# Utilization of an Aromatic [4.4.4]Propellane as Thermally Stable Hole-Transport Materials in OLEDs

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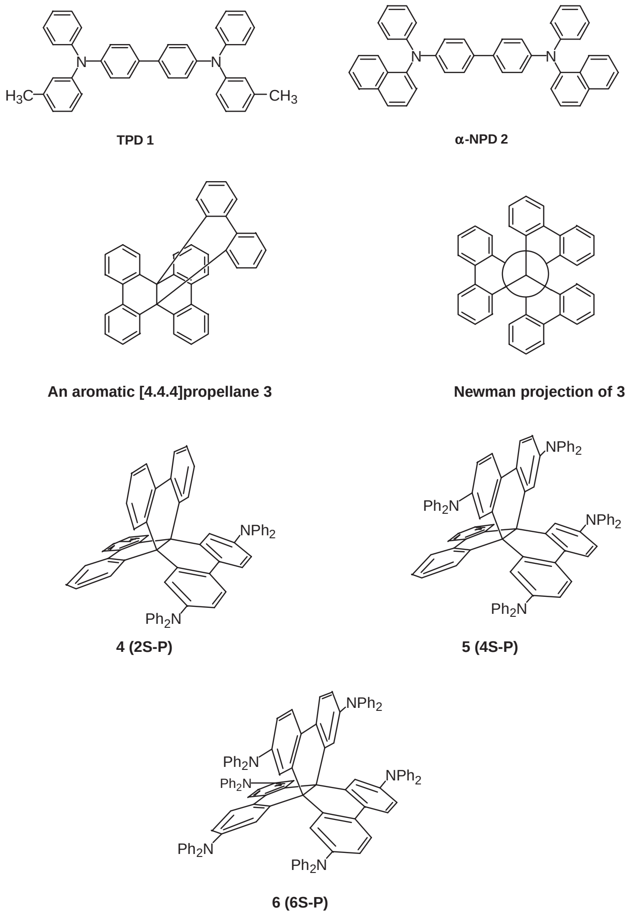
In order to develop the thermally stable hole-transport materials (HTMs) in organic light-emitting diodes (OLEDs), hexabenzo-annulated [4.4.4]propellane that has three-biphenyl substructures around the C–C hub has been exploited as the core substance. Introduction of bis-, tetrakis-, or hexakis(diphenylamino) substituents at the 4 and 4′-positions of each biphenyl moiety leads to monomeric, dimeric, and trimeric derivatives of *N*,*N*,*N*′,*N*′-tetraphenylbenzidine; *N*,*N*′-bis(3-methylphenyl)-*N*,*N*′-diphenylbenzidine (TPD) has excellent electroluminescent (EL) characteristics but low thermal stability. The key step in the preparation of these derivatives (2S-, 4S-, and 6S-P) was the coupling of appropriate fluorenes with requisite *ortho*-bromo biphenyl compounds. All of these had not only excellent EL characteristics, but also glass transition temperatures ($T_g$) of over 120 °C which was higher than that of TPD (62 °C) representative of the HTM. This result is consistent with that the parent hydrocarbon is unusually stable even at 300 °C. Structural effects of the present monomeric to trimeric TPD analogues on the thermal stability and EL characteristics are discussed.

Organic light-emitting diodes (OLEDs) have attracted much interest because of their use in the next generation of flat panel displays.[1] Materials for the devices need to be thermally stable and amorphous for long-life.[2–5] In multi-layered electroluminescent (EL) devices, since Tang and VanSlyke reported the diamine,[6] hole-transport materials (HTM) such as various triphenylamine derivatives, like the tetraphenylbenzidine family, including TPD[7] (**1**) and *N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenylbenzidine α-NPD[8] (**2**), a series of starburst molecules,[2,9,10] linear oligomers like TPTE,[11] spirocycle-incorporated derivatives,[12–14] tetrahedral,[15] fluorene core,[16,17] etc.[18,19] have been studied. Among the variety of HTMs, **2** was the first to be commercially used because of its excellent EL characteristics as well as its acceptable thermal stability, as shown by its glass transition temperature ($T_g$) of 95 °C.[20] The low $T_g$ (62 °C) of TPD has been overcome by dimeric and trimeric modifications.[11,13,14] It becomes important to know what effects the TPD unit has on the $T_g$ as well as EL characteristics. There has been, to our best knowledge, no study on the structural effects of monomeric to trimeric TPD units on an appropriate carbon skeleton.

