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Bistriphenylamine-substituted fluoranthene derivatives as electroluminescent emitters and dye-sensitized solar cells

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ABSTRACT

A novel series of compounds containing fluoranthene and triphenylamine were designed and synthesized as electroluminescent materials or sensitizers. Photophysical and electrochemical measurements were carried out on these compounds. **DPBF** exhibited a maximum current efficiency of 1.3 cd/A (1.00 lm/W at 5.17 V) and **D2** had the maximum light-to-electricity efficiency of 4.57% under AM 1.5 solar simulator (100 mW cm⁻²). The results suggest that bistriphenylamine-substituted fluoranthene derivatives have the potential application in optoelectronic materials.

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1. Introduction

Organic optoelectronic materials have attracted much attention in recent years, due to their essential role for optoelectronic devices, such as light-emitting diodes (OLEDs)¹ and dye-sensitized solar cells (DSSCs).² Unlike the conventional inorganic materials, the organic materials have showed obvious advantages of low cost, easy preparation, flexibility and so on. To date, a large number of novel organic photoelectric conversion materials have been developed and optimized, in order to achieve superior performance.³

Fluoranthene and its derivatives, one kind of polycyclic aromatic hydrocarbons (PAHs) with excellent fluorescent emission and carrier transport capacity, are of great interest in optoelectronic area.⁴ Hence, numerous fluoranthene-based PAH-type materials have been designed and investigated extensively for their potential application as organic nonlinear optical materials (NLO),⁵ fluorescent sensors,⁶ OLEDs,⁷ and DSSCs.⁸ More recently, we have applied benzo[*k*]fluoranthene derivatives into OLEDs⁹ and DSSCs¹⁰ and found that they can exhibit good performance in the area of optoelectronic materials.^{8,11}

As we know, triphenylamine derivatives, due to their outstanding thermal stability, mechanical property, and electrondonating ability, have become more and more important in the field of organic optoelectronics.¹² Based on the merits of combining fluoranthene and triphenylamine in one unit, we designed a series of bistriphenylamine-substituted fluoranthene derivatives (shown in Fig. 1). We synthesized 4,4'-(benzo[*k*]fluoranthene-7,12-diyl) bis(*N*,*N*-diphenylaniline) (**DPBF**), and fabricated it into three OLED devices. Meanwhile, we employed the organic sensitizers D-D π -A design concept¹³ and synthesized a series of dyes **D1**, **D2**, and **D3**, expecting that the extra triphenylamine moiety in dyes can form a tightly packed insulating monolayer blocking the I₃⁻ or cations approaching the TiO₂. They have been successfully applied to the



Fig. 1. Molecular structures of DPBF and D1–D3.





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sensitization of nanocrystalline TiO₂-based solar cells and the corresponding photovoltaic properties, electronic and optical properties are also presented.

2. Results and discussions

2.1. Synthesis

The synthetic route to these compounds containing the bistriphenylamine-substituted fluoranthene is depicted in Scheme 1. The synthesis of these dyes was similar to the procedures reported before.¹⁴ Compound **1** was prepared by Friedel–Crafts acylation. Then it was deoxidized and compound 2 was generated by intramolecular esterification. Compound 3 was obtained by Grignard reaction. **DPBF** and compounds **4** and **5** were synthesized and purified according to the established procedure.¹⁵ In the next step, the bromo-exposed intermediate 4 was reacted with 5-formylthiophen-2-ylboronicacid or 4-formylphenylboronic acid by Suzuki coupling reaction.¹⁶ Finally, the target products (D1–D3) were synthesized via the Knoevenagel condensation reaction of aldehydes 5, 6, and 7 with cyanoacetic acid in the presence of acetic acid and ammonium acetate. All the key intermediates and four final products (DPBF, D1–D3) were confirmed by ¹H NMR, ¹³C NMR, and high-resolution mass spectrometry.

2.2. Photophysical properties

The UV-vis absorption and fluorescence spectra of all compounds in dilute CH₂Cl₂ solution are shown in Fig. 2 (Table 1). The four compounds have very similar absorption properties. The lowest absorption maxima for them occur at 375-447 nm. and are assigned to the $\pi - \pi^*$ transition of conjugated molecular backbone. Compared to **D3**, the absorption band of **D2**, bearing a thiophene moiety instead of a phenyl ring, presented red-shift absorption and higher maximum extinction coefficients (ε_{max}), suggesting that the thiophene unit is more effective in increasing conjugation than the phenyl.¹⁷ In **D3**, there is a larger dihedral angle due to H–H steric hindrance effect from fluoranthene and benzene. However, the dihedral angle between fluoranthene and thiophene in **D2** is smaller to result in a larger conjugation length. Upon irradiation at 447, 445, 426, and 430 nm, the PL spectra of **D1–D3** and **DPBF** in solution were found to exhibit emission with the peak maxima at 470, 608, 611, and 590 nm, respectively. The quantum yields of these compounds in CH₂Cl₂ solution have been measured and summarized in Table 1.

