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Synthesis and photophysical properties of novel butterfly-shaped blue emitters based on pyrene

Xing Feng, Jian-Yong Hu, Hirotugu Tomiyasu, Nobuyuki Seto, Carl Redshaw, Mark R. J. Elsegood and Takehiko Yamato

Using 1,3,5,9-tetraaryl substituted pyrene derivatives were synthesized by the Suzuki-Miyaura cross-coupling reaction. Their thermal, photophysical, electrochemical and related properties were systematically investigated. All compounds were found to exhibit high thermal stabilities with decomposition temperatures (T_d) of up to 300 °C. All compounds show highly blue fluorescence emissions in the spectral region of 412–469 nm in solutions (Φ_f: 0.45–0.92) and 410–470 nm in the solid-state (Φ_f: 0.48–0.75). In particular, the compounds 4c, 4f and 5 show much greater red shifts because of the presence of the larger π-conjugated acceptor groups, which were verified by theoretical calculations. It is noteworthy that these butterfly-shaped pyrenes 4 possess low-lying HOMO levels ranging from −4.76 to −5.93 eV, which make them promising candidates in OLED applications.

Introduction

The design and synthesis of efficient organic semiconductors based on polycyclic aromatic hydrocarbons (PAHs) has attracted considerable interest, owing to their potential applications in optoelectronic devices, such as organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), organic field-effect transistors (OFETs), etc. In the past two decades, significant efforts have been devoted to explore novel electroluminescent (EL) materials with specific optoelectronic properties. To realize full-color OLED displays, the development of efficient and pure red, green and blue emitters is a significant milestone. However, only the red and green materials have been implemented in devices capable of sufficient efficiencies and lifetimes for commercial value, whilst the availability of blue emitters with satisfactory multifunctional properties for high-performance OLEDs still remains a challenge.

Pyrenes as classical members of the PAHs have attracted great interests from the scientific community, not only because of their planar structure, but also their excellent fluorescence properties, which has led to their wide utilization as fluorescence probes. Recently, a number of synthetic methods for the synthesis of novel PAHs based on pyrene have been reported, and their potential uses as chemosensors were exploited.

However, the flat structure of pyrene has restricted its use for developing EL materials for OLED applications, primarily because of the tendency towards π-stacking and excimer formations, which would quench the emission intensity with low fluorescence quantum efficiency. One strategy to suppress the passive π-π stacking interactions in condensed media is to introduce appropriate substituents into the pyrene core. The methods tend to attach substituents at the 1-, 3-, 6- and 8-positions of the pyrene so as to affect both the overall photophysical properties and the geometrical structures. For example, 1,3,6,8-tetraphenylpyrene (TPPy) exhibited a pure blue fluorescence with a high quantum yield (Φ_f = 0.90 in cyclohexane). Bulky aryl groups have been located at the 1,3,6,8-positions for the preparation of tetraaryl-functionalized pyrenes which showed high efficiencies with deep-blue emission, low turn-on voltages and high brightness in OLED devices. Sotoyam and co-workers have investigated different phenyl moieties 1,3,6,8-tetrasubstituted pyrene and how they affect the fluorescent properties by molecular orbitals (MOs) methods. The tert-Butyl groups located at the 2- or the 2- and 7-positions of the pyrene core play an important role in inhibiting the undesirable π-stacking interactions in the solid-state. Thus, the cruciform-, hand-, and Y-shaped pyrene derivatives were reported and can be potentially used as blue emitters in OLEDs.

Previously, a novel bromide precursor 1,3,5,9-tetrahydroxy-7-tert-butylpyrene was prepared from 2-tert-butylpyrene and Br₂ in CH₂Cl₂ in the presence of iron powder (6 equiv.) at room temperature. Based on this key intermediate, herein, we access a series of butterfly-shaped compounds of 1,3,5,9-tetraarylpyrenes with deep-blue fluorescence properties. Several 4-substituted phenyl groups were successfully introduced into the pyrene core at the 1,3,5,9-positions. Not only does this category of materials have great potential in organic materials, such as blue emitters for OLED applications, but will also be useful to understand the structure-property relationships of the current butterfly-shaped 1,3,5,9-tetraarylpyrenes relative to the other arylpyrenes.
Results and discussion

