Synthesis and fluorescence emission properties of 1,3,6,8-tetrakis(9*H*-fluoren-2-yl)pyrene derivative

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A novel pyrene-based highly pure blue fluorescent and stable molecule, 1,3,6,8-tetrakis[9,9-bis(3-methylbutyl)-9*H*-fluoren-2-yl]pyrene, was successfully synthesised via a Pd-catalysed Suzuki coupling reaction of 1,3,6,8-tetrabromopyrene with 2-[9,9-bis(3-methylbutyl)-9*H*-fluoren-2-yl]-4,4,5,5-tetramethyl[1,3,2]dioxaborolane. The photoproperties of this pyrene were examined in detail and these data indicated its potential application as blue-emitting materials in organic light-emitting diodes.

Keywords: pyrenes, Suzuki coupling reaction, tetraarylpyrene, fluorescence emission properties

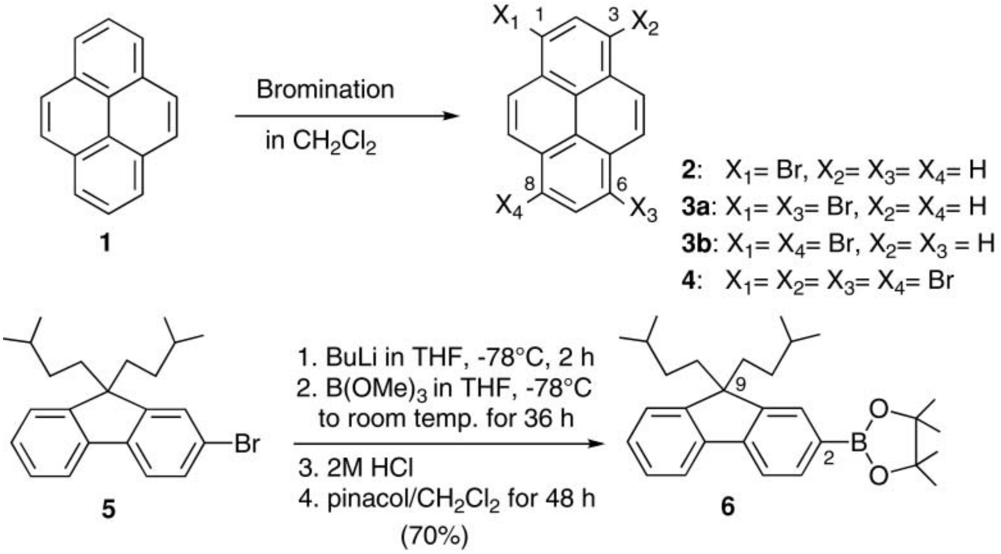
In recent years, organic materials such as the polycyclic aromatic hydrocarbons (PAHs) (*e.g.* naphthalene, anthracene, pyrene, perylene, *etc.*) and their derivatives have been used for developing emitters in organic light-emitting diodes (OLEDs) due to their fluorescent properties.[1–6] In particular, these compounds have strong π-electron delocalisation characteristics and can be substituted with a range of functional groups, which may be used for OLED materials with a tunable wavelength. At present, numerous materials derived from naphthalene, anthracene, perylene, and fluorene have been widely used as emitting materials in OLED, but the use of the pyrene molecules is very limited, because they easily formed π-aggregates/excimers in solid state and high concentration solutions, and the formation of π-aggregates/excimers leads to an additional emission band at a long wavelength and a decrease of quantum efficiency in electroluminescence. Recently, this problem has been mainly solved by the introduction of bulky or heavy branched side chains into pyrene molecules or co-polymerisation with a suitable bulky co-monomer. More recently, it was reported that pyrene derivatives were used as blue-emitting material in OLED by introducing long or branched side chains.[7–11] Recently, the synthesis of a pyrene-based fluorescent dendrimer has also been reported wherein the core unit is a 1,3,6,8-tetrasubstituted pyrene and the peripheral units contain monosubstituted pyrene units.[7,12–16]

On the other hand, recently, fluorene-based compounds have used in applications[17–21] such as highly thermal stable and efficient emissive materials for OLEDs and carrier transport materials for field effect transistors (FETs).[22–24] Chemically, fluorene derivatives are interesting since they contain a rigid biphenyl plane and a facial substitution at the C9 site, which provides the possibility of improving the solubility and processability, and of controlling interchain interactions to inhibit excimer formation in the excited state.[25–27]

Thus there is substantial interest in investigating the synthesis of fluorenyl-substituted pyrenes and studies undertaken on the electronic absorption and fluorescence emission properties of these molecules. We report here synthesis and fluorescence emission properties of 1-mono-, 1,6-bis-, 1,8-bis- and 1,3,6,8-tetrakis-fluorenyl-substituted pyrenes.

