



(19)대한민국특허청(KR)
(12) 등록특허공보(B1)

(51) 。 Int. Cl. C09K 11/06 (2006.01)	(45) 공고일자 (11) 등록번호 (24) 등록일자	2007년01월02일 10-0663721 2006년12월26일
---	-------------------------------------	--

(21) 출원번호 (22) 출원일자 심사청구일자	10-2005-0066176 2005년07월21일 2005년07월21일	(65) 공개번호 (43) 공개일자
----------------------------------	---	------------------------

(73) 특허권자 주식회사 이엘엠
 경기도 군포시 금정동 1-22

(72) 발명자 박종억
 경기 화성시 태안읍 병점리 860 구봉마을 우남퍼스트빌 104동203호

정수영
서울 강남구 개포3동 187 주공아파트 501동 906호

김정미
서울 강북구 미아1동 839-83호 7/3

백용구
경기 수원시 영통구 매탄1동 주공5단지 아파트 517동 806호

정준호
경기 수원시 장안구 조원동 782-16

민수현
서울 구로구 구로4동 746-20번지 401호

김진영
서울 강서구 내발산동 686-1 보람아파트 101동 1203호

(74) 대리인 정종욱

(56) 선행기술조사문헌 JP09241629 A JP2005093159 A * 심사관에 의하여 인용된 문헌	JP2003040845 A
--	----------------

심사관 : 손창호

전체 청구항 수 : 총 9 항

(54) 유기 발광 재료 및 유기 발광 다이오드

(57) 요약

본 발명은 유기 발광 다이오드(OLED)에 사용되는 화합물 유도체와 이를 이용한 유기 발광 다이오드에 관한 것으로, 더욱 자세하게는 높은 유리전이온도를 갖는 트리페닐렌 화합물 유도체를 제조하고 이를 유기 발광 다이오드의 정공전달물질로 사용하여 우수한 열안정성과 소자의 수명을 증가시키고, 발광 휘도와 발광 효율이 우수한 유기 발광 다이오드를 제공하는 것이다.

대표도

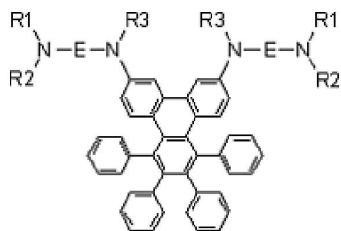
도 1

특허청구의 범위

청구항 1.

유기 발광 다이오드(OLED)의 정공전달물질로 사용되는 것을 특징으로 하는 하기 화학식 I로 표시되는 트리페닐렌 유도체.

[화학식 I]

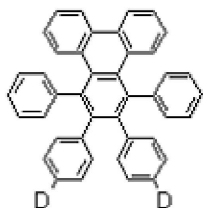


(상기 화학식 I에서, E는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R1 내지 R3는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R1과 R2는 서로, 또는 E와 R1은 서로 단일결합, 메틸렌기, 에틸렌기 또는 비닐기에 의하여 연결될 수 있다.)

청구항 2.

유기 발광 다이오드(OLED)의 정공전달물질로 사용되는 것을 특징으로 하는 하기 화학식 II로 표시되는 트리페닐렌 유도체.

[화학식 II]

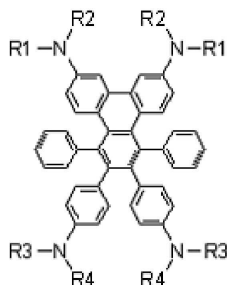


(상기 화학식 II에서, D는 디아민 유도체를 표시한다.)

청구항 3.

유기 발광 다이오드(OLED)의 정공전달물질로 사용되는 것을 특징으로 하는 하기 화학식 III로 표시되는 트리페닐렌 유도체.

[화학식 III]

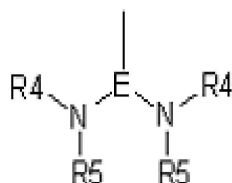


(상기 화학식 III에서, R1 내지 R4는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R1과 R2 는 서로, 또는 R3와 R4는 서로 단일결합, 메틸렌기, 에틸렌기 또는 비닐기에 의하여 연결될 수 있다.)

청구항 4.

제2항에 있어서, 상기 화학식 II의 D는 하기 화학식 1을 기본 골격으로 하는 디아민 유도체인 것을 특징으로 하는 트리페닐렌 유도체.

[화학식 1]



(상기 화학식 1에서, E는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R4 및 R5는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R4와 R5는 단일결합, 메틸렌기, 에틸렌기 또는 비닐기에 의하여 서로 연결될 수 있다.)

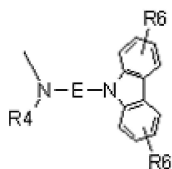
청구항 5.

제2항에 있어서, 상기 화학식 II의 D는 카바졸릴기를 포함하는 디아민 유도체인 것을 특징으로 하는 트리페닐렌 유도체.

청구항 6.

제5항에 있어서, 상기 카바졸릴기를 포함하는 디아민 유도체는 하기 화학식 2인 것을 특징으로 하는 트리페닐렌 유도체.

[화학식 2]

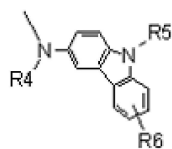


(상기 화학식 2에서, E는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R4는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R6는 수소원자, 알킬기, 알콕시기 또는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시한다.)

청구항 7.

제5항에 있어서, 상기 카바졸릴기를 포함하는 디아민 유도체는 하기 화학식 3인 것을 특징으로 하는 트리페닐렌 유도체.

[화학식 3]

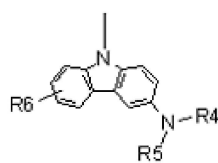


(상기 화학식 3에서, R4 및 R5는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R6는 수소원자, 알킬기, 알콕시기 또는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시한다.)

청구항 8.

제5항에 있어서, 상기 카바졸릴기를 포함하는 디아민 유도체는 하기 화학식 4인 것을 특징으로 하는 트리페닐렌 유도체.

[화학식 4]



(상기 화학식 4에서, R4 및 R5는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R4와 R5는 단일결합, 메틸렌기, 에틸렌기 또는 비닐기에 의하여 서로 연결될 수 있다. R6는 수소원자, 알킬기, 알콕시기 또는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시한다.)

청구항 9.

제1항 내지 제8항 중 어느 한 항에 따른 트리페닐렌 유도체를 정공주입재료, 정공수송재료 또는 발광층 재료로 이용하는 것을 특징으로 하는 유기 발광 다이오드.

명세서

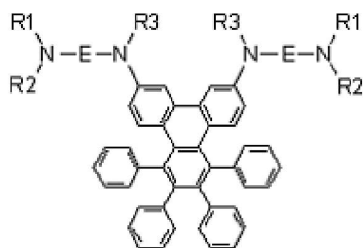
발명의 상세한 설명

발명의 목적

발명이 속하는 기술 및 그 분야의 종래기술

본 발명은 유기 발광 다이오드(OLED)에 사용되는 화합물 유도체와 이를 이용한 유기 발광 다이오드에 관한 것으로, 더욱 자세하게는 높은 유리전이온도를 갖는 트리페닐렌 유도체인 하기 화학식 I, 하기 화학식 II, 또는 하기 화학식 III의 화합물을 제조하고 이를 유기 발광 다이오드의 정공전달물질로 사용하여 우수한 열안정성과 소자의 수명을 증가시키고, 발광 휘도와 발광 효율이 우수한 유기 발광 다이오드를 제공하는 것이다. 정공전달물질은 정공주입층(HIL), 정공수송층(HTL)에 사용되는 물질을 말하며, 일부 경우에는 발광층(EML)에 사용되는 물질일수도 있다.

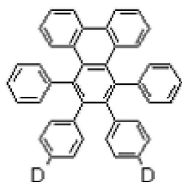
[화학식 I]



상기 화학식 I에서,

E는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R1 내지 R3는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R1과 R2는 서로, 또는 E와 R1은 서로 단일결합, 메틸렌기, 에틸렌기 또는 비닐기에 의하여 연결될 수 있다.

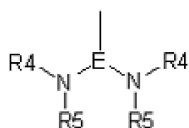
[화학식 II]



상기 화학식 II에서,

D는 하기 화학식 1을 기본 골격으로 하는 디아민 유도체 또는 카바졸릴기를 포함하는 디아민 유도체를 표시한다.

[화학식 1]

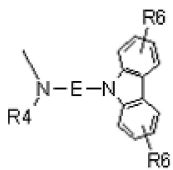


상기 화학식 1에서,

E는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R4 및 R5는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R4와 R5는 단일결합, 메틸렌기, 에틸렌기 또는 비닐기에 의하여 서로 연결될 수 있다.

D가 카바졸릴기를 포함하는 디아민 유도체의 예는 하기 화학식 2 내지 하기 화학식 4를 포함한다.

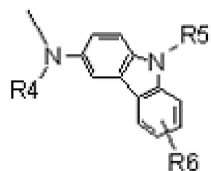
[화학식 2]



상기 화학식 2에서,

E는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R4는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R6는 수소원자, 알킬기, 알콕시기 또는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시한다.

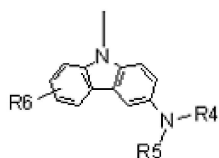
[화학식 3]



상기 화학식 3에서,

R4 및 R5는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R6는 수소원자, 알킬기, 알콕시기 또는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시한다.

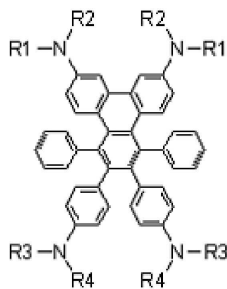
[화학식 4]



상기 화학식 4에서,

R4 및 R5는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R4와 R5는 단일결합, 메틸렌기, 에틸렌기 또는 비닐기에 의하여 서로 연결될 수 있다. R6는 수소원자, 알킬기, 알콕시기 또는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시한다.

[화학식 III]



상기 화학식 III에서,

R1 내지 R4는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R1과 R2 는 서로, 또는 R3와 R4는 서로 단일결합, 메틸렌기, 에틸렌기 또는 비닐기에 의하여 연결될 수 있다.

상기 화학식 I 내지 화학식 III와 상기 화학식 1 내지 화학식 4에서 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기의 예는 페닐기, 나프틸기, 페난트릴기, 안트릴기, 비페닐기 등을 포함한다.

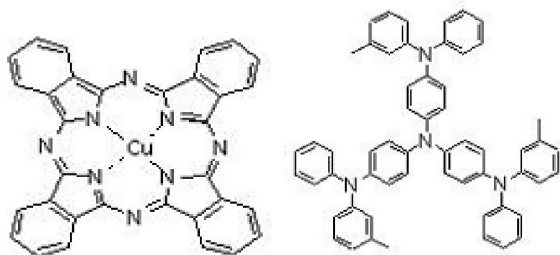
저 전압구동, 자기발광, 경량 박형, 광 시야각 그리고 빠른 응답속도 등의 여러 가지 장점을 가진 유기 발광 다이오드(OLED)는 LCD를 대체할 차세대 평판 디스플레이 중의 하나로서 최근 가장 연구가 활발히 이루어지고 있는 분야이다.

미국 특허 제 4,356,429 호에서, 탕(Tang)은 유기 발광 매체는 양극과 음극 사이에 놓인 2개의 유기층을 포함하는 이층구조의 유기 발광 다이오드를 개시하였다. 즉, 양극에 인접한 정공전달층은 정공전달물질을 함유하며 유기 발광 다이오드 장치 내에서 단지 정공(hole)만을 주로 발광층에 전달하는 기능을 갖는다. 이와 유사하게, 음극에 인접한 전자수송층은 전자 전달물질을 함유하며 유기 발광 다이오드 장치 내에서 단지 전자만을 주로 전달하도록 선택된 이층구조의 유기 발광 다이오드 장치는 높은 발광 효율을 달성하여 상당부분 유기 발광 다이오드의 기술을 개선시켰다. 따라서 발광효율적인 면에서 정공주입층(hole injection layer)과 정공수송층(hole transporting layer) 같은 정공전달층, 전자수송층(electron transporting layer), 정공차단층(hole blocking layer) 등을 포함하는 다층 구조(multilayer system)를 이용하지 않으면 고효율 및 고휘도의 발광특성을 기대하기는 불가능하다.

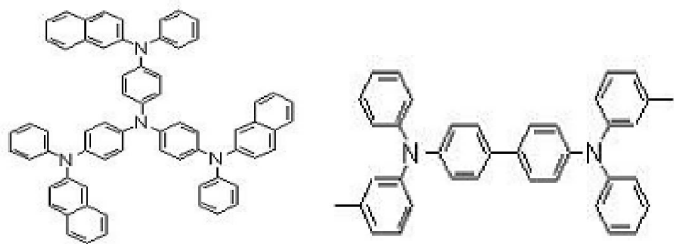
유기 발광 다이오드 장치를 실용화하기 위해서는 위의 다층 구조로 소자를 구성하는 것 이외에 소자 재료 특히, 정공전달 물질이 열적 그리고 전기적으로 안정성을 지니고 있어야한다. 왜냐하면 전압을 걸어주었을 때 소자에서 발생하는 열로 인하여 열안정성이 낮은 분자는 결정 안정성이 낮아 재배열현상이 일어나게 되고, 결국 국부적으로 결정화가 발생되어 불균질 부분이 존재한다면, 전기장이 이 부분에 집중하여 소자의 열화 및 파괴를 가져오는 것으로 받아들여지기 때문이다. 따라서 유기층은 통상적으로 비결정질 상태로 사용된다. 더욱이, 유기 발광 다이오드는 전류주입형 소자이기 때문에, 만약 사용되는 재료가 낮은 유리전이온도(Tg)를 갖는다면, 사용 중 발생하는 열이 유기 발광 다이오드의 열화를 초래하여 소자의 수명을 단축시키게 된다. 이런 점에서, 높은 유리전이온도를 갖는 재료가 바람직하다.

기준에 사용되고 있는 정공전달 물질의 대표적인 예로는 하기 화학식 5의 CuPC[구리 프탈로시아닌], 하기 화학식 6의 m-MTDATA[4,4',4"-트리스(*N*-3-메틸페닐-*N*'-페닐아미노)-트리페닐아민], 하기 화학식 7의 2-TNATA[4,4',4"-트리스(*N*-(나프틸렌-2-일)-*N*'-페닐아미노)-트리페닐아민], 하기 화학식 8의 TPD[*N,N'*-디페닐-*N,N'*-디(3-메틸페닐)-4,4'-디아미노비페닐] 그리고 하기 화학식 9의 NPB[*N,N'*-디(나프탈렌-1-일)-*N,N'*-디페닐벤지딘] 등이 있다.

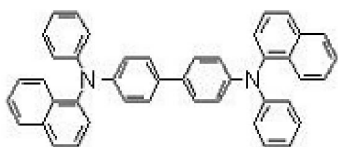
[화학식 5] [화학식 6]



[화학식 7] [화학식 8]



[화학식 9]



CuPC는 금속착화합물이므로 ITO 기판과의 접착성이 우수하고 가장 안정하기 때문에 널리 사용되지만 가시광선 영역에서 흡수가 일어나므로 총 천연색을 구현하는 것이 어렵고, m-MTDATA나 2-TNATA는 유리전이온도가 78℃ 및 108℃로 낮을 뿐만 아니라 대량화 하는 과정에서 문제점이 많이 발생하기 때문에 역시 총 천연색을 구현하는 데는 문제점이 있다. 또한, TPD나 NPB 역시 유리전이온도(Tg)가 각각 60℃ 및 96℃로 낮기 때문에 상기와 같은 이유로 소자의 수명을 단축시킨다는 치명적인 단점이 있다.

상기와 같이 종래의 유기 발광 다이오드에 사용되는 정공전달물질은 여전히 많은 문제점을 내포하고 있으며, 우수한 물적 특성을 가지는 성능 개량이 요구되고 있다. 따라서 유기 발광 다이오드의 발광효율을 향상시키고, 높은 열안정성과 높은 유리전이온도를 갖는 우수한 재료에 대한 개발이 절실히 요구된다.

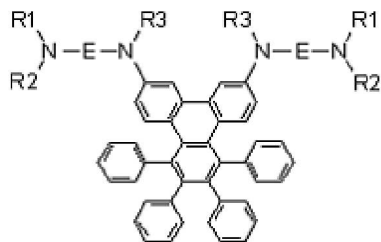
발명이 이루고자 하는 기술적 과제

본 발명은 종래의 상기와 같은 문제점들을 해결하고자 본 발명가들이 예의 연구를 거듭하여 얻은 결과로서, 신규 유기 발광 다이오드용 재료를 제공하는데 그 목적이 있다. 본 발명의 다른 목적은 유기 발광 다이오드의 발광 효율을 향상시키고 소자의 수명을 증가시킬 수 있는 우수한 열안정성을 가진 유기 발광 다이오드용 정공전달 물질 및 그 제조방법을 제공하는 것이다. 본 발명의 또 다른 목적은 높은 발광 효율을 나타내는 유기 발광 다이오드를 제공하는 것이다. 본 발명의 또 다른 목적은 연장된 수명을 갖는 유기 발광 다이오드를 제공하는 것이다. 본 발명에서 정공전달물질은 정공주입층 또는 정공수송층에 사용되는 물질을 말하며, 일부 경우에 발광층에 사용되는 물질일 수도 있다.

발명의 구성

본 발명은 유기 발광 다이오드에서 정공전달물질로 유용한 하기 화학식 I, 하기 화학식 II 또는 하기 화학식 III로 표시되는 트리페닐렌 유도체에 관한 것으로서, 이들 트리페닐렌 유도체는 높은 유리 전이 온도(145℃ 이상)와 우수한 정공 주입, 수송 능력을 갖고 있으므로 이를 정공전달물질로 사용하여 유기 발광 다이오드를 제작하면 발광 효율을 높이고 소자의 수명을 증가시킬 수 있는 것이다.

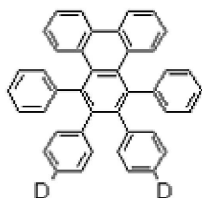
[화학식 I]



상기 화학식 I에서,

E는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R1 내지 R3는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R1과 R2는 서로, 또는 E와 R1은 서로 단일결합, 메틸렌기, 에틸렌기 또는 비닐기에 의하여 서로 연결될 수 있다.

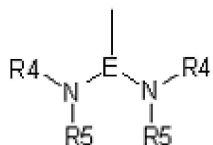
[화학식 II]



상기 화학식 II에서,

D는 하기 화학식 1을 기본 골격으로 하는 디아민 유도체 또는 카바졸릴기를 포함하는 디아민 유도체를 표시한다.

[화학식 1]

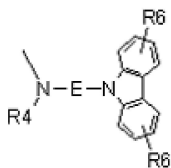


상기 화학식 1에서,

E는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R4 및 R5는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R4와 R5는 단일결합, 메틸렌기, 에틸렌기 또는 비닐기에 의하여 서로 연결될 수 있다.

D가 카바졸릴기를 포함하는 디아민 유도체의 예는 하기 화학식 2 내지 하기 화학식 4를 포함한다.

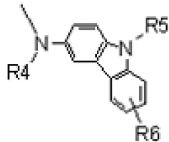
[화학식 2]



상기 화학식 2에서,

E는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R4는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R6는 수소원자, 알킬기, 알콕시기 또는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시한다.

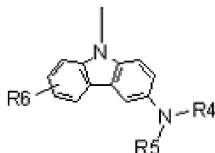
[화학식 3]



상기 화학식 3에서,

R4 및 R5는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R6는 수소원자, 알킬기, 알콕시기 또는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시한다.

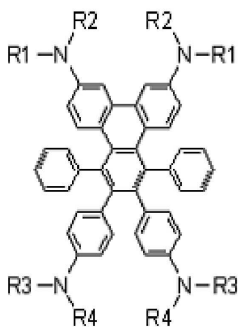
[화학식 4]



상기 화학식 4에서,

R4 및 R5는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R4와 R5는 단일결합, 메틸렌기, 에틸렌기 또는 비닐기에 의하여 서로 연결될 수 있다. R6는 수소원자, 알킬기, 알콕시기 또는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시한다.

[화학식 III]



상기 화학식 III에서,

R1 내지 R4는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R1과 R2는 서로, 또는 R3와 R4는 서로 단일결합, 메틸렌기, 에틸렌기 또는 비닐기에 의하여 연결될 수 있다.

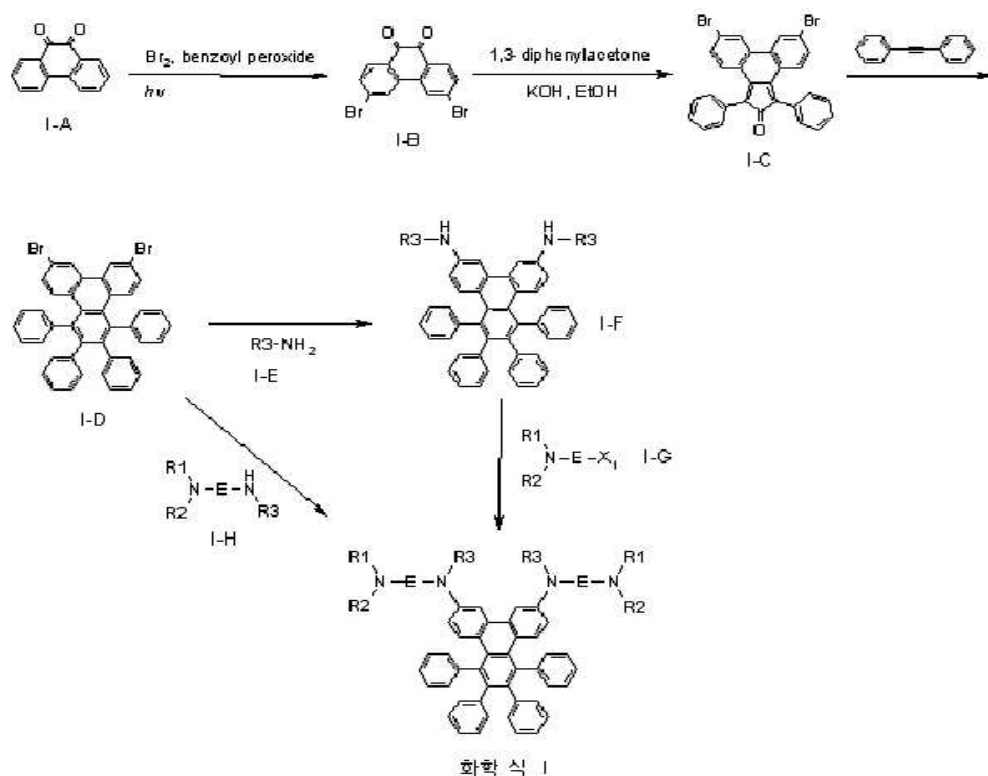
상기 화학식 I 내지 화학식 III와 상기 화학식 1 내지 화학식 4에서 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기의 예는 페닐기, 나프틸기, 페난트릴기, 안트릴기, 비페닐기 등을 포함한다.

본 발명에 따른 높은 발광 효율과 긴 수명의 유기 발광 다이오드를 가능하게 하는 트리페닐렌 유도체의 정공전달물질을 제조하는 과정을 이하에서 설명하기로 한다.

상기 화학식 I을 제조하는 방법은 하기 단계로 이루어진다.

본 발명자들은 하기의 반응식 1과 같은 합성 경로로 화학식 I의 일반 구조식을 갖는 화합물을 페난트렌퀴논(I-A)으로부터 제조할 수 있었다.

[반응식 1]



상기 반응식 1에서,

E는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아틸기를 표시하고, R1 내지 R3는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아틸기를 표시하고, R1과 R2는 서로, 또는 E와 R1은 서로 단일결합, 메틸렌기, 에틸렌기 또는 비닐기에 의하여 연결될 수 있다. X₁은 이탈기로 바람직하게는 할로젠 원자이다.