Synthesis

The synthetic route to the butterfly-shaped pyrene derivatives 4a–f are illustrated in Scheme 1. By using the 1,3,5,9-tetramethyl-7,7'-tert-butylpyrene (2) as the key intermediate, the compounds of type 4 were synthesized by the Suzuki-Miyaura cross-coupling reaction with the corresponding arylboronic acids (3) in 48–72% yields. To investigate the effect of a terminal moiety on the structure-property relationships in these butterfly-shaped pyrenes systems, the reaction of 4f with 17.0 equiv. of hydroxylamine hydrochloride in ethanol solution afforded the corresponding oxime 5 in 76% yield according to the literature approach. Furthermore, in order to investigate the effect of the tert-butyl group of the pyrene on photophysical properties, 6 was synthesized from 4a, in which the bulky steric tert-butyl group has been removed by Nafion-H catalyzing. The chemical structures of all synthesized compounds were confirmed by their 1H/13C NMR spectra, FT-IR spectroscopy, mass spectrometry, as well as elemental analysis.

Thermal properties

Thermal stability is an important physical parameter to evaluate EL materials for OLED applications. We investigated the thermal stability of these butterfly-shaped pyrene derivatives 4 and 5 by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹. The TGA data revealed that the butterfly-shaped compounds 4 showed high thermal stabilities in the range of 250–450 °C, with a 5% weight loss. (Fig. 1), and the following stability order CN > OMe > t-Bu > H > CHO > CF₃ > 5. From the TGA data, the amount of carbonized residue (char yield) of 4c, 4e, 4f and 5 in a nitrogen atmosphere was higher (20% for 4c, 4f, 37% for 4e and 64% for 5) than 4a, 4b and 4d with almost complete loss, which means that 4c, 4e, 4f and 5 possess more aromatic components than 4a, 4b and 4d. Ascribe from the substituent group [What does this mean? Please re-write.] at para-position of the phenyl would affect the thermal property. No glass transition temperature (Tg) was observed for any of the compounds.

Photophysical properties

We measured the UV-vis absorption and fluorescence (FL) spectra of compounds 4–6 in both dichloromethane solutions (~10⁻⁵ M) and thin films. The key data are summarized in Table 1.
Table 1 The photophysical and electrochemical properties of compounds 4, 5 and 6.

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ_{max}^{abs} (nm)</th>
<th>λ_{max}^{PL} (nm)</th>
<th>QY</th>
<th>Stokes shift (cm^{-1})</th>
<th>τ (ns)</th>
<th>T_{m}^{l}/T_{f} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>373 / 380</td>
<td>412 / 410</td>
<td>0.92 / 0.75</td>
<td>39 / 30</td>
<td>4.57</td>
<td>335/350</td>
</tr>
<tr>
<td>4b</td>
<td>378 / 379</td>
<td>416 / 435</td>
<td>0.45 / nd</td>
<td>38 / 56</td>
<td>5.18</td>
<td>332/407</td>
</tr>
<tr>
<td>4c</td>
<td>379 / 369</td>
<td>421 / 443</td>
<td>0.90 / 0.72</td>
<td>42 / 74</td>
<td>5.82</td>
<td>330/410</td>
</tr>
<tr>
<td>4d</td>
<td>370 / 358</td>
<td>418 / 466</td>
<td>0.91 / nd</td>
<td>48 / 108</td>
<td>12.2</td>
<td>258/328</td>
</tr>
<tr>
<td>4e</td>
<td>378 / 387</td>
<td>437 / 460</td>
<td>0.89 / nd</td>
<td>59 / 73</td>
<td>7.51</td>
<td>378/450</td>
</tr>
<tr>
<td>4f</td>
<td>386 / 400</td>
<td>469 / 471</td>
<td>0.56 / 0.48</td>
<td>83 / 71</td>
<td>4.04</td>
<td>302/329</td>
</tr>
<tr>
<td>5</td>
<td>381 / nd</td>
<td>440 / nd</td>
<td>0.63 / nd</td>
<td>59 / nd</td>
<td>4.53</td>
<td>214/250</td>
</tr>
<tr>
<td>6</td>
<td>371 / nd</td>
<td>411 / nd</td>
<td>0.26 / nd</td>
<td>40 / nd</td>
<td>5.10</td>
<td>244/nd</td>
</tr>
</tbody>
</table>

* Maximum absorption wavelength measured in dichloromethane at room temperature. * Measured as thin neat films. * Measured in dichloromethane and as neat thin films, respectively. * Melting temperature (T_m) obtained from differential scanning calorimetry (DSC) measurements. * Decomposition temperature (T_f) obtained from thermogravimetric analysis (TGA). nd: not determined.

Fig. 3 (a) Normalized UV-vis absorption and (b) emission spectra of 4a–f as thin neat films.