Results and discussion

1-Bromopyrene **2** was prepared by brominating pyrene **1** with *N*-bromosuccinimide (NBS) in DMF at room temperature for 24 h following the reported procedure.[28] Bromination of pyrene **1** with 1.1 equivalents of 1,3-dibromo-5,5-dimethylhydantoin (DBMH)[29] in CH_2Cl_2 at room temperature for 1h afforded a mixture of 1,6-di- and 1,8-dibromopyrene **3a**, **3b** in 97% yield. 1,3,6,8-Tetrabromopyrene **4** was readily obtained by the exhaustive bromination of pyrene **1** with 4.5 equivalents of bromine in nitrobenzene at 120°C for 12 h using a reported procedure (Scheme 1).[7,30,31] Although attempted separation of the mixture of 1,6- and 1,8-dibromopyrene (**3a** and **3b)** into each pure form failed, the mixture of isomers of 1,6-di- and 1,8-dibromopyrene (**3a** and **3b)** was directly used to carry out next Suzuki coupling reaction.



Scheme 1

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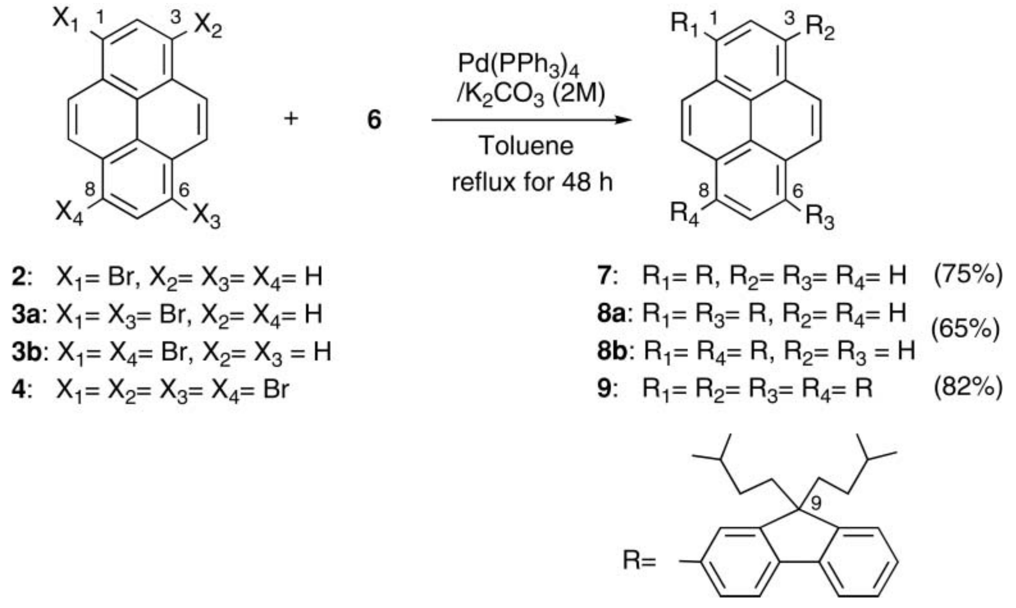

Scheme 2

The detailed synthesis of the fluorene boronic ester, **6**, is also shown in Scheme 1. Thus, compound **5** was prepared following a reported procedure,[32] underwent halogen–lithium exchange of 2-bromofluorene **5** with n-BuLi at –78 °C in THF and subsequent reaction of the anion with $B(OMe)_3$ gave the corresponding fluorene boronic acid, from which esterification with pinacol afforded the target boronic ester **6** (70% yield) as a white solid. The structure of this compound was determined on the basis of their elemental analysis and spectral data.

A Suzuki coupling reaction was employed between the 1-bromopyrene **2** and the fluorene boronic ester **6** under modified reaction conditions[33–35] to afford the desired compound, 1-fluorenyl-subsituted pyrene **7** in 75% yield. Similarly, the 1,3,6,8-tetrakis-fluorenyl-subsituted pyrene **9** was obtained in 72% yield under the same conditions. Both the mono- or tetrakis-fluorenyl-substituted pyrenes **7** and **9** were successfully purified by flash column chromatography. The mixture of **3a** and **3b** was also reacted with fluorene boronic ester **6** to afford bis-fluorenyl-subsituted pyrenes **8a/8b** in 65% yield. Although several attempted isolation of the mixture of 1,6-bis- and 1,8-bis-fluorenyl-substituted pyrenes **8a/8b** in each pure failed, the mixture of compounds, **8a/8b** was directly used to determine their photophysical properties.

