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New 9-fluorene-type trispirocyclic compounds for thermally stable hole transport materials in OLEDs

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A novel trispirocyclic hydrocarbon having three 9-fluorene moieties around the core of truxene (**5**) was prepared readily *via* coupling of truxenone with 2-bromobiphenyl; **5** was a high melting (>500 °C) solid. For the application of **5** to an effective hole transport material (HTM) in the OLED, a triphenylamine derivative carrying six diphenylamino groups at the 2- and 7-positions of each 9-fluorene moiety (**6**) was designed in order to get high thermal stability as an improved material of the TPD type HTM. The synthesis of **6** was easily achieved using 4,4′-bis(diphenylamino)-2-bromobiphenyl (**9**). The trispirocyclic **6** was found to show a glass transition temperature as high as 170 °C. It effects the formation of its stable cation radical upon electrooxidation in solution, and amorphous thin films in solid. A multi-layered EL device for **6** as an HTM using Alq$_3$ as an electron transporting emitter showed good EL characteristics such as the maximum luminance of 37 000 cd m^{-2} at 14 V. Thus, the hexakis(diphenylamino)substituted trispirocycle **6** (TX-F6S) can be used as an efficient and thermally stable HTM in OLEDs.

Introduction

Highly thermally durable and amorphous thin-film materials have recently been actively developed in organic light emitting diodes (OLEDs) with the aim of long-life and full-color flat panel displays.[1–4] Since Tang's pioneering work, typical multi-layered devices involving appropriate organic substances have been fabricated on a transparent anode, like an indium tin oxide (ITO) glass substrate, by successive vapor deposition of a hole transport material (HTM), a light emitting and electron transport material (that is, tris(8-quinolinolato) aluminium(III) (Alq3)) and finally a metallic cathode.[5] Various triphenylamine derivatives have been prepared for the effective HTM, for example: (1) diamine TCTA,[5] (2) *N*,*N*,*N*′,*N*′-tetraphenylbenzidine family such as TPD[6] (**1**, Fig. 1), α-NPD or NPB[7] (**2**), CPB[8] *etc.*,[9] (3) Shirota's starburst molecules with various core[1,10,11] and shells,[12] (4) linear oligomeric amines,[13] (5) spiro-linked or spirocyclic benzidines,[14,15] (6) 9,9-diphenylfluorenes,[16,17] (7) tetrahedral aromatic amines[18,19] and (8) others including dibenzo[*g*,*p*]chrysene[20] and indolocarvazoles,[21] and so on.[22]

A representative HTM, *i.e.*, TPD **1**, is known to effect quite excellent elcctroluminescence (EL). However, **1** has a problem with thermal stability as shown by its low glass transition temperature (T_g) of 62 °C.[23] Therefore, the modified α-NPD **2** possessing a higher T_g of 95 °C[24] is used as the incipient commercial HTM in mono-color displays. On the other hand, the 9-fluorene framework has recently been utilized in OLED materials as the molecular core[14–17] or shell[12] as well as numerous macromolecular poly(9-fluorenes).[25] Truxene (**3**)[26] has a structure of threefold 9-fluorene (see Fig. 1). It is only recently that the chemistry of the old known **3** has been extended into materials chemistry.[27–29] Since spirobi-9-fluorene looking like double fluorene has been used as the thermally stable framework of various materials[30–34] including HTMs