Fig. 2 illustrates the normalized absorption and FL spectra of 4, 5 and 6 in dilute dichloromethane solutions. The absorption spectra of these butterfly-shaped pyrene derivatives 4 and 6 exhibited well-resolved profiles in the range of 280–480 nm. The short wavelength absorption peak located at 277–279 nm and the long wavelength maximum (λ_{max}) occur at 370–381 nm, assigned to the π-π* and the n-π* transitions (Fig. 2a), respectively. Noticeably, 4f and 5 showed slightly red shifts of ~10 nm compared to the other compounds due to the effective increase in conjugation length. It is noteworthy that the compound 6 exhibited a blue shift (8 nm) after the removal of the tert-butyl group from the 2-position of the pyrene core compared to 4c, arising from the improved energies of both S_1 ← S_0 excitations and S_2 ← S_0 excitations.

Upon excitation at the absorption maximum in CH_2Cl_2, all compounds exhibited deep-blue to sky-blue FL with sharp emission maximum peaks at 412 nm for 4a, 416 nm for 4b, 421 nm for 4c, 418 nm for 4d, 437 nm for 4e, 440 nm for 5 and 411 nm for 6 (Fig. 2b). In the case of 4f, which showed a maximum peak at 469 nm, there was a larger Stokes shift of 83 nm relative to the other butterfly-shaped compounds, suggesting that its electronic structure in the ground state is significantly different from that in the excited state. It is noted that 4e and 5 showed almost the same emission peaks, suggesting that the –C=O groups make similar electronic contributions. This result implies that changing the terminal group at the para-position of the phenyl moiety can affect the electronic transition absorption, which also agrees with our previous report. Furthermore, a substituent effect involving S_1 ← S_0 was also observed in the emission spectra, and without the tert-butyl group in compound 6, the emission maximum displayed a lower red shift of ~10 nm compared to the corresponding compound 4c.

We also investigated the photophysical properties of 4 in the solid-state. The UV-vis absorption and photoluminescence (PL) spectra data are also listed in Table 1. As shown in Fig. 3, the absorption spectra of these butterfly-shaped pyrenes 4, possessing similar frameworks (pyrene-based core), exhibited a similar absorption band with a slight red shift (~14 nm) to those in dilute solutions. Compared with the FL in solutions, the PL spectra of 4a–f and 5 in thin films exhibited highly blue emissions with a maximum peak in the range of 410–471 nm, without extra excimer emissions, while compounds 4b–e displayed a red-shift (~48 nm), ascribed to the tert-butyl group located at the 7-position and the tetraaryl moieties at the 1,3,5,9-positions which can prevent π-aggregations via the intra/intermolecular interactions in the solid-state. The single-crystal packing revealed that no π-π stacking was observed, however, the aggregations cannot be sufficiently suppressed due to the small blocking group of the arylphenyl located at the 1,3,5,9-positions. Thus, larger red-shifts occurred in 4c and 4d. Fig. 2b and 3b revealed that these butterfly-shaped compounds 4 and 5 emit very bright and sharp blue fluorescence in both solution and the solid-state. The newly developed butterfly-shaped pyrenes 4a–e and 5 have very high quantum yields (Φ) in the range of 0.89–0.92 in solutions and 0.72–0.78 in the solid-state. Due to the presence of...
the –CHO in 4f that has efficient intramolecular conjugation and increased π–π intermolecular interactions that would quench the FL with quantum yields of 0.56 in solution and 0.48 in the solid-state. However, 6 exhibited a lower quantum yield of 0.26 compared with the TPPy (Φf = 0.90) which is probably due to the strong intermolecular interactions without the bulky steric tert-butyl group. Fluorescence lifetimes of 4–6 were determined in dichloromethane solution at 10−5 M with τ = 4.04–12.2 ns.

Table 2 Optical and electrochemical properties of compounds 4, 5 and 6.