먼저, M. V. Bhatt, Tetrahedron, 803(1964)를 참조로 하여, 페난트렌퀴논(I-A)에 브롬화 반응을 통하여 I-B로 표시되는 디브로모 화합물을 제조하고, 1,3-디페닐아세톤을 알콜성 수산화칼륨에서 반응시켜 I-C로 표시되는 디브로모펜사이클론 화합물을 제조한 다음 벤젠, 톨루엔 또는 자일렌 등의 적당한 용매에서 가열하여 I-D로 표시되는 디브로모트리페닐렌 유도체를 제조하였다. 이 디브로모트리페닐렌 유도체와 I-E로 표시되는 1차 아민과의 아민화 반응을 통하여 I-F로 표시되는 디아미노트리페닐렌 유도체를 제조하고, 이 화합물에 I-G로 표시되는 3차 아민과의 아민화 반응을 통하여 화학식 I을 제조하거나 또는 I-D로 표시되는 디브로모트리페닐렌 유도체와 I-H로 표시되는 디아민과의 아민화 반응을 통하여 최종적으로 본 발명에 따른 트리페닐 유도체의 한 가지 형태인 화학식 I로 표시되는 유기 발광 다이오드의 재료를 제조하였다. 본 제조과정에서 I-F를 합성하는 단계와 최종적으로 화학식 I을 합성하는 단계에 사용되는 아민화 반응의 조건은 크게 두 가지 방법이 있다.

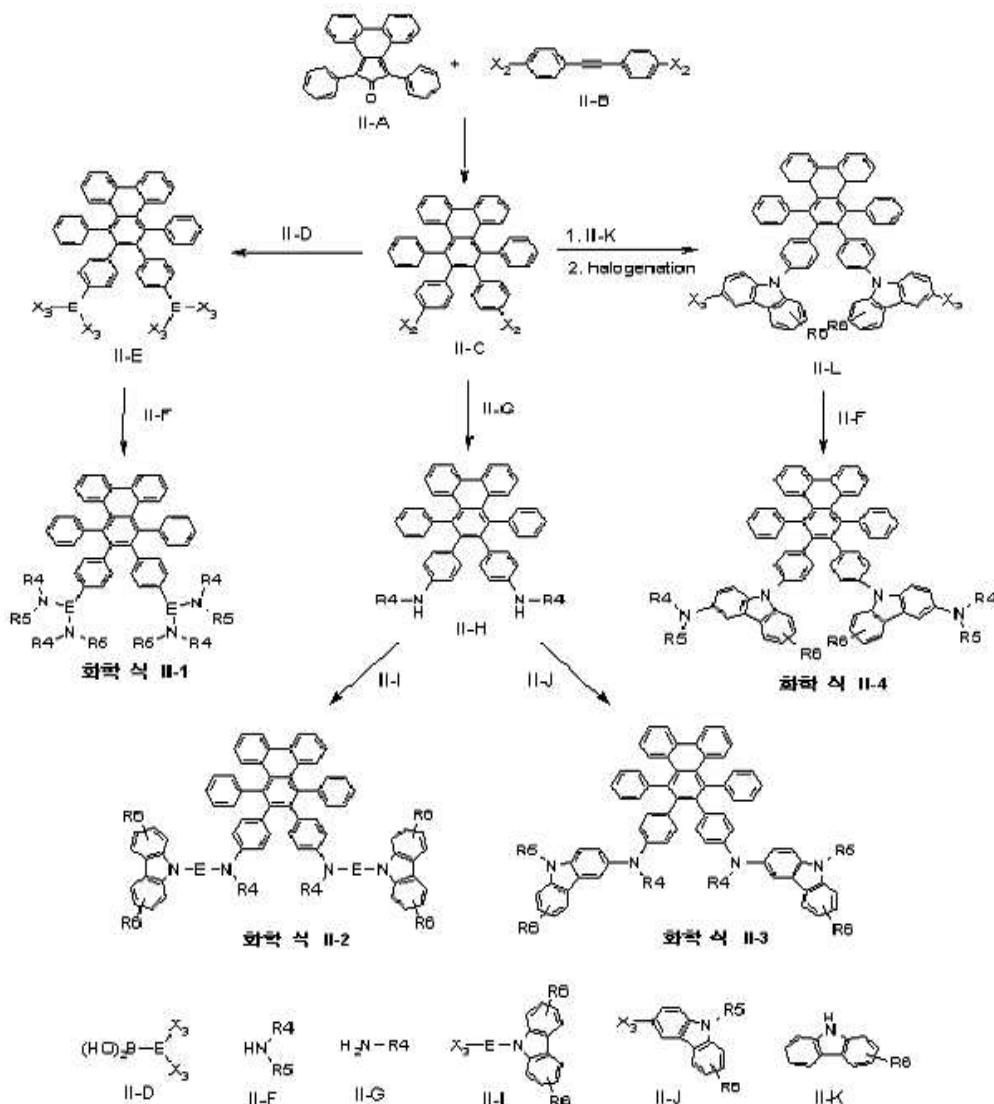
첫 번째 방법은 구리 촉매를 이용한 울만반응(Ullmann reaction)으로, 특별히 제한되지는 않지만 반응에 사용되는 구리 촉매는 구리 분말이나 황산구리(CuSO_4)가 적당하고 반응 염기는 포타시움 카보네이트나 소듐 카보네이트가 가장 적당하며, 반응 용매는 사용하지 않거나 고온의 끓는점을 가진 *N,N*-디메틸설폭사이드, 나이트로벤젠 또는 데칼린을 사용한다. 때로는 반응을 좀 더 원활히 수행하기 위하여 크라운 에테르나 폴리(에틸렌 글리콜)을 사용하기도 한다.

두 번째 방법은 팔라듐 촉매를 이용한 방법으로, 적당한 반응 용매 하에서 팔라듐 촉매, 포스핀 촉매 및 염기를 사용하여 아민화 반응을 수행하는 것으로 반응에 사용되는 팔라듐 촉매는 특별히 제한되지는 않지만 주로 팔라듐 아세테이트나 트리스(디벤질리덴아세톤)팔라듐(0)을 사용하고 포스핀 촉매도 특별히 제한되지는 않고 트리-(*o*-톨릴)포스핀, 2,2'-비스(디페닐포스포노)-1,1'-비나프틸, 트리-(*n*-부틸)포스핀 또는 트리-(*t*-부틸)포스핀 등을 사용한다. 반응 염기는 소듐 *t*-부톡시드 또는 포타시움 *t*-부톡시드 등의 금속 알콕시드를 사용한다. 반응용매는 특별히 제한되지 않고 사용되는 시약에 대하여 반응성이 없고 반응을 원활히 진행될 수 있을 정도의 용해도를 가지고 있으면 된다. 구체적인 예로는 벤젠, 톨루엔, 자일렌, *N,N*-디메틸포름아마이드, *N,N*-디메틸설폭사이드 등이 있다. 상기 반응에 사용되는 시약이나 반응 용매는 특별히 이에 한정되는 것은 아니다.

상기 화학식 II를 제조하는 방법은 하기 단계로 이루어진다.

본 발명자들은 하기의 반응식 2와 같은 합성 경로로 화학식 II의 일반 구조식을 갖는 트리페닐렌 유도체를 펜사이클론(II-A)으로부터 제조할 수 있었다.

[반응식 2]



상기 반응식 2에서,

E는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R4 및 R5는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R4와 R5는 단일결합, 메틸렌기, 에틸렌기 또는 비닐기에 의하여 서로 연결될 수 있다. R6는 수소원자, 알킬기, 알콕시기 또는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시한다. X₂ 및 X₃는 이탈기로 바람직하게는 할로젠 원자이다.

먼저, 펜사이클론(II-A)과 비스-(4-할로페닐)-아세틸렌(II-B)을 벤젠, 톨루엔 또는 자일렌 등의 적당한 용매 하에서 가열하여 II-C로 표시되는 디할로트리페닐렌 유도체를 제조하였다. 이 중간체로부터 다양한 아민기를 도입하여 기본 구조식이 화학식 II로 표시되는 본 발명의 트리페닐렌 유도체를 제조하는 것이 가능하였다. 화학식 II는 화합물의 특성을 이루는 기본 골격의 차이에 의하여 다시 화학식 II-1 내지 화학식 II-4의 4가지로 구분할 수 있다(반응식 2). 각각의 제조 방법은 아래와 같다.

화학식 II-1의 제조방법은 다음과 같다.

상기 반응식 2에서, II-C로 표시되는 디할로트리페닐렌 유도체에 II-D로 표시되는 보론산을 이용한 스즈키 반응을 통하여 II-E로 표시되는 테트라할로 화합물을 제조하고 여기에 II-F로 표시되는 2차 아민과의 아민화 반응을 통하여 화학식 II-1로 표시되는 트리페닐렌 유도체의 제조가 가능하였다.

화학식 II-2 및 화학식 II-3의 제조방법은 다음과 같다.

상기 반응식 2에서, I-C로 표시되는 디할로트리페닐렌 유도체에 II-G로 표시되는 1차 아민과의 아민화 반응을 통하여 II-H로 표시되는 2차 아민 화합물을 제조하고 II-I 및 II-J로 표시되는 카바졸 유도체와의 아민화 반응을 통하여 화학식 II-2 및 화학식 II-3로 표시되는 트리페닐렌 유도체를 각각 제조할 수 있었다.

화학식 II-4의 제조방법은 다음과 같다.

상기 반응식 2에서, II-C로 표시되는 디할로트리페닐렌 유도체에 II-K로 표시되는 카바졸 유도체의 아민화 반응과 할로젠화 반응을 통하여 II-L로 표시되는 화합물을 제조하고 II-F로 표시되는 2차 아민과의 아민화 반응을 다시 수행하여 화학식 II-4로 표시되는 트리페닐렌 유도체를 제조할 수 있었다.

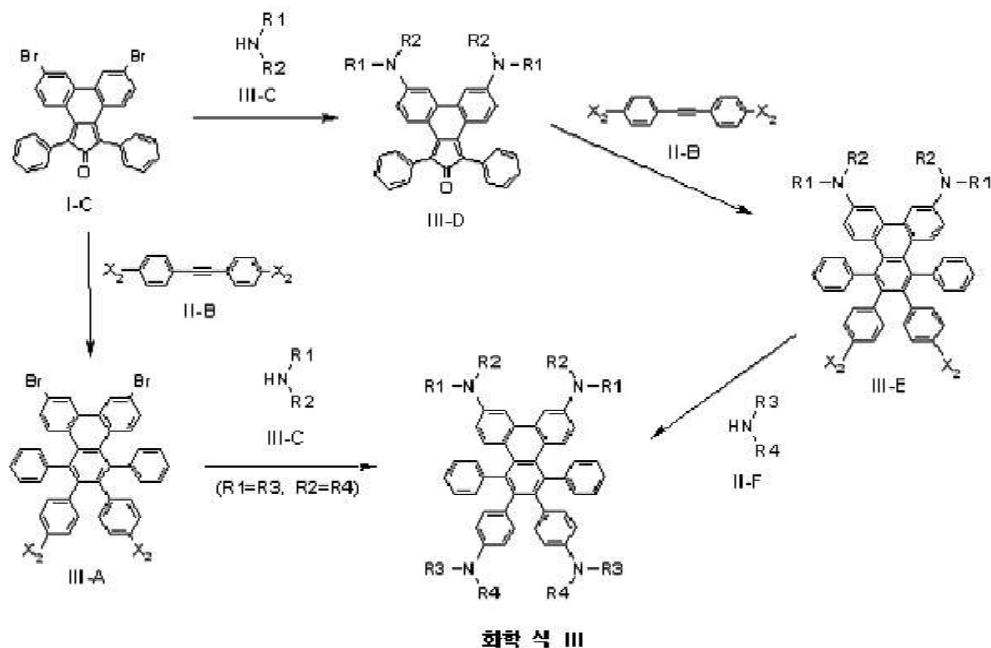
상기와 같은 방법으로 본 발명의 트리페닐렌 유도체의 한 예인 화학식 II로 표시되는 유기 발광 다이오드의 재료를 제조할 수 있었다.

상기에서, 화학식 II의 트리페닐렌 유도체 및 그 중간체를 제조하기 위하여 사용되는 아민화 반응의 조건은 화학식 I의 트리페닐렌 유도체를 제조하기 위하여 사용된 아민화 반응의 조건과 동일하다.

상기 화학식 III를 제조하는 방법은 하기 단계로 이루어진다.

본 발명자들은 하기의 반응식 3과 같은 합성 경로로 화학식 III의 일반 구조식을 갖는 화합물을 디브로모펜사이클론(I-C)으로부터 합성할 수 있었다.

[반응식 3]



상기 반응식 3에서,

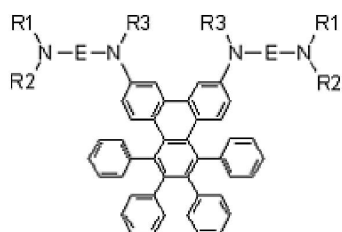
R1 내지 R4는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R1과 R2는 서로, 또는 R3와 R4는 서로 단일결합, 메틸렌기, 에틸렌기 또는 비닐기에 의하여 연결될 수 있다. X₂는 이탈기로 바람직하게는 할로겐 원자이다.

반응식 1에서 화학식 I를 제조하기 위한 중간체인 디브로모펜사이클론(I-C)으로부터 화학식 III의 제조하기 위한 방법은 최종 목적 화합물인 화학식 III의 구조적 특성상 2가지로 분류할 수 있다. 첫째로 아민의 치환기인 R1과 R3가 동일하고 R2와 R4가 동일할 경우는 II-B로 표시되는 아세틸렌 화합물과의 디엘스-알더 반응(Diels-Alder reaction)을 통하여 III-A로 표시되는 테트라할로 화합물을 제조하고 III-C로 표시되는 2차 아민과의 아민화 반응을 통하여 최종적으로 화학식 III의 화합물을 제조하는 것이 가능하였다. 둘째로 아민의 치환기인 R1 내지 R4가 각각 독립적인 경우는 III-C로 표시되는 2차 아민과의 아민화 반응을 통하여 III-D로 표시되는 디아미노펜사이클론 화합물을 제조하고 II-B로 표시되는 아세틸렌 화합물과의 디엘스-알더 반응을 통하여 디아미노트리페닐렌 유도체를 제조한 다음 II-F로 표시되는 2차 아민과의 아민화 반응을 통하여 본 발명의 트리페닐렌 유도체의 한 예인 화학식 III로 표시되는 유기 발광 다이오드의 재료를 제조할 수 있었다.

상기에서, 화학식 III의 트리페닐렌 유도체 및 그 중간체를 제조하기 위하여 사용되는 아민화 반응의 조건은 화학식 I의 트리페닐렌 유도체를 제조하기 위하여 사용된 아민화 반응의 조건과 동일하다.

상기와 같은 방법으로 제조하여 최종적으로 높은 발광 효율과 긴 수명의 유기 발광 다이오드를 가능하게 하는 정공전달물질의 구체적인 예는 하기의 표 1 내지 표 72에 표시되는 화합물을 포함한다. 하지만 본 발명은 이들로 한정되지는 않는다. 이하에서는 이들의 구체적인 예를 살펴본다.

[화학식 I]

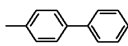
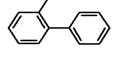
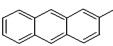
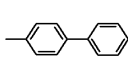
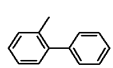
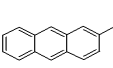
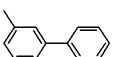
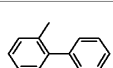


상기 화학식 I에서,

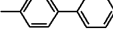
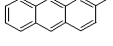
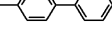
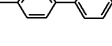
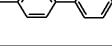
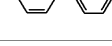
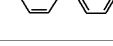
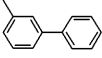
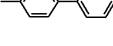
E는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R1 내지 R3는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R1과 R2는 서로, 또는 E와 R1은 서로 단일결합, 메틸렌기, 에틸렌기 또는 비닐기에 의하여 연결될 수 있다.

상기 화학식 I의 구체적인 예는 하기의 표1 내지 표 39에 표시되는 화합물을 포함한다.

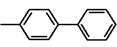
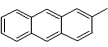
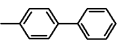
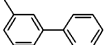
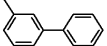
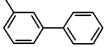
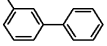
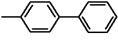
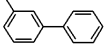
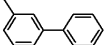
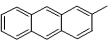
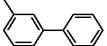
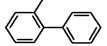
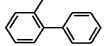
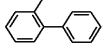
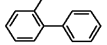
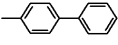
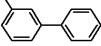
[표 1]

화학식	E	R1	R2	R3
I-1				
I-2				
I-3				
I-4				
I-5				
I-6				
I-7				
I-8				
I-9				
I-10				
I-11				
I-12				
I-13				
I-14				

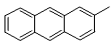
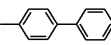
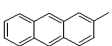
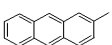
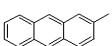
[표 2]

화학식	E	R1	R2	R3
I-15				
I-16				
I-17				
I-18				
I-19				
I-20				
I-21				
I-22				
I-23				
I-24				
I-25				
I-26				
I-27				
I-28				

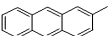
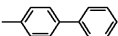
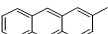
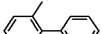
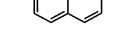
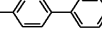
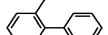
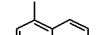
[표 3]

화학식	E	R1	R2	R3
I-29				
I-30				
I-31				
I-32				
I-33				
I-34				
I-35				
I-36				
I-37				
I-38				
I-39				
I-40				
I-41				
I-42				

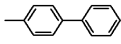
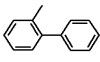
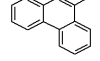
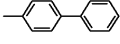
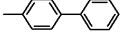
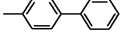
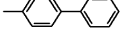
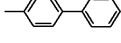
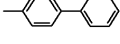
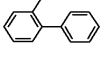
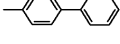
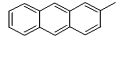
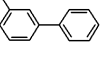
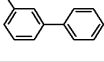
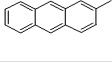
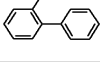
[표 4]

화학식	E	R1	R2	R3
I-43				
I-44				
I-45				
I-46				
I-47				
I-48				
I-49				
I-50				
I-51				
I-52				
I-53				
I-54				
I-55				
I-56				

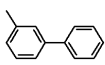
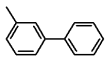
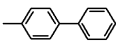
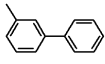
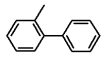
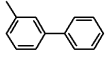
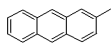
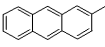
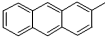
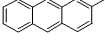
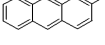
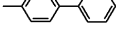
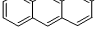
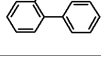
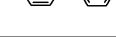
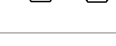
[표 5]

화학식	E	R1	R2	R3
I-57				
I-58				
I-59				
I-60				
I-61				
I-62				
I-63				
I-64				
I-65				
I-66				
I-67				
I-68				
I-69				
I-70				

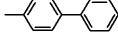
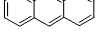
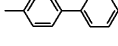
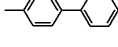
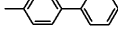
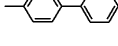
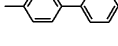
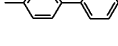
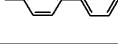
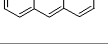
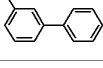
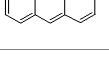
[표 6]

화학식	E	R1	R2	R3
I-71				
I-72				
I-73				
I-74				
I-75				
I-76				
I-77				
I-78				
I-79				
I-80				
I-81				
I-82				
I-83				
I-84				

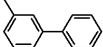
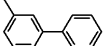
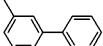
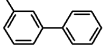
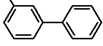
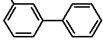
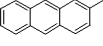
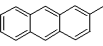
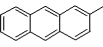
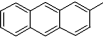
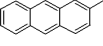
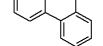
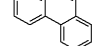
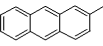
[표 7]

화학식	E	R1	R2	R3
I-85				
I-86				
I-87				
I-88				
I-89				
I-90				
I-91				
I-92				
I-93				
I-94				
I-95				
I-96				
I-97				
I-98				

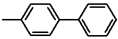
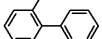
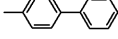
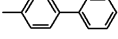
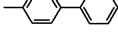
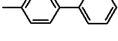
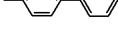
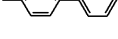
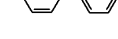
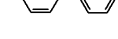
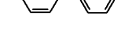
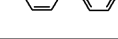
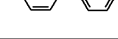
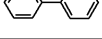
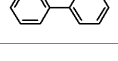
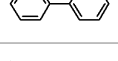
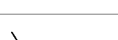
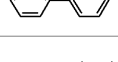
[표 8]

화학식	E	R1	R2	R3
I-99				
I-100				
I-101				
I-102				
I-103				
I-104				
I-105				
I-106				
I-107				
I-108				
I-109				
I-110				
I-111				
I-112				

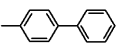
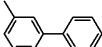
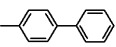
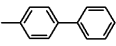
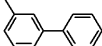
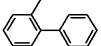
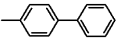
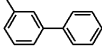
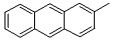
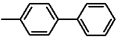
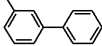
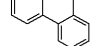
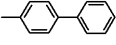
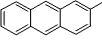
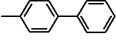
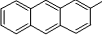
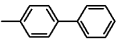
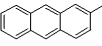
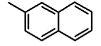
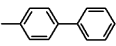
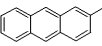
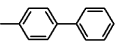
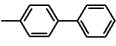
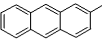
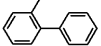
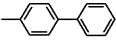
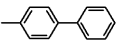
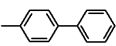
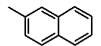
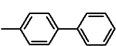
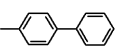
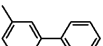
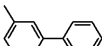
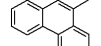
[표 9]

화학식	E	R1	R2	R3
I-113				
I-114				
I-115				
I-116				
I-117				
I-118				
I-119				
I-120				
I-121				
I-122				
I-123				
I-124				
I-125				
I-126				

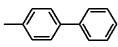
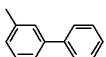
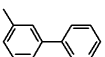
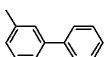
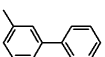
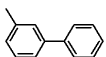
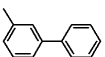
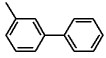
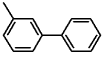
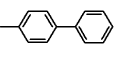
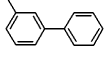
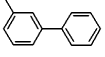
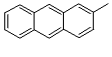
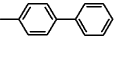
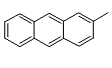
[표 10]

화학식	E	R1	R2	R3
I-127				
I-128				
I-129				
I-130				
I-131				
I-132				
I-133				
I-134				
I-135				
I-136				
I-137				
I-138				
I-139				
I-140				

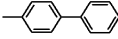
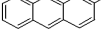
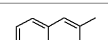
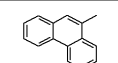
[표 11]

화학식	E	R1	R2	R3
I-141				
I-142				
I-143				
I-144				
I-145				
I-146				
I-147				
I-148				
I-149				
I-150				
I-151				
I-152				
I-153				
I-154				

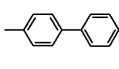
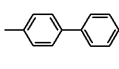
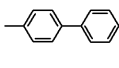
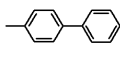
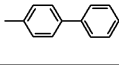
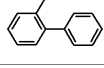
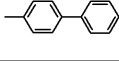
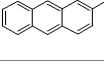
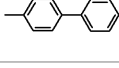
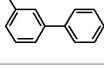
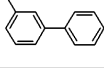
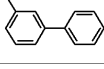
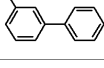
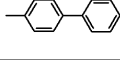
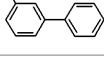
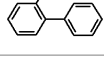
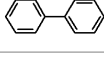
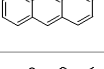
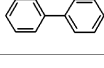
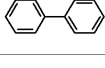
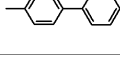
[표 12]

화학식	E	R1	R2	R3
I-155				
I-156				
I-157				
I-158				
I-159				
I-160				
I-161				
I-162				
I-163				
I-164				
I-165				
I-166				
I-167				
I-168				

