

(19)
(12)

(KR)
(B1)

(51) 。 Int. Cl. ⁷
C09K 11/06

(45)
(11)
(24)

2003 03 03
10 - 0374018
2003 02 15

(21)
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10 - 2000 - 0020606
2000 04 19

(65)
(43)

2001 - 0096922
2001 11 08

(73)

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614 - 2

373 - 1

(72)

99

132 - 1302

373 - 1

2 200 - 89

(74)

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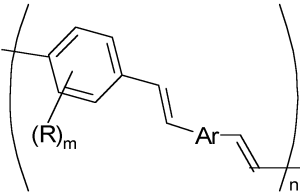
(54)

,

가

1

1



, R , , m 1~4 , Ar . , , , 가 가 , , .

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UV

3

PL

4

EL

5

-

6

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1: 2:

3: 4:

5: 6:

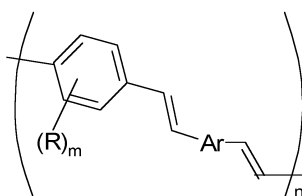
, , 가 , , , , ,

가 (PT) - 가 가 (1,4 -) (PPV), (PPP),
 가 . PPV 가 PPV ,
 가 ,
 .

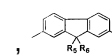
5,247,190 (1,4 -)
 , Macromolecules vol.31, p631, (1998)
 Macromolecules vol.32, p5162, (1999)

가 가 .

1



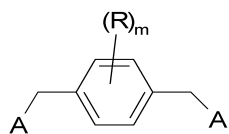
, R , , m 1~4 , Ar ,
 R₄, R₅ R₆ C1 C20



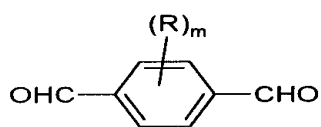
2

3

2



3



, R' R , , m 1~4 . , A - P + R'3 - PO(OR')2 .

, , .

, , 가 , 가 . ,

, , ,

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. , 가 . ,

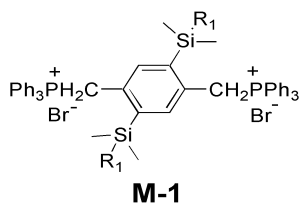
. ,

가 가 .

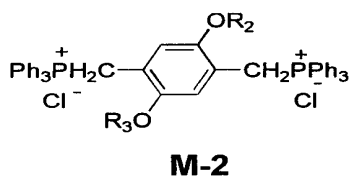
3 (Wittig) 2 (Wittig - Emons) ,

4 , 2 가 5 가 .

4



5

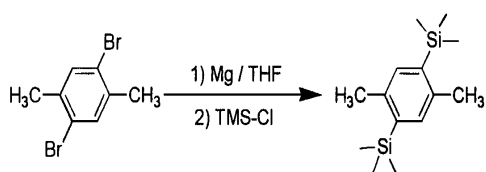


, R_1 , R_2 R_3 , C1 C20 .

4 , 2 (R_1) . 가

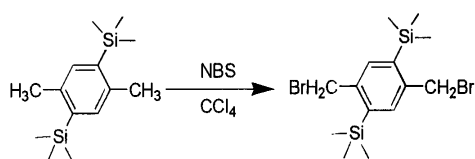
1 2,5 - - - (Grignard) 2,5 - 가 2,5 -
- () - - .

1



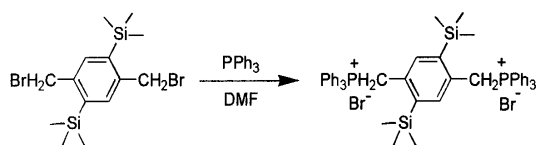
2 , 1 2,5 - - () - - N -
(N - bromosuccinimide, NBS) 2,5 - () - 1,4 - ()

2



3 , 2 2,5 - () - 1,4 - ()