<table>
<thead>
<tr>
<th></th>
<th>λedge/nm</th>
<th>E1/2</th>
<th>Eem</th>
<th>E2(CT)/eV</th>
<th>E1(CT)/eV</th>
<th>E1(homo)/eV</th>
<th>E2(homo)/eV</th>
<th>E2(CT)/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>399</td>
<td>1.42</td>
<td>1.35</td>
<td>3.11</td>
<td>−5.56</td>
<td>−5.01</td>
<td>3.43</td>
<td></td>
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<tr>
<td>4b</td>
<td>405</td>
<td>1.35</td>
<td>1.27</td>
<td>3.06</td>
<td>−5.51</td>
<td>−4.90</td>
<td>3.40</td>
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<tr>
<td>4c</td>
<td>411</td>
<td>1.28</td>
<td>1.20</td>
<td>3.01</td>
<td>−5.44</td>
<td>−4.76</td>
<td>3.40</td>
<td></td>
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<tr>
<td>4d</td>
<td>403</td>
<td>1.66</td>
<td>1.58</td>
<td>3.08</td>
<td>−5.82</td>
<td>−5.61</td>
<td>3.40</td>
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<tr>
<td>4e</td>
<td>418</td>
<td>1.71</td>
<td>1.63</td>
<td>2.97</td>
<td>−5.87</td>
<td>−5.93</td>
<td>3.32</td>
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<tr>
<td>4f</td>
<td>431</td>
<td>1.67</td>
<td>1.58</td>
<td>2.88</td>
<td>−5.82</td>
<td>−5.66</td>
<td>3.21</td>
<td></td>
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<tr>
<td>5</td>
<td>419</td>
<td>1.41</td>
<td>1.29</td>
<td>2.96</td>
<td>−5.56</td>
<td>−5.25</td>
<td>3.24</td>
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<tr>
<td>6</td>
<td>397</td>
<td>–</td>
<td></td>
<td>3.12</td>
<td>−5.06</td>
<td>3.43</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Measured in CH2Cl2. † CV measured in 0.1 M n-Bu4NPF6/CH2Cl2 with a scan rate of 100 mV s−1. ‡ Calculated from λedge−δ values calculated using the ferrocene HOMO level. Calculated from the empirical formulae HOMO = -(4.8 + E−1/2 − Eox (Fc)−1/2), " DFT/B3LYP/6-31G* using Gaussian 03.

Concentration-dependent UV-vis absorption and FL spectra studies in CH2Cl2 confirmed that these compounds did not change with concentration in solution, even on increasing the concentrations from 10−6 M to 10−3 M (See Supporting Information). On the other hand, we examined the solvatochromism of 4 and 5 in various solvents, such as cyclohexane, tetrahydrofuran (THF), CH2Cl2, CH3CN, and N,N-dimethylformamide (DMF) (Fig. 4a). In the compounds 4a–e and 5, the emission maxima were slightly shifted by ~5 nm depending on the solvent polarity. However, although the absorption spectrum of compound 4f does not show any change, the solvent dependence in the emission spectra of 4f is remarkable with large bathochromic shifts of ~36 nm on going from non-polar solvents (cyclohexane) to polar solvents (DMF). The linear relationship of Stokes shift (Δνs) against the solvent parameter Δ(ε, n)13 was determined by the Lippert–Mataga plot (Fig. 4b), which evaluated the effect of solvent molecules for day molecules fluorescence by hydrogen bond [This does not make any sense – please re- write].18 This solvatochromism can be attributed to the decrease in the energy of the singlet-excited states as a function of an increase in the polarity of the solvents.19

Electrochemical properties

We investigated the electrochemical properties of these compounds by cyclic voltammetry (CV) recorded in CH2Cl2 solution using ferrocene (Fc/Fc+) as the internal standard with a scan rate of 100 mVs−1 at room temperature. Fig. 5 displays the cyclic voltammograms (CVs) of 4 and 5. All compounds exhibited quasi-reversible oxidations in CH2Cl2. Interestingly, the compounds 4b and 4e, with electron-donating groups, showed two reversible oxidation waves, while the compounds 4d–f and 5, with electron-withdrawing groups, have only one reversible oxidation each. These results differ from the Y-shaped compounds that we recently reported.10c Obviously, the substituent positions play a significant role in affecting the
electronic structure and reversible oxidation characteristics. They are also clearly affected by the donor/acceptor groups of the arylphenyl moieties at the 5,9-positions of the pyrene core in the current butterfly-shaped pyrenes.\textsuperscript{15} Accordingly, the HOMO and LUMO energy levels were estimated from the CVs and the UV-vis absorption and the data are summarized in Table 2. The HOMO energy levels increased from \(-5.36\) to \(-5.79\) eV in the order: 4\(e > 4\)d > 4\(f > 4\)a > 4\(b = 5 > 4\)c, and their LUMO energy levels were in the range \(-2.36\) to \(-2.96\) eV. Based on the HOMO and LUMO energy levels, it can be proposed that these newly developed blue emitters 4 and 5 could be used as blue emitters in OLEDs.