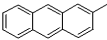
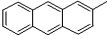
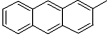
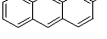
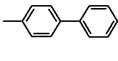
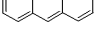
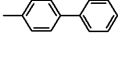
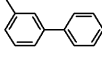
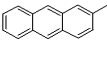
[표 13]

화학식	E	R1	R2	R3
I-169				
I-170				
I-171				
I-172				
I-173				
I-174				
I-175				
I-176				
I-177				
I-178				
I-179				
I-180				
I-181				
I-182				

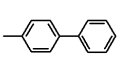
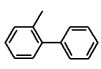
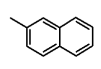
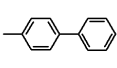
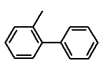
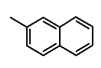
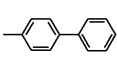
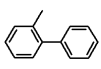
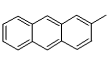
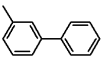
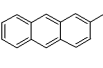
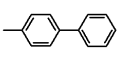
[표 14]

화학식	E	R1	R2	R3
I-183				
I-184				
I-185				
I-186				
I-187				
I-188				
I-189				
I-190				
I-191				
I-192				
I-193				
I-194				
I-195				
I-196				

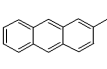
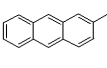
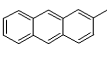
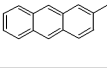
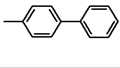
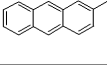
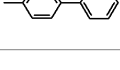
[표 15]

화학식	E	R1	R2	R3
I-197				
I-198				
I-199				
I-200				
I-201				
I-202				
I-203				
I-204				
I-205				
I-206				
I-207				
I-208				
I-209				
I-210				

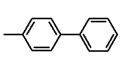
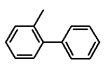
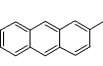
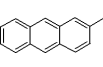
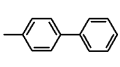
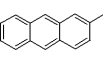
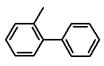
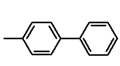
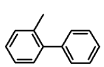
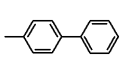
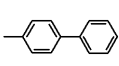
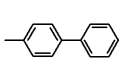
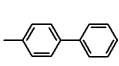
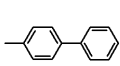
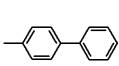
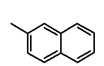
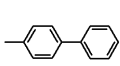
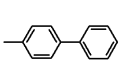
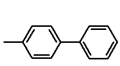
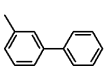
[표 16]

화학식	E	R1	R2	R3
I-211				
I-212				
I-213				
I-214				
I-215				
I-216				
I-217				
I-218				
I-219				
I-220				
I-221				
I-222				
I-223				
I-224				

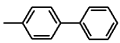
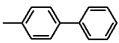
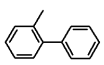
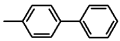
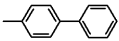
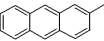
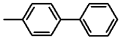
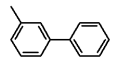
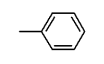
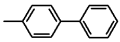
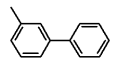
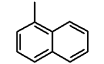
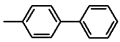
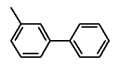
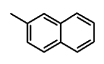
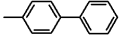
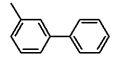
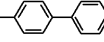
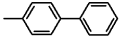
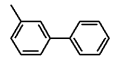
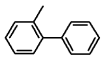
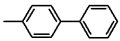
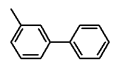
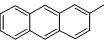
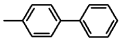
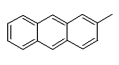
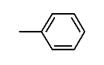
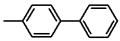
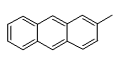
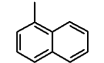
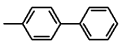
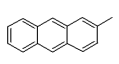
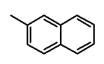
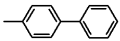
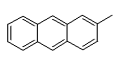
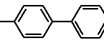
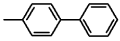
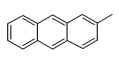
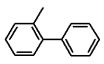
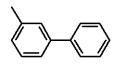
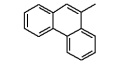
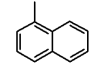
[표 17]

화학식	E	R1	R2	R3
I-225				
I-226				
I-227				
I-228				
I-229				
I-230				
I-231				
I-232				
I-233				
I-234				
I-235				
I-236				
I-237				
I-238				

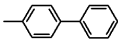
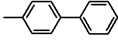
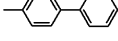
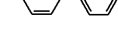
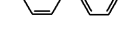
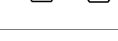
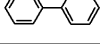
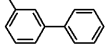
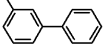
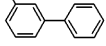
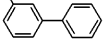
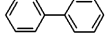
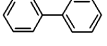
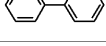
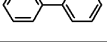
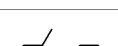
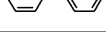
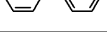
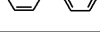
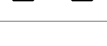
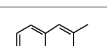
[표 18]

화학식	E	R1	R2	R3
I-239				
I-240				
I-241				
I-242				
I-243				
I-244				
I-245				
I-246				
I-247				
I-248				
I-249				
I-250				
I-251				
I-252				

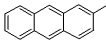
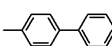
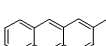
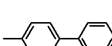
[표 19]

화학식	E	R1	R2	R3
I-253				
I-254				
I-255				
I-256				
I-257				
I-258				
I-259				
I-260				
I-261				
I-262				
I-263				
I-264				
I-265				
I-266				

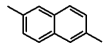
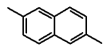
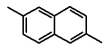
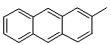
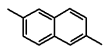
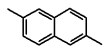
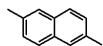
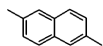
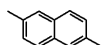
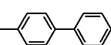
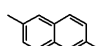
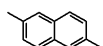
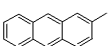
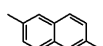
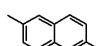
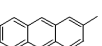
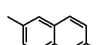
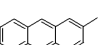
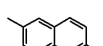
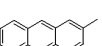
[표 20]

화학식	E	R1	R2	R3
I-267				
I-268				
I-269				
I-270				
I-271				
I-272				
I-273				
I-274				
I-275				
I-276				
I-277				
I-278				
I-279				
I-280				

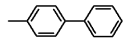
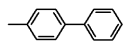
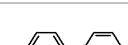
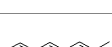
[표 21]

화학식	E	R1	R2	R3
I-281				
I-282				
I-283				
I-284				
I-285				
I-286				
I-287				
I-288				
I-289				
I-290				
I-291				
I-292				
I-293				
I-294				

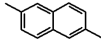
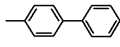
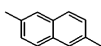
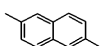
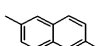
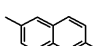
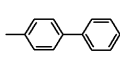
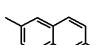
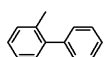
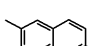
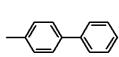
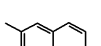
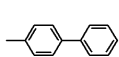
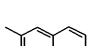
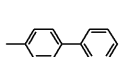
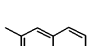
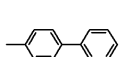
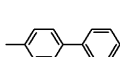
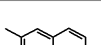
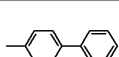
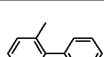
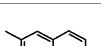
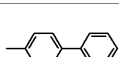
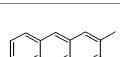
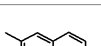
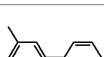
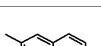
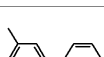
[표 22]

화학식	E	R1	R2	R3
I-295				
I-296				
I-297				
I-298				
I-299				
I-300				
I-301				
I-302				
I-303				
I-304				
I-305				
I-306				
I-307				
I-308				

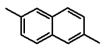
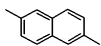
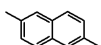
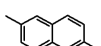
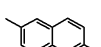
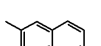
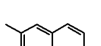
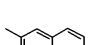
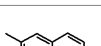
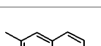
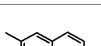
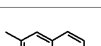
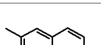
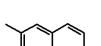
[표 23]

화학식	E	R1	R2	R3
I-309				
I-310				
I-311				
I-312				
I-313				
I-314				
I-315				
I-316				
I-317				
I-318				
I-319				
I-320				
I-321				
I-322				

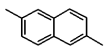
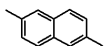
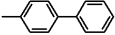
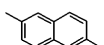
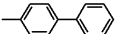
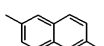
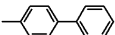
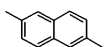
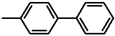
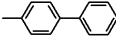
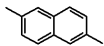
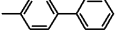
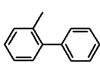
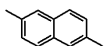
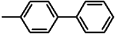
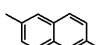
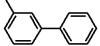
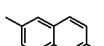
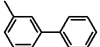
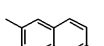
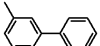
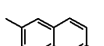
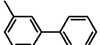
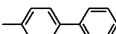
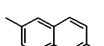
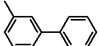
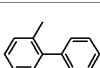
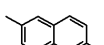
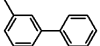
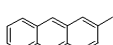
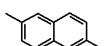
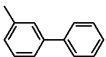
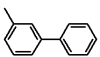
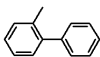
[표 24]

화학식	E	R1	R2	R3
I-323				
I-324				
I-325				
I-326				
I-327				
I-328				
I-329				
I-330				
I-331				
I-332				
I-333				
I-334				
I-335				
I-336				

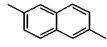
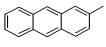
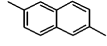
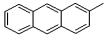
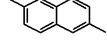
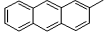
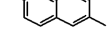
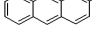
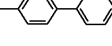
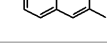
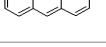
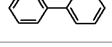
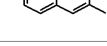
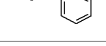
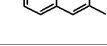
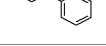
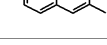
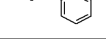
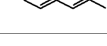
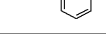
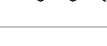
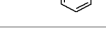
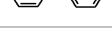
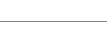
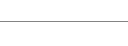
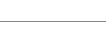
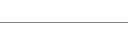
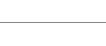
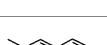
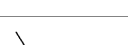
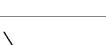
[표 25]

화학식	E	R1	R2	R3
I-337				
I-338				
I-339				
I-340				
I-341				
I-342				
I-343				
I-344				
I-345				
I-346				
I-347				
I-348				
I-349				
I-350				

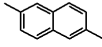
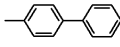
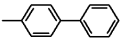
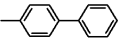
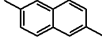
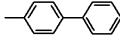
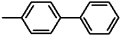
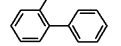
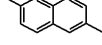
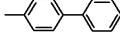
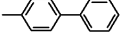
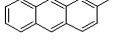
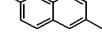
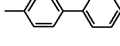
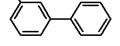
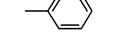
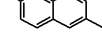
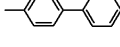
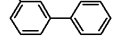
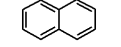
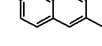
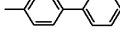
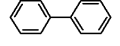
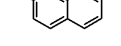
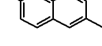
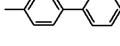
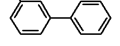
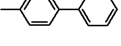
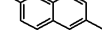
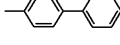
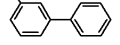
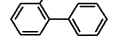
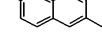
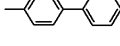
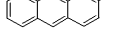
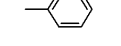
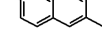
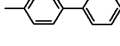
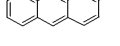
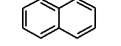
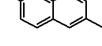
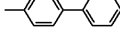
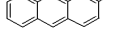
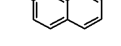
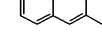
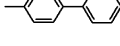
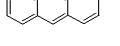
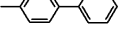
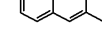
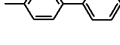
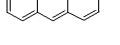
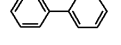
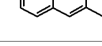
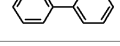
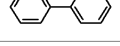
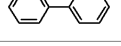
[표 26]

화학식	E	R1	R2	R3
I-351				
I-352				
I-353				
I-354				
I-355				
I-356				
I-357				
I-358				
I-359				
I-360				
I-361				
I-362				
I-363				
I-364				

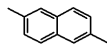
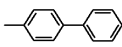
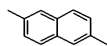
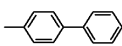
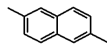
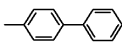
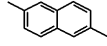
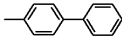
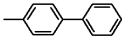
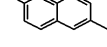
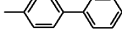
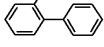
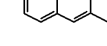
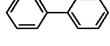
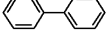
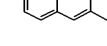
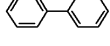
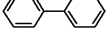
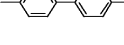
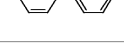
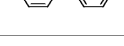
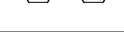
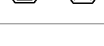
[표 27]

화학식	E	R1	R2	R3
I-365				
I-366				
I-367				
I-368				
I-369				
I-370				
I-371				
I-372				
I-373				
I-374				
I-375				
I-376				
I-377				
I-378				

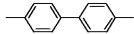
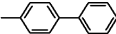
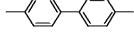
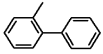
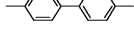
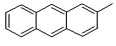
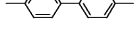
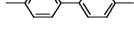
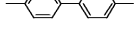
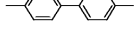
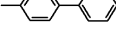
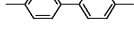
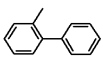
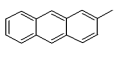
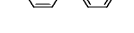
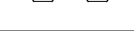
[표 28]

화학식	E	R1	R2	R3
I-379				
I-380				
I-381				
I-382				
I-383				
I-384				
I-385				
I-386				
I-387				
I-388				
I-389				
I-390				
I-391				
I-392				

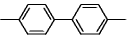
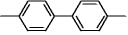
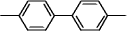
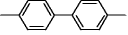
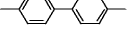
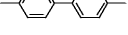
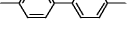
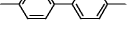
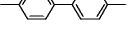
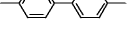
[표 29]

화학식	E	R1	R2	R3
I-393				
I-394				
I-395				
I-396				
I-397				
I-398				
I-399				
I-400				
I-401				
I-402				
I-403				
I-404				
I-405				
I-406				

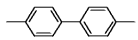
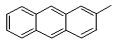
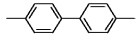
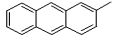
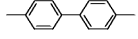
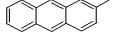
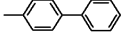
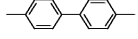
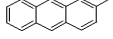
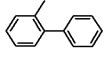
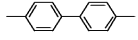
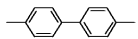
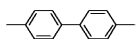
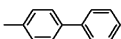
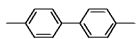
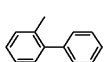
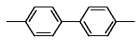
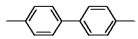
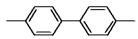
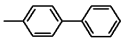
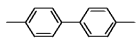
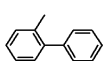
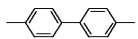
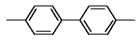
[표 30]

화학식	E	R1	R2	R3
I-407				
I-408				
I-409				
I-410				
I-411				
I-412				
I-413				
I-414				
I-415				
I-416				
I-417				
I-418				
I-419				
I-420				

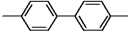
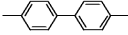
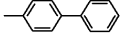
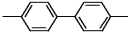
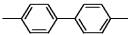
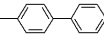
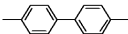
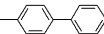
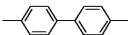
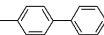
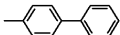
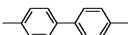
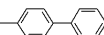
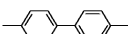
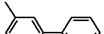
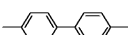
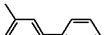
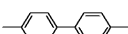
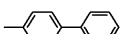
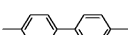
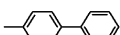
[표 31]

화학식	E	R1	R2	R3
I-421				
I-422				
I-423				
I-424				
I-425				
I-426				
I-427				
I-428				
I-429				
I-430				
I-431				
I-432				
I-433				
I-434				

[표 32]

화학식	E	R1	R2	R3
I-435				
I-436				
I-437				
I-438				
I-439				
I-440				
I-441				
I-442				
I-443				
I-444				
I-445				
I-446				
I-447				
I-448				

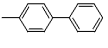
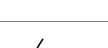
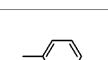
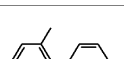
[표 33]

화학식	E	R1	R2	R3
I-449				
I-450				
I-451				
I-452				
I-453				
I-454				
I-455				
I-456				
I-457				
I-458				
I-459				
I-460				
I-461				
I-462				

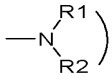
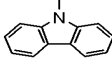
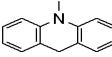
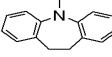
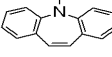
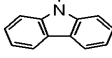
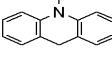
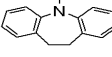
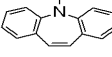
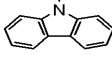
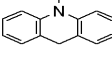
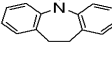
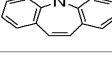
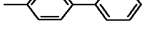
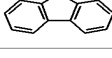
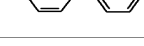
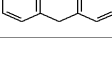
[표 34]

화학식	E	R1	R2	R3
I-463				
I-464				
I-465				
I-466				
I-467				
I-468				
I-469				
I-470				
I-471				
I-472				
I-473				
I-474				
I-475				
I-476				

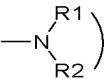
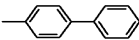
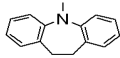
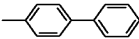
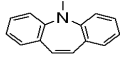
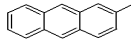
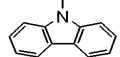
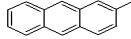
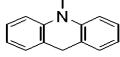
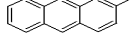
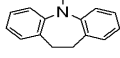
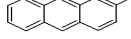
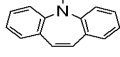
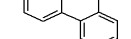
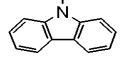
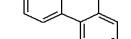
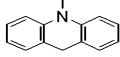
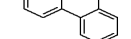
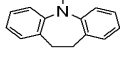
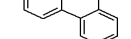
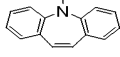
[표 35]

화학식	E	R1	R2	R3
I-477				
I-478				
I-479				
I-480				
I-481				
I-482				
I-483				
I-484				
I-485				
I-486				
I-487				
I-488				

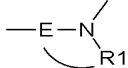
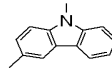
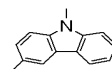
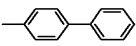
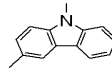
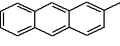
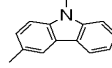
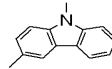
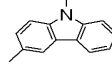
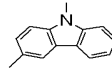
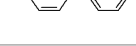
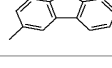
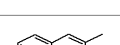
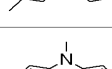
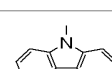
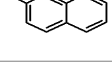
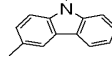
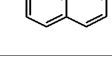
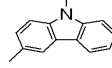
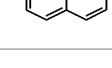
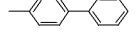
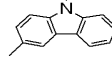
[표 36]

화 학 식	E	R3	
I-489			
I-490			
I-491			
I-492			
I-493			
I-494			
I-495			
I-496			
I-497			
I-498			
I-499			
I-500			
I-501			
I-502			

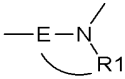
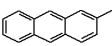
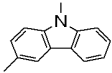
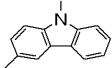
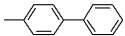
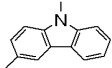
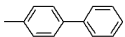
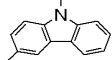
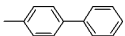
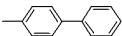
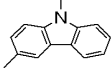
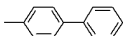
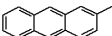
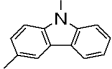
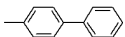
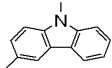
[표 37]

화학식	E	R3	
I-503			
I-504			
I-505			
I-506			
I-507			
I-508			
I-509			
I-510			
I-511			
I-512			

[표 38]

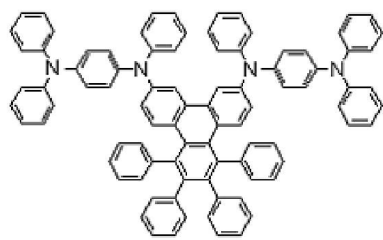
화학식	R2	R3	
I-513			
I-514			
I-515			
I-516			
I-517			
I-518			
I-519			
I-520			
I-521			
I-522			
I-523			
I-524			
I-525			

[표 39]

화학식	R2	R3	
I-526			
I-527			
I-528			
I-529			
I-530			
I-531			
I-532			

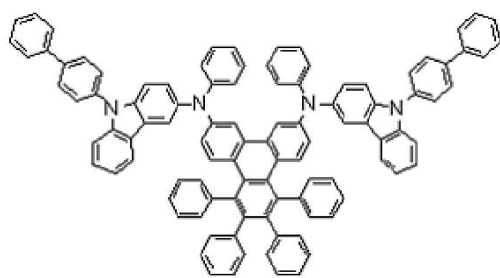
상기 표에서 설명하는 화학식을 구체적으로 표현하면 다음과 같다.

[화학식 I-1]



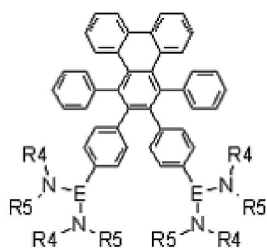
(E, R1, R2, R3가 각각 페닐기인 경우)

[화학식 I-528]



(E, R1, R3가 각각 페닐기이고, R2가 4-비페닐기인 경우)

[화학식 II-1]

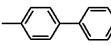
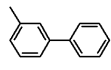
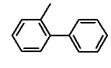
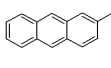
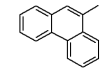
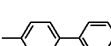
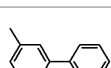
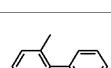


상기 화학식 II-1에서,

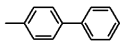
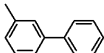
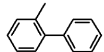
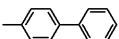
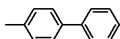
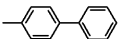
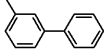
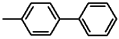
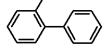
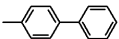
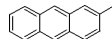
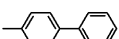
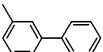
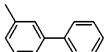
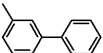
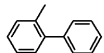
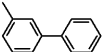
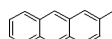
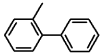
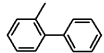
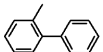
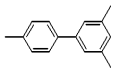
E는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R4 및 R5는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R4와 R5는 단일결합, 메틸렌기, 에틸렌기 또는 비닐기에 의하여 서로 연결될 수 있다.

상기 화학식 II-1의 구체적인 예는 하기의 표 40 내지 표 43에 표시되는 화합물을 포함한다.