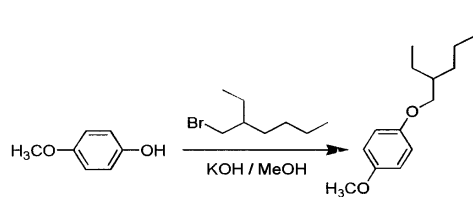
3



, 2 5 가

) - 1 - 4 4 - 2 - 4 - (2 -

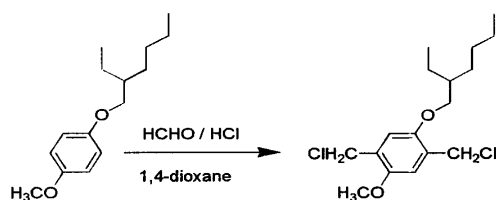
4



10

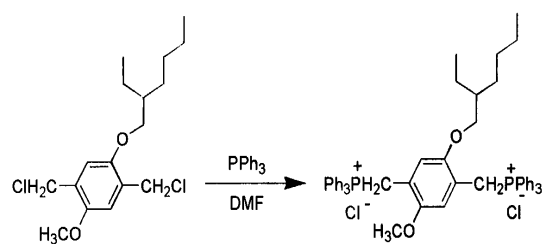
5 1, 4 , 4 4 - (2 -) - 1 -
(- CH_2Cl) 1,4 - () - 5 - (2 -
) - 2 -

5



6 , 5 가 1,4 - () - 5 - (2 -) - 2 -

6



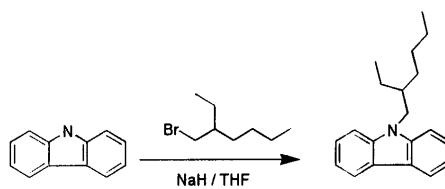
가

9 - (2 -)

7

2 -

7



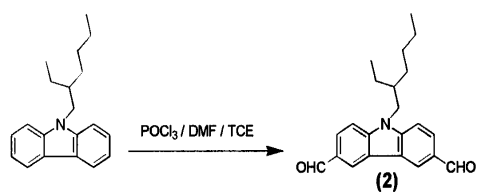
8

7
가

9 - (2 -)

(Vilsmeier)

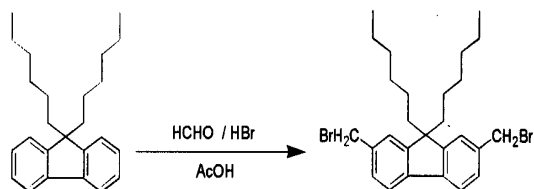
8



9

9,9 - n - (bromomethylation) - CH₂Br
2,7 - () - 9,9 - n -

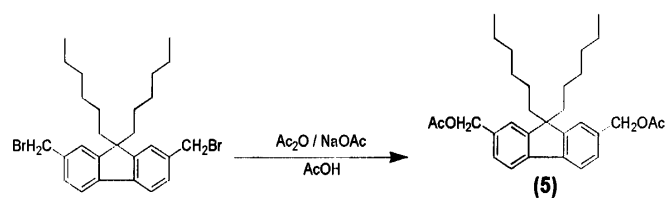
9



10 (acetic anhydride) 9 2,7 - () - 9,9 - n -
[7 - () - 9,9 - n - - 2 -

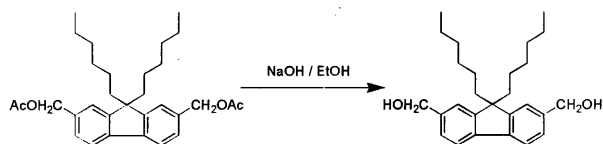
]

10



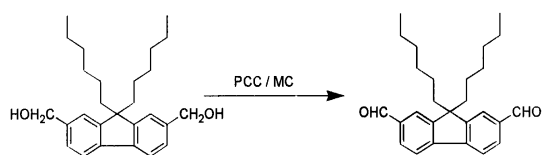
([9,9 - 7 - () - 9,9 - n - - 2 -] NaOH
11