An aromatic [4.4.4]propellane[21] (**3**) possesses three equivalent biphenyl moieties around the central ethane hub (see Fig. 1). Based on a molecular modeling, **3** has negligible strain in the stable state in which the two benzene rings of each biphenyl are twisted by about 30° (24° based on PM-3 calculation) due to van der Waals repulsion. However, to the best of our knowledge, no applications of this stable substance have been reported. Functionalization of diphenylamino groups at the 4 and 4′ positions of each biphenyl substructure can give rise to monomeric (**4**), dimeric (**5**), and trimeric (**6**) TPD



**TPD 1**

**α-NPD 2**

**An aromatic [4.4.4]propellane 3**

**Newman projection of 3**

**4 (2S-P)**

**5 (4S-P)**

**6 (6S-P)**

Fig. 1. The chemical structure of compounds **1**–**6**.

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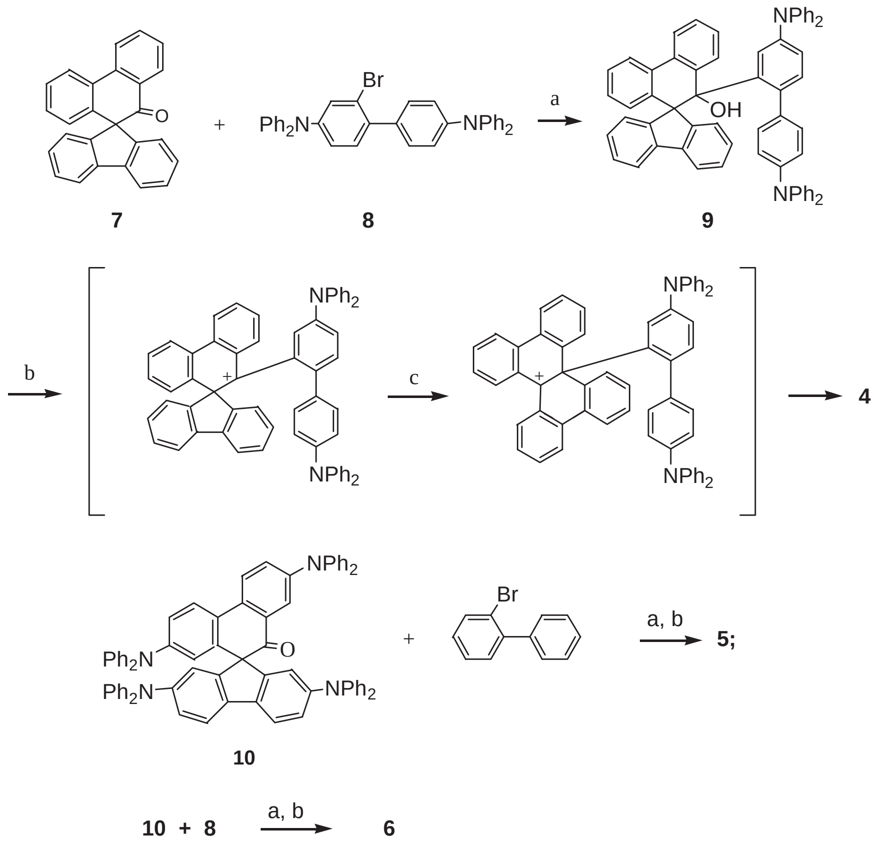

a) BuLi/THF; then $H_3O^+$ b) $CH_3SO_3H$ cat. AcOH reflux

Scheme 1.