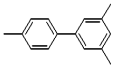
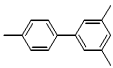
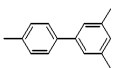
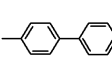
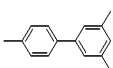
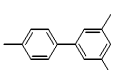
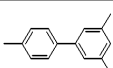
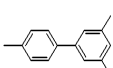
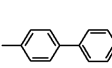
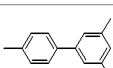
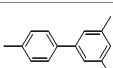
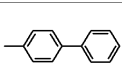
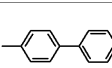
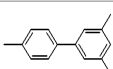
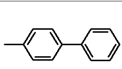
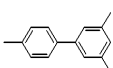
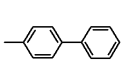
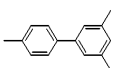
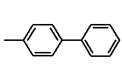
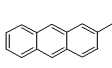
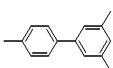
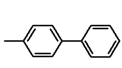
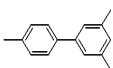
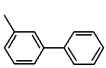
[표 40]

화학식	E	R4	R5
II-1-1			
II-1-2			
II-1-3			
II-1-4			
II-1-5			
II-1-6			
II-1-7			
II-1-8			
II-1-9			
II-1-10			
II-1-11			
II-1-12			
II-1-13			
II-1-14			

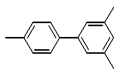
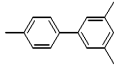
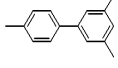
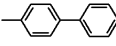
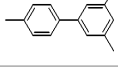
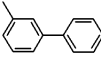
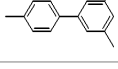
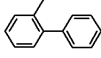
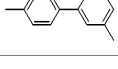
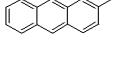
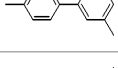
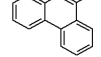
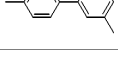
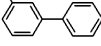
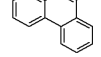
[표 41]

화학식	E	R4	R5
II-1-15			
II-1-16			
II-1-17			
II-1-18			
II-1-19			
II-1-20			
II-1-21			
II-1-22			
II-1-23			
II-1-24			
II-1-25			
II-1-26			
II-1-27			
II-1-28			

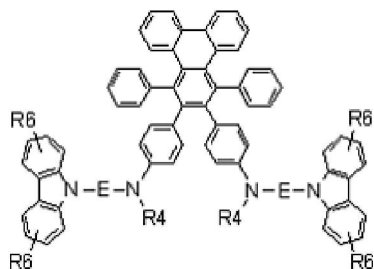
[표 42]

화학식	E	R4	R5
II-1-29			
II-1-30			
II-1-31			
II-1-32			
II-1-33			
II-1-34			
II-1-35			
II-1-36			
II-1-37			
II-1-38			
II-1-39			
II-1-40			
II-1-41			
II-1-42			

[표 43]

화학식	E	R4	R5
II-1-43			
II-1-44			
II-1-45			
II-1-46			
II-1-47			
II-1-48			
II-1-49			
II-1-50			

[화학식 II-2]

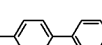
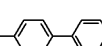


상기 화학식 II-2에서,

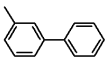
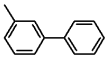
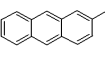
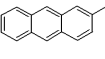
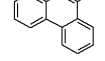
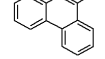
E는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R4는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R6는 수소원자, 알킬기, 알콕시기 또는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시한다.

상기 화학식 II-2의 구체적인 예는 하기의 표 44 내지 표 47에 표시되는 화합물을 포함한다.

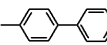
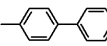
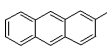
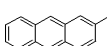
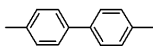
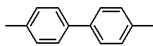
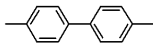
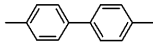
[표 44]

화학식	E	R4	R6
II-2-1			H
II-2-2			
II-2-3			CH ₃
II-2-4			OCH ₃
II-2-5			t-Bu
II-2-6			H
II-2-7			
II-2-8			CH ₃
II-2-9			OCH ₃
II-2-10			H
II-2-11			
II-2-12			CH ₃
II-2-13			H
II-2-14			

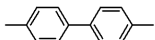
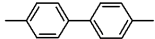
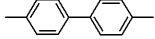
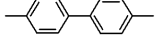
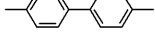
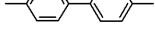
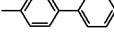
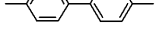
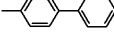
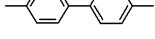
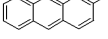
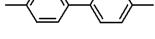
[표 45]

화학식	E	R4	R6
II-2-15			H
II-2-16			
II-2-17			H
II-2-18			
II-2-19			H
II-2-20			
II-2-21			H
II-2-22			
II-2-23			CH ₃
II-2-24			OCH ₃
II-2-25			t-Bu
II-2-26			H
II-2-27			
II-2-28			CH ₃

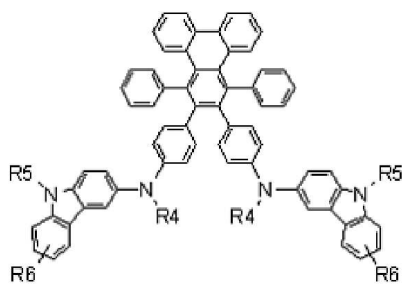
[표 46]

화학식	E	R4	R6
II-2-29			OCH ₃
II-2-30			H
II-2-31			
II-2-32			CH ₃
II-2-33			H
II-2-34			
II-2-35			H
II-2-36			
II-2-37			H
II-2-38			
II-2-39			H
II-2-40			
II-2-41			CH ₃
II-2-42			OCH ₃

[표 47]

화학식	E	R4	R6
II-2-43			H
II-2-44			
II-2-45			CH ₃
II-2-46			H
II-2-47			
II-2-48			H
II-2-49			
II-2-50			H
II-2-51			H
II-2-52			H
II-2-53			
II-2-54			H
II-2-55			
II-2-56			H

[화학식 II-3]

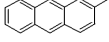


상기 화학식 II-3에서,

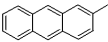
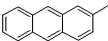
R4 및 R5는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R6는 수소원자, 알킬기, 알콕시기 또는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시한다.

상기 화학식 II-3의 구체적인 예는 하기의 표 48 내지 표 50에 표시되는 화합물을 포함한다.

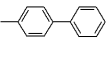
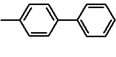
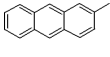
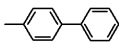
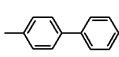
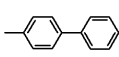
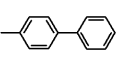
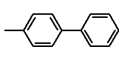
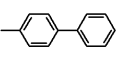
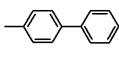
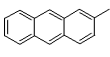
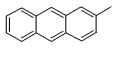
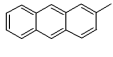
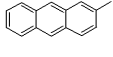
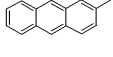
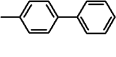
[표 48]

화학식	R4	R5	R6
II-3-1			H
II-3-2			
II-3-3			CH ₃
II-3-4			OCH ₃
II-3-5			t-Bu
II-3-6			H
II-3-7			
II-3-8			CH ₃
II-3-9			OCH ₃
II-3-10			H
II-3-11			
II-3-12			CH ₃
II-3-13			H
II-3-14			
II-3-15			H

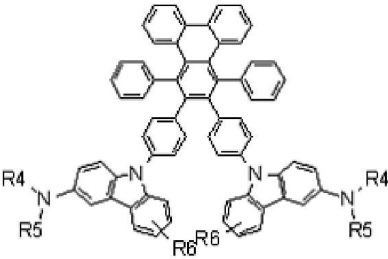
[표 49]

화학식	R4	R5	R6
II-3-16			H
II-3-17			
II-3-18			H
II-3-19			
II-3-20			H
II-3-21			
II-3-22			H
II-3-23			
II-3-24			CH ₃
II-3-25			OCH ₃
II-3-26			t-Bu
II-3-27			H
II-3-28			
II-3-29			CH ₃

[표 50]

화학식	R4	R5	R6
II-3-30			H
II-3-31			
II-3-32			H
II-3-33			
II-3-34			H
II-3-35			H
II-3-36			H
II-3-37			
II-3-38			H
II-3-39			
II-3-40			H
II-3-41			H
II-3-42			
II-3-43			CH ₃
II-3-44			

[화학식 II-4]



상기 화학식 II-4에서,

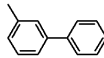
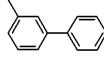
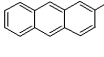
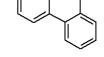
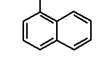
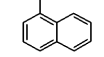
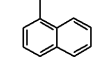
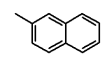
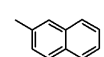
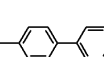
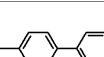
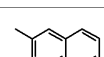
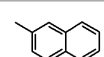
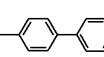
R4 및 R5는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R4와 R5는 단일결합, 메틸렌기, 에틸렌기 또는 비닐기에 의하여 서로 연결될 수 있다. R6는 수소원자, 알킬기, 알콕시기 또는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시한다.

상기 화학식 II-4의 구체적인 예는 하기의 표 51 내지 표 53에 표시되는 화합물을 포함한다.

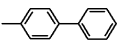
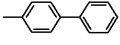
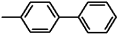
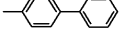
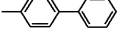
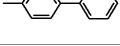
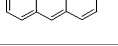
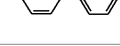
[표 51]

화학식	R4	R5	R6
II-4-1			H
II-4-2			
II-4-3			CH ₃
II-4-4			OCH ₃
II-4-5			t-Bu
II-4-6			H
II-4-7			
II-4-8			CH ₃
II-4-9			OCH ₃
II-4-10			H
II-4-11			
II-4-12			CH ₃
II-4-13			H
II-4-14			

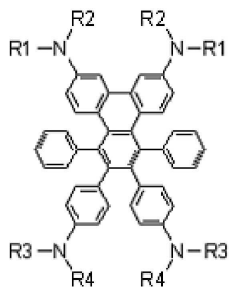
[표 52]

화학식	R4	R5	R6
II-4-15			H
II-4-16			
II-4-17			H
II-4-18			H
II-4-19			H
II-4-20			
II-4-21			CH ₃
II-4-22			H
II-4-23			
II-4-24			H
II-4-25			
II-4-26			H
II-4-27			
II-4-28			H

[표 53]

화학식	R4	R5	R6
II-4-29			
II-4-30			H
II-4-31			
II-4-32			H
II-4-33			H

[화학식 III]

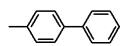
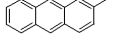
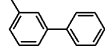
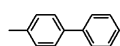
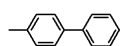


상기 화학식 III에서,

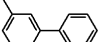
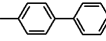
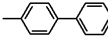
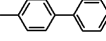
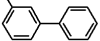
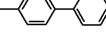
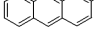
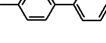
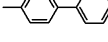
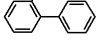
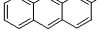
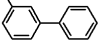
R1 내지 R4는 치환되거나 비치환된 6 내지 14개의 핵 탄소 원자를 갖는 아릴기를 표시하고, R1과 R2 는 서로, 또는 R3와 R4는 서로 단일결합, 메틸렌기, 에틸렌기 또는 비닐기에 의하여 연결될 수 있다.

상기 화학식 III의 구체적인 예는 하기의 표 54 내지 표 72에 표시되는 화합물을 포함한다.

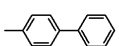
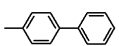
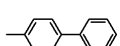
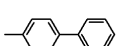
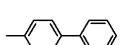
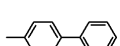
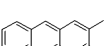
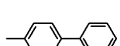
[표 54]

화학식	R1	R2	R3	R4
III-1				
III-2				
III-3				
III-4				
III-5				
III-6				
III-7				
III-8				
III-9				
III-10				
III-11				
III-12				
III-13				
III-14				

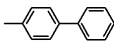
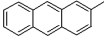
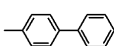
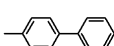
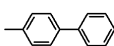
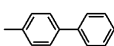
[표 55]

화학식	R1	R2	R3	R4
III-15				
III-16				
III-17				
III-18				
III-19				
III-20				
III-21				
III-22				
III-23				
III-24				
III-25				
III-26				
III-27				
III-28				

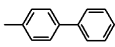
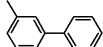
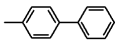
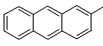
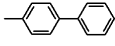
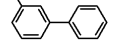
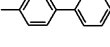
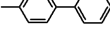
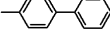
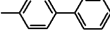
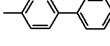
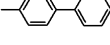
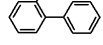
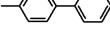
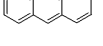
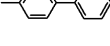
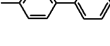
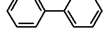
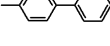
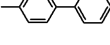
[표 56]

화학식	R1	R2	R3	R4
III-29				
III-30				
III-31				
III-32				
III-33				
III-34				
III-35				
III-36				
III-37				
III-38				
III-39				
III-40				
III-41				
III-42				

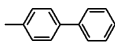
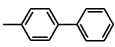
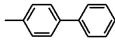
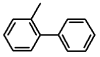
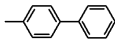
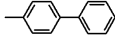
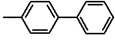
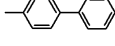
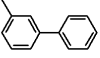
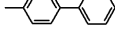
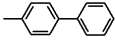
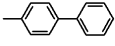
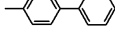
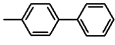
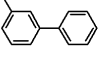
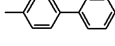
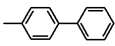
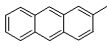
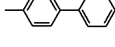
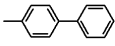
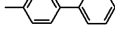
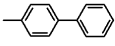
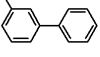
[표 57]

화학식	R1	R2	R3	R4
III-43				
III-44				
III-45				
III-46				
III-47				
III-48				
III-49				
III-50				
III-51				
III-52				
III-53				
III-54				
III-55				
III-56				

[표 58]

화학식	R1	R2	R3	R4
III-57				
III-58				
III-59				
III-60				
III-61				
III-62				
III-63				
III-64				
III-65				
III-66				
III-67				
III-68				
III-69				
III-70				

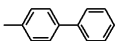
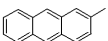
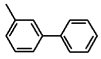
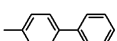
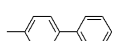
[표 59]

화학식	R1	R2	R3	R4
III-71				
III-72				
III-73				
III-74				
III-75				
III-76				
III-77				
III-78				
III-79				
III-80				
III-81				
III-82				
III-83				
III-84				

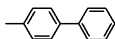
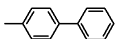
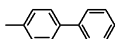
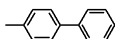
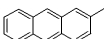
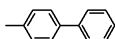
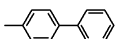
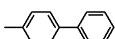
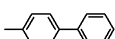
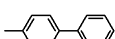
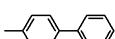
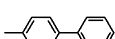
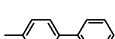
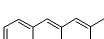
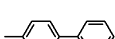
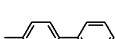
[표 60]

화학식	R1	R2	R3	R4
III-85				
III-86				
III-87				
III-88				
III-89				
III-90				
III-91				
III-92				
III-93				
III-94				
III-95				
III-96				
III-97				
III-98				

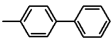
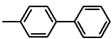
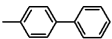
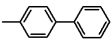
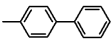
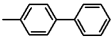
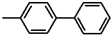
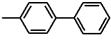
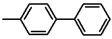
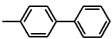
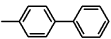
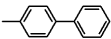
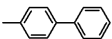
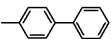
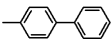
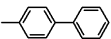
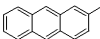
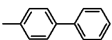
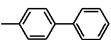
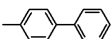
[표 61]

화학식	R1	R2	R3	R4
III-99				
III-100				
III-101				
III-102				
III-103				
III-104				
III-105				
III-106				
III-107				
III-108				
III-109				
III-110				
III-111				
III-112				

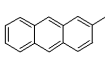
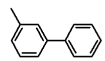
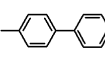
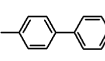
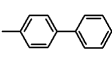
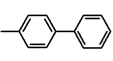
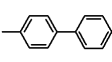
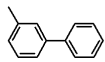
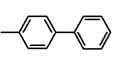
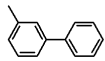
[표 62]

화학식	R1	R2	R3	R4
III-113				
III-114				
III-115				
III-116				
III-117				
III-118				
III-119				
III-120				
III-121				
III-122				
III-123				
III-124				
III-125				
III-126				

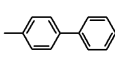
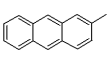
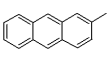
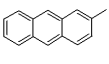
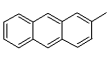
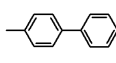
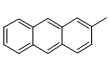
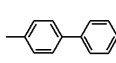
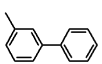
[표 63]

화학식	R1	R2	R3	R4
III-127				
III-128				
III-129				
III-130				
III-131				
III-132				
III-133				
III-134				
III-135				
III-136				
III-137				
III-138				
III-139				
III-140				

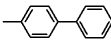
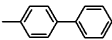
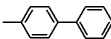
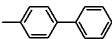
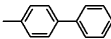
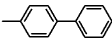
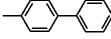
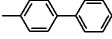
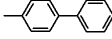
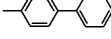
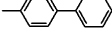
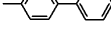
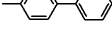
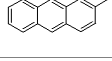
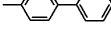
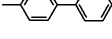
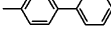
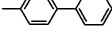
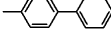
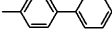
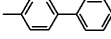
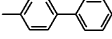
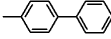
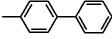
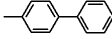
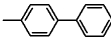
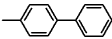
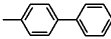
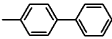
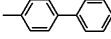
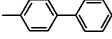
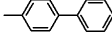
[표 64]

화학식	R1	R2	R3	R4
III-141				
III-142				
III-143				
III-144				
III-145				
III-146				
III-147				
III-148				
III-149				
III-150				
III-151				
III-152				
III-153				
III-154				

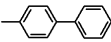
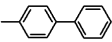
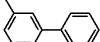
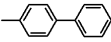
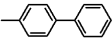
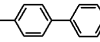
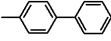
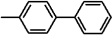
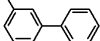
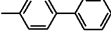
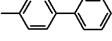
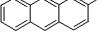
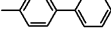
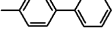
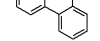
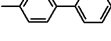
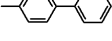
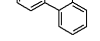
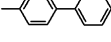
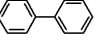
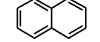
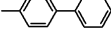
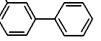
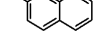
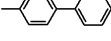
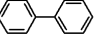
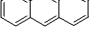
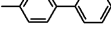
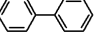
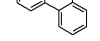
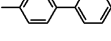
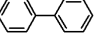
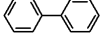
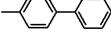
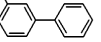
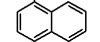
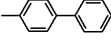
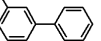
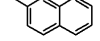
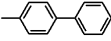
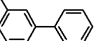
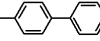
[표 65]

화학식	R1	R2	R3	R4
III-155				
III-156				
III-157				
III-158				
III-159				
III-160				
III-161				
III-162				
III-163				
III-164				
III-165				
III-166				
III-167				
III-168				

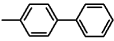
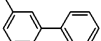
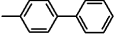
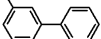
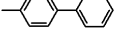
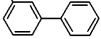
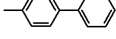
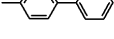
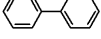
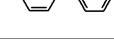
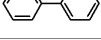
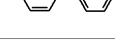
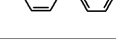
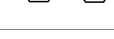
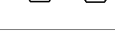
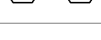
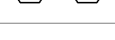
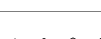
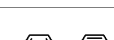
[표 66]

화학식	R1	R2	R3	R4
III-169				
III-170				
III-171				
III-172				
III-173				
III-174				
III-175				
III-176				
III-177				
III-178				
III-179				
III-180				
III-181				
III-182				

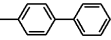
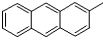
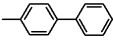
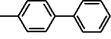
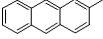
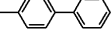
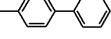
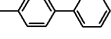
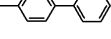
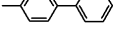
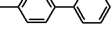
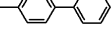
[표 67]

화학식	R1	R2	R3	R4
III-183				
III-184				
III-185				
III-186				
III-187				
III-188				
III-189				
III-190				
III-191				
III-192				
III-193				
III-194				
III-195				
III-196				

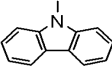
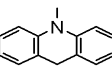
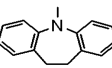
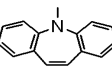
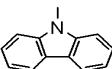
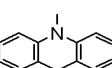
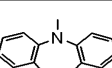
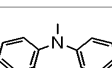
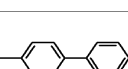
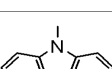
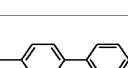
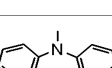
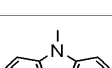
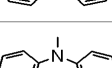
[표 68]

화학식	R1	R2	R3	R4
III-197				
III-198				
III-199				
III-200				
III-201				
III-202				
III-203				
III-204				
III-205				
III-206				
III-207				
III-208				
III-209				
III-210				

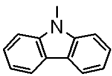
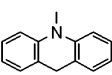
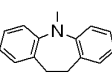
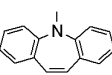
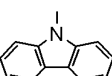
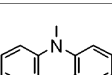
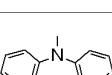
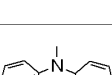
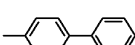
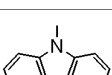
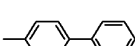
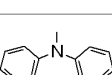
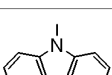
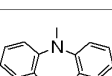
[표 69]

화학식	R1	R2	R3	R4
III-211				
III-212				
III-213				
III-214				
III-215				
III-216				
III-217				
III-218				

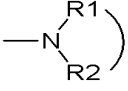
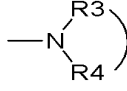
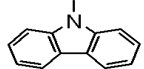
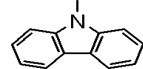
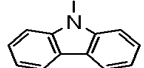
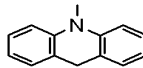
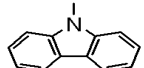
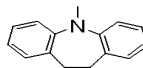
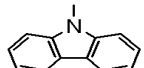
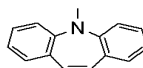
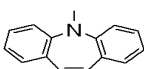
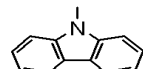
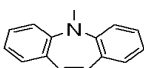
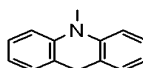
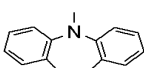
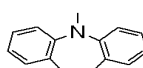
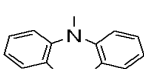
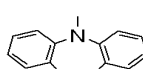
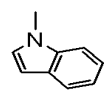
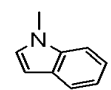
[표 70]

화학식	R1	R2	
III-219			
III-220			
III-221			
III-222			
III-223			
III-224			
III-225			
III-226			
III-227			
III-228			
III-229			
III-230			

[표 71]

화학식	R3	R4	$\begin{array}{c} \text{R1} \\ \text{---N} \\ \text{R2} \end{array}$
III-231			
III-232			
III-233			
III-234			
III-235			
III-236			
III-237			
III-238			
III-239			
III-240			
III-241			
III-242			

[표 72]

화학식		
III-243		
III-244		
III-245		
III-246		
III-247		
III-248		
III-249		
III-250		
III-251		

본 발명의 상기 화학식 I, 화학식 II 및 화학식 III로 표시되는 트리페닐렌 유도체는 상기와 같은 방법으로 제조가 가능하며, 이를 유기 발광 다이오드의 정공전달물질로 사용하면 고 발광 효율을 얻을 수 있고 유리전이 온도가 높기 때문에 우수한 내구성능을 갖는 소자를 제작할 수 있다. 여기에서 정공전달물질은 정공주입층, 정공수송층은 물론 때로는 발광층에 사용하는 재료를 말한다. 또한 상기 화학식 I, 화학식 II 및 화학식 III로 표시되는 화합물은 발광층에 사용되는 발광 재료의 발광색상 즉, 청색, 녹색 또는 적색에 관계없이 모두 정공전달물질로 사용이 가능하므로 총 천연색의 표시장치를 제작하는데 효과적으로 사용되어 내구성능이 우수한 고성능의 총 천연색 표시장치 제작을 가능하게 한다.

상기와 같은 방법으로 합성된 본 발명의 상기 화학식 I, 화학식 II 및 화학식 III으로 표시되는 트리페닐렌 유도체들은 고순도를 요구하는 유기 발광 다이오드의 특성상 재결정과 승화법을 이용하여 정제를 실시하였다. 합성에 대한 자세한 설명은 아래의 합성예에서 기술하였다. 이러한 정제과정을 거쳐 제조된 본 발명에 따른 화합물의 물성 및 광화학적 특성을 측정하였고, 그 중 대표적으로 화학식 I-1, 화학식 II-1-1, 화학식 II-2-6, 화학식 II-3-22, 화학식 III-43의 트리페닐렌 유도체에 대한 광화학적 특성 결과를 설명한다.