11



([9,9 - 7 - () - 2 -]) PCC
12

12



2

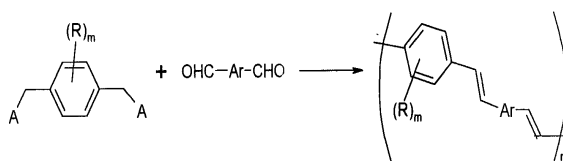
3

가

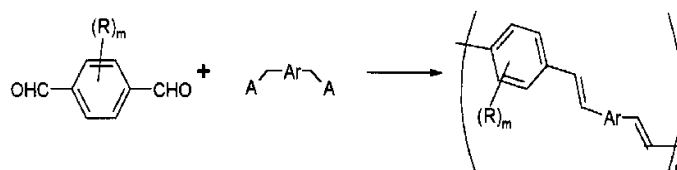
2

3

13



14



, R, Ar, A m

(M - 3)

(M - 2)

15 16

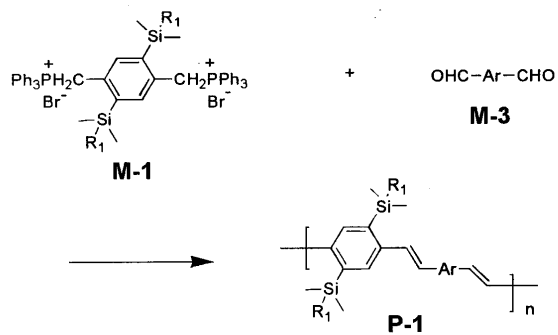
(P - 1)
(M - 3)

가

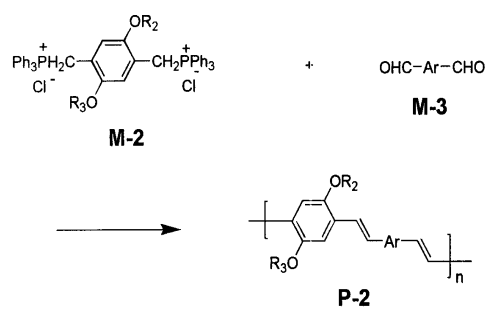
(M - 1)

(P - 2) 가

15



16



가

가

가

가

가

가

가
가

가

1

(6)

(1)

(2),

(3),

(4),

(5)

(4)

PVK (polyvinylcarbazole)

(1)

2,5 - () -

5.5 g (0.2274 mol) Mg 가 10 mL THF
 , 20.0 g (0.0758 mol) 2,5 - - p - THF
 Mg - THF . 3 (suspension) 가 . 30
 mL 가 5 HCl
 Mg MgSO₄
 (14.1 g, 74%)

Mp 56 - 57 : ¹H - NMR (CDCl₃) δ 7.25 (s, 2H), 2.43 (s, 6H), 0.33 (s, 18H). ¹³C - NMR (CDCl₃) δ 139.50, 139.14, 135.67, 22.55, - 0.16. C₁₄H₂₆Si₂ : C, 67.12; H, 10.46. : C, 66.88; H, 10.63.

(2)

2,5 - () - 1,4 - ()

2,5 - - - p - 5.0 g (0.02 mol) 7.1 g (0.0404 mol) N -
 (NBS) 40 mL .
 90 3
 가 MeOH
 . 5.1 g (62 %).

Mp 96 - 97 . ¹H - NMR (CDCl₃) δ 7.53 (s, 2H), 4.61 (s, 4H), 0.40 (s, 18H). ¹³C - NMR (CDCl₃) δ 142.12, 140.89, 137.40, 34.08, 0.28. C₁₄H₂₄Si₂Br₂ : C, 41.18; H, 5.92. : C, 39.91; H, 5.73.

(3)

2,5 - () - 1,4 - ()

4.3 g (0.0163 mol) 2 2,5 - () - 1,4 - ()
 7.4 g (0.0074 mol) 30 mL DMF , 24 .
 가
 . 6.1 g (89 %).

Mp 299 - 300 . ¹H - NMR (DMSO - d₆) δ 7.94 - 7.55 (m, 30H), 7.05 (s, 2H), 5.01 (d, 4H), - 0.31 (s, 18H).
 . C₅OH₅₄Si₂Br₂P₂ : C, 64.35; H, 5.79. : C, 63.02; H, 6.04.

(4)

4 - (2 -) - 1 -

20.0 g 4 - (0.016 mol) 12.8 g KOH (1.2 eq) MeOH 41 mL 2 -
 (1.3 eq) 80 12
 .30.0 g (79 %).