analogues. Another structural feature of **3** is the large rotation of the benzene rings in two triphenylmethyl moieties connected at the ortho positions of each biphenyl group (see the Newman's projection of **3** as well as the structural formulae of **4**–**6** in Fig. 1). Three benzene rings on the same carbon stand near perpendicularly (over 60°) to each other. Such a molecular geometry may prevent thermal decomposition due to dissociation to two sets of triphenylmethyl radicals that should acquire conjugative stabilization with a near planar configuration. Therefore, one can expect **3** to have good thermal stability due to the triphenylmethyl moieties. Here, we report the preparation of three biphenyl-fused [4.4.4]propellane-type TPD analogues **4**–**6**. Their thermal and electrochemical properties were examined for the device design. Some EL characteristics for **4**–**6** in multilayered devices were also evaluated in order to determine the structural effects of the TPD moiety.

## Results and Discussion

**Parent Propellane.** In our preliminary study, **3** was shown to be chiral based on its Newman's projection, of the Fig. 1, of which only the right-hand spiral *P*-form is illustrated. Resolution of enantiomeric pair was accomplished by chromatography with chiral cellulose derivatives.[22] As for the thermal stability or amorphousness of **3**, the racemization experiment was of interest apart from its mechanism. Surprisingly, the resolved enatiomers of **3** do not racemize under normal conditions, which contradicts molecular modeling that indicated flipping is possible about the ethane hub. Racemization did not even occur at 300 °C resulted in recovery without racemization. However, [4.4.4]propellahexaene is reported to undergo facile racemization at room temperature with an activation energy of 14.9 kcal mol$^{-1}$.[23] Relevant compounds 9,9,10,10-tetraphenyl-9,10-dihydrophenanthrenes are known to undergo cleavage at the 9,10-bond leading to 2,2′-bis(diphenylmethyl) cation or radical-substituted biphenyl.[24] Calculation of activation energy for **3** by AM1 and B3LYP/6-3G* gave unusually large values of 47.3 and 60.1 kcal mol$^{-1}$, respectively. Thus, the carbon skeleton of **3** is more rigid and fixed than analogous compounds. The striking stability of **3** can be explained in terms of a clamping effect[25] in which three equivalent biphenyl moieties show cooperative resistance to dissociation to two stable triphenylmethyl-type radicals upon heating. Therefore, the framework of **3** is useful for thermally stable materials if adequately functionalized.

**Preparation of 4–6.** The reported preparative method[21] for **3** was used to prepare of **4**–**6** using appropriate spirocyclic ketones and *ortho*-bromobiphenyls (Scheme 1). For the preparation of **4** and **6**, the *ortho*-bromobiphenyl[14] **8** was *ortho*-lithiated and coupled with known spirocyclic ketone[26] **7** or tetrakis(diphenylamino)-substituted ketone[13] **10**. The resulting tertiary alcohol, like **9**, was subjected to acid catalysis, which ensured the formation of intermediate cations, followed by the subsequent Wagner–Meerwein rearrangement and Friedel–Crafts type cyclization to afford **4** and **6**. In turn, **5** was ob-

Table 1. Thermal Properties of Propellane Derivative **4**–**6**

| | | Mw | Mp/°C | $T_g$/°C |
|---|---|---|---|---|
| TPB[a)] | | 489 | 173–174 | 67 |
| TPF[b)] | | 502 | 245–246 | 78 |
| Propellane | **4** (mono-) | 815 | 349–352 | 121 |
| | **5** (di-) | 1149 | 354–355 | 129 |
| | **6** (tri-) | 1484 | 377–379 | 159 |

a) *N,N,N′,N′*-Tetraphenylbenzidine as a simple analogue of TPD molecule. b) 2,7-Bis(diphenylamino)-9-fluorene as a monomeric TPD.