The absorption spectra of **D1–D3** on TiO₂ films after 18 h adsorption are shown in Fig. 3. The maximum absorption peaks of **D1–D3** on the TiO₂ film are at 440, 419, and 437 nm, respectively. Compared to those of the corresponding solution spectra, the



Scheme 1. The synthetic routes of DPBF and D1-D3.



Fig. 2. Normalized absorption and PL spectra of compounds DPBF and D1-D3.

and 1.10 V versus NHE, respectively. The HOMO levels of the three dyes are much more positive than the iodine/iodide redox potential value (0.4 V), ensuring that there is enough driving force for the dye regeneration efficiently through the recapture of the injected electrons from I⁻ by the dye cation radical. The excitation transition energies (E_{0-0}) of **D1–D3** estimated from their absorption thresholds of dyes-sensitized TiO₂ films are 2.27, 2.28, and 2.43 eV, respectively. The estimated excited state potential corresponding to the LUMO levels of **D1–D3**, calculated from $E_{HOMO}-E_{0-0}$, are –1.21, –1.20, and –1.33 V versus NHE, respectively. The LUMO levels of the dyes are sufficiently more negative than the conduction-band-edge energy level (E_{cb}) of the TiO₂ electrode (–0.5 V vs NHE), which implies that electron injection from the excited dyes into the conduction-band of TiO₂ is feasible.²⁰

2.4. Application in OLED

To study the electroluminescent performance of **DPBF**, we fabricated three devices (1-3), with the following device configura-

Optical and electrochemical properties of DPBF and D1–D3							
Dye	$\lambda_{\rm max}^{\rm UV}{}^{\rm a}/{ m nm}~(\epsilon{ imes}10^{-4}~{ m M}^{-1}~{ m cm}^{-1})$	λ_{max}^{b}/nm	$\lambda_{\max}^{FL} a, c/nm$	${\Phi_{\mathrm{f}}}^{\mathrm{a,d}}$	HOMO ^e /V	E_{0-0}^{f}/eV	LUMO ^g /V
DPBF	325, 375, 425	_	470	0.66	-5.14(eV)	2.88	-2.26(eV)
D1	297(5.8), 447(1.2)	440	608	0.13	1.06	2.27	-1.21
D2	300(5.4), 445(2.1)	439	611	0.03	1.08	2.28	-1.20
D3	303(5.1), 426(1.4)	417	590	0.02	1.10	2.43	-1.33

^a As measured in CH₂Cl₂ solution.

^b Absorption maximum on TiO₂ film.

^c **DPBF** and **D1–D3** are excited at 447, 445, 426, and 430 nm, respectively.

^d **DPBF**, with anthracene in ethanol ($\phi_{f}=0.31$) as standard and **D1–D3**, with rhodamine B in ethanol ($\phi_{f}=0.89$) as a standard.

^e HOMO of **DPBF**(eV) was measured in CH₂Cl₂ solution and HOMO of **D1–D3**(vs NHE) was measured on TiO₂ film.

 $^{\rm f}$ E_{0-0} of **D1–D3** was estimated from the absorption thresholds from absorption spectra of dyes adsorbed on the TiO₂ film.

^g LUMO is estimated by subtracting E_{0-0} to HOMO.

absorption peaks of the dyes on the TiO_2 films are slightly blueshifted, which is probably due to the H-aggregation.^{18,19}

2.3. Electrochemical properties

The HOMO levels and LUMO levels measured by cyclic voltammetry are listed in Table 1. The HOMO value of **DPBF** measured in CH_2CI_2 is -5.14 eV, and its LUMO value calculated from the optical band gap and the HOMO value, is -2.26 eV. The HOMO levels of **D1–D3** corresponding to their first redox potential are 1.06, 1.08,



Fig. 3. Normalized absorption spectra of dyes on TiO₂ film.

tions: ITO/CFx/NPB (50 nm)/DPBF(40 nm)/TPBI (15 nm)/LiF (1 nm)/ Al (device 1); ITO/CFx/NPB (50 nm)/DPBF (40 nm)/TPBI (40 nm)/LiF (1 nm)/Al (device 2); ITO/CFx/DPBF (40 nm)/TPBI (40 nm)/LiF (1 nm)/Al (device 3), where indium tin oxide (ITO) was used as the anode, polymerized fluorocarbon (CFx) was the hole-injection layer, 4,4'-bis[*N*-(1-naphthyl)-*N*-phenyl-1-amino]biphenyl (NPB) was used as the hole transporting layer, 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) was used as the electron injecting layer. The detailed device structures are shown in Fig. S1. Additionally we tested **DPBF**'s thermal property and it exhibits high thermal stabilities with decomposition temperature (T_d) over 510 °C, which is helpful to improve the device lifetime. However, no glass transition was observed in differential scanning calorimetry.