^1H - NMR (CDCl_3 , ppm) δ 6.8 (s, 4H), 3.8 (d, 2H), 3.7 (s, 3H), 1.6 - 1.2 (m, 9H), 0.9 (m, 6H).
 $\text{C}_{15}\text{H}_{24}\text{O}_2$: C, 76.22; H, 10.26. : C, 75.11; H, 10.23.

(5)

1,4 - () - 5 - (2 -) - 2 -

30.0 g (0.13 mol) 4 HCl HCHO 1,4 - (dioxane)
 90 12 MeOH
 .30.0 g (71%)

Mp 67 - 68 . ^1H - NMR (CDCl_3 , ppm) δ 6.8 (d, 2H), 4.5 (s, 4H), 3.8 (d, 2H), 3.7 (s, 3H), 1.6 - 1.3 (m, 9H), 0.9 (m, 6H).
 $\text{C}_{17}\text{H}_{26}\text{O}_2\text{Cl}_2$: C, 61.26; H, 7.88. : C, 60.89; H, 7.57.

(6)

1 - (2 -) - 4 - - 2,5 - ()

5.0 g (0.015 mol) 5 8.7 g (0.033 mol) 30 mL DM
 F 24 가 , diethyl ether
 가 (11.2 g, 87%)

Mp 218 - 219 . ^1H - NMR (CDCl_3 , ppm) δ 7.87 - 7.54 (m, 30H), 6.75 (s, 1H), 6.53 (s, 1H), 5.06 (d, 2H), 4.95 (d, 2H), 2.94 (s, 2H), 2.79 (s, 3H), 1.30 - 0.95 (m, 9H), 0.84 (t, 3H), 0.71 (t, 3H).
 $\text{C}_{53}\text{H}_{56}\text{O}_2\text{Cl}_2\text{P}_2$: C, 74.19; H, 6.53. : C, 70.32; H, 6.45.

(7)

9 - (2 -)

20.0 g (0.12 mol) 30.3 (0.016 mol) 2 - 250 mL THF
 6.5 g (0.16 mol) NaH . 48 h .

2 - (vacuum distillation) (40 /3 mmHg)
 (15.1 g, 45%) 가 .

^1H NMR (CDCl_3 , ppm): δ 8.11 (d, 2H, Ar H), 7.43 (m, 4H, Ar H), 7.26 (m, 2H, Ar H), 4.17 (d, 2H, - NC H₂CH(Et) -), 2.08 (m, 1H, - NCH₂CH(Et) -), 1.35 (m, 8H, - CH₂ -), 0.87 (m, 6H, - CH₃).
 $\text{C}_{25}\text{H}_{25}\text{N}_1\text{O}_2$: C, 85.96; H, 9.04; N, 5.01. : C, 86.01; H, 9.01; N, 4.99.

(8)

9 - (2 -) - 3,6 - [9 - (2 - ethylhexyl) - carbazole - 3,6 - dicarbaldehyde]

(Ice bath) 16.7 mL (0.22 mol) DMF 500 mL
 16.8 mL (0.18 mol) (phosphorous oxychloride) 30 가
 5.0 g (0.0018 mol) 30 mL 1,1,2 -
 90 2
 가 pH 6 - 8 가
 MgSO₄
 n - / (10/1,)
 (2.9 g, 48%) 가

Mp: 112 . ¹H NMR (CDCl₃, ppm): δ 10.12 (s, 2H, - CHO), 8.65 (s, 2H, Ar H), 8.05 (d, 2H, Ar H), 7.51 (d, 2H, Ar H), 4.24 (d, 2H, - NCH₂CH(Et) -), 2.05 (m, 1H, - NCH₂CH(Et) -), 1.32 (m, 8H, - CH₂ -), 0.87 (m, 6H, - CH₃). C₂₂H₂₅NO₂ : C, 78.77; H, 7.53; N, 4.18. : C, 79.02; H, 7.89; N, 4.37.