The structures for these pyrene-based π-conjugated compounds **7–9** were fully characterised based on their ^{1}H NMR, mass spectroscopy and elemental analysis. In particular, due to their D_{2d} point-group symmetric structure, the ^{1}H NMR spectrum of the 1,3,6,8-tetrakis-fluorenyl-subsituted pyrene **9** is much simpler than those of asymmetrical compounds **7** and **8**. For example, compound 1,3,6,8-tetrakis[9,9-bis(3-methylbutyl)-9*H*-fluoren-2-yl]pyrene **9** displays two singlets at δ = 8.16 and 8.19 ppm in the ratio of 1:2 for the pyrene ring protons at 2,7-positions and 4,5,9,10-positions, respectively. But the fluorene ring protons and the eight terminal methyl protons of 9,9-bis(3-methylbutyl) groups both appear in the region at δ = 7.31–7.88 ppm and at around δ = 1.68 ppm as a multiplet, respectively. Simultaneously, the structures of **7**, **8a/8b** and **9** were also established on the basis of the base peak molecular ion at *m/z* 506, 810, and 1420 in their mass spectrum. Interestingly, these three types of fluorenyl-substituted pyrenes **7–9** are all stable solids that can be stored in air at room temperature for a prolonged period of time. Furthermore, compounds **7** and **9** have a good solubility in all the common organic solvents including hexane with high melting point. However, the isomeric 1,6-bis-, and 1,8-bis-fluorenyl-substituted pyrenes **8a** and **8b** have a limited solubility in organic solvents.

The UV-Vis absorption and fluorescence spectra of these three types of fluorenyl-substituted pyrenes **7–9** were measured in dichloromethane (CH_2Cl_2) at 25 °C and are shown in Figs 1 and 2, respectively. The corresponding spectroscopic data are summarised in Table 1.

As shown in Table 1 and Fig. 1, the absorption spectra of these fluorenyl-substituted pyrenes **7–9** show a π–π* band at ~346–395 nm and the absorption maxima of **7** (346 nm) and **9** (395 nm) are significantly red-shifted *ca* 10 nm and *ca* 60 nm compared with that of unsubstituted parent pyrene **1** (336 nm) respectively. Similarly, in the case of **8a/8b**, the absorption spectra maxima (371 nm) is redshifted about 35 nm from that of pyrene **1**. Thus, from the mono-substituted pyrene **7** to

Table 1 Optical absorption and emission spectroscopic data for compounds **7–9** and pyrene **(1)**[a]

Compound	Absorption λ_{max}/nm[b]	Fluorescence emission λ_{max}/nm[c]	log ε M^{-1} cm^{-1} [d]	Stokes-shift/nm	PLQY[e]
1	336	374	nd	38	nd
7	346	402	4.63	56	0.93
8a/8b	371	427	4.75	56	0.98
9	395	456	4.80	61	0.75

[a] All spectra were recorded for ~10^{-5}–10^{-6} M concentration in dilute CH_2Cl_2 solution at room temperature.
[b] At ~10^{-5} M, λ_{abs} is the absorption band appearing at the longest wavelength.
[c] At ~10^{-6} M, λ_{abs} is the fluorescence band appearing at the shortest wavelength.
[d] Calculated at concentration of 1.0 × 10^{-5} M.
[e] Fluorescence quantum yield, determined at 1.0 × 10^{-6} M concentration, relative that of 9,10-diphenylanthrathcene (0.90 in cyclohexane).
nd, not determined.

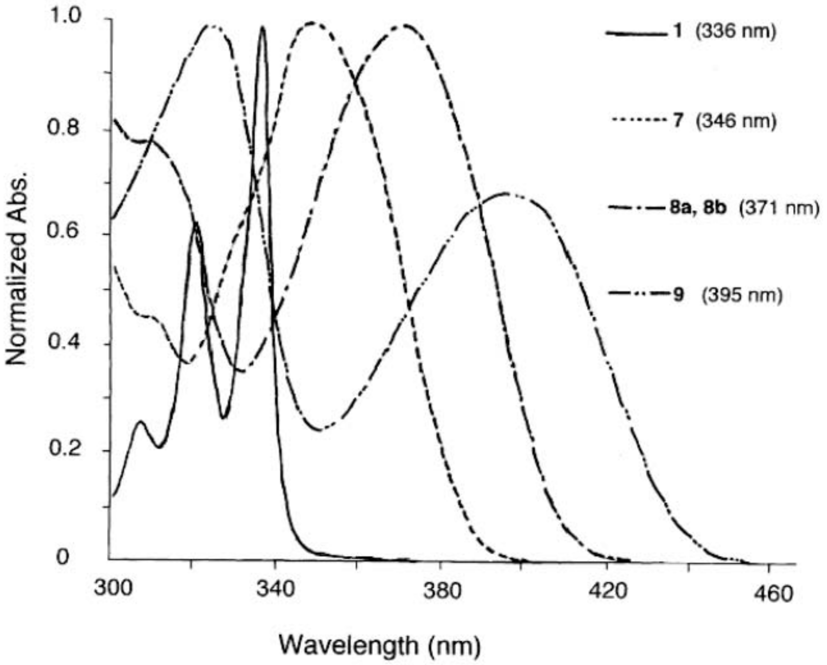

Fig. 1 UV-Vis absorption spectra of compounds **7**, **8a/8b** and **9**; All compounds are measured in dichloromethane at ~10^{-5} M concentration at 25 °C, compared with that of pyrene **1**.

the tetrakis-substituted pyrene **9**, the absorption spectrum shows gradually redshift due to the increasing π-conjugation length, along with the increasing number of the fluorenyl-substituents.