The current density–voltage–luminance (I-V-L) characteristics for the devices 1–3 are shown in Fig. S2. The device 1 presented hole transporting layer (NPB) and the decreasing thickness of electron transporting layer (TPBI). Meanwhile, from the device 3, we can also find that DPBF showed good hole transporting property. Detailed EL performances of all the three devices were summarized in Table 2 and device 1 showed the highest efficiency among the three types of devices. The maximum current and power efficiencies of device 1 were 1.30 cd/A and 1.00 lm/W with a maximum luminance of 1254 cd/m² at 15 V, respectively.

2.5. Application in DSSC

To investigate the sensitized performance of **D1–D3**, we fabricated them into a sandwich-type two-electrode cells. Fig. 4 shows the action spectra of incident photo-to-current conversion efficiency (IPCE) for DSSCs with **D1–D3**. The dye-coated TiO₂ film was used as working electrode, platinized FTO glass as the counter

Table 1

Table 2EL performance of devices 1–3

Device	$V_{\mathrm{on}}{}^{\mathrm{a}}\left(\mathrm{V}\right)$	$\eta_{l,\max}^{b}$ (cd/A)	$\eta_{p,max}{}^c(lm/W)$	$\frac{L_{max}^{d}}{(cd/m^2)}$	λ _{EL} (fwhm) ^e (nm)	CIE _{x,y}
1	5.17	1.30	1.00	1254	464(84)	0.18, 0.25
2	4.39	1.36	0.97	943	460(68)	0.18, 0.19
3	4.55	0.98	0.60	717	476(76)	0.18, 0.26

^a Turn-on voltage at which emission starts to be detectable.

^b Maximum current efficiency.

^c Maximum power efficiency.

^d Maximum luminance.

^e Full-width at half-maximum.



Fig. 4. Photocurrent action spectra of the TiO₂ electrodes sensitized by D1–D3.

electrode, and 0.6 M PMII, 0.05 M I₂, 0.10 M LiI, and 0.5 M 4-*tert*butylpyridine in acetonitrile and methoxypropionitrile (volume ratio, 7:3) mixture solution as the redox electrolyte. As shown in Fig. 4, **D2** has more efficiency converting visible light to photocurrent in the region from 400 to 600 nm, which reaches its maximum of 70% at 450 nm. The IPCE of **D1** and **D3** is less than 60% in the spectral range 400–600 nm, which reach their maximum at 450 and 440 nm, respectively. The rather high IPCE value for **D2** dye indicates that thiophene is a good link bridge in DSSC.

The current–voltage characteristics of DSSCs fabricated with these dyes (**D1–D3**) as sensitizers under standard global AM 1.5 solar light condition are presented in Fig. 5. The detailed parameters of short-circuit current density (J_{sc}), open-circuit voltages (V_{oc}), fill factor (ff), and photovoltaic conversion efficiency (η) are summarized in Table 3. **D2** has the highest light-harvesting efficiency and short-circuit current J_{sc} among the three dyes, as the J_{sc} is related to the molar extinction coefficient of the dye molecule, in which a higher molar extinction coefficient has good light-harvesting ability and yields a higher short circuit. Compared with **D3**, **D1** has a little lower molar extinction, but its photovoltaic performance is higher than **D3**.

This is probably because **D1** has a much higher maximum values of IPCE spectrum than **D3**, which can be attributed to the good injection efficiency of **D1** and its HOMO might be beneficial for retarding the electron transfer from TiO_2 to the oxidized dye or electrolyte.

3. Conclusion

In summary, we have synthesized a series of bistriphenylaminesubstituted fluoranthene derivatives, which can be used as DSSC or OLED materials and studied their electro-optical properties. Our



Fig. 5. Photocurrent density versus voltage curves of DSSCs sensitized by the dyes **D1–D3** with electrolyte containing 0.1 M Lil, 0.05 M I₂, 0.6 M PMII, 0.5 M TBP in the mixed solvent of acetonitrile and 3-methoxypropionitrile (7:3, v/v) under light (100 mW cm⁻² simulated AM 1.5 G solar light) and dark.

 Table 3

 Optical properties and performance parameters of dye-sensitized solar cells of D1–D3^a

Dye	$J_{\rm sc}/{ m mAcm^{-2}}$	$V_{\rm oc}/{\rm V}$	ff	η /%
D1	7.59	0.73	0.72	4.00
D2	8.57	0.76	0.70	4.57
D3	5.56	0.69	0.69	2.72
N79	17.41	0.74	0.63	8.00

 $^{\rm a}$ Illumination: 100 mW cm $^{-2}$ simulated AM 1.5 G solar light; electrolyte containing: 0.1 M LiI+0.05 M I_2+0.6 M PMII+0.5 M TBP in the mixed solvent of aceto-nitrile and 3-methoxypropionitrile (7:3, v/v).

findings show that device 1 with hole transporting layer and thin electron injecting layer achieves better EL performance. We also obtained a maximum solar energy to electricity conversion efficiency of 4.57% (J_{sc} =8.57 mA cm⁻², V_{oc} =0.76 V, ff=0.70) under AM 1.5 solar simulator (100 mW cm⁻²) based on **D2** and the future improvement of the power conversion efficiency in dye-based TiO₂ cell will be possible by modification of the structure, and these works are now in progress.