먼저, 본 발명에 따른 트리페닐렌 유도체의 광화학적 특성을 확인하기 위하여 상기 화학식 II-1-1, 화학식 II-3-22 와 화학식 III-43의 화합물에 대해 각각의 UV 최대 흡수 파장(λ_{max})을 측정된 결과가 각각 326nm, 312nm, 351nm이었고, 이 최대 흡수파장을 여기파장으로 하여, 상기 화학식 II-1-1, 화학식 II-3-22 와 화학식 III-43의 화합물 각각에 대해 광 발광(PL) 스펙트럼을 측정하였고, 각각의 최대피크는 413nm, 461nm, 439nm에서 측정되었다. 도 1에서는 상기 화학식 II-1-1의 화합물에 대한 UV/Vis. 및 형광 스펙트럼 측정 결과를, 도 2에서는 상기 화학식 II-3-22의 화합물에 대한 결과를, 도 3에서는 상기 화학식 III-43의 화합물에 대한 결과를 나타내었으며, 이로부터 본 발명에 따른 상기 화합물은 청색 내지 청록색으로 발광을 하고 있음을 알 수 있다.

또한, 각각의 재료에 대하여 열적 안정성을 확인하기 위하여 시차주사열량계(DSC)와 열중량분석기(TGA)를 이용하여 측정하였다. 시차주사열량계 측정 결과, 화학식 I-1 화합물과 화학식 II-2-6의 녹는점은 각각 218.9℃와 371℃이고, 화학식 I-1, 화학식 II-1-1, 화학식 II-2-6, 화학식 II-3-22의 화합물에 대한 유리전이온도는 각각 170.3℃, 181℃, 202℃와 213℃로 모두 170℃ 이상에서 관측되었다. 따라서 종래의 정공전달물질로 사용되었던 것 중에서 비교적 높은 유리전이온도를 갖고 있는 2-TNATA[4,4',4''-트리스(N-(나프틸렌-2-일)-N-페닐아미노)-트리페닐아민]보다도 현저하게 높은 유리전이온도를 갖고 있으므로 열적안정성이 우수하여 이를 소자에 적용하면 긴 수명의 소자 제작이 가능하다. 화학식 I-1, 화학식 II-1-1, 화학식 II-2-6과 화학식 II-3-22의 화합물에 대한 시차주사열량계 측정 결과는 도 4 내지 도 7에 나타내었다.

다음으로, 열중량분석기(TGA) 측정 결과, 본 발명에 의한 상기 화학식에 따른 화합물의 1% 중량 손실은 모두 500℃ 이상 범위에서 관측되었다. 따라서, 본 발명은 고온에서도 열적 안정성을 갖고 있으므로 소자 제작 과정에서 진공 증착 시킬 때 분해 될 우려가 없어서 효과적인 소자의 제작이 가능하다. 상기 화학식 I-1, 화학식 II-2-6, 화학식 II-3-22와 화학식 III-43의 화합물에 대한 열중량분석기 측정 결과는 도 8 내지 도 11에 나타내었다.

한편, 위와 같은 본 발명에 따른 정공전달물질을 이용하여 아래의 실시예와 같은 방법으로 유기 발광 다이오드를 제작하였고, 이렇게 제작된 본 발명의 바람직한 하나의 예로써 유기 발광 다이오드의 구조는 도 12에 나타난 바와 같다. 즉, 투명기판 위에 음극과 양극이 존재하고, 상기 음극과 양극 사이에 발광층, 정공수송층, 정공주입층이 적층될 수 있으며, 본 발명에 따른 트리페닐렌 유도체는 상기 발광층, 정공수송층 또는 정공주입층의 재료로 사용될 수 있는 것이다.

더불어서, 상술한 정제과정 및 제조방법을 거쳐서 본 발명에 따른 화합물로 제작된 유기 발광 다이오드의 물성 및 전기 발광 특성을 측정하였고, 이를 종래 기술로써 2-TNATA를 사용한 소자의 발광 특성과 비교하였다. 본 발명에 따른 화합물을 정공전달물질로 사용한 경우, 증착 두께에 관계없이 비교물질인 2-TNATA보다 전류 밀도, 휘도, 최고 휘도 그리고 발광 효율 모든 면에서 아주 우수한 발광 특성을 나타내었다. 구체적으로, 도 13의 전기발광(EL) 스펙트럼에 나타난 바와 같이 본 발명에 따라 화학식 I-1(실시예 1), 화학식 I-161(실시예 3) 그리고 화학식 III-43(실시예 10)의 화합물에 의한 EL 피크는 종래기술에 따른 2-TNATA(비교예 1)보다 높은 강도를 보이고 있다.

이하, 본 발명을 합성예, 실시예와 비교예를 참조하여 더욱 상세히 설명한다. 본 발명은 하기의 합성예, 실시예와 비교예에 의하여 보다 더 잘 이해될 수 있으며, 하기의 합성예와 실시예는 본 발명을 예시하기 위한 것이며 첨부된 특허청구범위에 의하여 한정되는 보호범위를 제한하고자 하는 것은 아니다.

[합성예 1]

3,6-디브로모페난트렌퀴논(화학식 I-B)의 제조

1000-ml, 4구 둥근바닥플라스크에 페난트렌퀴논 45.0g(0.216mol), 니트로벤젠 400ml와 벤조일퍼록사이드 0.52g (2.16mmol)을 투입하고 교반시킨 후 브롬 24.36ml(0.475mol)를 서서히 투입하였다. 이 반응액에 200W 텅스텐 램프로 빛을 조사하여 광반응을 3시간 동안 실시하였다. 반응액을 실온으로 냉각시킨 후 진공여과하고 메탄올로 세척하여 얻어진 고체를 분리하여 메탄올에서 교반시켰다. 다시 진공여과하여 분리된 고체를 진공건조하여 목적화합물 64.0g(수율 81%)을 얻었다.

$^1\text{H NMR}$ (DMSO- d_6): δ 8.67(d, J = 1.4Hz, 2H), 7.93(d, J = 8.3Hz, 2H), 7.76(dd, J = 8.3, 1.5Hz, 2H).

MALDI-TOF mass($M+H^+$) : $\text{C}_{14}\text{H}_6\text{Br}_2\text{O}_2$: 364.8902(364.8735)

[합성예 2]

6,9-디브로모-1,3-디페닐-사이클로펜타[1]페난트렌-2-온(화학식 I-C)의 제조

1000-ml, 4구 둥근바닥플라스크에 3,6-디브로모페난트렌퀴논 45.0g(0.123mol), 1,3-디페닐아세톤 28.44g(0.135mol)과 에탄올 630ml를 투입하고 교반시켰다. 이 용액에 수산화칼륨 41.4g(0.738mol)을 투입하고 50℃에서 1시간 동안 교반하였다. 반응액을 실온으로 냉각 후 생성된 고체를 여과하고 메탄올로 충분히 세척하였다. 얻어진 고체를 진공건조하여 목적화합물 47.8g(수율 72%)을 얻었다.

^1H NMR (CDCl_3): δ 7.87(d, J = 1.9Hz, 2H), 7.44~7.35(m, 12H), 7.10(dd, J = 8.6, 1.9Hz, 2H).

MALDI-TOF mass($\text{M} + \text{H}^+$) : $\text{C}_{29}\text{H}_{16}\text{Br}_2\text{O}$: 538.9752(538.9568)

[합성예 3]

7,10-디브로모-1,2,3,4-테트라페닐-트리페닐렌(화학식 I-D)의 제조

500-ml, 3구 둥근바닥플라스크에 질소 분위기 하에서 6,9-디브로모-1,3-디페닐-사이클로펜타[1]페난트렌-2-온(화학식 I-C) 30.0g(0.0555mol)을 *o*-자일렌 240ml로 희석시키고 디페닐아세틸렌 9.90g(0.0555mol)을 투입하였다. 이 혼합액을 16시간 동안 환류시키고 실온으로 냉각한 다음 과량의 메탄올에 투입하여 고체를 석출시켰다. 석출된 고체를 여과하고 메탄올로 세척한 다음 진공건조하여 목적화합물 30.1g(수율 78.5%)을 얻었다.

^1H NMR ($\text{DMSO}-d_6$): δ 8.83(d, J = 1.8Hz, 2H), 7.38(d, J = 9.1Hz, 2H), 7.20(dd, J = 9.0, 1.7Hz, 2H), 7.15~7.10(m, 6H), 7.02(d, J = 6.5Hz, 4H), 6.90~6.88(m, 6H), 6.72(d, J = 4.9Hz, 4H).

MALDI-TOF mass($\text{M} + \text{H}^+$) : $\text{C}_{42}\text{H}_{26}\text{Br}_2$: 689.2538(689.0401)

[합성예 4]

5,6,7,8,*N,N'*-헥사페닐-트리페닐렌-2,11-디아민의 제조

본 합성예는 상기 화학식 I-F로 표시되는 화학식에서 R3가 페닐기인 경우이다.

500-ml, 3구 둥근바닥플라스크를 완전히 건조시킨 후 질소분위기 하에서 7,10-디브로모-1,2,3,4-테트라페닐-트리페닐렌(화학식 I-D) 46.0g(66.6mmol)을 투입하고 무수 톨루엔 370ml로 용해시켰다. 이 용액에 아닐린(화학식 I-E, R3 = 페닐) 14.89g(160mmol), 트리(*o*-톨릴)포스핀 0.203g(0.666mmol), 트리스(디벤질리덴아세톤)디팔라디움(0) 0.305g(0.333mmol) 및 소듐 *t*-부톡사이드 16g(167mmol)을 투입하였다. 이 혼합액을 6시간 동안 환류시키고 실온으로 냉각한 다음 톨루엔을 농축하였다. 이 농축액에 아세톤을 투입하였다. 생성된 고체를 여과하고 아세톤으로 세척하여 조생성물을 얻었다. 얻어진 조생성물을 에틸 아세테이트와 헥산을 이용하여 재결정화하고 진공건조하여 목적화합물 39.5g(수율 83%)을 얻었다.

^1H NMR ($\text{DMSO}-d_6$): δ 8.43(s, 2H), 7.95(s, 2H), 7.29~7.26(m, 6H), 7.17(d, J = 8.0Hz, 4H), 7.11(d, J = 1.8Hz, 6H), 7.04~7.03(m, 4H), 6.90(t, J = 7.3Hz, 2H), 6.87(s, 6H), 6.71~6.63(m, 6H).

MALDI-TOF mass($\text{M} + \text{H}^+$) : $\text{C}_{54}\text{H}_{38}\text{N}_2$: 715.9147(715.8930)

[합성예 5]

N,N'-디-나프탈렌-1-일-5,6,7,8-테트라페닐-트리페닐렌-2,11-디아민의 제조

본 합성예는 상기 화학식 I-F로 표시되는 화학식에서 R3가 1-나프틸기인 경우이다.

500-ml, 3구 둥근바닥플라스크를 완전히 건조시킨 후 질소분위기 하에서 7,10-디브로모-1,2,3,4-테트라페닐-트리페닐렌(화학식 I-D) 17g(24.6mmol)을 투입하고 무수 톨루엔 160ml로 용해시켰다. 이 용액에 1-아미노나프탈렌(화학식 I-E, R3 = 1-나프틸) 8.46g(59.0mmol), 트리(*o*-톨릴)포스핀 0.748mg(2.46mmol), 트리스(디벤질리덴아세톤)디팔라디움(0) 112mg(0.124mmol) 및 소듐 *t*-부톡사이드 5.92g(61.6mmol)을 투입하였다. 이 혼합액을 7시간 동안 환류시키고 실온으로 냉각한 다음 메탄올 800ml를 투입하였다. 생성된 고체를 여과하고 메탄올로 세척하여 조생성물을 얻었다. 얻어진 조생성물을 에틸 아세테이트와 헥산을 이용하여 재결정화하고 진공건조하여 목적화합물 16.3g(수율 81%)을 얻었다.

^1H NMR (DMSO- d_6): δ 8.44(s, 2H), 8.11(d, J = 8.3Hz, 2H), 7.89(d, J = 7.8Hz, 2H), 7.83(s, 2H), 7.58(t, J = 4.5Hz, 2H), 7.51~7.39(m, 10H), 7.23(d, J = 9.1Hz, 2H), 7.20~7.04(m, 10H), 6.87(d, J = 3.1Hz, 6H), 6.71~6.67(m, 4H).

MALDI-TOF mass($M+H^+$) : $\text{C}_{62}\text{H}_{42}\text{N}_2$: 815.4878(815.3348)

[합성예 6]

4-브로모트리페닐아민의 제조

본 합성예는 상기 화학식 I-G로 표시되는 일반식에서 R1, R2, E가 페닐기이고 할로젠 원자 X_1 이 브롬 원자인 경우이다.

5000-ml, 4구 둥근바닥플라스크를 완전히 건조시킨 후 질소분위기 하에서 디페닐아민 300g(1.77mol)을 투입하고 무수 톨루엔 3000ml로 용해시켰다. 이 용액에 1-브로모-4-아이오도벤젠 651g(2.30mol), 트리(*o*-톨릴)포스핀 10.77g(35.4mmol), 트리스(디벤질리덴아세톤)디팔라디움(0) 16.2g(17.7mmol) 및 소듐 *t*-부톡시드 255.7g(2.66mol)을 투입하였다. 이 혼합액을 1일 동안 환류시킨 후 40℃로 냉각하고 톨루엔 500ml와 증류수 1000ml를 투입하고 목적화합물을 추출하였다. 분리된 유기층을 건조하고 감압 하에서 톨루엔 잔량이 약 500ml가 되도록 농축한 다음 3000ml의 메탄올을 가하여 고체를 생성시켰다. 생성된 고체를 여과 후 메탄올로 세척하고 진공건조하여 목적화합물 441.9g(수율 77%)을 얻었다.

^1H NMR (CDCl_3): δ 7.33(d, J = 8.9Hz, 2H), 7.28~7.25(m, 4H), 7.08(d, J = 7.6Hz, 4H), 7.05(t, J = 7.4Hz, 2H), 6.95(d, J = 8.9Hz, 2H).

MALDI-TOF mass($M+H^+$) : $\text{C}_{18}\text{H}_{14}\text{BrN}$: 323.9308(324.0310)

[합성예 7]

N,N,N'-트리페닐-벤젠-1,4-디아민의 제조

본 합성예는 상기 화학식 I-H로 표시되는 일반식에서 R1, R2, R3, E가 각각 페닐기인 경우이다.

500-ml, 3구 둥근바닥플라스크를 완전히 건조시킨 후 질소분위기 하에서 앞에서 제조된 4-브로모트리페닐아민 20g(61.7mmol)을 투입하고 무수 톨루엔 170ml로 용해시켰다. 이 용액에 아닐린 6.74ml(74.0mmol), 트리(*o*-톨릴)포스핀 0.374mg(1.23mmol), 트리스(디벤질리덴아세톤)디팔라디움(0) 0.565g(0.617mmol) 및 소듐 *t*-부톡시드 7.41g(77.1mmol)을 투입하였다. 이 혼합액을 65℃에서 1시간 동안 교반시키고 실온으로 냉각한 다음 셀라이트를 통과시켜 진공 여과하고 여액에 톨루엔 150ml와 증류수 150ml를 투입하여 추출하였다. 유기층을 분리하여 건조, 농축하여 생성된 조질 결정체를 에틸 아세테이트와 헥산을 이용하여 재결정화하고 진공건조하여 목적화합물 14.1g(수율 68%)을 얻었다.

^1H NMR (DMSO- d_6): δ 8.14(s, NH, 1H), 7.26~7.20(m, 6H), 7.07~7.04(m, 4H), 6.98~6.93(m, 8H), 6.80(t, J = 7.2Hz, 1H).

MALDI-TOF mass($M+H^+$) : $\text{C}_{24}\text{H}_{20}\text{N}_2$: 337.2194(337.1626)

[합성예 8]

N,N-디페닐-N'-(1-나프틸)벤젠-1,4-디아민의 제조

본 합성예는 상기 화학식 I-H로 표시되는 일반식에서 R1, R2, E는 페닐기이고 R3는 1-나프틸기인 경우이다.

1000-ml, 3구 둥근바닥플라스크를 완전히 건조시킨 후 질소분위기 하에서 앞에서 제조된 4-브로모트리페닐아민 50g(0.154mol)을 투입하고 무수 톨루엔 400ml로 용해시켰다. 이 용액에 1-아미노나프탈렌 26.5g(0.185mol), 트리(*t*-부

틸)포스핀(10%, 헥산 용액) 6.24g(30.8mmol), 트리스(디벤질리텐아세톤)디팔라디움(0) 1.41g (1.5mmol) 및 소듐 t-부톡시드 35.6g(0.370mol)을 투입하였다. 이 혼합액을 75℃에서 1시간 동안 교반시키고 실온으로 냉각한 다음 셀라이트를 통과시켜 진공 여과하고 여액에 톨루엔 300ml와 증류수 300ml를 투입하여 추출하였다. 유기층을 분리하여 건조, 농축하여 생성된 조질 결정을 에틸 아세테이트와 헥산을 이용하여 재결정화하고 진공건조하여 목적화합물 45.3g(수율 76%)을 얻었다.

^1H NMR (DMSO- d_6): δ 8.24(s, NH, 1H), 8.22~8.20(m, 1H), 7.90~7.88(m, 1H), 7.54~7.49(m, 3H), 7.40(t, J =6.4Hz, 1H), 7.32(d, J = 6.2Hz, 1H), 7.27(t, J = 6.8Hz, 4H), 7.09(d, J = 7.3Hz, 2H), 7.00~6.95(m, 8H).

MALDI-TOF mass($M+H^+$) : C₂₈H₂₂N₂: 387.2134(387.1783)

[합성예 9]

화학식 I-1의 제조

본 합성예는 위에서 제조된 7,10-디브로모-1,2,3,4-테트라페닐-트리페닐렌(화학식 I-D)에, 디아민류로 아민화 반응을 유도하여, 본 발명에 따라 화학식 I로 표시되는 트리페닐렌 유도체의 바람직한 실시형태 중 하나로써 화학식 I-1을 제조하는 일 합성예에 관한 것이다. 본 합성예에서 아민화 반응의 조건으로는 구리촉매를 이용한 울만반응을 이용하였다.

250-ml, 3구 둥근바닥플라스크에 앞에서 제조된 7,10-디브로모-1,2,3,4-테트라페닐-트리페닐렌 30.0g(0.0434mol)에, 역시 앞에서 제조한 N,N,N'-트리페닐-벤젠-1,4-디아민 32.2g(0.0956mol)과, 포타시움 카보네이트 18.02g(0.130mol) 그리고 구리 분말 0.414g(6.5mmol)을 투입한다. 반응 용기를 가열하여 220℃~230℃에서 20시간 동안 교반 후 반응액이 굳지 않도록 적당량의 N,N-디메틸포름아마이드를 투입하면서 60℃로 반응액을 냉각시켰다. 현탁액에 테트라하이드로퓨란을 투입하고 여과하여 불용성 물질을 제거시켰다. 여과액을 적당히 농축하고 과량의 메탄올을 투입하여 목적화합물을 고체로 석출시켰다. 얻어진 고체를 여과하고 증류수와 메탄올로 차례로 세척한 후 진공건조하여 목적화합물 46.4g(수율 89%)을 얻었다.

^1H NMR (DMSO- d_6): δ 7.47(d, J = 2.1Hz, 2H), 7.29~7.22(m, 14H), 7.07(d, J = 3.0Hz, 6H), 7.02~6.98(m, 22H), 6.90(dd, J = 19.3, 8.9Hz, 8H), 6.85~6.84(m, 6H), 6.67(t, J = 3.6Hz, 4H), 6.54(dd, J = 9.2, 1.9Hz, 2H).

MALDI-TOF mass($M+H^+$) : C₉₀H₆₄N₄: 1201.5563(1201.5131)

EA : C, 89.8741%; H, 5.3812%; N, 4.7065%(C, 89.97%; H, 5.37%; N, 4.66%)

UV($\lambda_{\max}$) : 356nm PL : 502nm 녹는점(mp) : 219℃

유리전이온도(Tg, DSC에 의한 측정) : 170℃

1% 중량손실온도(TGA에 의한 측정) : 514℃

[합성예 10]

화학식 I-1의 다른 제조

본 합성예는 위의 합성예 9와 같이 화학식 I-1을 제조하는 일 실시예에 관한 것이지만, 본 합성예에서는 아민화 반응의 조건으로는 구리 촉매 대신 팔라디움 촉매를 사용하였다.

1000-ml, 4구 둥근바닥플라스크에 앞에서 제조된 7,10-디브로모-1,2,3,4-테트라페닐-트리페닐렌(화학식 I-D) 52.0g (0.0753mol), 역시 앞에서 제조한 N,N,N'-트리페닐-벤젠-1,4-디아민 55.7g(0.166mol), 트리스(디벤질리텐아세톤)디팔라디움(0) 0.345g (0.377mmol), 트리-(*o*-톨릴)포스핀 0.229g(0.753mmol), 소듐 t-부톡시드 17.4g(0.181mol) 그리고 톨루엔 420ml를 투입하였다. 반응액을 6시간 동안 환류 시킨 후 냉각하고 과량의 메탄올에 부어 고체를 석출시켰다. 얻어진 고체를 여과하고 진공건조하여 목적화합물 85g(수율 94%)을 얻었다.

[합성예 11]

화학식 I-1의 또 다른 제조

본 합성예는 반응 촉매로 상기 합성예 10에서 사용한 트리스(디벤질리덴아세톤)디팔라디움(0)과 트리-(*o*-톨릴)포스핀 대신에 팔라디움 아세테이트와 트리-(*t*-부틸)포스핀을 사용한 것을 제외하고는 합성예 10과 동일한 방법으로 제조하여 목적화합물 83.2g(수율 92%)을 얻었다.

[합성예 12]

화학식 I-1의 또 다른 제조

본 합성예는 위에서 제조된 5,6,7,8,*N,N'*-헥사페닐-트리페닐렌-2,11-디아민(화학식 I-F의 한 종류)과 4-브로모트리페닐아민(화학식 I-G의 한 종류)의 아민화 반응을 실시하여 화학식 I-1를 제조하는 일 실시예에 관한 것이다.

1000-ml, 4구 둥근바닥플라스크에 앞에서 제조된 5,6,7,8,*N,N'*-헥사페닐-트리페닐렌-2,11-디아민 39.40g (0.0552mol)에, 역시 앞에서 제조한 4-브로모트리페닐아민 39.4g(0.1215mol), 트리스(디벤질리덴아세톤)디팔라디움(0) 0.253g(0.276mmol), 트리-(*o*-톨릴)포스핀 0.168g(0.552mmol), 소듐 *t*-부톡사이드 12.7g(0.133mol) 그리고 톨루엔 350ml를 투입하였다. 반응액을 8시간 동안 환류 시킨 후 냉각하고 과량의 메탄올에 부어 고체를 석출시켰다. 얻어진 고체를 여과하고 진공건조하여 목적화합물 64.3g(수율 97%)을 얻었다.

[합성예 13]

화학식 I-2의 제조

본 합성예는 위에서 제조된 7,10-디브로모-1,2,3,4-테트라페닐-트리페닐렌(화학식 I-D)과 디아민류(화학식 I-H)로 아민화 반응을 유도하여, 본 발명에 따라 화학식 1로 표시되는 트리페닐렌 유도체의 바람직한 실시형태 중 하나로써 화학식 I-2를 제조하는 일 실시예에 관한 것이다. 본 합성예에서 아민화 반응의 조건으로는 구리촉매를 이용한 울만반응을 이용하였다.