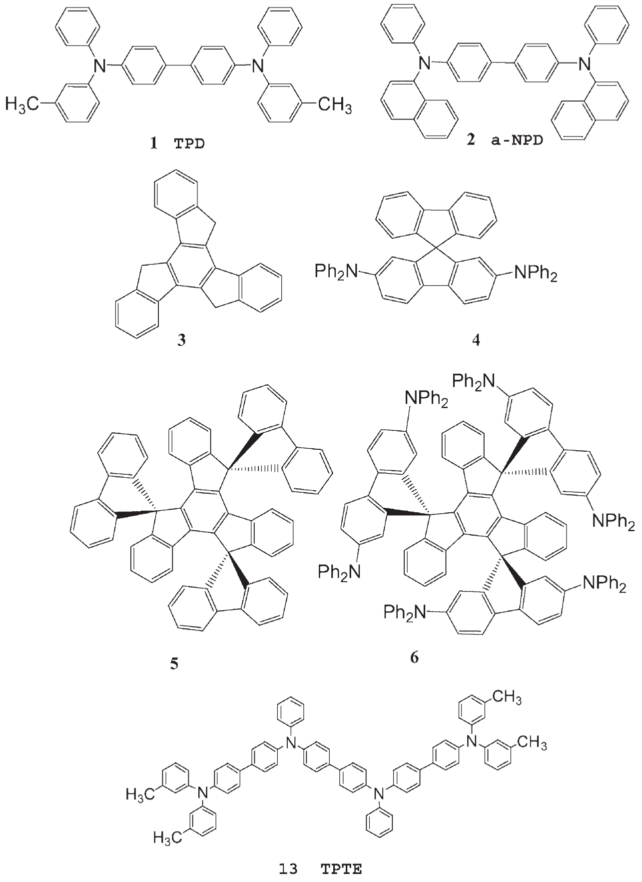

Fig. 1 Chemical structures of compounds for **1–6** and **13**.

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*ktakagi@apchem.nagoya-u.ac.jp (Makoto Kimura) (for example **4**),[14,15] a new trispirocyclic hydrocarbon **5** can be designed as the threefold spirobifluorene. Its hexakis(diphenylamino) substituted derivative **6** can be expected not only to retain the excellence in EL characteristics due to the TPD moiety, but also to exhibit an enhanced T_g leading to thermal stability in devices over the previous spirobifluorene derivative.[14] We report here the preparation of hydrocarbon **5** and its HTM derivative **6**. Thermal and electrochemical properties of **6** are also described. Conventional devices using **6** as an HTM were fabricated and EL characteristics of **6** (named here as TX-F6S) were obtained in detail.

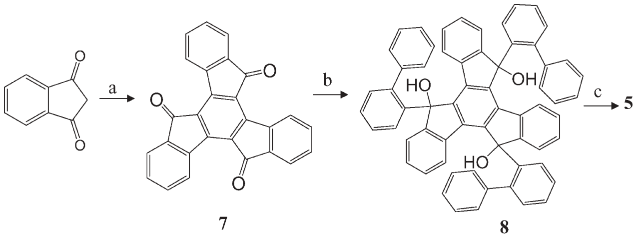
Results and discussion

Synthesis

The method for the preparation of threefold spirobifluorene **5** is the use of truxenone (**7**, truxenequinone)[29] and its coupling with 2-lithiobiphenyl, followed by acid-catalyzed cyclization of the resulting alcohol to a spirocycle (Scheme 1). The coupling of **7** with 2-bromobiphenyl took place smoothly in THF using toluene as co-solvent. The resulting triol **8** was probably a mixture of two isomers (α,α,α- and α,α,β-), and underwent the expected spirocyclization quantitatively. The aromatic hydrocarbon **5**[35,36] was a colorless solid, sparingly soluble in common organic solvents, and did not melt up to 500 °C.

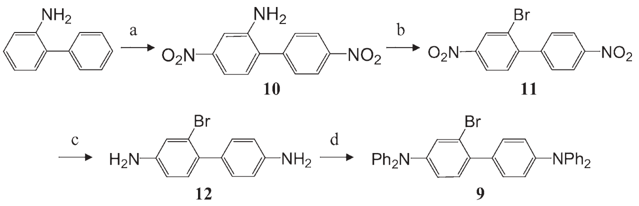
For the synthesis of **6**, 4,4′-hexakis(diphenylamino) substituted 2-bromobiphenyl compound **9** was prepared in several steps (Scheme 2). 2-Aminobiphenyl turned out as a good starting material for the key material synthesis of **9**. Classical nitration of it fortunately gave rise to di-functionalization at the 4- and 4′-positions cleanly; attempts to brominate selectively appropriate biphenyl compounds as the starting materials were in vain to give inseparable mixtures. The product 2-amino-4,4′-dinitrobiphenyl (**10**)[37] was easily purified by recrystallization, and obtained in a good yield, in turn being converted into dinitrobromide **11**.[38] Reduction of dinitro compound **11** with iron powder and hydrochloric acid gave 2-bromobenzidine (**12**). Desired **9** was obtained after reaction of **12** with an excessive amount of iodobenzene under the tri-*tert*-butylphosphine palladium catalysis.[15]