4. Experiment section

4.1. General information

¹H NMR and ¹³C NMR spectra were recorded on a Bücker AM 400 spectrometer. Mass spectra were measured with an HP5989 mass spectrometer. The UV-vis spectra were recorded with a Varian Cary 500 spectrophotometer and fluorescence emission spectra were conducted on Varian Cary Eclipse fluorescence spectrophotometer. Cyclic voltammograms were performed with a Versastat II electrochemical workstation. The differential scanning calorimetry (DSC) analysis was performed under a nitrogen atmosphere on a TA Instruments DSC 2920. Thermogravimetric analysis was undertaken using a TGA instrument. To measure the fluorescence quantum yields (Φ_f), degassed solutions of the compounds in CH_2Cl_2 were prepared. Rhodamine B in ethanol ($\Phi_f=0.89$) and anthracene in ethanol ($\phi_{f=0.31}$) were used as standard. Detailed device fabrications and the photoelectrochemical measurements are written in Supplementary data. Fluorine-doped SnO₂ conducting glass (FTO glass, transmission >90% in the visible, sheet resistance 15 $\Omega/square)$ was obtained from Geao Science and Educational Co. Ltd. of China. Tetra-n-butylammonium hexafluorophosphate (TBAPF₆), 4-*tert*-butylpyridine (4-TBP), and lithium iodide were bought from Fluka and iodine, 99.999%, was purchased from Alfa Aesar. All other solvents and chemicals used were produced by Sinopharm Chemical Reagent Co., Ltd., China (reagent grade) and used as received. Solvents were distilled from appropriate reagents.

4.2. Synthesis

4.2.1. 2-(4-(*Diphenylamino*)*benzoyl*)*benzoic acid* (**1**). Phthalic anhydride (7.4 g, 50 mmol), anhydrous aluminum chloride (8.67 g, 65 mmol), and dry CH₂Cl₂ (150 mL) were added to a three-neck flask. The mixture was stirred for 1 h at room temperature and was treated dropwise with a solution of triphenylamine (10.23 g, 41.7 mmol) in CH₂Cl₂ (50 mL) at 0 °C. After the addition was complete, the reaction mixture was stirred for another 4 h at room temperature, poured over ice-contained HCl solution, and extracted with CH₂Cl₂. The organic layer was collected, dried over anhydrous Na₂SO₄. It was purified by column chromatography on silica (CH₂Cl₂/petrol ether=4:1) to yield **1** as a white solid (12.30 g, 75%). ¹H NMR (400 MHz, CDCl₃, δ): 8.08–8.10 (d, *J*=7.6 Hz, 1H), 7.61–7.65 (t, 1H), 7.51–7.57 (m, 3H), 7.37–7.38 (d, *J*=7.2 Hz, 1H), 7.29–7.32 (t, 4H), 7.11–7.17 (m, 6H), 6.91–6.93 (d, *J*=8.4 Hz, 1H). HRMS (*m/z*): [M+H]⁺ calcd for C₂₆H₁₉NO₃: 394.1443, found: 394.1449.

4.2.2. 3-(4-(Diphenylamino)phenyl)isobenzofuran-1(3H)-one (**2**). A solution of compound **1** (11.8 g, 30 mmol) in THF/EtOH (2:5) (140 mL) was treated with NaBH₄(5.67 g, 150 mmol) in portions. It was refluxed for 12 h, cooled to room temperature, and then cautiously acidified with 12% aqueous hydrochloric acid to pH 2. The mixture was stirred for 1 h at room temperature, and extracted with EtOAc. The organic layer was collected, dried over anhydrous MgSO₄. It was purified by column chromatography on silica (hexane/EtOAc=9:1) to yield **2** as a white solid (7.65 g, 68%). ¹H NMR (400 MHz, CDCl₃, δ): 7.95–7.97 (d, *J*=7.6 Hz, 1H), 7.65–7.69 (t, 1H), 7.54–7.58 (t, 1H), 7.37–7.39 (d, *J*=7.6 Hz, 1H), 7.24–7.28 (t, 4H), 7.01–7.09 (m, 10H). HRMS (*m/z*): [M+H]⁺ calcd for C₂₆H₁₉NO₂: 378.1494, found: 378.1499.

4.2.3. 4,4'-(Isobenzofuran-1,3-diyl)bis(N,N-diphenylaniline) (3). 4-Bromo-N,N-diphenylaniline (9.73 g, 30 mmol) with dry THF(25 mL) was added slowly to a refluxing mixture of magnesium turnings (0.87 g, 36 mmol) and iodine (10 mg) in dry THF(20 mL) under argon. After the formation of the Grignard reagent (1 h reflux), the cooled reagent was added slowly via an addition funnel to a solution of lactone **2** (7.55 g, 20 mmol) in THF (50 mL) at 0 °C. The reaction mixture was stirred for 6 h at room temperature and was acidified with HCl. The mixture was stirred for 15 min at room temperature, and extracted with CH₂Cl₂. The organic layer was collected, dried over anhydrous MgSO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica (hexane) to yield **3** as an orange solid (6.05 g, 50%). The intermediate is unstable, so we have no characterization data.