250-ml, 3구 둥근바닥플라스크에 앞에서 제조된 7,10-디브로모-1,2,3,4-테트라페닐-트리페닐렌 20.0g(0.0290mol)에, 역시 앞에서 제조한 *N,N'*-디페닐-*N'*-(1-나프틸)벤젠-1,4-디아민(화학식 I-H의 한 종류) 24.6g(0.0637mol)과, 포타시움 카보네이트 12.0g(0.087mol) 그리고 구리 분말 0.276g(4.3mmol)을 투입한다. 반응 용기를 가열하여 220℃~230℃에서 26시간동안 교반 후 반응액이 굳지 않도록 적당량의 *N,N'*-디메틸포름아마이드를 투입하면서 60℃로 반응액을 냉각시켰다. 현탁액에 테트라하이드로퓨란을 투입하고 여과하여 불용성 물질을 제거시켰다. 여과액을 적당히 농축하고 과량의 메탄올을 투입하여 목적화합물을 고체로 석출시켰다. 얻어진 고체를 여과하고 증류수와 메탄올로 차례로 세척한 후 진공건조하여 목적화합물 131.3g(수율 83%)을 얻었다.

¹H NMR (DMSO-*d*₆): δ 7.90(d, *J* = 8.3Hz, 2H), 7.83(d, *J* = 8.3Hz, 2H), 7.64(d, *J* = 8.4Hz, 2H), 7.49(d, *J* = 8.6Hz, 2H), 7.42~7.32(m, 16H), 7.23(d, *J* = 9.1Hz, 2H), 7.06~6.82(m, 40H), 6.71~6.51(m, 6H).

MALDI-TOF mass(*M*+*H*⁺) : C₉₈H₆₈N₄: 1301.2983(1301.5444)

EA : C, 90.5531%; H, 5.3041%; N, 4.2457%(C, 90.43%; H, 5.27%; N, 4.30%)

UV(λ_{max}) : 367nm PL : 504nm

[합성예 14]

화학식 I-2의 다른 제조

본 합성예는 위의 합성예 13과 같이 화학식 I-2를 제조하는 일 실시예에 관한 것이지만, 합성예 13과 다르게 본 합성예에서는 아민화 반응의 조건으로는 구리 촉매 대신 팔라듐 촉매를 사용하였다.

1000-ml, 4구 둥근바닥플라스크에 앞에서 제조된 7,10-디브로모-1,2,3,4-테트라페닐-트리페닐렌 22.0g(0.0319mol)에, 역시 앞에서 제조한 N,N-디페닐-N'-(1-나프틸)벤젠-1,4-디아민(화학식 I-H의 한 종류) 27.1g(0.0701mol), 트리스(디벤질리덴아세톤)디팔라듐(0) 0.146g(0.159mmol), 트리-(o-톨릴)포스핀 0.097g(0.319mmol), 소듐 t-부톡사이드 7.35g(0.077mol) 그리고 톨루엔 220ml를 투입하였다. 반응액을 22시간 동안 환류 시킨 후 냉각하고 과량의 메탄올에 부어 고체를 석출시켰다. 얻어진 고체를 여과하고 진공건조하여 목적화합물 39.4g(수율 95%)을 얻었다.

[합성예 15]

화학식 I-2의 또 다른 제조

본 합성예는 반응 촉매로 상기 합성예 14에서 사용한 트리스(디벤질리덴아세톤)디팔라듐(0) 대신에 팔라듐 아세테이트를 사용한 것을 제외하고는 합성예 14와 동일한 방법으로 제조하여 목적화합물 38.2g(수율 92%)을 얻었다.

[합성예 16]

화학식 I-2의 또 다른 제조

본 합성예는 위에서 제조된 N,N'-디-나프탈렌-1-일-5,6,7,8-테트라페닐-트리페닐렌-2,11-디아민(화학식 I-F의 한 종류)과 4-브로모트리페닐아민(화학식 I-G의 한 종류)의 아민화 반응을 실시하여 화학식 I-2를 제조하는 일 실시예에 관한 것이다.

1000-ml, 4구 둥근바닥플라스크에 앞에서 제조된 N,N'-디-나프탈렌-1-일-5,6,7,8-테트라페닐-트리페닐렌-2,11-디아민 45.0g(0.0552mol)에, 역시 앞에서 제조한 4-브로모트리페닐아민 39.4g(0.1215mol), 트리스(디벤질리덴아세톤)디팔라듐(0) 0.253g(0.276mmol), 트리-(o-톨릴)포스핀 0.168g(0.552mmol), 소듐 t-부톡사이드 12.7g(0.133mol) 그리고 톨루엔 400ml를 투입하였다. 반응액을 8시간 동안 환류 시킨 후 냉각하고 과량의 메탄올에 부어 고체를 석출시켰다. 얻어진 고체를 여과하고 진공건조하여 목적화합물 63.2g(수율 88%)을 얻었다.

[합성예 17]

화학식 I-2의 또 다른 제조

본 합성예는 반응 촉매로 상기 합성예 16에서 사용한 트리-(o-톨릴)포스핀 대신에 트리-(t-부틸)포스핀을 사용한 것을 제외하고는 합성예 16과 동일한 방법으로 제조하여 목적화합물 66.8g(수율 93%)을 얻었다.

[합성예 18]

3-브로모-9-페닐-9H-카바졸의 제조

본 합성예에서는 상기 화학식 I-G로 표시되는 일반식에서 R1, R2, E는 페닐기이고 R1과 E가 단일 결합에 의하여 연결된 경우이다.

1000-ml, 3구 둥근바닥플라스크에 9-페닐카바졸 68g(0.281mol), N-브로모숙신이미드(NBS) 52g(0.292mol)과 클로로포름 500ml를 투입하고 이 반응액을 1시간 동안 환류시켰다. 진공여과하여 불용성물질을 제거시키고 여과액에 증류수를 투입하여 추출하였다. 분리된 유기층을 농축하고 헥산을 투입하여 고체 형태로 분리시켰다. 얻어진 고체를 진공건조하여 목적화합물 90.5g(수율 89%)을 얻었다.

¹H NMR (DMSO-d₆): δ 8.51(d, J = 1.9Hz, 1H), 8.31(d, J = 7.8Hz, 1H), 7.68(t, J = 8.0Hz, 2H), 7.61(d, J = 7.4Hz, 2H), 7.57~7.53(m, 2H), 7.47(t, J = 7.2Hz, 1H), 7.36(d, J = 8.2Hz, 1H), 7.32~7.29(m, 2H).

[합성예 19]

화학식 I-514의 제조

본 합성예는 위에서 제조된 *N,N'*-디-나프탈렌-1-일-5,6,7,8-테트라페닐-트리페닐렌-2,11-디아민(화학식 I-F의 한 종류)과 3-브로모-9-페닐-9H-카바졸(화학식 I-G의 한 종류)의 아민화 반응을 실시하여 화학식 I-514를 제조하는 일 실시예에 관한 것이다.

100-ml, 3구 둥근바닥플라스크에 앞에서 제조된 *N,N'*-디-나프탈렌-1-일-5,6,7,8-테트라페닐-트리페닐렌-2,11-디아민 4.4g(5.40mmol)에, 역시 앞에서 제조한 3-브로모-9-페닐-9H-카바졸 3.65g(11.34mmol), 팔라듐(II) 아세테이트 6.1mg(0.027mmol), 트리-(*o*-톨릴)포스핀 16mg(0.054mmol), 소듐 *t*-부톡시드 1.25g(13.0mmol) 그리고 *o*-자일렌 40ml를 투입하였다. 반응액을 16시간 동안 환류 시킨 후 냉각하고 과량의 메탄올에 부어 고체를 석출시켰다. 얻어진 고체를 여과하고 진공건조하여 목적화합물 6.52g(수율 93%)을 얻었다.

$^1\text{H NMR}$ (DMSO- d_6): δ 8.05(d, J = 7.7Hz, 2H), 7.93(s, 2H), 7.82(d, J = 7.8Hz, 2H), 7.72~7.12(m, 36H), 7.03~6.65(m, 20H), 6.33(d, J = 9.4Hz, 2H).

MALDI-TOF mass($M+H^+$): C₉₈H₆₄N₄: 1298.2980(1297.5131)

EA : C, 90.5636%; H, 5.0114%; N, 4.2856%(C, 90.71%; H, 4.97%; N, 4.32%)

UV($\lambda_{\max}$) : 314nm PL : 460nm

[합성예 20]

(4-브로모-페닐에티닐)-트리메틸-실란의 제조

250-ml, 3구 둥근바닥플라스크에 질소분위기 하에서 1-브로모-4-아이오도벤젠 50g(0.177mol)를 투입하고 피페리딘 350ml로 희석시켰다. 이 희석액에 코퍼(I)아이오다이드 1.68g(8.84mmol), 테트라키스(트리페닐포스핀)팔라듐(0) 4.08g(3.50mmol)과 트리메틸실릴아세틸렌 25ml(0.177mol)를 투입하고 2시간 동안 실온에서 교반하였다. 반응액을 포화 암모니움 클로라이드 수용액에 투입하고 디클로로메탄으로 추출하였다. 분리된 유기층을 포화 암모니움 클로라이드 수용액과 증류수로 연속 세척하고 마그네슘 설페이트로 건조시켰다. 이 유기층을 감압 하에서 농축시켜 흰색의 목적화합물 44.3g(수율 99%)을 얻었다.

$^1\text{H NMR}$ (CDCl₃): δ 7.44(d, J = 8.5Hz, 2H), 7.32(d, J = 8.5Hz, 2H), 0.26(s, 9H).

[합성예 21]

4-(브로모)페닐아세틸렌의 제조

250-ml, 3구 둥근바닥플라스크에 앞에서 제조된 (4-브로모-페닐에티닐)-트리메틸-실란 43g (0.170mmol), 테트라하이드로퓨란 160ml, 메탄올 200ml와 포타슘 카보네이트 45g을 차례로 투입하였다. 실온에서 1시간 동안 교반 후 여과하여 불용성 물질을 제거시키고 여과액을 감압 농축시켰다. 농축액에 증류수와 디클로로메탄을 투입하여 추출하고 유기층을 분리하였다. 분리된 유기층을 건조 후 다시 감압 농축하여 흰색의 목적화합물을 30.8g(수율 94%) 얻었다.

$^1\text{H NMR}$ (CDCl₃): δ 8.47(d, J = 8.5Hz, 2H), 7.36(d, J = 8.5Hz, 2H), 3.13(s, 1H).

[합성예 22]

비스-(4-브로모페닐)아세틸렌(화학식 II-B의 한 종류)의 제조

본 합성예에서는 비스-(4-브로모페닐)아세틸렌을 제조하였으며, 이는 화학식 II-B에서 할로젠 원자 X_2 가 브롬 원자인 경우이다.

250-ml, 3구 둥근바닥플라스크에 질소분위기 하에서 앞에서 제조한 4-(브로모)페닐아세틸렌 28g(0.155mol)을 투입하고 트리에틸아민 120ml로 희석시켰다. 이 희석액에 1-브로모-4-아이오도벤젠 43.8g(0.155mol), 코퍼(I)아이오다이드 1.47g (7.74mmol)과 테트라키스(트리페닐포스핀)팔라듐(0) 3.57g(3.09mmol)을 투입하고 2시간 동안 실온에서 교반하였다. 반응액에 메탄올을 가하고 얻어진 결정을 여과한 다음 메탄올로 세척하였다. 이 고체를 진공 건조하여 목적화합물 46.9g(수율 90%)을 얻었다.

$^1\text{H NMR}$ (CDCl_3): δ 7.50(d, J = 8.3Hz, 2H), 7.39(d, J = 8.2Hz, 2H).

[합성예 23]

2,3-비스-(4-브로모페닐)-1,4-디페닐-트리페닐렌(화학식 II-C의 한 종류)의 제조

본 합성예는 화학식 II-C의 한 종류를 제조하는 일 실시예로, 이는 화학식 II-C에서 할로젠 원자 X_2 가 브롬 원자인 경우이다.

500-ml, 3구 둥근바닥플라스크에 질소 분위기 하에서 펜사이클론(phencyclone) 40g(0.105mol)을 *o*-자일렌 350ml로 희석시키고 앞에서 제조된 비스-(4-브로모페닐)아세틸렌 37.2g(0.110mol)을 투입하였다. 이 혼합액을 16시간 동안 환류시키고 실온으로 냉각한 다음 *o*-자일렌을 감압 하에서 농축하였다. *o*-자일렌이 약 40ml 정도 잔류하면 농축을 중단하고 다시 실온으로 냉각한다. 이 농축액에 메탄올 2000ml를 투입하여 고체를 석출시켰다. 석출된 고체를 여과하고 메탄올로 세척한 다음 진공건조하여 목적화합물 66.4g(수율 92%)을 얻었다.

$^1\text{H NMR}$ (CDCl_3): δ 8.41(d, J = 7.8Hz, 2H), 7.56(d, J = 7.9Hz, 2H), 7.40(t, J = 8.0Hz, 2H), 7.14~7.09(m, 6H), 7.06(d, J = 6.8Hz, 4H), 7.03~7.00(m, 6H), 6.54(d, J = 6.8Hz, 4H).

MALDI-TOF mass($M+H^+$) : $\text{C}_{42}\text{H}_{26}\text{Br}_2$: 689.2557(689.0401)

[합성예 24]

2,3-비스-(3',5'-디클로로페닐-비페닐-4-일)-1,4-디페닐-트리페닐렌(화학식 II-E의 한 종류)의 제조

본 합성예는 화학식 II-E에서 할로젠 원자 X_3 가 염소 원자인 경우이다.

250-ml, 3구 둥근바닥플라스크에 앞에서 제조한 2,3-비스-(4-브로모페닐)-1,4-디페닐-트리페닐렌 8.5g(12.3mmol)를 투입하고 톨루엔 340ml와 에탄올 136ml로 현탁시켰다. 이 현탁액에 3,5-디클로로벤젠보론산 5.17g(27.1mmol)을 투입 후 탄산 칼륨 13.61g(98.5mmol)을 증류수 204ml에 완전히 녹인 수용액을 투입하였다. 위의 현탁액에 테트라키스(트리페닐포스핀)팔라듐(0) 1.14g(0.98mmol)을 투입 후 빛을 차단시킨 상태에서 반응액을 1일 동안 환류시켰다. 반응액을 실온으로 냉각 후 유기층을 분리하고 수분을 제거시킨 후 농축시켰다. 이 농축액에 테트라하이드로퓨란을 투입하여 희석시킨 후 메탄올을 투입하여 고체를 석출시켰다. 얻어진 고체 화합물을 진공건조하여 목적화합물 8.2g(수율 81%)을 얻었다.

$^1\text{H NMR}$ (CDCl_3): δ 8.43(d, J = 7.9Hz, 2H), 7.60(d, J = 8.3Hz, 2H), 7.42(d, J = 7.2Hz, 2H), 7.34(d, J = 1.8Hz, 4H), 7.25(d, J = 1.8Hz, 2H), 7.12~7.02(m, 16H), 6.79(d, J = 8.2Hz, 4H).

[합성예 25]

화학식 II-1-1의 제조

본 합성에는 앞에서 제조된 2,3-비스-(3',5'-디클로로페닐-비페닐-4-일)-1,4-디페닐-트리페닐렌(화학식 II-E의 한 종류)과 디페닐아민(화학식 II-F의 한 종류)의 아민화 반응을 실시하여 화학식 II-1-1을 제조하는 일 실시예에 관한 것이다.

100-ml, 3구 둥근바닥플라스크에 앞에서 제조된 2,3-비스-(3',5'-디클로로페닐-비페닐-4-일)-1,4-디페닐-트리페닐렌 5.5g(6.69mmol), 디페닐아민 4.98g(29.4mmol), 팔라듐(II) 아세테이트 7.5mg(0.033mmol), 트리-(*t*-부틸)포스핀 (10%, 헥산 용액) 0.14ml(0.067mmol), 소듐 *t*-부톡시드 3.08g(32.1mmol) 그리고 *o*-자일렌 500ml를 투입하였다. 반응액을 18시간 동안 환류 시킨 후 냉각하고 과량의 메탄올에 부어 고체를 석출시켰다. 얻어진 고체를 여과하고 진공건조하여 목적화합물 7.4g(수율 82%)을 얻었다.

$^1\text{H NMR}$ (DMSO- d_6): δ 8.53(d, J = 8.0Hz, 2H), 7.42(t, J = 8.5Hz, 4H), 7.27~7.24(m, 14H), 7.05~6.95(m, 34H), 6.85~6.74(m, 8H), 6.69(d, J = 7.5Hz, 4H), 6.64(s, 4H), 6.56(s, 2H).

MALDI-TOF mass($M+H^+$) : C₁₀₂H₇₂N₄: 1353.3242(1353.5757)

UV(λ_{max}) : 326nm PL : 413nm 녹는점(mp) : 387°C

유리전이온도(Tg, DSC에 의한 측정) : 181°C

1% 중량손실온도(TGA에 의한 측정) : 512°C

[합성예 26]

2,3-비스-(4-(1-나프틸아미노)페닐)-1,4-디페닐-트리페닐렌(화학식 II-H의 한 종류)의 제조

본 합성에는 상기 화학식 II-H로 표시되는 일반식에서 R₄가 1-나프틸기인 경우이다.

250-ml, 3구 둥근바닥플라스크를 완전히 건조시킨 후 질소분위기 하에서 앞에서 제조된 2,3-비스-(4-브로모페닐)-1,4-디페닐-트리페닐렌(화학식 II-C) 8.5g(12.3mmol)을 투입하고 무수 톨루엔 80ml로 용해시켰다. 이 용액에 1-아미노나프탈렌 4.23g(29.5mmol), 트리(*o*-톨릴)포스핀 37.4mg(0.123mmol), 트리스(디벤질리덴아세톤)디팔라듐(0) 56mg(0.062mmol) 및 소듐 *t*-부톡시드 2.96g(30.8mmol)을 투입하였다. 이 혼합액을 6시간 동안 환류시키고 실온으로 냉각한 다음 메탄올 400ml를 투입하였다. 생성된 고체를 여과하고 메탄올로 세척하여 조생성물을 얻었다. 얻어진 조생성물에 에틸 아세테이트와 헥산을 이용하여 재결정화하고 진공건조하여 목적화합물 8.8g(수율 88%)을 얻었다.

$^1\text{H NMR}$ (DMSO- d_6): δ 8.55(d, J = 7.6Hz, 2H), 8.09(d, J = 7.4Hz, 2H), 8.01(s, 2H), 7.82(d, J = 7.3Hz, 2H), 7.53~7.38(m, 10H), 7.25~7.02(m, 16H), 6.68(d, J = 8.5Hz, 4H), 6.61(d, J = 8.5Hz, 4H).

MALDI-TOF mass($M+H^+$) : C₆₂H₄₂N₂: 815.4881(815.3348)

[합성예 27]

9-(4-클로로페닐)-9H-카바졸(화학식 II-I의 한 종류)의 제조

본 합성에는 상기 화학식 II-I로 표시되는 일반식에서 E가 페닐기, R₆가 수소 원자이고 X₃가 염소 원자인 경우이다.

250-ml, 3구 둥근바닥플라스크를 완전히 건조시킨 후 질소분위기 하에서 카바졸 4.5g(26.9mmol)을 투입하고 무수 *o*-자일렌 40ml로 용해시켰다. 이 용액에 1-클로로-4-아이오도벤젠 7.06g(29.6mmol), 트리(*o*-톨릴)포스핀 82mg(0.27mmol), 트리스(디벤질리덴아세톤)디팔라듐(0) 123mg(0.135mmol) 및 소듐 *t*-부톡시드 3.1g(32.3mmol)을 투입하였다. 이 혼합액을 15시간 동안 환류시키고 실온으로 냉각한 다음 반응액을 농축시켰다. 이 농축액을 소량의 테트라하이드로퓨란으로 용해시키고 헥산을 투입하여 불용성 물질을 제거시킨 후 모아진 여과액을 다시 농축시켰다. 이 농축액을 에틸 아세테이트와 헥산을 전개용매로 이용하여 실리카 겔 판 크로마토그래피를 이용하여 목적화합물 3.8g(수율 62%)을 얻었다.

^1H NMR (DMSO- d_6): δ 8.25(d, J = 7.7Hz, 2H), 7.73(d, J = 8.7Hz, 2H), 7.67(d, J = 8.6Hz, 2H), 7.44(t, J = 7.7Hz, 2H), 7.38(d, J = 8.1Hz, 2H), 7.30(t, J = 7.5Hz, 2H).

MALDI-TOF mass($M+H^+$) : C₁₈H₁₂ClN: 278.2381(278.0658)

[합성예 28]

화학식 II-2-6의 제조

본 합성예는 앞에서 제조된 2,3-비스-(4-(1-나프틸아미노)페닐)-1,4-디페닐-트리페닐렌(화학식 II-H의 한 종류)과 역시 앞에서 제조된 9-(4-클로로페닐)-9H-카바졸(화학식 II-I의 한 종류)의 아민화 반응을 실시하여 화학식 II-2-6을 제조하는 일 실시예에 관한 것이다.

250-ml, 3구 둥근바닥플라스크에 2,3-비스-(4-(1-나프틸아미노)페닐)-1,4-디페닐-트리페닐렌 14.0g(17.2mmol), 9-(4-클로로페닐)-9H-카바졸 10.5g(37.8mmol), 팔라듐(II) 아세테이트 19.3mg(0.086mmol), 트리-(*t*-부틸)포스핀 (10%, 헥산 용액) 0.35ml(0.172mmol), 소듐 *t*-부톡시드 4.0g(41.2mmol) 그리고 *o*-자일렌 126ml를 투입하였다. 반응액을 6시간 동안 환류 시킨 후 냉각하고 잔사가 100ml가 될 때까지 감압 농축시켰다. 이 잔사에 메탄올을 투입하고 석출된 고체를 진공여과 후 건조시켜 목적화합물 19.9g(수율 89%)을 얻었다.

^1H NMR (DMSO- d_6): δ 8.54(d, J = 8.2Hz, 2H), 8.18(d, J = 7.7Hz, 4H), 7.90(d, J = 8.2Hz, 2H), 7.79(t, J = 7.5Hz, 4H), 7.53(d, J = 8.5Hz, 2H), 7.46~7.41(m, 6H), 7.30~7.17(m, 26H), 7.08~7.06(m, 4H), 7.02(t, J = 7.4Hz, 2H), 6.87(d, J = 8.6Hz, 4H), 6.76(d, J = 8.3Hz, 4H), 6.65(d, J = 8.3Hz, 4H).

MALDI-TOF mass($M+H^+$) : C₉₈H₆₄N₄: 1296.7032(1296.5131)

UV(λ_{max}) : 321nm PL : 440nm 녹는점(mp) : 371°C

유리전이온도(Tg, DSC에 의한 측정) : 202°C

1% 중량손실온도(TGA에 의한 측정) : 557°C

[합성예 29]

화학식 II-3-22의 제조

본 합성예는 앞에서 제조된 2,3-비스-(4-(1-나프틸아미노)페닐)-1,4-디페닐-트리페닐렌(화학식 II-H의 한 종류)과 역시 앞에서 제조된 3-브로모-9-페닐-9H-카바졸(화학식 II-J의 한 종류)의 아민화 반응을 실시하여 화학식 II-3-22를 제조하는 일 실시예에 관한 것이다.

250-ml, 3구 둥근바닥플라스크에 2,3-비스-(4-(1-나프틸아미노)페닐)-1,4-디페닐-트리페닐렌 14.0g(17.2mmol), 3-브로모-9-페닐-9H-카바졸 12.2g(37.8mmol), 팔라듐(II) 아세테이트 19.3mg(0.086mmol), 트리-(*t*-부틸)포스핀 (10%, 헥산 용액) 0.35ml(0.172mmol), 소듐 *t*-부톡시드 4.0g(41.2mmol) 그리고 *o*-자일렌 126ml를 투입하였다. 반응액을 5시간 동안 환류 시킨 후 냉각하고 아세톤으로 희석시켰다. 이 희석액을 메탄올에 부어 석출된 고체를 진공여과 후 건조시켜 목적화합물 18.5g(수율 83%)을 얻었다.

^1H NMR (DMSO- d_6): δ 8.53(d, J = 8.4Hz, 2H), 7.91(d, J = 8.2Hz, 2H), 7.80~7.70(m, 8H), 7.53(d, J = 7.8Hz, 6H), 7.47~7.21(m, 26H), 7.08~7.01(m, 12H), 6.52(d, J = 8.3Hz, 4H), 6.47(d, J = 8.3Hz, 4H).