(9)

2,7 - () - 9,9 - - n -

4 g (10 mmol) 9,9 - - n - 3 g (100 mmol)
 (ice bath) 30% HBr 80 mL 가 60 - 70 24
 4.2 g (81%) (viscous)

¹H NMR (CDCl₃, ppm): δ 7.61 (d, 2H, Ar H), 7.34 (d, 4H, Ar H), 4.58 (s, 4H, - CH₂Br), 1.92 (m, 4H; 9 - α - CH₂), 1.06 (12H; β ~ δ - CH₂), 0.76 - 0.75 (10H; ε - CH₂ and CH₃). C₂₇H₃₆Br₂ : C, 62.32; H, 6.97. : C, 62.36; H, 6.92.

(10)

[7 - () - 9,9 - - n - - 2 -]

9 4.0 g (7.7 mmol) (3.2 g, 38.6 mmol) (2.
 17 mL, 23.1 mmol) (40 mL) 90 3
 3.1 g (83.7%)

¹H NMR (CDCl₃, ppm): δ 7.65 (d, 2H, Ar H), 7.34 (d, 4H, Ar H), 5.15 (s, 4H, - CH₂O -), 2.12 (s, 6H, - OCOCH₃), 1.93 (m, 4H; 9 - α - CH₂), 1.02 (12H; β ~ δ - CH₂), 0.77 - 0.70 (10H; ε - CH₂ and CH₃). C₃₁H₄₂O₄ : C, 77.79; H, 8.84. : C, 77.71; H, 8.87.

(11)

([9,9 - - 7 - () - 2 -])

10 (5.2 g, 10.7 mmol) (2.17 g, 54.3 mmol) 80 mL
 40 2 100 mL HCl
 pH가 7 가 3.1 g (78.9%)
 가

^1H NMR (CDCl_3 , ppm): δ 7.64 (d, 2H, Ar H), 7.28 (d, 4H, Ar H), 4.74 (s, 4H, -CH₂OH), 1.93 (m, 4H; α - CH₂), 1.03 (12H; $\beta \sim \delta$ - CH₂), 0.77 - 0.70 (10H; ϵ - CH₂ and CH₃).
 . C₂₇ H₃₈ O₂ : C, 82.18; H, 9.71; : C, 82.19; H, 9.69.

(12)

9,9 - - n - - 2,7 - (9,9 - di - n - hexyl fluorene - 2,7 - dicarbaldehyde)

11 (3.0 g, 8.2 mmol) 100 mL PCC (5.3 g, 24.
 6 mmol) 20 가 . 8 가 TLC
 . (suspension) 150 mL 30 가
 . 100 mL 1N - HCl M
 gSO₄ . 2.1 g (70.
 0%) .

^1H NMR (CDCl_3 , ppm): δ 10.07 (s, 2H, -CHO), 7.89 (s, 6H, Ar H), 2.04 (m, 4H; α - CH₂), 0.98 (12H; $\beta \sim \delta$ - CH₂), 0.74 - 0.50 (10H; ϵ - CH₂ and CH₃).
 : C, 82.37; H, 8.85. : C, 82.33; H, 8.81. 9 -
 . C₂₅ H₃₂ O₂

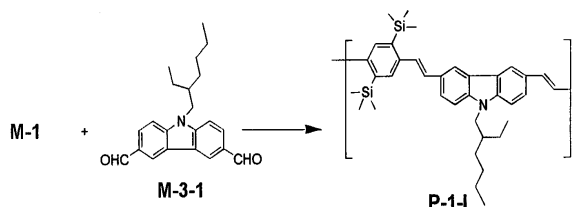
(13)

P - 1 - I

2,5 - () - 1,4 - () 1.00 g (1.1 mmol)
 9 - (2 -) - 3,6 - 0.36 g (1.1 mmol) 10 mL
 . 10 mL 0.62 g (5.5 mmol) t - BuOK 가 . 48
 . (Soxhlet) 3 0.42 g
 . 69% .

17 .