4.2.4. 4,4'-(3-Bromobenzo[k][fluoranthene-7,12-diyl)bis(N,N-diphenylaniline) (**4**). Compound **3** (3.02 g, 5 mmol) and 5-bromoacenaphthylene (1.16 g, 5 mmol) were refluxed in toluene (30 mL) for 24h. After cooling to room temperature, trifluoroacetic acid (0.78 mL) was added and heated at 60 °C for 3h. After cooling to room temperature, the mixture was evaporated under reduced pressure. The crude product was purified by column chromatography on silica (hexane/CH₂Cl₂ = 6:1) to yield **4** as a green solid (1.23 g, 30%). ¹H NMR (400 MHz, CDCl₃, δ): 7.91–7.93 (d, *J*=8.4 Hz, 1H), 7.76–7.79 (m, 2H), 7.64–7.66 (d, *J*=7.6 Hz, 1H), 7.45–7.53 (m, 4H), 7.35–7.40 (m, 15H), 7.28–7.31 (m, 8H), 7.09–7.12 (t, *J*=6.8 Hz, 4H), 6.88–6.90 (d, *J*=7.2 Hz, 1H), 6.66–6.68 (d, *J*=7.6 Hz, 1H). HRMS (*m*/*z*): [M+H]⁺ calcd for C₅₆H₃₇BrN₂: 817.2218, found: 817.2237.

4.2.5. 7,12-Bis(4-(diphenylamino)phenyl)benzo[k]fluoranthene-3carbaldehyde (**5**). A procedure similar to that for the compound **4** but with acenaphthylene-5-carbaldehyde (0.45 g, 2.5 mmol) instead of 5-bromoacenaphthylene giving the compound **5** as a yellow solid (1.34 g, 70%). ¹H NMR (400 MHz, CDCl₃, δ): 10.35 (s, 1H), 8.83–8.85 (d, *J*=8.4 Hz, 1H), 7.91–7.92 (d, *J*=7.6 Hz, 1H), 7.76–7.79 (m, 2H), 7.46–7.56 (m, 3H), 7.35–7.39 (m, 16H), 7.29–7.31 (m, 8H), 7.08–7.13 (dd, *J*₁=7.2 Hz, *J*₂=12 Hz, 4H), 6.94–6.96 (d, *J*=7.2 Hz, 1H), 6.87–6.89 (d, *J*=7.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, δ): 193.11, 147.88, 147.72, 147.69, 143.54, 138.11, 136.95, 136.90, 136.13, 135.44, 135.13, 134.02, 133.58, 133.25, 131.76, 131.52, 130.73, 130.68, 130.60, 130.37, 129.55, 129.51, 127.57, 127.35, 127.05, 126.78, 126.22, 124.88, 124.79, 124.58, 123.86, 123.63, 123.42, 123.30, 123.14, 120.94. HRMS (*m*/*z*): [M+H]⁺ calcd for C₅₇H₃₈N₂O: 767.3062, found: 767.3065.

4.2.6. 4,4'-(Benzo[k]fluoranthene-7,12-diyl)bis(N,N-diphenylaniline) (**DPBF**). A procedure similar to that for the compound **4** but with acenaphthylene (0.76 g, 5 mmol) instead of acenaphthylene-5-carbaldehyde giving the compound **DPBF** as a yellow-green solid (1.23 g, 68%). ¹H NMR (400 MHz, CDCl₃, δ): 7.79–7.81 (m, 2H), 7.74–7.76 (d, J=8 Hz, 2H), 7.29–7.47 (m, 28H), 7.07–7.11 (t, J=7.2 Hz, 4H), 6.88–6.90 (d, J=6.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, δ): 147.82, 147.54, 136.82, 135.66, 135.07, 134.70, 133.12, 132.63, 130.90, 130.19, 129.44, 129.31, 127.84, 126.88, 125.94, 125.78, 124.63, 124.49, 124.31, 124.12, 124.01, 123.11, 122.99, 122.24. HRMS (*m*/*z*): [M+H]⁺ calcd for C₅₆H₃₈N₂: 739.3113, found: 739.3121.

4.2.7. 3-(7,12-Bis(4-(diphenylamino)phenyl)benzo[k]fluoranthen-3yl)-2-cyanoacrylic acid D1. Compound 5 (0.77 g, 1 mmol), 2cyanoacetic acid (0.6 g, 7 mmol), and ammonium acetate (100 mg) were refluxed in acetic acid (15 mL) at 120 °C for 12 h. After cooling the solution, water was added to quench the reaction. The precipitate was filtered and washed with water. The residue was purified by column chromatography on silica gel (CH₂Cl₂/ $CH_3OH=20:1$) to yield **D1** as an orange solid (0.67 g, 81%). ¹H NMR (400 MHz, DMSO-*d*₆, δ): 8.74 (s, 1H), 8.10–8.12 (d, *J*=7.6 Hz, 1H), 7.82-7.84 (d, J=6.8 Hz, 1H), 7.60-7.65 (m, 2H), 7.48-7.50 (m, 3H), 7.38–7.43 (m, 8H), 7.10–7.32 (m, 20H), 6.62–6.68 (m, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆, δ): 147.19, 147.05, 147.01, 138.67, 136.07, 135.21, 134.53, 134.45, 134.04, 133.30, 132.75, 132.32, 131.28, 131.01, 130.44, 130.35, 130.26, 129.81, 129.63, 129.51, 129.01, 128.97, 128.38, 128.32, 127.94, 126.72, 126.64, 126.42, 124.31, 124.10, 123.88, 123.36, 123.28, 122.10, 120.83. HRMS (m/z): $[M+H]^+$ calcd for $C_{60}H_{39}N_3O_2$: 834.3121, found: 834.3116.