MALDI-TOF mass($M+H^+$) : C₉₈H₆₄N₄: 1296.6893(1296.5131)

UV($\lambda_{\max}$) : 312nm PL : 461nm 녹는점(mp) : 369℃

유리전이온도(Tg, DSC에 의한 측정) : 213℃

1% 중량손실온도(TGA에 의한 측정) : 560℃

[합성예 30]

2,3-비스-(4-(카바졸-9-일)-페닐)-1,4-디페닐-트리페닐렌의 제조

본 합성예는 상기 화학식 II-L로 표시되는 일반식에서 R6와 X₃가 수소원자인 경우이다.

500-ml, 3구 둥근바닥플라스크를 완전히 건조시킨 후 질소분위기 하에서 앞에서 제조된 2,3-비스-(4-브로모페닐)-1,4-디페닐-트리페닐렌(화학식 II-C) 20g(29.0mmol)을 투입하고 o-자일렌 180ml로 용해시켰다. 이 용액에 카바졸 10.66g(63.7mmol), 트리(o-톨릴)포스핀 88mg(0.290mmol), 트리(디벤질리덴아세톤)디팔라디움(0) 133mg(0.145mmol) 및 소듐 t-부톡시드 6.68g(69.5mmol)을 투입하였다. 이 혼합액을 20시간 동안 환류시키고 실온으로 냉각한 다음 아세톤으로 희석시킨 후 메탄올을 투입하였다. 생성된 고체를 여과하고 메탄올로 세척하여 조생성물을 얻었다. 얻어진 조생성물을 진공건조하여 목적화합물 25g(수율 100%)을 얻었다.

¹H NMR (DMSO-d₆): δ 8.63(d, J = 8.4Hz, 2H), 8.21(d, J = 8.1Hz, 4H), 7.70(d, J = 8.5Hz, 2H), 7.51(d, J = 7.7Hz, 2H), 7.30~7.23(m, 22H), 7.14~7.10(m, 6H), 7.06(d, J = 8.3Hz, 4H).

MALDI-TOF mass(M+ H⁺) : C₆₆H₄₂N₂: 863.4725(863.3348)

[합성예 31]

2,3-비스-(4-(3-브로모카바졸-9-일)-페닐)-1,4-디페닐-트리페닐렌(화학식 II-L의 한 종류)의 제조

본 합성예는 상기 화학식 II-L로 표시되는 일반식에서 R6가 수소원자이고 X₃가 브롬원자인 경우이다.

500-ml, 3구 둥근바닥플라스크에 2,3-비스-(4-(카바졸-9-일)-페닐)-1,4-디페닐-트리페닐렌 25g(29.0mmol), N-브로모숙신이미드(NBS) 10.4g(58.5mmol)과 클로로포름 200ml를 투입하고 이 반응액을 1.5시간 동안 환류시켰다. 진공여과하여 불용성물질을 제거시키고 여과액에 증류수를 투입하여 추출하였다. 분리된 유기층을 농축하고 헥산을 투입하여 고체 형태로 분리시켰다. 얻어진 고체를 진공건조하여 목적화합물 28.7g(수율 97%)을 얻었다.

¹H NMR (DMSO-d₆): δ 8.62(d, J = 8.0Hz, 2H), 8.47(d, J = 1.9Hz, 2H), 8.27(d, J = 8.9Hz, 2H), 7.70(d, J = 8.5Hz, 2H), 7.51(t, J = 7.4Hz, 2H), 7.29~7.19(m, 20H), 7.13~7.03(m, 8H), 6.91(d, J = 8.6Hz, 2H).

[합성예 32]

화학식 II-4-1의 제조

본 합성예는 앞에서 제조된 2,3-비스-(4-(3-브로모카바졸-9-일)-페닐)-1,4-디페닐-트리페닐렌(화학식 II-L의 한 종류)과 디페닐아민(화학식 II-F의 한 종류)의 아민화 반응을 실시하여 화학식 II-4-1을 제조하는 일 실시예에 관한 것이다.

500-ml, 3구 둥근바닥플라스크에 2,3-비스-(4-(3-브로모카바졸-9-일)-페닐)-1,4-디페닐-트리페닐렌 28.0g(27.4mmol), 디페닐아민 10.2g(60.3mmol), 팔라디움(II) 아세테이트 30.8mg(0.137mmol), 트리-(t-부틸)포스핀(10%, 헥산 용액) 0.56ml(0.274mmol), 소듐 t-부톡시드 6.3g(65.8mmol) 그리고 o-자일렌 250ml를 투입하였다. 반응액을 5시간 동안 환류시킨 후 냉각하고 아세톤으로 희석시켰다. 이 희석액을 메탄올에 부어 석출된 고체를 진공여과 후 건조시켜 목적화합물 28.9g(수율 88%)을 얻었다.

^1H NMR (DMSO- d_6): δ 8.61(d, J = 8.2Hz, 2H), 8.08(d, J = 6.8Hz, 2H), 7.96(s, 2H), 7.69(d, J = 8.5Hz, 2H), 7.49(t, J = 7.2Hz, 2H), 7.27~7.21(m, 22H), 7.11~7.09(m, 10H), 6.99~6.92(m, 18H).

MALDI-TOF mass($M+H^+$) : C₉₀H₆₀N₄: 1197.6656(1197.4818)

UV(λ_{max}) : 325nm PL : 415nm 녹는점(mp) : 240℃

유리전이온도(Tg, DSC에 의한 측정) : 191℃

1% 중량손실온도(TGA에 의한 측정) : 470℃

[합성예 33]

2,3-비스-[4-(*N*-페닐-1-나프틸아미노)-페닐]-1,4-디페닐-트리페닐렌의 제조

500-ml, 3구 둥근바닥플라스크를 완전히 건조시킨 후 질소분위기 하에서 앞에서 제조된 2,3-비스-(4-브로모페닐)-1,4-디페닐-트리페닐렌(화학식 II-C) 20g(29.0mmol)을 투입하고 *o*-자일렌 180ml로 용해시켰다. 이 용액에 *N*-페닐-1-나프틸아민 14.0g(63.7mmol), 트리(*o*-톨릴)포스핀 88mg(0.290mmol), 트리스(디벤질리텐아세톤)디팔라디움(0) 133mg(0.145mmol) 및 소듐 *t*-부톡사이드 6.68g(69.5mmol)을 투입하였다. 이 혼합액을 5시간 동안 환류시키고 실온으로 냉각한 다음 아세톤으로 희석시킨 후 메탄올을 투입하였다. 생성된 고체를 여과하고 메탄올로 세척하여 조생성물을 얻었다. 얻어진 조생성물을 진공건조하여 목적화합물 28g(수율 100%)을 얻었다.

^1H NMR (DMSO- d_6): δ 8.50(d, J = 8.2Hz, 2H), 7.90(d, J = 8.4Hz, 2H), 7.78(d, J = 8.0Hz, 2H), 7.62(d, J = 8.4Hz, 2H), 7.50(d, J = 8.2Hz, 2H), 7.44~7.38(m, 6H), 7.21~7.14(m, 12H), 7.07(d, J = 7.3Hz, 2H) 7.00(d, J = 7.4Hz, 6H), 6.89(d, J = 7.1Hz, 2H), 6.70(d, J = 7.8Hz, 4H), 6.50(s, 8H).

MALDI-TOF mass($M+H^+$) : C₇₄H₅₀N₂: 967.5152(967.3974)

UV(λ_{max}) : 302nm PL : 429nm 녹는점(mp) : 212℃

유리전이온도(Tg, DSC에 의한 측정) : 150℃

1% 중량손실온도(TGA에 의한 측정) : 432℃

[합성예 34]

7,10-디브로모-2,3-비스(4-브로모페닐)-1,4-디페닐-트리페닐렌(화학식 III-A)의 제조

500-ml, 3구 둥근바닥플라스크에 질소 분위기 하에서 앞에서 제조한 6,9-디브로모-1,3-디페닐-사이클로펜타[*l*]페난트렌-2-온(화학식 I-C) 69g(0.128mol)을 *o*-자일렌 550ml로 희석시키고, 역시 앞에서 제조한 비스-(4-브로모페닐)아세틸렌(화학식 II-B의 한 종류) 45.5g(0.135mol)을 투입하였다. 이 혼합액을 15시간 동안 환류시키고 실온으로 냉각한 다음 아세톤으로 희석 후 과량의 메탄올에 투입하여 고체를 석출시켰다. 석출된 고체를 여과하고 메탄올로 세척한 다음 진공건조하여 목적화합물 73.8g(수율 68%)을 얻었다.

^1H NMR (DMSO- d_6): δ 8.44(d, J = 2.0Hz, 2H), 7.39(d, J = 9.1Hz, 2H), 7.15~7.11(m, 8H), 7.06(d, J = 8.4Hz, 4H), 6.98~6.96(m, 4H), 6.53(d, J = 8.4Hz, 4H).

[합성예 35]

화학식 III-1의 제조

본 합성예는 앞에서 제조된 7,10-디브로모-2,3-비스(4-브로모페닐)-1,4-디페닐-트리페닐렌(화학식 III-A)과 디페닐아민(III-C의 한 종류)의 아민화 반응을 실시하여 화학식 III-1을 제조하는 일 실시예에 관한 것이다.

500-ml, 3구 둥근바닥플라스크에 7,10-디브로모-2,3-비스(4-브로모페닐)-1,4-디페닐-트리페닐렌 20.0g(23.6mmol), 디페닐아민 16.8g(99.0mmol), 팔라듐(II) 아세테이트 26.5mg(0.118mmol), 트리-(t-부틸)포스핀(10%, 헥산 용액) 0.48ml(0.236mmol), 소듐 t-부톡사이드 10.4g(0.108mol) 그리고 o-자일렌 180ml를 투입하였다. 반응액을 6시간 동안 환류 시킨 후 냉각하고 아세톤으로 희석시킨 후 메탄올을 투입하였다. 석출된 고체를 진공여과 후 건조시켜 목적화합물 24.8g(수율 88%)을 얻었다.

^1H NMR (DMSO- d_6): δ 7.58(s, 2H), 7.42(d, J = 9.2Hz, 2H), 7.19~7.14(m, 26H), 7.04(d, J = 7.9Hz, 8H), 6.99(t, J = 7.4Hz, 4H), 6.94~6.91(m, 12H), 6.72~6.68(m, 6H), 6.60(d, J = 8.3Hz, 4H).

MALDI-TOF mass($M+H^+$) : C₉₀H₆₄N₄: 1201.9764(1201.5131)

UV(λ_{max}) : 351nm PL : 431nm 녹는점(mp) : 366℃

유리전이온도(Tg, DSC에 의한 측정) : 167℃

1% 중량손실온도(TGA에 의한 측정) : 529℃

[합성예 36]

화학식 III-43의 제조

본 합성예는 앞에서 제조된 7,10-디브로모-2,3-비스(4-브로모페닐)-1,4-디페닐-트리페닐렌(화학식 III-A)과 *N*-페닐-2-나프틸아민(III-C의 한 종류)의 아민화 반응을 실시하여 화학식 III-43을 제조하는 일 실시예에 관한 것이다.

500-ml, 3구 둥근바닥플라스크에 7,10-디브로모-2,3-비스(4-브로모페닐)-1,4-디페닐-트리페닐렌 20.0g(23.6mmol), *N*-페닐-2-나프틸아민 22.2g(0.101mol), 팔라듐(II) 아세테이트 26.5mg(0.118mmol), 트리-(t-부틸)포스핀(10%, 헥산 용액) 0.48ml(0.236mmol), 소듐 t-부톡사이드 10.4g(0.108mol) 그리고 o-자일렌 180ml를 투입하였다. 반응액을 9시간 동안 환류 시킨 후 냉각하고 아세톤으로 희석시킨 후 메탄올을 투입하였다. 석출된 고체를 진공여과 후 건조시켜 목적화합물 32.5g(수율 98%)을 얻었다.

MALDI-TOF mass($M+H^+$) : C₁₀₆H₇₂N₄: 1401.7420(1401.5757)

UV(λ_{max}) : 351nm PL : 439nm 녹는점(mp) : 391℃

유리전이온도(Tg, DSC에 의한 측정) : 166℃

1% 중량손실온도(TGA에 의한 측정) : 546℃

[합성예 37]

화학식 III-251의 제조

본 합성예는 앞에서 제조된 7,10-디브로모-2,3-비스(4-브로모페닐)-1,4-디페닐-트리페닐렌(화학식 III-A)과 인돌(III-C의 한 종류)의 아민화 반응을 실시하여 화학식 III-251을 제조하는 일 실시예에 관한 것이다.

500-ml, 3구 둥근바닥플라스크에 7,10-디브로모-2,3-비스(4-브로모페닐)-1,4-디페닐-트리페닐렌 18.0g(21.2mmol), 인돌 10.4g(89.1mmol), 팔라듐(II) 아세테이트 23.8mg(0.106mmol), 트리-(t-부틸)포스핀(10%, 헥산 용액) 0.43ml

(0.212mmol), 소듐 t-부톡사이드 9.38g(97.6mmol) 그리고 o-자일렌 160ml를 투입하였다. 반응액을 21시간 동안 환류시킨 후 냉각하고 아세톤으로 희석시킨 후 메탄올을 투입하였다. 석출된 고체를 진공여과 후 건조시켜 목적화합물 18g(수율 86%)을 얻었다.

^1H NMR (DMSO- d_6): δ 8.85(s, 2H), 7.87(d, J = 3.2Hz, 2H), 7.78(d, J = 8.9Hz, 2H), 7.69(dd, J = 15.3, 8.4Hz, 4H), 7.61(d, J = 7.9Hz, 2H), 7.49(d, J = 3.1Hz, 2H), 7.38(d, J = 9.2Hz, 2H), 7.28~7.19(m, 18H), 7.15(t, J = 7.5Hz, 2H), 7.07~7.02(m, 6H) 6.92(t, J = 7.4Hz, 2H), 6.74(d, J = 3.1Hz, 2H), 6.64(d, J = 2.9Hz, 2H).

MALDI-TOF mass($M+H^+$) : C₇₄H₄₈N₄: 994.1043(993.3879)

UV(λ_{max}) : 326nm PL : 406nm 녹는점(mp) : 244℃

유리전이온도(Tg, DSC에 의한 측정) : 164℃

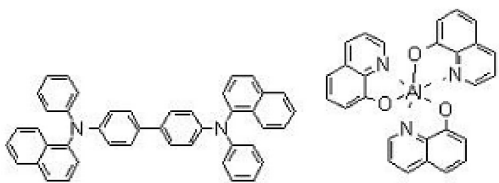
1% 중량손실온도(TGA에 의한 측정) : 500℃

[실시예 1]

화학식 I-1을 이용한 유기 발광 다이오드 제작

25mm × 75mm × 1.1mm 크기의 유리 기판 상에 막 두께가 750Å 인 인듐 주석 산화물(ITO)의 투명성 양극을 형성시켰다. 상기 유리 기판을 진공 증착장치에 넣어 약 10^{-7} torr로 감압하였다. 이어서 본 발명의 상기 화학식 I-1을 두께가 600Å 이 되도록 증착시켜 정공주입층을 형성시켰다. 이어서 하기 화학식 9의 NPB[N,N'-디(나프탈렌-1-일)-N,N'-디페닐벤지딘]를 두께가 200Å 이 되도록 증착시켜 정공수송층을 형성하였다. 하기 화학식 10의 Alq₃[트리스(8-히드록시퀴놀린) 알루미늄(III)]를 두께가 500Å 이 되도록 증착시켜 발광층을 형성하였다. 최종적으로 알루미늄과 리튬을 동시에 증착시켜 1000Å의 두께를 갖는 음극을 형성시켰다. 상기와 같이 제작된 유기 발광 다이오드에 0 ~ 17V의 전압을 인가하여 발광시험을 실시하였다. 즉, 각각의 전압에서 전류밀도, 휘도, 발광효율, EL 피크 그리고 최고휘도를 측정하였다. 10V 인가전압에서, 전류밀도는 154mA/cm², 휘도는 6079cd/m², 최고휘도는 24660cd/m², 발광효율은 3.95cd/A, 1.24lm/W이었다.

[화학식 9] [화학식 10]



[실시예 2]

화학식 I-2를 이용한 유기 발광 다이오드 제작

본 실시예 2에서는 상기 실시예 1에서 화학식 I-1 대신 화학식 I-2를 사용한 것을 제외하고는 실시예 1과 동일하게 유기 발광 다이오드를 제작하고 평가하였다. 10V 인가전압에서, 전류밀도는 166mA/cm², 휘도는 5511cd/m², 최고휘도는 22890cd/m², 발광효율은 3.32cd/A, 1.04lm/W이었다.

[실시예 3]

화학식 I-161을 이용한 유기 발광 다이오드 제작

본 실시예에서는 상기 실시예 1에서 화학식 I-1 대신 화학식 I-161을 사용한 것을 제외하고는 실시예 1과 동일하게 유기 발광 다이오드를 제작하고 평가하였다. 10V 인가전압에서, 전류밀도는 $58.7\text{mA}/\text{cm}^2$, 휘도는 $1837\text{cd}/\text{m}^2$, 최고휘도는 $21210\text{cd}/\text{m}^2$, 발광효율은 $3.13\text{cd}/\text{A}$, $0.98\text{lm}/\text{W}$ 이었다.

[실시예 4]

화학식 I-514를 이용한 유기 발광 다이오드 제작

본 실시예에서는 상기 실시예 1에서 화학식 I-1 대신 화학식 I-514를 사용한 것을 제외하고는 실시예 1과 동일하게 유기 발광 다이오드를 제작하고 평가하였다. 10V 인가전압에서, 전류밀도는 $43.5\text{mA}/\text{cm}^2$, 휘도는 $1736\text{cd}/\text{m}^2$, 최고휘도는 $26480\text{cd}/\text{m}^2$, 발광효율은 $3.99\text{cd}/\text{A}$, $1.28\text{lm}/\text{W}$ 이었다.

[실시예 5]

화학식 II-1-1을 이용한 유기 발광 다이오드 제작

본 실시예에서는 상기 실시예 1에서 화학식 I-1 대신 화학식 II-1-1을 사용한 것을 제외하고는 실시예 1과 동일하게 유기 발광 다이오드를 제작하고 평가하였다. 10V 인가전압에서, 전류밀도는 $3.84\text{mA}/\text{cm}^2$, 휘도는 $136\text{cd}/\text{m}^2$, 최고휘도는 $18310\text{cd}/\text{m}^2$, 발광효율은 $3.71\text{cd}/\text{A}$, $1.11\text{lm}/\text{W}$ 이었다.

[실시예 6]

화학식 II-2-6을 이용한 유기 발광 다이오드 제작

본 실시예에서는 상기 실시예 1에서 화학식 I-1 대신 화학식 II-2-6을 사용한 것을 제외하고는 실시예 1과 동일하게 유기 발광 다이오드를 제작하고 평가하였다. 10V 인가전압에서, 전류밀도는 $1.50\text{mA}/\text{cm}^2$, 휘도는 $45.2\text{cd}/\text{m}^2$, 최고휘도는 $15900\text{cd}/\text{m}^2$, 발광효율은 $3.01\text{cd}/\text{A}$, $0.95\text{lm}/\text{W}$ 이었다.

[실시예 7]

화학식 II-3-22를 이용한 유기 발광 다이오드 제작

본 실시예에서는 상기 실시예 1에서 화학식 I-1 대신 화학식 II-3-22를 사용한 것을 제외하고는 실시예 1과 동일하게 유기 발광 다이오드를 제작하고 평가하였다. 10V 인가전압에서, 전류밀도는 $48.2\text{mA}/\text{cm}^2$, 휘도는 $1990\text{cd}/\text{m}^2$, 최고휘도는 $16170\text{cd}/\text{m}^2$, 발광효율은 $4.13\text{cd}/\text{A}$, $1.30\text{lm}/\text{W}$ 이었다.

[실시예 8]

화학식 II-4-1을 이용한 유기 발광 다이오드 제작

본 실시예에서는 상기 실시예 1에서 화학식 I-1 대신 화학식 II-4-1을 사용한 것을 제외하고는 실시예 1과 동일하게 유기 발광 다이오드를 제작하고 평가하였다. 10V 인가전압에서, 전류밀도는 $30.8\text{mA}/\text{cm}^2$, 휘도는 $1359\text{cd}/\text{m}^2$, 최고휘도는 $31970\text{cd}/\text{m}^2$, 발광효율은 $4.41\text{cd}/\text{A}$, $1.38\text{lm}/\text{W}$ 이었다.

[실시예 9]

화학식 III-2를 이용한 유기 발광 다이오드 제작

본 실시예에서는 상기 실시예 1에서 화학식 I-1 대신 화학식 III-2를 사용한 것을 제외하고는 실시예 1과 동일하게 유기 발광 다이오드를 제작하고 평가하였다. 10V 인가전압에서, 전류밀도는 $42.6\text{A}/\text{cm}^2$, 휘도는 $1695\text{cd}/\text{m}^2$, 최고휘도는 $26550\text{cd}/\text{m}^2$, 발광효율은 $3.98\text{cd}/\text{A}$, $1.25\text{lm}/\text{W}$ 이었다.

[실시예 10]

화학식 III-43을 이용한 유기 발광 다이오드 제작

본 실시예에서는 상기 실시예 1에서 화학식 I-1 대신 화학식 III-43을 사용한 것을 제외하고는 실시예 1과 동일하게 유기 발광 다이오드를 제작하고 평가하였다. 10V 인가전압에서, 전류밀도는 $13.5\text{A}/\text{cm}^2$, 휘도는 $481\text{cd}/\text{m}^2$, 최고휘도는 $19160\text{cd}/\text{m}^2$, 발광효율은 $3.57\text{cd}/\text{A}$, $1.12\text{lm}/\text{W}$ 이었다.

[실시예 11]

화학식 III-251을 이용한 유기 발광 다이오드 제작

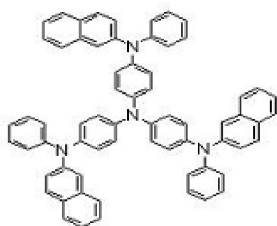
본 실시예에서는 상기 실시예 1에서 화학식 I-1 대신 화학식 III-251을 사용한 것을 제외하고는 실시예 1과 동일하게 유기 발광 다이오드를 제작하고 평가하였다. 10V 인가전압에서, 전류밀도는 $9.83\text{A}/\text{cm}^2$, 휘도는 $396\text{cd}/\text{m}^2$, 최고휘도는 $22750\text{cd}/\text{m}^2$, 발광효율은 $4.03\text{cd}/\text{A}$, $1.27\text{lm}/\text{W}$ 이었다.

[비교예 1]

화학식 2-TNATA(화학식 7)를 이용한 유기 발광 다이오드 제작

본 비교예에서는 상기 실시예 1에서 화학식 I-1 대신 종래에 널리 알려진 2-TNATA를 사용한 것을 제외하고는 실시예 1과 동일하게 유기 발광 다이오드를 제작하고 평가하였다. 10V 인가전압에서, 전류밀도는 $1.42\text{A}/\text{cm}^2$, 휘도는 $21.1\text{cd}/\text{m}^2$, 최고휘도는 $15780\text{cd}/\text{m}^2$, 발광효율은 $1.49\text{cd}/\text{A}$, $0.47\text{lm}/\text{W}$ 이었다.