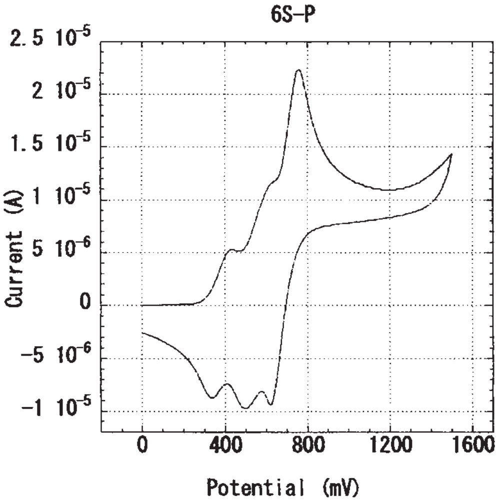

Fig. 2. Cyclic voltammogram of **6** (6S-P).

tained by coupling **10** with 2-bromobiphenyl. The overall yields of **4**–**6** were 57, 76, and 32%, respectively, after chromatograpy or recrystallization.

**Properties.** These new triphenylamine derivatives **4**–**6** were all high melting solids, (mp > 350 °C). Differential scanning calorimetry (DSC) analyses of **4**–**6** gave $T_g$ values of 121, 129, and 159 °C, respectively (Table 1). These values are conspicuously high as compared to the $T_g$'s of **1** (62 °C) and **2** (95 °C). Clearly, **4**–**6** have higher thermal stability than TPD and could be put to practical use in EL devices.[27] The reported $T_g$'s of spirobifluorene derivatives with one or two TPD moiety is 111[13] and 133 °C,[12] respectively. In other words, the selection of core hydrocarbon framework is important in establishing a high $T_g$ for HTM, and the high $T_g$ of a trispirocyclic HTM which is a trimeric TPD (170 °C) supports it.[14] In addition, the $T_g$ (129 °C) of **5** as a dimeric TPD corresponds to the $T_g$ (130 °C) of TPTE which is a single-bonded dimer of TPD. From Table 1, materials with higher mps lead to higher $T_g$. Addition of two diphenylamino groups to the parent propellane hydrocarbon to make the mono-, di-, and tri-TPD moieties caused the enhancement of $T_g$. The increase in $T_g$ from **4** to **6** is mainly attributed to the of increase in molecular weights.[28] Thus, the free rotating diphenylamino groups exert not only glassy nature[14] but also increase $T_g$.

Cyclic voltammetry (CV) of **4**–**6** was carried out in dichloromethane (for **6**, Fig. 2). Compound **4** has two reversible waves similar to *N,N,N′,N′*-tetraphenylbenzidine (TPB). In contrast, three waves were obtained in the CV of **5** and **6**, and the wave separation suggests that there is intramolecular interaction between the TPB moieties. The oxidation potentials of **4**–**6** were almost the same with their difference < 0.1 V.