4.2.8. 5-(7,12-Bis(4-(diphenylamino)phenyl)benzo[k]fluoranthen-3yl)thiophene-2-carbaldehyde (6). A stirred mixture of 4 (0.41 g, 5-formylthiophen-2-ylboronicacid 0.50 mmol), (0.078 g, 0.50 mmol), Pd(PPh₃)₄ (0.0075 g, 0.0065 mmol), Na₂CO₃ (65 mg, 0.6 mmol), THF(10 mL), and H₂O (2 mL) was heated at reflux for 12 h. When the reaction was completed, water was added and the reaction mixture was extracted three times with CH₂Cl₂. The combined organic layer was washed with H₂O and brine, dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica (hexane/CH₂Cl₂=1:1) to yield **6** as an orange solid (0.21 g, 49%). ¹H NMR (400 MHz, CDCl₃, δ): 9.96 (s, 1H), 8.07–8.09 (d, *J*=8.4 Hz, 1H), 7.84–7.85 (d, J=4 Hz, 1H), 7.78–7.81 (m, 2H), 7.59–7.61 (d, J=7.2 Hz, 1H), 7.51-7.55 (m, 1H), 7.46-7.49 (m, 3H), 7.25-7.42 (m, 24H), 7.08–7.12 (m, 4H), 6.89–6.93 (t, *J*=7.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, δ): 182.89, 151.95, 147.77, 147.74, 147.70, 143.58, 138.36, 137.39, 136.84, 136.04, 135.41, 135.07, 134.92, 134.19, 133.44, 133.25,

132.17, 132.06, 130.79, 129.91, 129.83, 129.48, 129.03, 128.39, 127.89, 127.05, 127.00, 126.19, 126.07, 124.78, 124.75, 124.50, 123.97, 123.89, 123.79, 123.30, 123.25, 122.75, 121.80. HRMS (m/z): $[M+H]^+$ calcd for C₆₁H₄₀N₂OS: 849.2940, found: 849.2940.

4.2.9. 3-(5-(7,12-Bis(4-(diphenylamino)phenyl)benzo[k]fluoranthen-3-yl)thiophen-2-yl)-2-cyanoacrylic acid**D2**. The synthesis method resembles compound**D1**, and the compound was purified by column chromatography on silica (CH₂Cl₂/CH₃OH=20:1) to yield**D2** $as an orange solid (85%). ¹H NMR (400 MHz, DMSO-<math>d_6$, δ): 8.16 (s, 1H), 7.95–7.97 (d, J=7.6 Hz, 1H), 7.77–7.78 (d, J=3.6 Hz, 1H), 7.68–7.70 (d, J=7.2 Hz, 1H), 7.61–7.62 (m, 2H), 7.34–7.51 (m, 14H), 7.12–7.27 (m, 18H), 6.76–6.78 (d, J=7.6 Hz, 1H), 6.64–6.66 (d, J=6.8 Hz, 1H). ¹³C NMR (100 MHz, THF- d_8 , δ): 147.50, 147.43, 147.39, 147.33, 146.48, 138.41, 137.86, 137.77, 136.97, 134.36, 133.70, 132.92, 131.63, 130.21, 130.06, 130.02, 129.75, 129.16, 129.13, 129.08, 128.95, 128.90, 128.82, 128.71, 126.34, 126.24, 125.40, 124.31, 124.27, 123.92, 123.79, 123.45, 123.23, 123.14, 123.02, 122.76, 122.70, 118.67, 113.18, 112.43. HRMS (m/z): [M+H]⁺ calcd for C₆₄H₄₁N₃O₂S: 916.2998, found: 916.2996.