[화학식 7]



발명의 효과

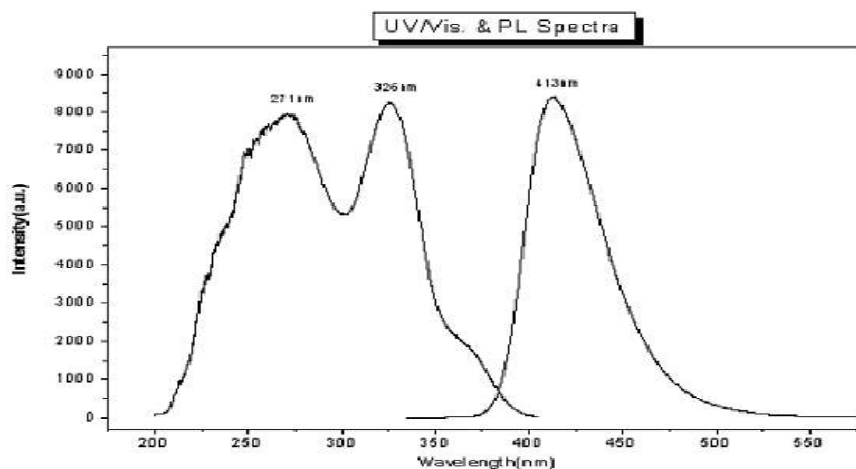
본 발명에 따른 트리페닐렌 유도체로써 정공전달물질은 145°C 이상의 높은 유리전이온도와 높은 열분해 온도를 갖고 있으므로 열적안정성이 우수하고 이를 사용하여 유기 발광 다이오드를 제작하고 발광특성을 평가한 결과, 기존의 정공전달물질인 화학식 7의 2-TNATA보다 전류 밀도, 휘도, 최고 휘도 그리고 발광 효율 모든 면에서 아주 우수한 발광 특성을 나타내었다. 따라서 본 발명의 트리페닐렌 유도체를 정공주입층으로 사용하여 유기 발광 다이오드를 제작하면, 기존의 유기 발광 다이오드의 가장 큰 단점인 발광 휘도와 발광 효율이 낮은 문제를 동시에 해결할 수 있을 뿐만 아니라, 유리전이온도도 높기 때문에 유기 발광 다이오드의 열적 안정성까지 뛰어나므로, 고성능의 유기 발광 다이오드의 제작이 가능하여 고효율, 고휘도 및 장수명이 요구되는 종전연색의 유기 발광 다이오드의 상용화에 크게 기여할 수 있다. 본 발명의 단순한 변형 또는 변경은 이 분야의 통상의 지식을 가진 자에 의하여 용이하게 실시될 수 있으며, 이러한 변형이나 변경은 모두 본 발명의 영역에 포함될 수 있다.

도면의 간단한 설명

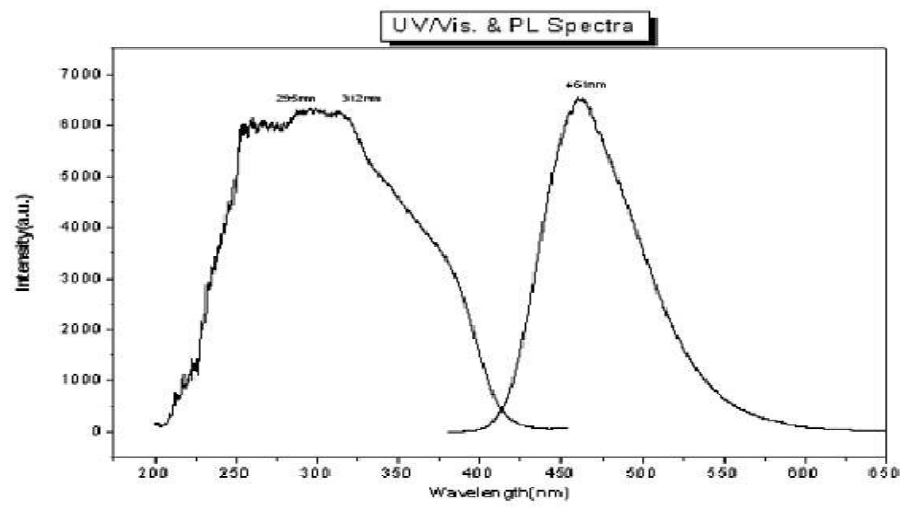
- 도 1은 본 발명에 따른 화학식 II-1-1의 트리페닐렌 유도체에 대한 UV/Vis. 및 형광 스펙트럼 그래프이다.
- 도 2는 본 발명에 따른 화학식 II-3-22의 트리페닐렌 유도체에 대한 UV/Vis. 및 형광 스펙트럼 그래프이다.
- 도 3은 본 발명에 따른 화학식 III-43의 트리페닐렌 유도체에 대한 UV/Vis. 및 형광 스펙트럼 그래프이다.
- 도 4는 본 발명에 따른 화학식 I-1의 트리페닐렌 유도체에 대한 시차주사열량계(DSC) 곡선 그래프이다.
- 도 5는 본 발명에 따른 화학식 II-1-1의 트리페닐렌 유도체에 대한 시차주사열량계 곡선 그래프이다.
- 도 6은 본 발명에 따른 화학식 II-2-6의 트리페닐렌 유도체에 대한 시차주사열량계 곡선 그래프이다.
- 도 7은 본 발명에 따른 화학식 II-3-22의 트리페닐렌 유도체에 대한 시차주사열량계 곡선 그래프이다.
- 도 8은 본 발명에 따른 화학식 I-1의 트리페닐렌 유도체에 대한 열중량분석기(TGA) 곡선 그래프이다.
- 도 9는 본 발명에 따른 화학식 II-2-6의 트리페닐렌 유도체에 대한 열중량분석기 곡선 그래프이다.
- 도 10은 본 발명에 따른 화학식 II-3-22의 트리페닐렌 유도체에 대한 열중량분석기 곡선 그래프이다.
- 도 11은 본 발명에 따른 화학식 III-43의 트리페닐렌 유도체에 대한 열중량분석기 곡선 그래프이다.
- 도 12는 본 발명에 따른 트리페닐렌 유도체를 이용하여 제작된 유기 발광 다이오드의 다층 구조를 나타내는 도면이다.
- 도 13은 본 발명에 따른 트리페닐렌 유도체를 이용하여 제작된 유기 발광 다이오드의 전기발광(EL) 스펙트럼 그래프이다.

도면

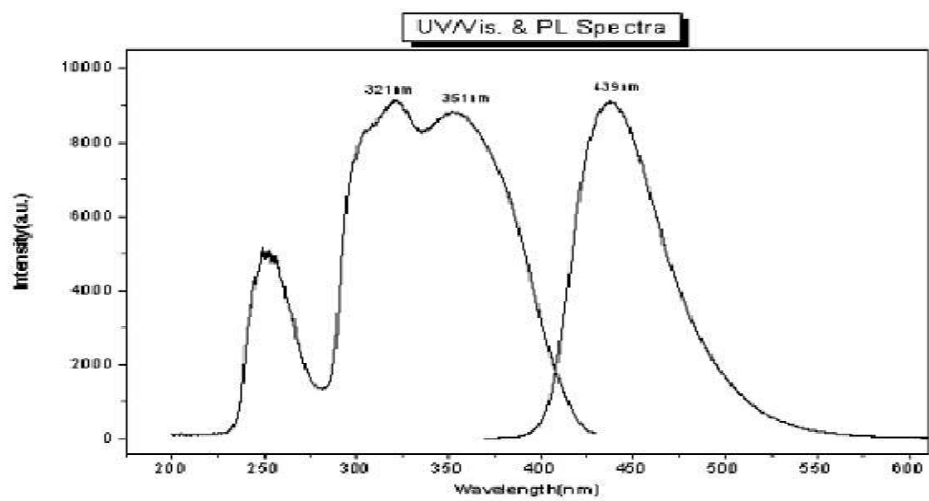
도면1



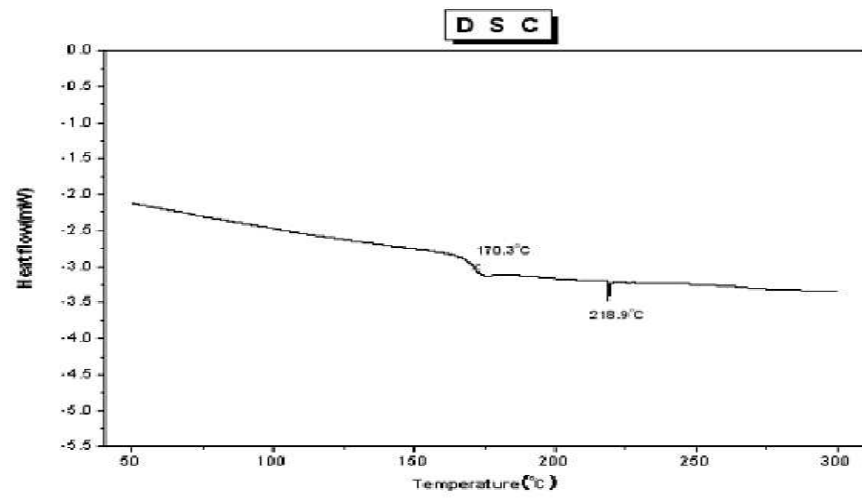
도면2



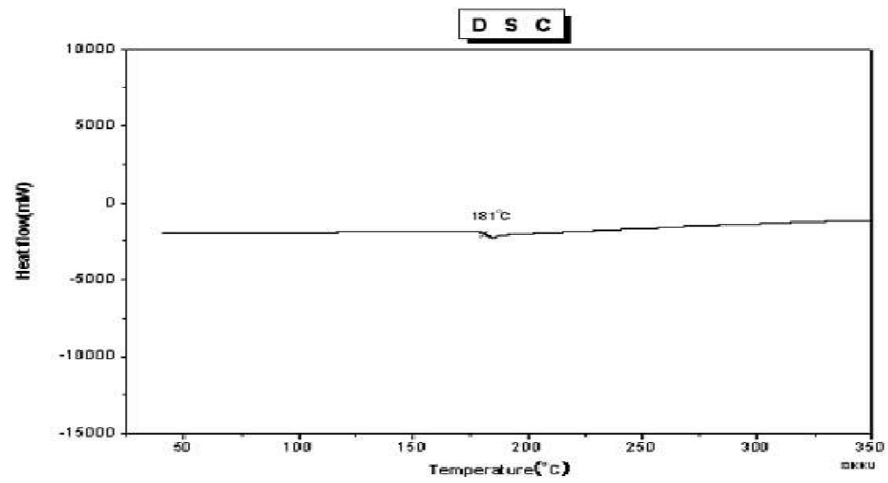
도면3



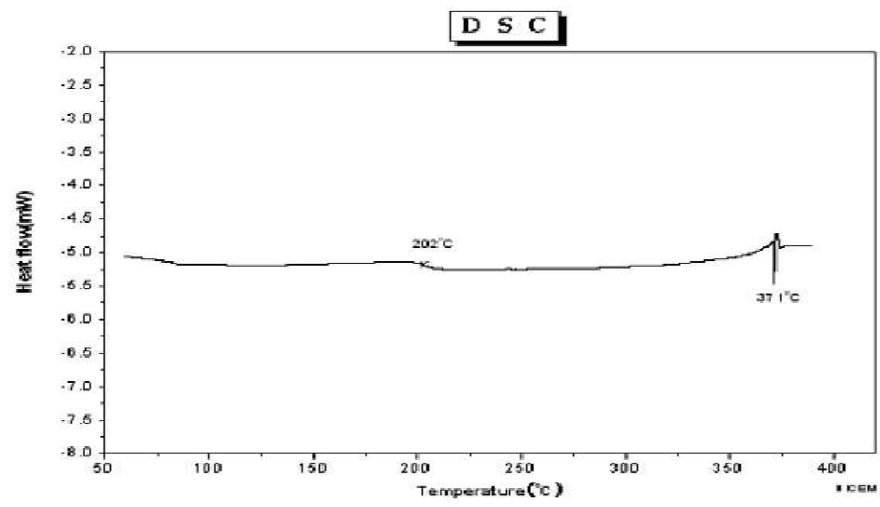
도면4



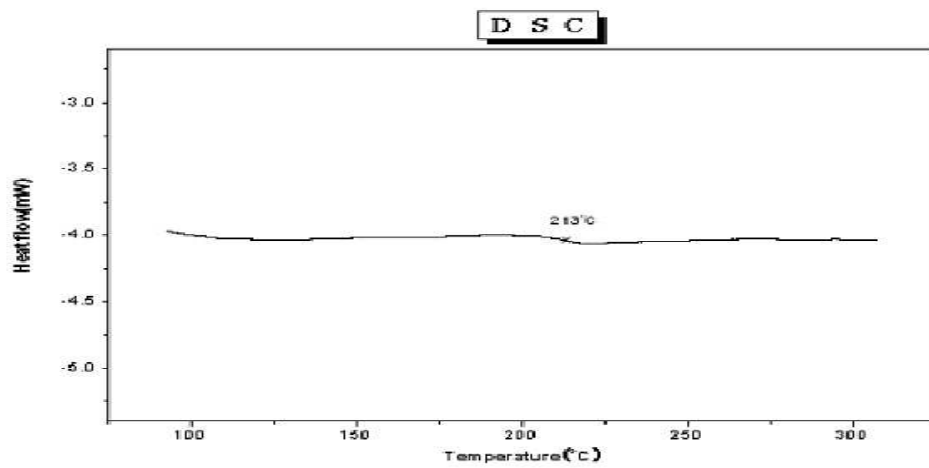
도면5



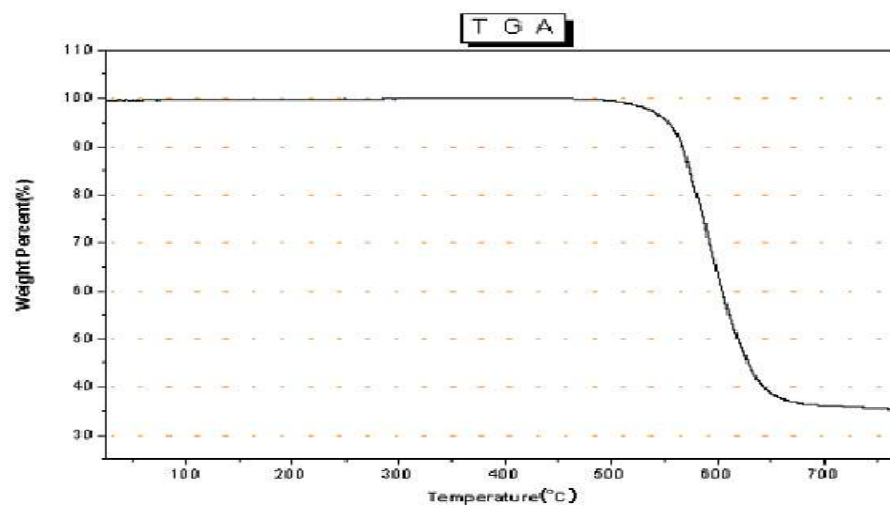
도면6



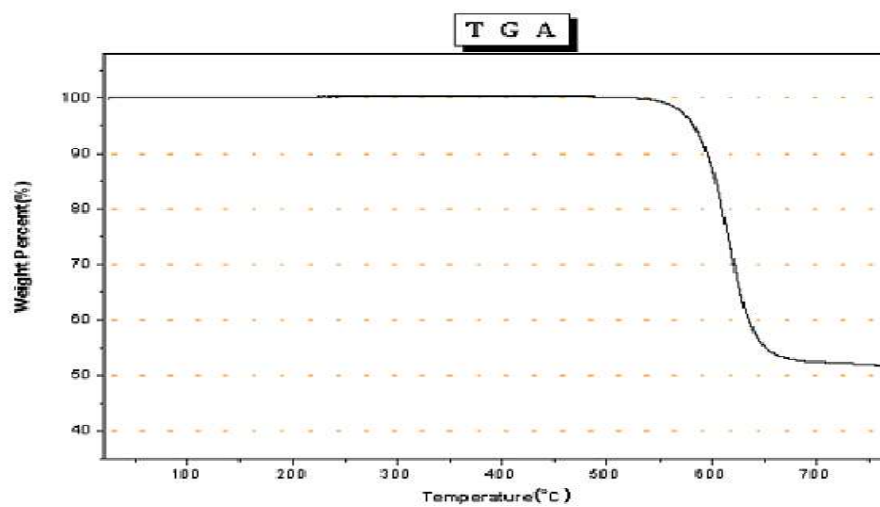
도면7



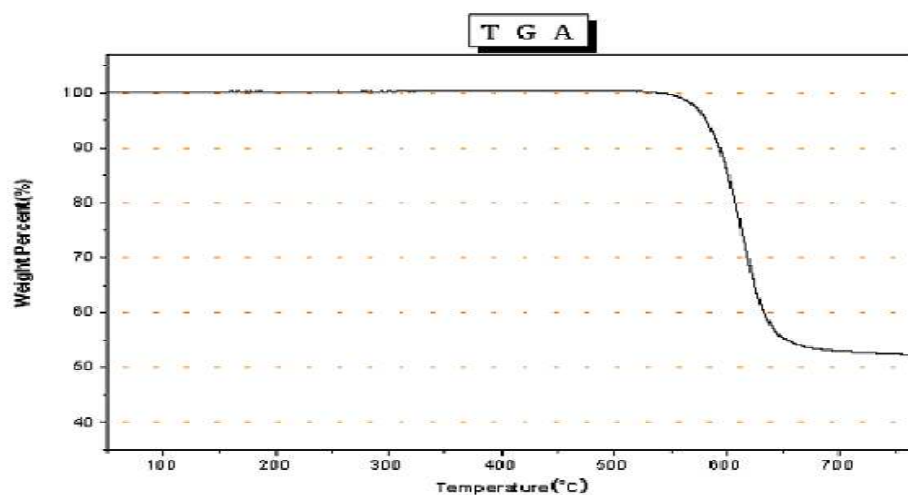
도면8



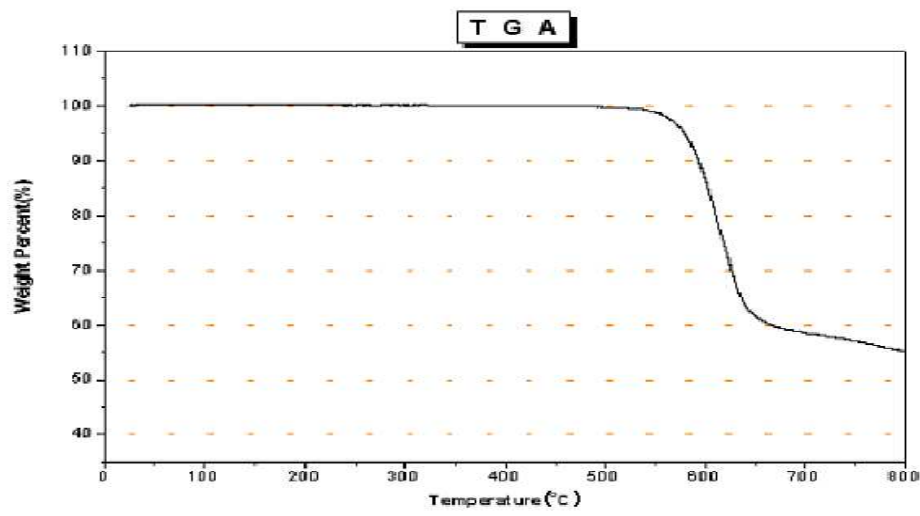
도면9



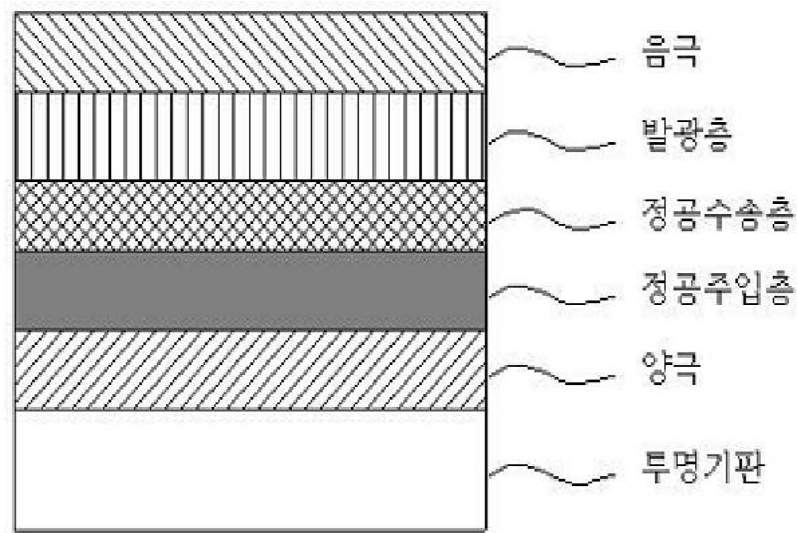
도면10



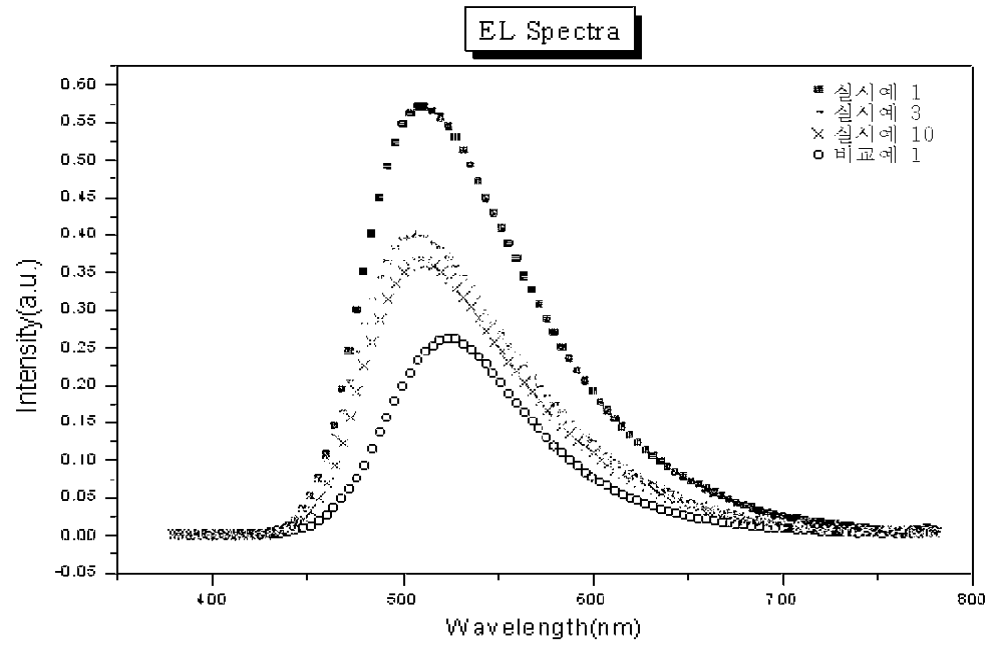
도면11



도면12



도면13



专利名称(译)	有机发光材料和有机发光二极管		
公开(公告)号	KR100663721B1	公开(公告)日	2007-01-02
申请号	KR1020050066176	申请日	2005-07-21
[标]申请(专利权)人(译)	有限公司ELM		
申请(专利权)人(译)	M. ELK公司		
当前申请(专利权)人(译)	M. ELK公司		
[标]发明人	PARK JONG YEK 박종억 JEONG SOO YOUNG 정수영 KIM JEONG MI 김정미 BAEK YONG GU 백용구 JUNG JOON HO 정준호 MIN SOO HYUN 민수현 KIM JIN YOUNG 김진영		
发明人	박종억 정수영 김정미 백용구 정준호 민수현 김진영		
IPC分类号	C09K11/06		
外部链接	Espacenet		

摘要(译)

本发明提供一种具有高玻璃化转变温度的三亚苯化合物衍生物作为空穴传输材料，因此赋予有机发光二极管优异的热稳定性，寿命，亮度和发光效率。三亚苯衍生物由下式I表示，并用作有机发光二极管（OLED）中的空穴传输材料。在式1中，E代表取代或未取代的C6-C14芳基；R1-R3各自代表取代或未取代的C6-C14芳基，其中E和R1可以通过单键，亚甲基，亚乙基或乙烯基相互连接。