When excited, dilute solutions of **7–9** in dichloromethane solution shown high fluorescence from deep-blue to sky-blue emission (Fig. 2). In all of the fluorescence spectra, only one strong emission band is observed in the visible region, which indicates that the emission occurs from the lowest excited state with the largest oscillator strength. The emission spectra show systematic bathochromic redshifts with the conjugation length increase arising from the increasing number of substituents, in the present fluorenyl-substituted pyrenes (**7–9**), that is **7** < **8a/8b** < **9**, implying that the energy gap between ground and excited states decreases in this order (Table 1). For example, the emission maxima of the fluorenyl-substituted pyrenes, **7**, **8a/8b** and **9**, consecutively shifted to longer wavelengths at 402, 427 and 456 nm, in a manner similar to their absorption maxima, respectively. These results are also observed in some carbozole-based dendrimers[36] and several phenylethynyl-substituted pyrenes derivatives.[37,38]

The fluorescence quantum yields (Φ_F) of **7–9** recorded in dichloromethane are listed in Table 1, along with their absorption (A_{max}) and emission (λ_{max}) maxima. The quantum yield Φ_F

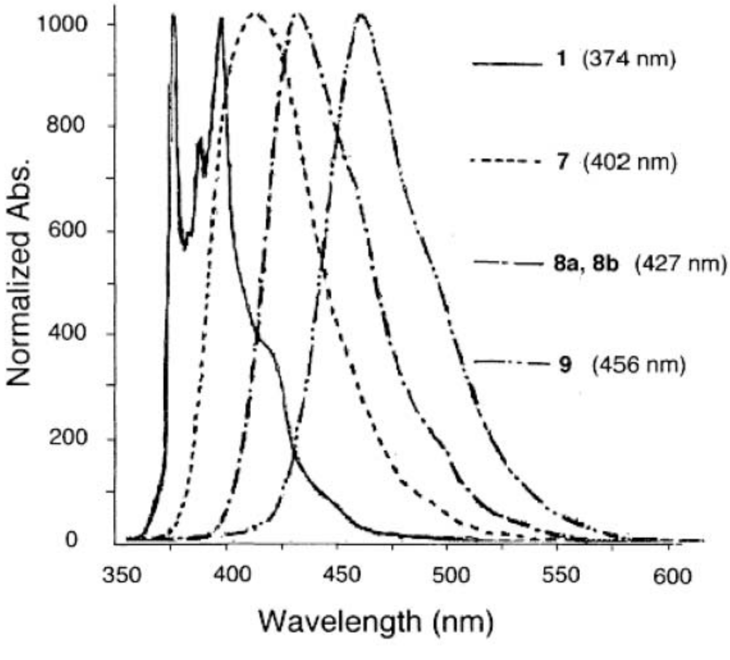

Fig. 2 Normalised fluorescence-emission spectra of compounds **7**, **8a/8b** and **9**. All compounds are measured in dichloromethane at ~10^{-6} M concentration at 25 °C, compared with that of pyrene **1**.

Table 2 Optical absorption and emission spectroscopic data for compounds **7** and **9** in various solvents at 25 °C[a]

Compound	Solvent	Absorption λ_{max}/nm[b]	Fluorescence emission λ_{max}/nm[c]	log ε M^{-1} cm^{-1} [d]	Stokes-shift/nm
7	Cyclohexane	345	401	4.60	56
	CH_2Cl_2	346	402	4.63	56
	THF	348	402	4.65	54
	$CHCl_3$	**349**	**405**	4.75	56
	DMF	350	418	4.84	68
9	Cyclohexane	394	455	4.67	61
	CH_2Cl_2	395	456	4.80	61
	THF	395	457	5.16	62
	$CHCl_3$	397	458	5.31	61
	DMF	397	459	5.56	62

[a] All spectra were measured for ~10^{-5}–10^{-6} M concentration in different solvents at 25 °C.

[b] ~10^{-5} M in different solvents, λ_{abs} is the absorption band appearing at the longest wavelength.

[c] ~10^{-6} M in different solvents, λ_{abs} is the fluorescence band appearing at the shortest wavelength.

[d] Calculated at concentration of 1 × 10^{-5} M in different solvents.

values of **7–9** were found in the range of 0.75–0.98 relative to that of 9, 10-diphenylanthrathcene (0.90 in cyclohexane).[39]

In order to obtain the detailed electronic spectroscopic properties of these fluorene-substituted pyrene derivatives, the influence of solvents on the UV-Vis absorption and fluorescence emissions were investigated. The mono-fluorenyl-substituted pyrene **7** and the tetrakis-fluorenyl-substituted pyrene **9**, were selected to as representative compounds, and their optical absorption and emission spectroscopic data measured in various solvents are listed in Table 2.