4.2.10. 4-(7,12-Bis(4-(diphenylamino)phenyl)benzo[k]fluoranthen3vl)benzaldehyde (7). A stirred mixture of 4 (0.41 g, 0.50 mmol), 4formylphenylboronic acid (0.075 g, 0.50 mmol), Pd(PPh₃)₄ (0.0075 g, 0.0065 mmol), Na2CO3 (65 mg, 0.6 mmol), THF(10 mL), and H₂O (2 mL) was heated at reflux for 12 h. When the reaction was completed, water was added and the reaction mixture was extracted three times with CH₂Cl₂. The combined organic layer was washed with H₂O and brine, dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica (hexane/CH₂Cl₂=1:1) to yield **6** as an orange solid (0.30 g, 71%). ¹H NMR (400 MHz, CDCl₃, δ): 10.13 (s, 1H), 8.02–8.04 (d, *J*=8 Hz, 2H), 7.78–7.83 (m, 3H), 7.73-7.75 (d, J=8.4 Hz, 2H), 7.46-7.50 (m, 3H), 7.41-7.44 (m, 5H), 7.29–7.39 (m, 20H), 7.07–7.11 (m, 4H), 6.92–6.96 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, δ): 192.05, 147.77, 147.67, 147.65, 146.35, 137.68, 137.30, 137.24, 135.98, 135.25, 135.03, 134.96, 134.49, 133.29, 133.21, 132.34, 130.85, 130.82, 129.86, 129.48, 128.95, 128.53, 128.12, 126.98, 126.02, 125.98, 124.72, 124.13, 124.02, 123.22, 122.51, 121.95. HRMS (m/z): $[M+H]^+$ calcd for C₆₃H₄₂N₂O: 843.3375, found: 843.3376.

4.2.11. 3-(4-(7,12-Bis(4-(diphenylamino)phenyl)benzo[k]fluoranthen-3-yl)phenyl)-2-cyanoacrylic acid**D3**. The synthesis methodresembles compound**D1**, and the compound was purified by column chromatography on silica (CH₂Cl₂/CH₃OH=20:1) to yield**D3**as $an orange solid (69%). ¹H NMR (400 MHz, DMSO-d₆, <math>\delta$): 8.16–8.18 (d, J=7.6 Hz, 2H), 7.82–7.84 (d, J=7.6 Hz, 1H), 7.76–7.78 (d, J=8 Hz, 2H), 7.69–7.71(m, 2H), 7.63–7.65 (d, J=7.2 Hz, 1H), 7.55–7.58 (m, 3H), 7.41–7.44 (m, 11H), 7.25–7.30 (m, 12H), 7.11–7.15 (m, 4H). ¹³C NMR (100 MHz, DMSO-d₆, δ): 147.31, 147.22, 147.09, 143.06, 143.01, 137.38, 136.21, 136.03, 135.04, 134.52, 134.45, 134.09, 133.58, 132.54, 132.48, 131.39, 131.05, 130.63, 129.72, 127.53, 126.47, 126.42, 124.39, 123.39. HRMS (*m*/*z*): [M+H]⁺ calcd for C₆₆H₄₃N₃O₂: 910.3434, found: 910.3431.

Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.09.013.