17



UV (P - 1 - I) , 8,400 가 1.76 .
 0 nm 2 355 nm , 3 48

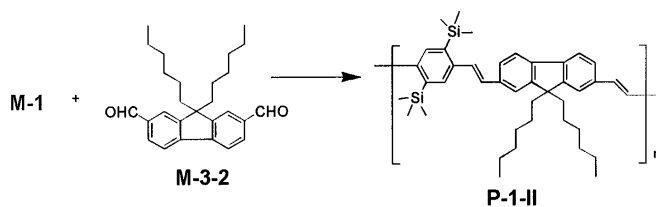
(14)

P - 1 - II

2,5 - () - 1,4 - () 1.00 g (1.1 mmol)
 9,9 - - n - - 2,7 - 0.42 g (1.1 mmol) 10 mL
 . 10 mL 0.62 g (5.5 mmol) t - BuOK 가 . 48
 (Soxhlet) 3 0.43 g
 64% .

18 .

18



(P - 1 - II) 8,800 가 1.90 .
 UV 2 385 nm , 3 49
 5 nm .

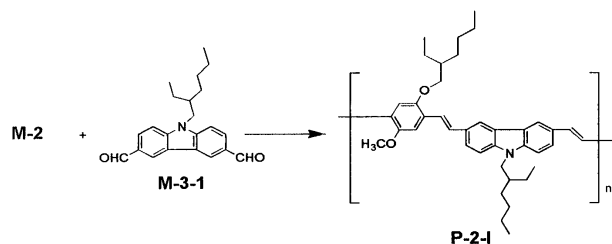
(15)

P - 2 - I

1 - (2 -) - 4 - - 2,5 - () 1.00 g (1.2 mmol)
 9 - (2 -) - 3,6 - 0.39 g (1.2 mmol) 10 mL
 . 10 mL 0.62 g (5.5 mmol) t - BuOK 가 . 4
 8 (Soxhlet) 3 0.39 g
 57% .

19 .

19



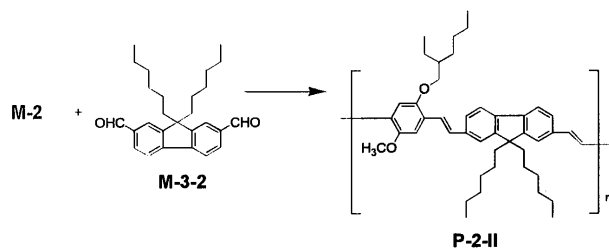
UV (P - 2 - I) 2 410 nm , 6,800 가 2.05 . 52
 0 nm .
 (16)

P - 2 - II

1 - (2 -) - 4 - - 2,5 - () 1.00 g (1.2 mmol)
 9,9 - - n - - 2,7 - 0.47 g 10 mL
 10 mL 0.62 g (5.5 mmol) t - BuOK 가 . 48
 (Soxhlet) 3 0.39 g
 42% .

20

20



UV (P - 2 - II) 2 430 nm , 6,600 가 1.95 . 54
 0nm . 3

가 P - 1 - II . P - 1 - I, P - 1
 - II, P - 2 - I P - 2 - II PMMA (diphenylanthracene)

, P - 1 - II $\Phi = 0.81$
 , PPV 가 (: J. Chem.
 Soc. Chem. Comm. 1996, 35, 2241; J. Am. Chem. Soc. 1998, 120, 231).
 (UV - visible) , 1 .

[1]

	UV - visible $\lambda_{\max}$ (nm) ^a	$\lambda_{\max}$ (nm) ^a	Φ_{pl} ^a
P - 1 - I	355(310 250) ^b	480	0.64
P - 1 - II	385	495	0.81
P - 2 - I	410(310 250) ^b	520	0.59
P - 2 - II	430	540	0.26

a (quartz)

b

1 , , 가 P - 1 - I P -
 1 - II PPV , PPV

(17)

1 (P - 1 - I) 2 (P - 1 - II)
 , ITO가 100nm , ITO 100nm
 , Al 1000
 4 , - 5 , - 6 .

MEH - PPV([2 - - 5 - (2 -) - 1,4 -])
 P - 1 - I P - 1 - II , P - 1 - I
 MEH - PPV 13 , 가 P - 1 - II MEH - PPV
 32 , , , 2

[2]

		(V/m)	(nm)	
MEH - PPV	1	5×10^7	595	
P - 1 - I	13	1.8×10^8	480	
P - 1 - II	32	1.2×10^8	500	

2 , 가 P - 1 - I P -
 1 - II MEH - PPV 가 MEH - PPV

가 가

가

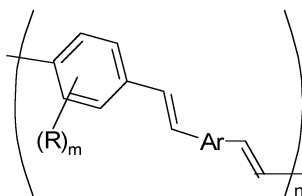
가
가
가
가

(57)

1.