It is well known that the solvatochromitic effect is not only depends on the molecular structure, but also depends on the nature of the chromophore, and the solvents.[39] Each monomer shows a slight positive solvatochromism in their absorption spectra and emission spectra (see Table 2), respectively. For example, a change in solvent from non-polar cyclohexane to polar *N,N*-dimethylformamide (DMF) causes only a very slight positive solvatochromic shift in the π–π^* absorption band from 345 to 350 nm ($\Delta\lambda_{abs}$ = 5 nm) for **7**. On the other hand, in the case of emission spectrum of **7**, a small positive solvatochromism behaviour was also observed with increasing solvent polarity, the emission spectrum of **7** was observed with a peak around 401 nm and a shoulder peak around 421 nm in cyclohexane. A broad and red-shifted emission of **7** was observed with only one peak at λ_{max}= 418 nm in the solvent of high polarity, DMF. Similar results in their absorption spectra and emission spectra were also observed for **9**.

These results indicated that the μ_e (dipole moment of **7** in the excited state) should be a little larger than the μ_g (the dipole moment of **7** in the ground state) because a positive solvatochromic effect was observed in the absorption spectra and emission spectra.[40,41] Although the dipole moments of **9** in either the ground or excited states are indeed zero because they are possessed centro-symmetric in the ideal D_{2d} symmetry, these current results obtained above indicated that the Q_e (the quadrupole moments of **9** in the excited state) should be larger than the Q_g (the quadrupole moments of **9** in the ground state) because positive solvatochromic effects were observed in both the absorption spectra and the emission spectra, which implies that there is a change in the quadropole moment upon excitation.[42] On the other hand, the fact that the solvatochromic effect is more important for emission than for absorption suggests that these current compounds are more solvated in the excited state than in the ground state.[43]

Conclusions

A series of fluorenyl-substituted pyrenes **7–9** have been synthesised in high yield by a modified Suzuki coupling reaction. Photoproperties studies of **7–9** indicated that there is a significant effect on the UV-Vis absorption spectra and emission spectra with increasing the number of fluorenyl substituents. Compounds **7–9** emit very bright, pure-blue fluorescence in solution ($\Phi_F \approx$ 0.75–0.98) and have good solubility in common organic solvents and high stability. A slight solvatochromic effect observed in **7–9** can be explained by these compounds being more solvated in the excited state than in the ground state. The herein-presented molecules are exciting new materials that combine excellent optical features and an improved thermal stability. Thus, application in OLEDs is possible and further explorations into this area are currently under study in our laboratory.

Experimental

All melting points are uncorrected. ^1H NMR spectra were recorded at 300 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in deuteriochloroform with Me_4Si as an internal reference. UV-Vis spectra were recorded on a Perkin Elmer Lambda 19 UV/VIS/NIR spectrometer. Emission spectra were performed in a semimicro fluorescence cell (Hellma®, 104F-QS, 10×4 mm, 1400µL) with a Varian Cary Eclipse spectrophotometer. Mass spectra were obtained on a Nippon Denshi JMS-HX110A Ultrahigh Performance Mass Spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed by Yanaco MT-5.

Mono-bromination of pyrene with NBS in DMF (NBS-DMF) (**2**): A solution of NBS (187 mg, 1.05 mmol) in dry DMF (5 mL) was added to a solution of pyrene (252 mg, 1.0 mmol) in dry DMF (10 mL) and stirred at room temperature 24 h. After reaction, the mixture was poured into water (50 mL) and extracted with dichloromethane (100 mL). The extract was washed well with water, dried ($MgSO_4$), and evaporated under reduced pressure to yield crude products (85%, G. C. Analysis) as a pale-yellow solid (332 mg, 85%); m.p.103–104°C (m.p. 102–104°C).[30]

Di-bromination of pyrene with 1,3-dibromo-5,5-dimethylhydantoin (DBMH) in CH_2Cl_2 (**3a/3b**): A solution of DBMH (308 mg, 1.1 mmol) in dry CH_2Cl_2 (10 mL) was added to a solution of pyrene (252 mg, 1.00 mmol) in dry CH_2Cl_2 (40 mL) and stirred at room temperature for 1 h. The mixture was poured into water (50 mL) and extracted with dichloromethane (200 mL). The extract was washed well with water, dried ($MgSO_4$), and evaporated under reduced pressure to yield crude products. The crude products were successfully washed with CH_2Cl_2 (15 mL) to give a mixture of 1,6-di- and 1,8-dibromopyrene **3a**, **3b** as an orange-yellow solid (398 mg, 97%); m.p.123–124°C. Separation of 1,6-di- and 1,8-dibromopyrene **3a** and **3b** was reported in the literature (m.p. 230–231 °C for **3a** and m.p. 210–211°C for **3b**).[31] However, several attempted separations of the mixture of **3a** and **3b** into each pure failed. The mixture of isomers of 1,6-di- and 1,8-dibromopyrene (**3a** and **3b**) was directly used to carry out next Suzuki coupling reaction.