**EL Devices.** Multi-layered devices containing HTMs **4**–**6** (nicknamed as 2S-, 4S-, and 6S-P) were fabricated by successive vapor deposition with aluminum(III) tris(8-quinolinolate) Alq3 as electron-transporting emitter. The device structure was a transparent indium tin oxide ITO anode/an HTM 60 nm/Alq3 60 nm/LiF 0.5 nm/Al cathode 150 nm. Upon application of direct current to these devices, green emission due to Alq3 was observed around 530 nm in each case. Figure 3a shows the luminance–applied voltage ($L/V$) characteristics of the devices containing **4**–**6**. Emission for **4**–**6** starts around 2.0 V, pass through a practical level of 100 cd m$^{-2}$ at 5.2, 4.0, and 3.5 V, respectively, and reach a maximum of over 20000 cd m$^{-2}$. The EL performance of **4**–**6** is comparable to that of TPD or TPTE;[11,14] in fact, the $L/V$ curve for **6** overlaps that for TPTE. Dimeric **5** and trimeric **6** that gave deformed CV waves have slightly higher luminance involving electron-conduction in the solid states. In the current density–voltage characteristics (Fig. 3b), the ability of hole-transport in the thin layer is enhanced in the order of **4** < **5** < **6**; this order is consistent with the number of TPD units. However, Figure 3c shows that the change in luminance against the amount of current injected goes in the order of **6** < **5** < **4**, that is, **4** is the most responsive at low of current densities (<60 mA cm$^{-2}$). Further detailed tests were carried out. The photometric efficiencies of devices measured at 300 cd m$^{-2}$ for **4**, **5**, and **6** were 3.7, 3.0, and 2.6 cd A$^{-1}$, respectively, referenced to TPTE (3.3 cd m$^{-2}$). In addition, the power efficiencies of **4**, **5**, and **6** at 300 cd m$^{-2}$ were 1.8, 1.7, and 1.8 lm W$^{-1}$, respectively, which are slightly less than that of TPTE (2.1 lm W$^{-1}$). From this, the difference in material efficiency can be negligible.

The differences among **4**–**6** are small as typically shown by the $L/V$ characteristics, though increasing in the order of **4** < **5** < **6**. This kind of level-ceiling effect on the EL properties suggests possible strategies for the molecular design of effective HTMs. As mentioned before, the $T_g$, which indicates thermal stability, can be improved by using a thermally stable rigid core like this aromatic [4.4.4]propellane. As far as EL characteristics are concerned, the incorporation of one effective HTM unit, such as TPD, can be sufficient on the basis of improve the photometric and power efficiencies. Thus, the only question that remains is how to design molecules that interact with each other in solids or on solid surfaces for efficient conduction of electrons and holes.

In conclusion, the aromatic [4.4.4]propellane core has high thermal stability. For a better HTM than TPD, the carbon skeleton has been modified by the addition of two to six diphenylamino groups at the 4 and 4′ positions of the biphenyl substructures. Hexakis(diphenylamino)-substituted compound (6S-P) shows, among those studied, the highest $T_g$ and good EL characteristics making it suitable for practical use. The present approach suggests that functionalization of the propellane will afford advanced materials for OLEDs and related devices.[5,12]

## Experimental

**General.** Commercially available reagents including dry solvents were used as received. NMR spectra were recoded on a 200