1

1



(, Ar , R , m 1~4)

2.

1



3.

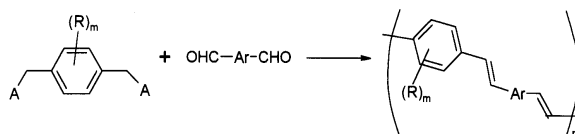
1

2

m 2 , R 가 2, 5 -

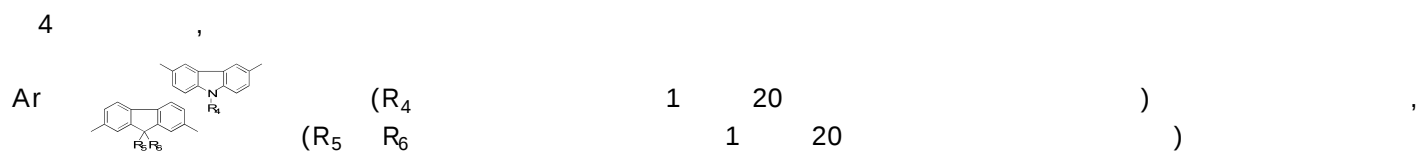
4.

가



(R , $-\text{Ar}-$, R , $-\text{PO}(\text{OR}')_2$, $-\text{P}^+\text{R}'_3$, R') , m 1~4 . , A

5.



6.

4 ,

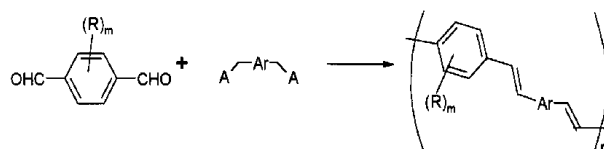
m 2 , R , 가 2, 5 -

7.

4 ,

A $-\text{P}^+(\text{C}_6\text{H}_5)_3$

8.

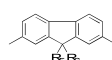
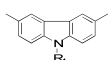


($\text{PO}(\text{OR}')_2$, $-\text{Ar}-$, R , R' , $\text{P}^+\text{R}'_3$, A , m 1~4)

9.

8

Ar



10.

8

m 2, R , 가 2, 5-

11.

8

A $-\text{P}^+(\text{C}_6\text{H}_5)_3$

12.

1

3

13.

12

14.

12 ,

, , ,

15.

12 ,

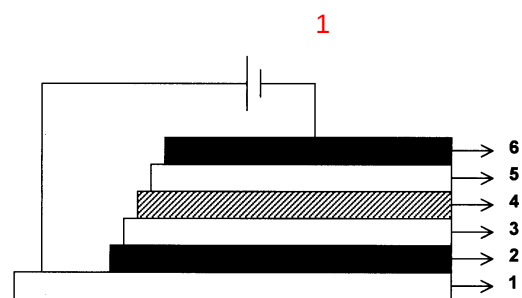
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16.

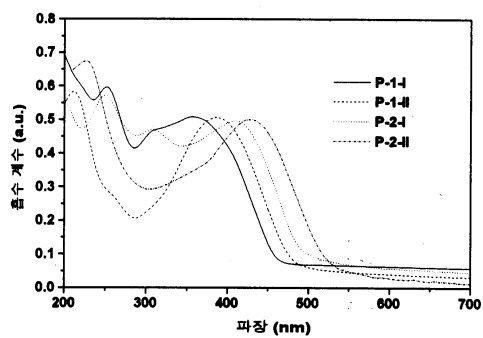
15 ,

PVK (polyvinylcarbazole)