The coupling component **9** was lithiated with *t*-BuLi in ether and then allowed to react with less than one-third equiv of triketone **7**. The resulting crude triol was treated with methanesulfonic acid as catalyst to afford the desired trispirocyclic compound **4** albeit in 23% yield. Such a low yield is presumably due to the low solubility of the intermediary product, since the monoketonic dispirocyclic compound was isolated as major side product.



a) conc H_2SO_4 , 90% b) 2-bromobiphenyl , BuLi , THF
c) CH_3SO_3H cat , AcOH , 58% (2 steps)

Scheme 1



a) KNO_3 2equiv , H_2SO_4 , 81% b) $NaNO_2$, H_2SO_4 , AcOH then Cu_2Br_2 HBr , 73%
c) Fe powder , HCl , THF-EtOH , 61%
d) PhI large excess , $Pd(OAc)_2$-P^tBu_3 cat , ^tBuONa , *o*-xylene , 120 °C 12 h , 71%

Scheme 2

Properties

The hexakis(diphenylamino)substituted trispirocycle **6** being of molecular weight of 1796 g mol^{-1} is a high melting colorless solid, mp 427–430 °C. Differential scanning calorimetry (DSC) analysis showed that the T_g of **6** was as high as 170 °C; the value considerably exceeds T_g's of common polymers such as poly(methyl methacrylate) (125 °C) and poly(Bisphenol A carbonate) (149 °C). The T_g's of monospiro-bifluorene analogues like **4** are reported to be 111–133 °C.[14,15] In the study on the oligomeric triphenylamine series, it is shown that the T_g of HTM increases with increasing molecular weights; for instance, the TPTE (**13**, see Fig. 1) as a linear dimeric derivative of TPD has 140 °C of T_g.[13] Thus, the higher T_g of trispirocycle **6** can be ascribed to an effect of its high molecular weight. Moreover, we propose that a contribution of the high melting nature of **6** is derived from that of the parent hydrocarbon **5**. Since light-emitting Alq3 is known to have 175 °C of T_g,[23,41] the trispirocycle **6** can be compatible with Alq3 when they are used in a device working at such high temperatures without crystallization causing dark spots.

The hexakis(diphenylamino) substituted **6** can form transparent and glassy thin films, judging from an X-ray diffraction (XRD) analysis. Although a powder sample of **6** showed several peaks indicative of a poly-crystalline structure, the film obtained by evaporating chloroform showed only a hollow curve. As for the molecular structure of **6**, six bulky diphenylamino groups attached at the fringes of 9-fluorene moieties can undergo free rotation in three dimensions, apart from the rigid trispirocyclic core. Accordingly, such an arrangement of diphenylamino groups can contribute to the glassy nature, whereas the rigid core of trispirocycle establishes a high T_g.

UV and visible absorption spectra of **6** in chloroform were recorded using *N*,*N*,*N*′,*N*′-tetraphenylbenzidine and 2,7-bis(diphenylamino)-9-fluorene as the standard compounds. The latter two samples showed their absorption maxima at 354 and 362 nm with extinction coefficients ε of 4.1 × 10^4 and 4.3 × 10^4, respectively. On the other hand, trispirocycle **6** exhibited two absorption maxima at 365 (ε = 9.6 × 10^4) and 380 (ε = 9.3 × 10^4) nm, being not simply a triplicate of the monomeric fluorene derivative. One reason for such absorption of **6** may result from possible contribution of the spiro-conjugation.[42] For the application to device design, the

HOMO–LUMO energy band gap of **6** can be roughly estimated to be smaller by 0.2–0.3 eV than that of TPD on the basis of their absorption onsets. Cyclic voltammetry (CV) of **6** was carried out in dichloromethane using tetrabutylammonium perchlorate as an electrolyte (Fig. 2). Notably, three reversible waves for **6** were observed, being in contrast to the result of popular two waves for TPD. This may be due to possible interaction among free rotating diphenylamino groups present at each fluorene shell. The standard TPD shows two peaks at 0.63 (oxidation potential, the average of anodic and cathodic peak potentials) and 0.91 (anodic peak potential) V *vs.* Ag–AgCl electrode, suggesting a successive formation of the cation radical and then dication species of TPD molecule. In the case of **6**, the first, second and third peak oxidation peaks appeared at 0.60 (oxidation potential), 0.88 (peak potential) and 1.07 (peak potential) V *vs.* Ag–AgCl, in Fig. 2, appeared at 420, 650 and 860 mV, respectively. From the first peak, the oxidation potentials of **6** can be regarded as almost equal to that of TPD. The stability of the hole, *i.e.*, cation radicals generated, can be deduced by the ratio of cathodic and anodic peak current i_{pc}/i_{pa}.[43] In fact, the measured ratios were 0.92 and 0.95 for **6** and TPD, respectively. These results indicate that **6** can form stable cation radicals in its tetraphenylbenzidine moieties like TPD. In case of the device design,[44] the HOMO level of **6** is nearly the same as that of TPD family compounds. On the basis of the results of the absorption spectra and electrochemical CV, **6** may undergo a sort of space interaction among three electrophores, *i.e.*, TPD moieties at its activated state.