Synthesis of 1,3,6,8-tetrabromopyrene (**4**): Bromine (8.75 g, 0.055 mol) was added dropwise, with vigorous stirring to a solution of pyrene (2.5 g, 12.3 mmol) in nitrobenzene (50 mL) at 80°C. Then the mixture was heated to 120 °C and kept for 12 h. After cooled to room temperature, the mixture was filtered, washed with ethanol (100 mL), and dried under vacuum to afford **4** (6.04 g, 96%) as a pale-green solid; m.p. > 300 °C (Found C, 36.85; H, 1.23. $C_{16}H_6Br_4$ (517.84) requires C, 37.11; H, 1.17%).

This compound was quite insoluble in all common organic solvents. The ^{1}H NMR spectrum was not obtained in $CDCl_3$ due to the limited solubility of this compound.

Synthesis of 2-[9,9-bis(3-methyl-butyl)-9H-fluoren-2-yl]-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (**6**): Prepared in 70% yield from 2-bromo-9,9-bis(3-methylbutyl)-9*H*-fluorene **5** followed by the reported procedure, the synthetic method completely agreed with the reported literature procedure.[32] **6** was obtained from **5** in 70% yield as a colourless powder; m.p. 86–88°C; δ_H ($CDCl_3$) 0.36–0.54 (4H, m, CH_2), 0.65 (6H, d, *J*= 4.8 Hz, *Me*), 0.68 (6H, d, *J*= 4.8Hz, *Me*), 1.17–1.30 (2H, m, *CH*), 1.39 (12H, s, *Me*), 2.02 (4H, t, CH_2), 7.31–7.33 (3H, m, ArH), 7.68–7.83 (4H, m, ArH); *m/z*: 432 (M^+) (Found C, 80.60; H, 9.43. $C_{29}H_{41}O_2B$ (432.46) requires C, 80.54; H, 9.56%).

Synthesis of 1-(9,9-bis(3-methylbutyl)-9H-fluoren-2-yl)pyrene (**7**): 1-Bromopyrene **2** (200 mg, 0.70 mmol), 2-[9,9-bis(3-methylbutyl)-9*H*-fluoren-2-yl]-4,4,5,5-tetramethyl[1,3,2]dioxaborolane **6** (461 mg, 1.07 mmol) and $Pd(PPh_3)_4$ (23 mg, 0.07mmol) and aqueous 2.0 M K_2CO_3 (2 mL) were mixed in a flask containing with argon saturated toluene (15 mL). The reaction mixture was stirred at 90 °C for 48 h. After it was cooled to room temperature, the reaction mixture was quenched with saturated sodium bicarbonate solution and extracted with toluene (50 mL × 2). The combined organic extracts were dried with anhydrous $MgSO_4$ and evaporated. The crude product was purified by column chromatography using hexane as eluent and recrystallisation from methanol to afford the desired product **7** (265mg, 75%) as colourless prisms, m.p. 244–246°C; δ_H ($CDCl_3$): 0.64–0.75 (12H, m, *Me*), 0.30–1.37 (4H, m, CH_2), 2.02–2.07 (6H, m, CH_2 and *CH*), 7.35–7.42 (3H, m, ArH), 7.60–7.62 (4H, m, ArH), 7.78–8.27 (9H, m, Py-*H*); *m/z*: 506 (M^+) (Found C, 92.26; H, 7.34. $C_{39}H_{38}$ (506.74) requires C, 92.44; H, 7.56%).

Synthesis of isomer of 1,6-bis[9,9-bis(3-methylbutyl)-9H-fluoren-2-yl] pyrene and 1,8-bis[9,9-bis(3-methylbutyl)-9H-fluoren-2-yl]pyrene (**8a** and **8b**): Dibromopyrene (**3a** and **3b**) (200 mg, 0.44 mmol), 2-[9,9-bis(3-methylbutyl)-9*H*-fluoren-2-yl]-4,4,5,5-tetramethyl[1,3,2]dioxaborolane **6** (475 mg, 1.10mmol), and $Pd(PPh_3)_4$ (0.044 mmol) and aqueous 2.0 M K_2CO_3 (2 mL) were mixed in a flask containing with argon saturated toluene (15 mL). The reaction mixture was stirred at 90°C for 48 h. After it was cooled to room temperature, the reaction mixture was quenched with saturated sodium bicarbonate solution and extracted with toluene (50 mL × 2). The combined organic extracts were dried with anhydrous $MgSO_4$ and evaporated. The crude product was purified by column chromatography using hexane as eluent and recrystallisation from methanol and hexane to afford the desired product **8a/8b** (230 mg, 65%) as colourless prisms, m.p. 206–208 °C; δ_H($CDCl_3$): 0.60–0.78 (24H, m, *Me*), 1.23–1.40 (8H, m, CH_2), 1.99–2.09 (12H, m, CH_2 and *CH*), 7.30–7.43 (6H, m, ArH), 7.57–7.64 (8H, m, ArH), 7.76–8.28 (8H, m, Py-*H*); *m/z*: 810.48 (M^+) (Found C, 91.74; H, 8.17. $C_{62}H_{66}$ (811.22) requires C, 91.80; H, 8.20%).