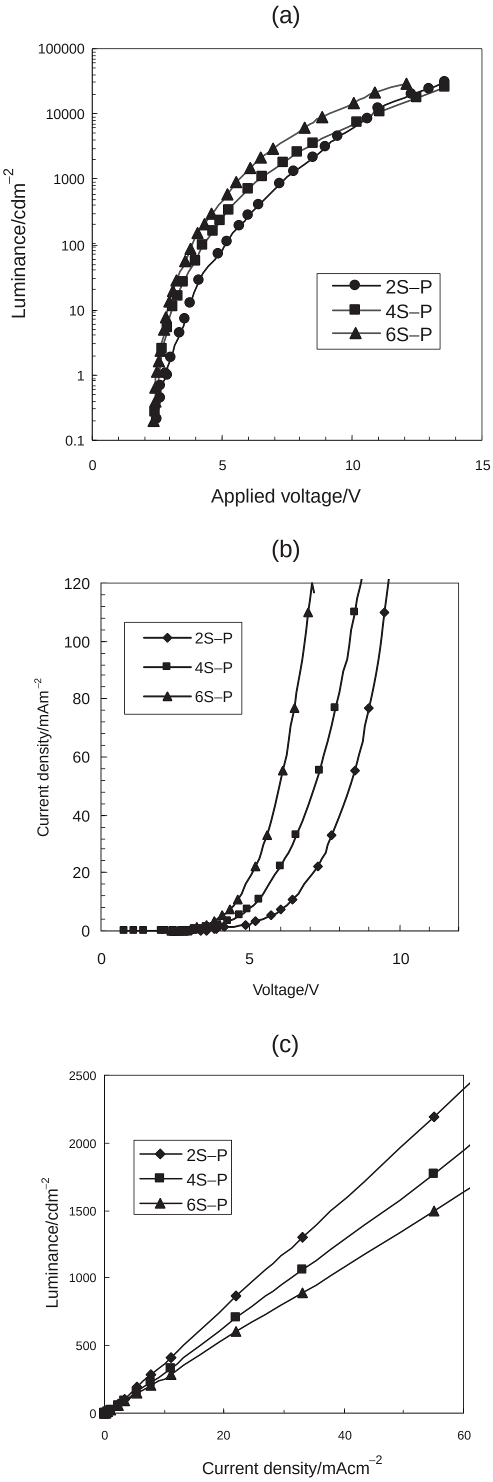

Fig. 3. Luminance–applied voltage characteristics (a), current density–voltage characteristics (b), and luminance–current density characteristics (c) of **4** (2S-P, ●), **5** (4S-P, ■), and **6** (6S-P, ▲). The device structure was ITO anode/an HTM (**4**–**6**) 60 nm/Alq3 60 nm/LiF 0.5 nm/Al cathode.

or 500 MHz spectrometer using TMS as an internal standard. DSC analyses were carried out on a SEIKO Exter 6200 model under nitrogen; the samples were heated above their melting points and cooled rapidly to room temperature. The heating rate was 10 °C min$^{-1}$. CV measurements were carried out on a BAS-50W electrochemical analyzer with 10 mL solutions (0.01 M) in dichloromethane containing tetrabutylammonium perchlorate (0.1 M) under nitrogen atmosphere with a scan rate of 0.2 V s$^{-1}$.

**Attempted Racemization of Three Biphenyl-Fused [4.4.4]-Propellane (3).** According to the literature,[21] **3** was prepared as white needles, mp (uncorrected) 472–475 °C (lit,[21] 473–475 °C). A dilute solution of the material in chloroform was subjected to preparative HPLC using a chiral column (Daicel OD, 0.46 cm in diameter and 25 cm in length) with methanol–water (9:1) as an eluant. The retention times were 23.0 and 24.9 min. Identification of *P*- or *M*-isomer is as yet. Accumulated aliquots were concentrated in vaccuo and dissolved in a new solvent such as *p*-cymene (bp 178 °C) and squalane (bp 350 °C). Attempting to racemize, a sealed tube of the enantiomer in squalane was heated at 300 °C for 4 h, but analysis by the chiral HPLC showed no significant change in the peak and retention time.

**Preparation of Bis(diphenylamino)-Substituted Propellane 4 (2S-P).** To a stirred solution of 4,4′-bis(diphenylamino)-2-bromobiphenyl[14] (**8**, 0.85 g, 1.5 mmol) in ether (10 mL) was added dropwise a hexane solution of *t*-butyllithium (1.6 M, 2.1 mL, 3.3 mmol) at −10 °C for 20 min under nitrogen atmosphere. The reaction mixture was stirred for 2 h and then a solution of spiroketone[26] **7** (0.516 g, 1.5 mmol) in toluene (8 mL) was added. The solution was then stirred for 0.5 h at room temperature. The resulting dark red solution was poured into benzene (150 mL) and ice water and acidified with dilute hydrochloric acid, followed by extractive work-up. The solvent was removed resulting in an orange colored solid. The material was admixed with acetic acid (300 mL) and methanesulfonic acid (0.5 mL) and heated at 90 °C for 2 h. The resulting precipitate was filtered and washed successively with water, methanol and benzene, giving a pale yellow solid (0.75 g). Upon recrystallization from benzene, 0.70 g of pure **4** was obtained in 57% yield; mp 349–352 °C, *m*/*z* 815 (M + 1). Anal. Found: C, 91.54; H, 5.18; N, 3.28%. Calcd for $C_{62}H_{42}N_2$: C, 91.37; H, 5.19; N, 3.44%.