EL devices

A conventional multi-layered device for **6** (nicknamed TX-F6S) was fabricated by successive vapor deposition onto an ITO transparent glass substrate in the order of ITO cathode/HTM **6** 60 nm/Alq3 60 nm/LiF 0.5 nm–Al 150 nm. Upon application of direct current voltage, the device emitted green light due to Alq3 with a peak wavelength around 530 nm. Figs. 3–6 show various EL characteristics of **6** including those of the former developed TPTE (**13**)[13] for comparison. Generally, the present HTM **6** shows excellent EL characteristics, being equivalent to those of TPTE. In the luminance-applied voltage characteristics (Fig. 3), the emission for both **6** and TPTE starts at a voltage lower than 3 V, passes through the practical use level of 200–300 cd m^{-2} at about 5 V, and finally reaches the maximum of 37 000 cd m^{-2} at 14 V. The current density–voltage characteristics in Fig. 4 show that the present **6** has almost the same or slightly better efficiency in hole injection and transport ability as compared with TPTE. The luminance–current density characteristics in Fig. 5 show a similar situation; the photometric efficiencies of **6** and TPTE were 3.4 and 3.3 cd A^{-1}, respectively. These values are remarkably high among fluorescence-based devices using Alq3 as electron transporting emitter. This new HTM **6** (TX-F6S)

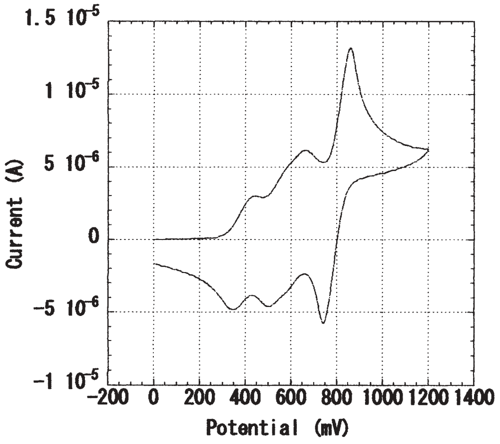


Fig. 2 Cyclic voltammogram of trispirocycle **6** measured in CH_2Cl_2 containing Bu_4ClO_4. The potential is recoded here *vs.* the ferrocene electrode after corrected potentials.

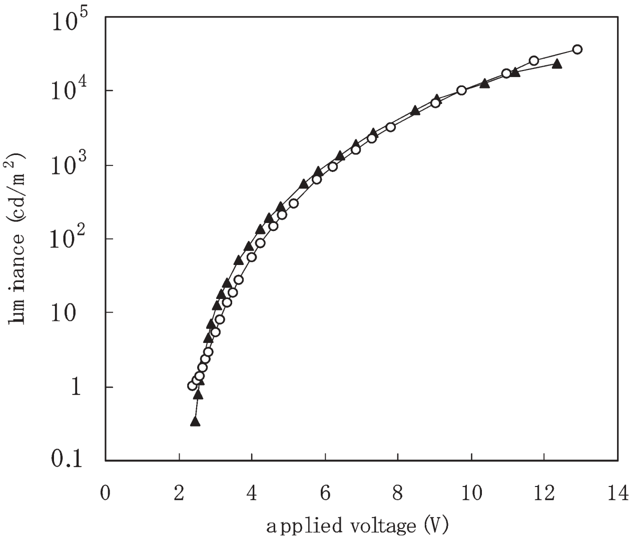


Fig. 3 Luminance–applied voltage characteristics of **6** (○) and TPTE (▲). As for the device structure, ITO/HTM (**6** or TPTE) 60 nm/Alq3 60 nm/LiF 0.5 nm–Al 150 nm.