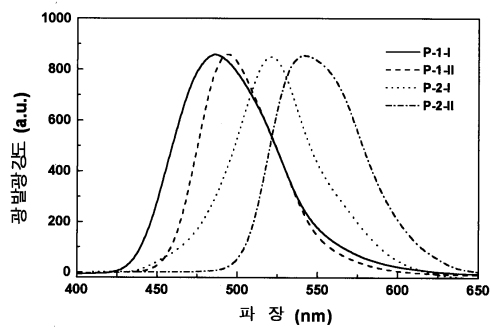
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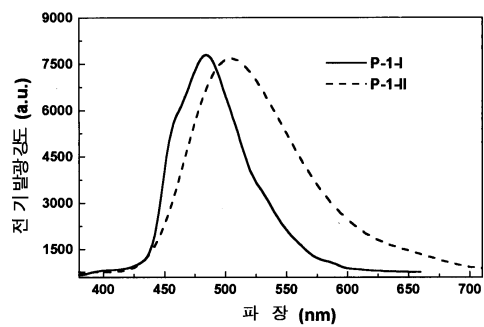
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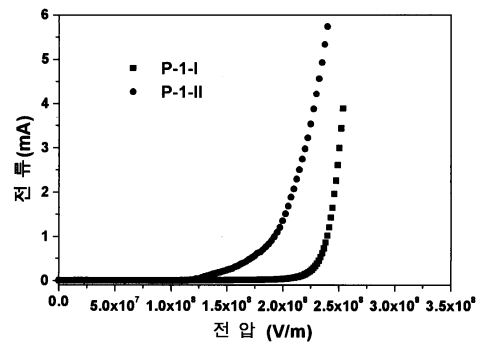
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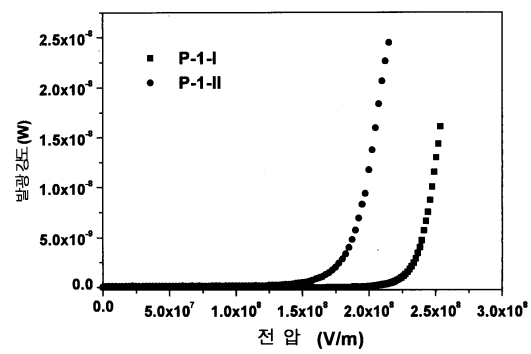
4



5



6



专利名称(译)	高效蓝色和绿色光致发光和电致发光聚合物，其制造方法以及使用该聚合物的电致发光装置		
公开(公告)号	KR100374018B1	公开(公告)日	2003-03-03
申请号	KR1020000020606	申请日	2000-04-19
[标]申请(专利权)人(译)	韩国科学技术院		
申请(专利权)人(译)	日进显示器有限公司 科学与韩国高等科技研究院		
当前申请(专利权)人(译)	日进显示器有限公司 科学与韩国高等科技研究院		
[标]发明人	SHIM HONGKU 심홍구 AHN TAEK 안택 SONG SEUNGYONG 송승용		
发明人	심홍구 안택 송승용		
IPC分类号	C09K11/06		
CPC分类号	E02B7/28 E02B7/54		
代理人(译)	JEONG JI WON 该专利事务所		
其他公开文献	KR1020010096922A		
外部链接	Espacenet		

摘要(译)

本发明提供了一种苯二胺骨架和亚芳基骨架，特别是咔唑或茚骨架通过亚乙基桥结构彼此连接，即，蓝，或绿色发光聚合物，如（1），其具有完全液化球结构式。一级方程式 - 1 - 其中R是甲硅烷基，烷基或烷氧基，m是1至4的整数，Ar是亚芳基。在本发明的聚合物，咔唑或茚骨架具有高的空穴传输和能力或能够表现出优异的发光效率，在亚烷基骨架取代的苯基甲硅烷基，烷基或烷氧基所希望的蓝色或绿色的发光波长区域发光。因此，通过选择适当的取代基可以获得所需的发光波长范围。此外，甲硅烷基取代的碳酸亚乙烯均聚物，本发明的一个绿色或橙色，甚至对比发光在发光波长范围内的红色，亚乙烯基，和芳撑亚乙烯基的发光聚合物的共聚物是蓝色的发光并在波长区域发光。 1 指数方面 发光聚合物，亚苯基亚乙烯基，亚芳基亚乙烯基，咔唑，茚，电致发光器件