**Preparation of Tetrakis(diphenylamino)-Substituted Propellane 5 (4S-P) and Hexakis(diphenylamino)-Substituted Propellane 6 (6S-P).** Spiroketone **10** was prepared previously.[13] Coupling reactions of **10** with 2-bromobiphenyl or its 4,4′-bis-(diphenylamino)-substituted derivative **8** were carried out in the same manner as above; **5**, 76% yield, mp 354–355 °C, *m*/*z* 1149 (M + 1). Anal. Found: C, 90.12; H, 5.21; N, 4.67%. Calcd for $C_{86}H_{60}N_4$: C, 89.86; H, 5.26; N, 4.87%. **6**, 32% yield, *m*/*z* 1485 (M + 1), Anal. Found: C, 89.28; H, 5.15; N, 5.54%. Calcd for $C_{110}H_{78}N_6$: C, 89.04; H, 5.30; N, 5.66%.

**Devices.** An ITO-coated glass substrate was treated by r.f. plasma of argon/oxygen gas for 30 s at a pressure of 7 × $10^{-2}$ Torr for cleaning of the surface. A hole-transport layer of 60 nm and then an Alq3 layer of 60 nm were formed under a vacuum of 5 × $10^{-7}$ Torr onto the ITO anode substrate. Finally, a 0.5 nm thick LiF layer and a 150 nm thick Al layer were deposited as the cathode. The emission area of the device was 0.09 cm$^2$. The luminance–current–voltage characteristics were measured using a current source (Keithley 2400) connected to a Minolta photometer and a microcomputer.

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## References

1 *Flat Panel Display: Advanced Organic Materials*, ed. by S. M. Kelly, Royal Society of Chemistry, **2000**.

2 Y. Shirota, *J. Mater. Chem.* **2000**, *10*, 1.

3 U. Mitschke, P. Bauerle, *J. Mater. Chem.* **2000**, *10*, 1471.

4 P. Strohriegel, J. V. Grazulcicius, *Adv. Mater.* **2002**, *14*, 1439.

5 E. Holder, B. M. W. Langeveld, U. S. Schubert, *Adv. Mater.* **2005**, *17*, 1109.

6 C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.* **1987**, *51*, 913.

7 C. Adachi, S. Tokito, T. Tsutsui, S. Saito, *Jpn. J. Appl. Phys.* **1988**, *27*, L269; C. Adachi, K. Nagai, N. Tamoto, *Appl. Phys. Lett.* **1995**, *66*, 2679.

8 S. A. Van Slyke, C. H. Chen, C. W. Tang, *Appl. Phys. Lett.* **1996**, *69*, 2160.

9 J. P. Chen, H. Tanabe, X.-C. Li, T. Thomas, Y. Okamura, K. Ueno, *Synth. Met.* **2003**, *132*, 173.

10 J. Li, C. Ma, J. Tang, C.-S. Lee, S. Lee, *Chem. Mater.* **2005**, *17*, 615; J. Li, D. Liu, Y. Li, C.-S. Lee, H.-L. Kwong, S. Lee, *Chem. Mater.* **2005**, *17*, 1208.

11 H. Tanaka, S. Tokito, Y. Taga, A. Okada, *Chem. Commun.* **1996**, 2175; S. Tokito, H. Tanaka, A. Okada, Y. Taga, *Appl. Phys. Lett.* **1996**, *69*, 878; See also: H. Fujikawa, M. Ishii, S. Tokito, Y. Taga, *Mater. Res. Soc. Symp. Proc.* **2000**, *621*, Q3.4.1.

12 T. Spehr, R. Pudzich, T. Fuhrmann, J. Salbeck, *Org. Electron.* **2003**, *4*, 61; N. Johanssen, J. Salbeck, J. Bauer, F. Weissortel, P. Prms, A. Anderson, W. R. Salaneck, *Adv. Mater.* **1998**, *10*, 1136; *Adv. Mater.* **2000**, *12*, 130; J. Salbeck, N. Yu, J. Baer, F. Weissortel, H. Bestgan, *Synth. Met.* **1997**, *91*, 209.