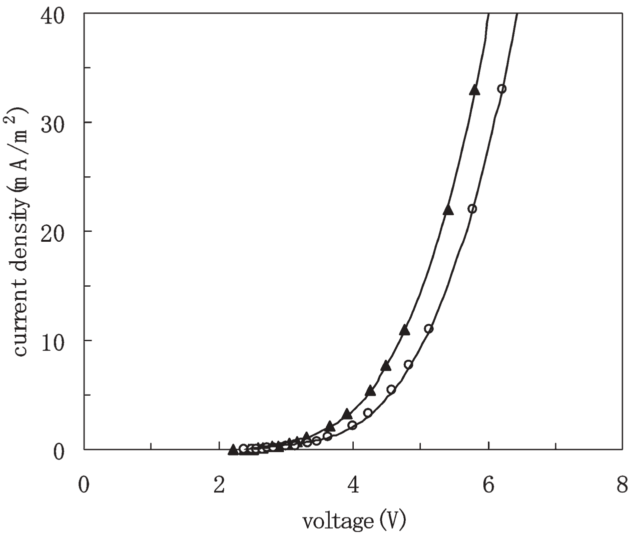


Fig. 4 Current density–applied voltage characteristics of **6** (○) and TPTE (▲). The device structure is shown in the caption of Fig. 3.

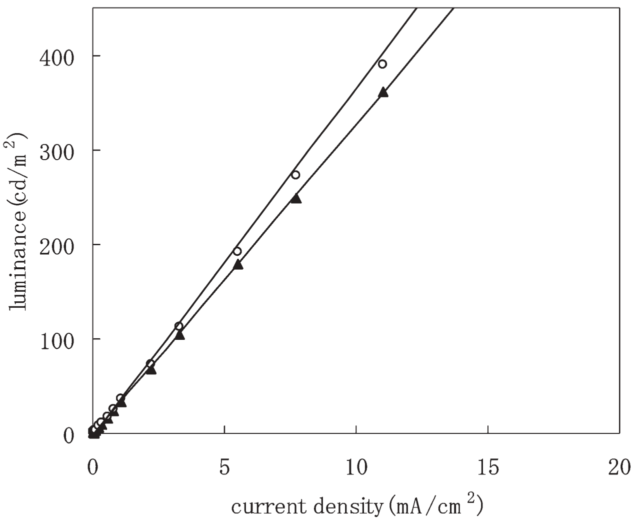


Fig. 5 Luminance–current density characteristics of **6** (○) and (▲) TPTE. See Fig. 3.

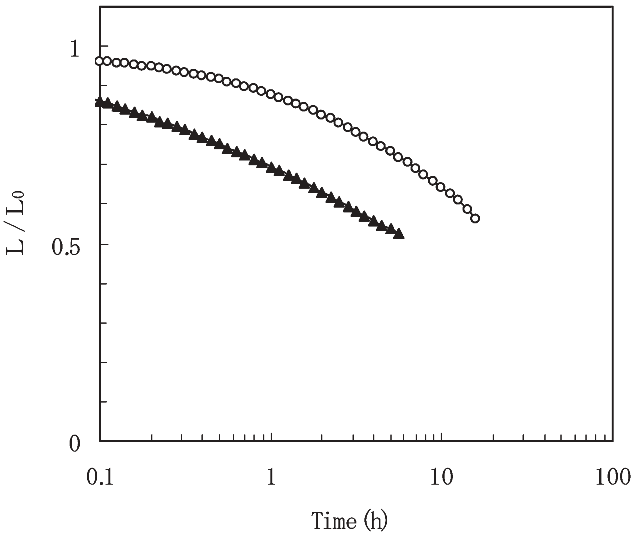


Fig. 6 Life times for devices of **6** (○) and TPTE (▲). The relative luminance L/L_0 is plotted, initial luminance L_0 being 3100 cd m^{-2}.

was examined with respect to the lifetime (Fig. 5). The half luminance of **6** was several tens of times longer than that of TPTE in an accelerated examination. At the practical use level of 200–300 cd m^{-2}, the value of **6** can be regarded to work about several hundred to thousand hours.[20] Since over ten thousand hours is necessary for full-color displays, the value is still insufficient. But, suitable design for thin-film configuration should enhance the durability. Hence, the new trispirocyclic HTM **6** can give better performance in device driving than the previously developed TPTE.