The ^{1}H NMR spectrum of this compound was not obtained due to its limited solubility in $CDCl_3$ solution. But a strong blue fluorescence emission was observed in CH_2Cl_2 solution condition.

Synthesis of 1,3,6,8-tetrakis-[9,9-bis(3-methylbutyl)-9H-fluoren-2-yl] pyrene (**9**): 1,3,6,8-Tetrabromopyrene **4** (200 mg, 0.39 mmol), 2-[9,9-bis(3-methylbutyl)-9*H*-fluoren-2-yl]-4,4,5,5-tetramethyl[1,3,2]dioxaborolane **6** (1003 mg, 2.32 mmol), and $Pd(PPh_3)_4$ (4 mg, 0.013 mmol) and aqueous 2.0 M K_2CO_3 (2 mL) were mixed in a flask containing with argon saturated toluene (50 mL). The reaction mixture was stirred at 90 °C for 48 h. After it was cooled to room temperature, the reaction mixture was quenched with saturated sodium bicarbonate solution and extracted with dichloromethane (100 mL × 2). The combined organic extracts were dried with anhydrous $MgSO_4$ and evaporated. The crude product was purified by column chromatography using hexane/dichloromethane (9:1) as eluent to provide **9** (452mg, 82%) as a pale green solid and recrystallisation from $CHCl_3$/EtOH (3:1 v/v) to afford **9** as pale yellow prisms, m.p. 276–278°C; δ_H($CDCl_3$): 0.66–0.69 (48H, m, *Me*), 1.23–1.35 (16H, m, CH_2), 2.01–2.06 (24H, m, CH_2 and *CH*), 7.31–7.41 (12H, m, ArH), 7.66–7.88 (16H, m, ArH), 8.16 (2H, s, Py-H_a), 8.19 (4H, s, Py-H_b); *m/z*: 1418.95 (M^+) (Found C, 88.70; H, 8.47. $C_{108}H_{122}\cdot 2H_2O$ (1456.21) requires C, 89.08; H, 8.72%).

Received 19 January 2010; accepted 21 April 2010
Paper 100053 doi: 10.3184/030823410X12743772163259