13 M. Kimura, S. Inoue, K. Shimada, S. Tokito, N. Noda, Y. Taga, Y. Sawaki, *Chem. Lett.* **2000**, 192.

14 M. Kimura, S. Kuwano, Y. Sawaki, H. Fujikawa, K. Noda, Y. Taga, K. Takagi, *J. Mater. Chem.* **2005**, *15*, 2393.

15 H. Zhao, C. Tanjuto, S. Thayumanavan, *Tetrahedron Lett.* **2001**, *42*, 4421; See also: S. Wang, W. J. Oldham, Jr., R. A. Hudack, Jr., G. C. Bazan, *J. Am. Chem. Soc.* **2000**, *122*, 5695; L.-H. Chen, R.-H. Lee, C.-F. Hieh, H.-C. Yeh, C.-T. Chen, *J. Am. Chem. Soc.* **2002**, *124*, 6419.

16 S. Okutsu, T. Onikubo, M. Tamano, T. Enokida, *IEEE Trans. Electron Devices* **1997**, *44*, 1302.

17 K.-T. Wong, Z.-J. Wang, Y.-Y. Chien, C.-L. Wang, *Org. Lett.* **2001**, *3*, 2285; D. E. Loy, B. E. Koene, M. E. Thompson, *Adv. Funct. Mater.* **2002**, *12*, 245.

18 S. Tokito, K. Noda, H. Fujikawa, Y. Taga, M. Kimura, K. Shimada, Y. Sawaki, *Appl. Phys. Lett.* **2000**, *77*, 160; S. Tokito, K. Noda, K. Shimada, S. Inoue, M. Kimura, Y. Sawaki, Y. Taga, *Thin Solid Films* **2000**, *363*, 290.

19 K. R. J. Thomas, J. T. Lin, Y.-T. Tao, C.-W. Ko, *J. Am. Chem. Soc.* **2001**, *123*, 9404.

20 S. A. Van Slyke, C.-H. Chen, C. W. Tang, *Appl. Phys. Lett.* **1996**, *69*, 2160.

21 G. Wittg, W. Schoch, *Justus Liebigs Ann. Chem.* **1971**, *749*, 38; The Chemical Abstracts name for **3** is 8b,16b-([1,2]benzeno[1,2]benzeno)dibenzo[*g*,*p*]chrysene. See also: W. D. Hounshell, D. A. Dougherty, J. P. Hummel, K. Mislow, *J. Am. Chem. Soc.* **1977**, *99*, 1916.

22 Y. Okamoto, M. Kawashima, K. Hatada, *J. Am. Chem. Soc.* **1984**, *106*, 5357.

23 L. A. Paquette, S. Liang, L. Waycole, G. DeLucca, H. Tendralla, R. D. Rogers, D. Kratz, R. Gleiter, *J. Org. Chem.* **1990**, *55*, 1598.

24 T. Suzuki, R. Yamamoto, H. Higuchi, E. Horita, M. Ohkita, T. Tsuji, *J. Chem. Soc., Perkin Trans. 2* **2002**, 1937.

25 D. Hounshell, D. A. Dougherty, J. H. Hummel, K. Mislow, *J. Am. Chem. Soc.* **1977**, *99*, 1916; G. Dyker, J. Koening, P. G. Jones, P. Bubenitschek, *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1733.

26 I. J. Borobitz, M. Anschel, P. D. Reado, *J. Org. Chem.* **1971**, *36*, 553.

27 P. F. Smith, P. Gerrior, S. Xie, A. M. Her, Z. Popovic, M. L. Hair, *Langmuir* **1998**, *14*, 5946.

28 K. Naito, A. Miura, *J. Phys. Chem.* **1993**, *97*, 6240.