The present results provide a clue how to design the HTM molecule possessing a high T_g. A decade ago, the amorphous thin film was associated with a symmetric globular structure with large molecular weight and small intermolecular cohesion.[23] The statement fairly falls in the tetrahedral-type HTM.[18,19] The design also holds true in the HTM **6**. Recently, Shirota *et al.* have illustrated that the T_g of HTM can be enhanced by the introduction of rigid groups like 9,9-dimethylfluorene into starburst molecules around those shell parts.[12] The reverse approach is our design using rigid spiro-linked molecules in the core. The thermal stability represented by high T_g is emphasized in our case, whereas glassy materials are stressed in Shirota's study. The glassy nature of **6** can be ascribed to the presence of six free rotating diphenylamino groups attached on the three-dimensional core hydrocarbon.

In conclusion, a unique trispirocyclic hydrocarbon $C_{63}H_{36}$ as a threefold molecule of spirobi-9*H*-fluorene was prepared favorably from truxenone and 2-bromobiphenyl. We prepared its hexakis(diphenylamino) substituted derivative **6** (TX-F6S) by employing the requisite 2-bromobiphenyl derivative as the coupling and spirocyclizing agent. The amine **6** exhibited a high T_g of 170 °C. According to our molecular design, this allows **6** to be used as a thermally durable HTM in combination with Alq3 at high temperatures. The EL characteristics of **6** as HTM proved to be like or better than the representative TPD. Therefore, the trispirocyclic amine **6** can be applied to advanced full-color EL displays.

Experimental

General

Commercially available reagents including dry solvents were used as received. NMR spectra were recorded on a 200 MHz spectrometer using TMS as an internal standard. XRD data were collected on a Rigaku Rint 2100 model using Cu Kα radiation with 60 kV and 50 mA. CV measurements were carried out on a BAS-50w electrochemical analyzer with 10 mL of dichloromethane solutions (0.01 M) containing tetrabutylammonium perchlorate (0.1 M) under nitrogen atmosphere. The scan rate was 0.2 V s^{-1}. The electrode potential was corrected using ferrocene as a standard (Fig. 2).

Materials

Trispirocyclic hydrocarbon 5. A solution of *t*-butyllithium in hexane (1.6 M, 11.3 mL, 18 mmol) was added dropwise into a cooled solution of 2-bromobiphenyl (2.1 g, 9 mmol) in ether (6 mL) at −10 °C with stirring. The reaction mixture was kept stirring for 2 h. Then a mixture of truxenone[29] (0.768 g, 2 mmol), prepared previously from indane-1,3-dione in conc. sulfuric acid, and toluene (10 mL) was treated with the resultant solution of 2-lithiobiphenyl at room temperature for 1 h. The reaction mixture was poured into water (50 mL) and benzene (80 mL) and neutralized with dilute hydrochloric acid. Extraction with benzene and subsequent work-up gave a brownish solid of the resulting triols. To the material acetic acid (25 mL) and methanesulfonic acid (60 mg) as catalyst were added and then heated at 90 °C for 1 h. After cooling, the precipitated solid was filtered and washed repeatedly with acetic acid , water, methanol and benzene. There was obtained pale-yellow powder of **5** (0.92 g, 58%), sufficiently pure; mp > 500 °C, ^{1}H NMR (CDCl$_3$) δ 6.35 (d, J = 7 Hz, 3H), 6.52 (d, J = 7 Hz, 3H), 6.60 (t-like, J = 7 Hz, 3H), 6.73 (t, J = 7 Hz, 3H), 6.85 (d, J = 7 Hz, 6H), 7.18 (t-like, J = 7 Hz, 6H), 7.40

(t, *J* = 7 Hz, 6H), 7.91 (d, *J* = 2 Hz, 6H). FAB-MS *m*/*z* = 792.61 (M+). HR-MS for $C_{63}H_{36}$ (+H), calced, 793.2886, found 793.2915.

Spirocycle-coupling component 9. 2-Amino 4,4′-dinitrobiphenyl (**10**) was prepared according to literature[37] mp 207–209 °C (lit.[37] 206 °C). This amine was converted by the Sandmeyer reaction to 2-bromo-4,4′-dinitrobiphenly (**11**)[38] in 73% yield, mp 144–146 °C (lit. 148–149 °C).