References

1 Q.-C. Zhou, A.-J. Qin, Q.-G. He, G.-T. Lei, L.-D. Wang, Y.Q. Cheng, F.-T. Ga and F.-L. Bai, *Lumine*., 2007, **674**, 122.
2 X.-Y. Jiang, Z.-L. Zhang, X.-Y. Zheng, Y.-Z. Wu and S.-H. Xu, *Thin Solid Films*, 2001, **401**, 251.
3 B. Balaganesan, W.-J. Shen and C.H. Chen, *Tetrahedron Lett.*, 2003, **44**, 5747.
4 Y. Shibano, T. Umeyama, Y. Matano and H. Imahori, *Org. Lett.*, 2007, **10**, 1971.
5 Y.-L. Liao, C.-Y. Lin, K.-T. Wong, T.-H. Hou and W.-Y. Hung, *Org. Lett.*, 2007, **10**, 4511.
6 K.R.J. Thomas, J.T. Lin, Y.-T. Tao and C.-W. Ko, *J. Am. Chem. Soc.*, 2001, **123**, 9404.
7 G. Venkataramana and S. Sankararaman, *Eur. J. Org. Chem.*, 2005, 4162.
8 G. Venkataramana and S. Sankararaman, *Org. Lett.*, 2006, **8**, 2739.
9 V.D. Halleux, J.-P. Calbert, P Brocorens, J. Cornil, J.-P Declercq, J.-L. Bredas and Y. Greets, *Adv. Funct. Mater.*, 2004, **14**, 649.
10 J.N. Moorthy, P. Natarajin, P. Venkatakrishnan, D.-F. Huang and T.J. Chow, *Org. Lett*., 2007, **9**, 5215.
11 C. Modrakowski, S.C. Flores, M. Beinhoff and A.D. Schlüter, *Synthesis*, 2001, 2143.
12 J. Hu, M. Era, M.R.J. Elsegood and T. Yamato, *Eur. J. Org. Chem.*, 2010, 72.
13 M. Beinhoff, W. Weigel, M. Jurczok, W. Rettig and A.D. Schlüter, *Eur. J. Org. Chem.*, 2001, 3819.
14 H. Shimizu, K. Fujimoto, M. Furusayo, H. Maeda, Y. Nanai, K. Mizuno and M. Inouye, *J. Org. Chem*., 2007, **72**, 1530.
15 A.C. Benniston, A. Harriman, D.J. Lawrie and S.A. Rostron, *Eur. J. Org. Chem.*, 2004, 2272.
16 E. Rivera, M. Belletete, X.X. Zhu, G. Durocher and R. Giasson, *Polymer*, 2002, **43**, 5059.
17 K.-T. Wong, Y.-Y. Chien, R.-T. Chen, C.-F. Wang, Y.-T. Lin, H.-H. Chiang, P.-Y. Hsieh, C.-C. Wu, C. H. Chou, Y. O. Su, G.-H. Lee, S.-M. Peng, *J. Am. Chem. Soc*., 2002, **124**, 11576.
18 D. Katsis, Y.H. Geng, J.J. Ou, S.W. Culligan, A. Trajkovska, S.H. Chen and L. Rothberg, *J. Chem. Mater.*, 2002, **14**, 1332.
19 Y. Geng, S.W. Culligan, A. Trajkovska, J.U. Wallace and S.H. Chen, *Chem. Mater.*, 2003, **15**, 542.
20 S.W. Culligan, Y. Geng, S.H. Chen, K. Klubek, K.M. Vaeth and C.W. Tang, *Adv. Mater*., 2003, **15**, 1176.
21 C.-C. Wu, Y.-T. Lin, K.-T. Wong, R.-T. Chen and Y.-Y. Chien, *Adv. Mater.*, 2004, **16**, 61.
22 Z.H. Li, M.S. Wong, H. Fukutani and Y. Tao, *Chem. Mater.*, 2005, **17**, 5032.
23 T. Yasuda, K. Fujita and T. Tsutsui, *Chem. Mater*., 2005, **17**, 264.
24 W.-Y. Lai, R. Zhu, Q.-L. Fan, L.-T. Hou, Y. Cao and W. Huang, *Macromolecules*, 2006, **39**, 3707.
25 G. Klaerner and R.D. Miller, *Macromolecules* 1998, **31**, 2007.
26 U. Lemmer, S. Hein, R.F. Mahrt, U. Scherf, M. Hopmeir, U. Wiegner, R.O. Göbel, K. Müllen and H. Bassler, *Chem. Phys. Lett*., 1995, **240**, 371.
27 S.A. Jenekhe and J.A. Osaheni, *Science*, 1994, **265**, 765.
28 R.H. Mitchell, Y.-H. Lai and R.V. Williams, *J. Org. Chem.*, 1979, **44**, 4733.
29 H. Eguchi, H. Kawaguchi, S. Yoshinaga, A. Nishida, T. Nishiguchi and S. Fujisaki, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 1918.
30 H. Volmmann, H. Becker, M. Corell and H. Streeck, *Justus Liebigs Ann. Chem.*, 1937, **531**, 1.
31 J. Grimshaw and J.T. Grimshaw, *J. Chem. Soc., Perkin Trans.* 1, 1972, 1622.
32 W.-L. Yu, J. Pei, Y. Cao, W. Huang and A.J. Heeger, *Chem. Commun.*, 1999, 1837.
33 N. Miyaura, T. Yanagi and A. Suzuki, *Synth. Commun.*, 1981, **11**, 513.
34 N. Miyaura, K. Yamada, H. Suginome and A. Suzuki, *J. Am. Chem. Soc.*, 1985, **107**, 972.
35 N. Miyaura and A. Suzuki, *Chem. Rev*., 1995, **95**, 2457.
36 R.M. Adihikari, R. Mondal, B.K. Shah and D.C. Neckers, *J. Org. Chem.*, 2007, **72**, 4727.
37 H. Maeda, T. Maeda, K. Mizuno, K. Fujimoto, H. Shimizu and M. Inouye, *Chem. Eur. J.*, 2006, **12**, 824.
38 H.M. Kim, Y.O. Lee, C.S. Lim, J.S. Kim and B.R. Cho, *J. Org. Chem.* 2008, **73**, 5127.
39 J.C. Sciano, *Handbook of Organic Photochemistry*; CRC Press: Boca Raton, FL, 1989; Vol. 1, p 231.
40 C. Reichardt, *Chem. Rev*., 1994, **94**, 2319.
41 T. Soujanya, R.W. Fessenden and A. Samanta, *J. Phys. Chem.*, 1996, **100**, 3507.
42 J. D. Jackson (Ed.), *Classical electrodynamics*, John Wiley & Sons, 1975.
43 S. Chew, P. Wang, Z. Hong, H.L. Kwong, J. Tang, S. Sun, C.S. Lee and S.T. Lee, *J. Lumin.*, 2007, **124**, 221.