References and notes

- (a) Zhong, H. L.; Lai, H.; Fang, Q. J. Phys. Chem. C 2011, 115, 2423–2477; (b) Bubniene, G.; Malinauskas, T.; Daskeviciene, M.; Jankauskas, V.; Getautis, V. Tetrahedron 2010, 66, 3199–3206.
- (a) Zhou, H. P.; Xue, P. C.; Zhang, Y.; Zhao, X.; Jia, J. H.; Zhang, X. F.; Liu, X. L.; Lu, R. *Tetrahedron* **2011**, 67, 8477–8483; (b) Lai, H.; Hong, J.; Liu, P.; Yuan, C.; Li, Y. X.; Fang, Q. *RSC Adv.* **2012**, *2*, 2427–2432; (c) Chou, H.-H.; Hsu, C.-Y.; Hsu, Y.-C.; Lin, Y.-S.; Lin, J. T.; Tsai, C. *Tetrahedron* **2012**, 767–773.
- (a) Zhu, X.-H.; Peng, J. B.; Cao, Y.; Roncali, J. Chem. Soc. Rev. 2011, 40, 3509–3524; (b) Yokoyama, D. J. Mater. Chem. 2011, 21, 19187–19202; (c) Heckmann, A.; Lambert, C. Angew. Chem., Int. Ed. 2012, 51, 326–392; (d) Clifford, J.; Martínez-Ferrero, E.; Viterisi, A.; Palomares, E. Chem. Soc. Rev. 2011, 40, 1635–1646; (e) Mishra, A.; Fischer, M. R.; Bäuerle, P. Angew. Chem., Int. Ed. 2009, 48, 2474–2499; (f) Wang, Z.-S.; Cui, Y.; Hara, K.; Dan-oh, Y.; Kasada, C.; Shinpo, A. Adv. Mater. 2007, 19, 1138–1141.
- (a) Watson, M. D.; Fechtenkötter, A.; Müllen, K. Chem. Rev. 2001, 101, 1267–1300; (b) Kim, J.-Y.; Lee, C.-W.; Jang, J. G.; Gong, M.-S. Dyes Pigments 2012, 94, 304–313; (c) Wang, Z. Q.; Xu, C.; Wang, W. Z.; Dong, X. M.; Zhao, B. T.; Ji, B. M. Dyes Pigments 2012, 92, 732–736; (d) Sonar, P.; Soh, M. S.; Cheng, Y. H.; Henssler, J. T.; Sellinger, A. Org. Lett. 2010, 12, 3292–3295; (e) Ramanan, C.; Smeigh, A. L.; Anthony, J. E.; Marks, T. J.; Wasielewski, M. R. J. Am. Chem. Soc. 2012, 134, 386–397; (f) Okujima, T.; Tomimori, Y.; Nakamura, J.; Yamada, H.; Uno, H.; Ono, N. Tetrahedron 2010, 66, 6895–6900.
- (a) He, G. S.; Tan, L. S.; Zheng, Q. D.; Prasad, P. N. Chem. Rev. 2008, 108, 1245–1330; (b) Mongin, O.; Porrès, L.; Charlot, M.; Katan, C.; Blanchard-Desce, M. Chem.—Eur, J. 2007, 13, 1481–1498; (c) Albota, M.; Beljonne, D.; Brédas, J. L.; Ehrlich, J. E.; Fu, J. Y.; Heikal, A. A.; Hess, S. E.; Kogej, T.; Levin, M. D.; Marder, S. R.; McCord-Maughon, D.; Perry, J. W.; Röckel, H.; Rumi, M.; Subramaniam, G.; Webb, W. W.; Wu, X. L.; Xu, C. Science 1998, 281, 1653–1656; (d) Pawlicki, M.; Collins, H. A.; Denning, R. G.; Anderson, H. L. Angew. Chem., Int. Ed. 2009, 48, 3244–3266; (e) Kim, H. M.; Lee, Y. O.; Lim, C. S.; Kim, J. S.; Cho, B. R. J. Org. Chem. 2008, 73, 5127–5130.
- Liu, X. C.; Yang, X.; Fu, Y.; Zhu, C. J.; Cheng, Y. X. Tetrahedron 2011, 67, 3181–3186.
- (a) Wu, J. S.; Pisula, W.; Müllen, K. Chem. Rev. 2007, 107, 718–747; (b) Debad, J. D.; Morris, J. C.; Lynch, V.; Magnus, P.; Bard, A. J. J. Am. Chem. Soc. 1996, 118, 2374–2379; (c) Liu, F.; Xie, L. H.; Tang, C.; Liang, J.; Chen, Q. Q.; Peng, B.; Wei, W.; Cao, Y.; Huang, W. Org. Lett. 2009, 11, 3850–3853; (d) Shah, B. K.; Neckers, D. C.; Shi, J. M.; Forsythe, E. W.; Morton, D. Chem. Mater. 2006, 18, 603–608.
- Wu, W. J.; Li, J.; Guo, F. L.; Zhang, L.; Long, Y. T.; Hua, J. L. Renewable Energy 2010, 35, 1724–1728.
- 9. Tang, C. W.; Vanslyke, S. A. Appl. Phys. Lett. 1987, 51, 913-915.
- 10. O'Regan, B.; Grätzel, M. Nature 1991, 353, 737-740.
- Xia, Z. Y.; Su, J. H.; Fan, H. H.; Cheah, K. W.; Tian, H.; Chen, C. H. J. Phys. Chem. C 2010, 114, 11602–11606.
- (a) Zhao, Y.; Ye, C. Q.; Qiao, Y. L.; Xu, W.; Song, Y. L.; Zhu, D. B. *Tetrahedron* **2012**, 68, 1547–1551; (b) Gao, B. X.; Xia, D. F.; Geng, Y. H.; Cheng, Y. X.; Wang, L. X. *Tetrahedron Lett.* **2010**, *51*, 1919–1921.
- 13. Ning, Z. J.; Zhang, Q.; Wu, W. J.; Pei, H. C.; Liu, B.; Tian, H. J. Org. Chem. 2008, 73, 3791–3797.
- Ma, X. M.; Wu, W. J.; Zhang, Q.; Guo, F. L.; Meng, F. S.; Hua, J. L. Dyes Pigments 2009, 82, 353–359.
- 15. Debad, J. D.; Morris, J. C.; Magnus, P.; Bard, A. J. J. Org. Chem. 1997, 62, 530-537.
- 16. Suzuki, A. J. Organomet. Chem. 1999, 576, 147-168.
- 17. Thomas, K. R. J.; Hsu, Y.-C.; Lin, J. T.; Lee, K.-M.; Ho, K.-C.; Lai, C.-H.; Cheng, Y.-M.; Chou, P.-T. *Chem. Mater.* **2008**, *20*, 1830–1840.
- Zhan, W. H.; Wu, W. J.; Hua, J. L.; Jing, Y. H.; Meng, F. S.; Tian, H. Tetrahedron Lett. 2007, 48, 2461–2465.
- Hwang, S.; Lee, J. H.; Park, C.; Lee, H.; Kim, C.; Park, C.; Lee, M. H.; Lee, W.; Park, J.; Kim, K.; Park, N. G.; Kim, C. Chem. Commun. 2007, 4887–4889.
- Li, R. Z.; Shi, D.; Zhou, D. F.; Cheng, Y. M.; Zhang, G. L.; Wang, P. J. Phys. Chem. C. 2009, 113, 7469–7479.