Reduction of dinitro compound **11** to diamine **12** as follows: To a solution of **11** (4.83 g, 15 mmol) in THF (50 mL) and ethanol (40 mL) and conc. HCl (90 mL), iron powder (55.9 g, 0.24 g-atm) was added in small portions for 2 h. The mixture was allowed to react at 75 °C overnight. After cooling and concentration, water and benzene were added and phases were separated. When the aqueous layer was made alkaline, the resulting insoluble material was filtered off and washed with benzene. The collected benzene layer was dried and removal of the solvent gave a viscous liquid of crude **12**,[39] 2.4 g, 61%, being deteriorated on standing.

A mixture of 2- bromobenzidine (**12** 2.67 g, 10 mmol), sodium *t*-butoxide (4.8 g, 50 mmol), iodobenzene (26.5 g, 0.13 mol) and *o*-xylene (12 mL), to which a solution of palladium acetate and tri-t-butylphosphine[40] (1 : 4 mol ratio, Pd cat. 0.05 mmol) was added under nitrogen atmosphere, was heated to reflux at 120 °C and kept stirring for 20 h. The reaction mixture was poured onto ice water and acidified with dilute hydrochloric acid. Extractive work-up with chloroform and solvent evaporation gave a brown residue. Isolation of **9** after column chromatography on silica gel using benzene–hexane (1 : 2) as eluent, followed by recrystallization from benzene, gave white crystals (4.01 g, 71% yield), mp 191–2 °C, *m*/*e* 567 and 569 (M + 1), ^{1}H NMR ($CDCl_3$), δ 6.9–7.5 (m), ^{13}C NMR, 122.01, 122.62, 122.91, 123.14, 123.67, 124.79, 124.92, 127.11, 129.44, 129.61, 130.42, 131.62, 134.70, 135.78, 137.66, 147.14, 147.38, 148.87, 147.97. Anal. calcd for $C_{36}H_{27}BrN$, C 76.19, H 4.99, N 4.94. Found, C 76.63, H 4.93, N 4.28.

Hexakis(diphenylamino) substituted spirocycle 6 (TX-F6S). To a solution of ortho-bromide **9** (3.1 g, 5.5 mmol) in ether (30 mL) was added a hexane solution of *t*-butyllithium (1.6 M, 6.9 mL, 11 mmol) at −10 °C under nitrogen, and the mixture was kept stirring for 3 h. A suspension of truxenone (0.58 g, 1.5 mmol) in toluene (15 mL) was added and the reaction mixture was allowed to react for 1 h at room temperature. The resulting orange red solution was diluted with benzene and acidified with dilute hydrochloric acid. Usual workup gave the adduct triol as an orange–red glassy solid. This material was admixed with acetic acid (25 mL) containing methanesulfonic acid (0.5 mL) and heated at 100 °C for 2 h. After extractive workup using chloroform, an orange-colored solid was obtained. Careful addition of acetonitrile to the chloroform solution caused precipitation of pale yellow crystals of **6**, mp 427–430 °C. The analytical sample depended on further purification by vacuum sublimation. FAB-MS *m*/*z* = 1796 (M+), ^{13}C NMR 119.60, 120.30, 121.94, 124.88, 126.29, 126.85, 128.32, 137.61, 138.80, 140.89, 148.72. Anal. calcd for $C_{135}H_{90}N_6$, C 90.27, H 5.05, N 4.68. Found, C 90.61, H 4.91, N 4.48.

Devices

An ITO-coated glass substrate was treated by r.f. plasma of argon and oxygen gas for 60 s at a pressure of 2×10^{-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 (Fig. 3–6) were measured using a source meter (Keithley 2400) and a luminance meter (Minolta LS-110).

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35 A possible IUPAC name of **5** is as follows, based on G. P. Moss, *Pure Appl. Chem.*, 1999, **71**, 531, trispiro[10,15-dihydro-5*H*-diindeno[1,2-a:1′,2′-c]fluorene-5,9′:10,9″:15,9‴-tri(9*H*-fluorene)]. In a recent CAS index name, the truxene part is 10,15-dihydro-5*H*-tribenzo[a,f,k,]triindene.

36 For the structural interest, Professor G. Yamamoto *et al.* at Kitasato University, Japan, prepared **5** independently, a part of their work being presented at the 81st Annual meeting of the Chemical Society of Japan in spring 2002. Until now we are not aware of the details.

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