To further understand the electronic properties of 4, 5 and 6, DFT calculations (B3LYP/6–31G* basis set) were carried out using Gaussian 03 for the geometry optimization.\textsuperscript{20} The optimized structures and orbital distributions of the HOMO and LUMO of these butterfly-shaped pyrenes are shown in both Fig. 6 and the supporting information. The dihedral angles between the arylphenyl and pyrene are in the range of 55–58\(^\circ\), which suggested that the different substituents equally contribute to the steric congestion in these system. The HOMO levels of 4, 5 and 6 mainly involve contributions of \(\pi\)-orbitals from the pyrene core, while the substituent aryl groups have limited contributions to these molecules. Similarly, the LUMO levels are also spread across the entire pyrene frameworks; however, acceptor groups with \(\pi\)-conjugation enlarged range from \(-\text{CF}_3\), \(-\text{CN}, \text{–CHO and –C=N–OH, the LUMOs located on entire molecules [I don’t understand this sentence – please re-write]. The HOMO-LUMO energy gaps were in the range of 3.21 eV to 3.43 eV in 4 and 5. Therefore, these theoretical calculations provided clear evidence that the red shift of the absorption and emission bands observed in compounds 4 and 5 are consistent with the experimental results.

Without the tert-butyl group in 6, the energy gap resembles that of 4\(a\), but with a lower LUMO energy level.

Conclusion

In summary, in this study, a series of novel butterfly-shaped pyrene derivatives was successfully synthesized by the classical Suzuki-Miyaura cross-coupling reaction. The introduction of several arylphenyl substituents located at the 1,3,5,9-positions of the pyrene influenced the FL emissions in solution and in the solid-state. The structure-property relationships of the donor–acceptor interactions play a curial role in determining the thermal, UV-vis absorption, electrochemical behavior, etc. These pyrenes possess high solubility, high stability, highly blue emissions with quantum efficiency of up to 70\%, and long fluorescence lifetimes in solution. These excellent qualities make them very promising for applications in OLED devices.

Experimental

General

All melting points (Yanagimoto MP-S\(_1\)) are uncorrected.\textsuperscript{1} \(^1\)H NMR spectra (300 MHz) were recorded on a Nippon Denshi JEOL FT-300 NMR
Lewis acid-catalysed bromination of 2-tert-butylpyrene (1). A mixture of 2-tert-butylpyrene (0.512 g, 2 mol) and iron powder (0.56 g, 10 mmol) was added while stirring for 15 min in chloroform (50 mL) at room temperature. Then, a solution of Br2 (0.63 mL, 12.1 mmol) in CH2Cl2 (15 mL) was slowly added dropwise with vigorous stirring. After this addition, the reaction mixture was continuously stirred for 4 h at room temperature. The reaction mixture was quenched with Na2S2O3 (10%) and extracted with dichloromethane (2 × 50 mL). The combined organic extracts were washed with water and brine and then evaporated. The crude product exhibits a gray color. The crude product was insoluble in general common organic solvents, such as benzene, hexane, methanol, etc. and only slightly dissolved in CH2Cl2 or CHCl3. The residue was dissolved in hot CHCl3 and filtered, then crystallization from CHCl3 to gave pure 7-tert-butyl-1,3,5,9-tetrambromopyrene 2 (978 mg, 84%) as colourless prisms. M.p. 303.4–305.0 °C; IR: νmax (KBr)/cm⁻¹: 2962, 2365, 1579, 1523, 1461, 1425, 1392, 1363, 1267, 1195, 1132, 1027, 1012, 941, 877, 809, 655 and 474; 1H NMR (300 MHz, CDCl3): δ = 1.65 (s, 9H, tBu), 8.47 (s, 1H, pyrene-H); 8.71 (s, 2H, pyrene-H) and 8.79 (s, 2H, pyrene-H) ppm. Due to the poor solubility, it was not further identified by 13C NMR spectroscopy. FABMS: m/z: 573.62 [M⁺]. C39H14Br4 (573.78): calc C 42.05, H 2.53.

Synthesis of 1,3,5,9-tetraaryl-7-tert-butylpyrylenes (4). The series of butterfly-shaped compound 4a–f were synthesized from 1,3,5,9-tetra bromo-7-tert-butylpyrene 2 with the corresponding arylyboronic acid 3 by a Suzuki-Miyaura cross-coupling reaction in high yield.

Synthesis 7-tert-butyl-1,3,5,9-tetraphenylpyrene (4a). 7-tert-Butyl-1,3,5,9-tetraphenylpyrene 2 (200 mg, 0.35 mmol), phenylboronic acid 3a (245 mg, 2.11 mmol), Pd(PPh3)4 (70 mg, 0.06 mmol), 85 °C for 24 h. After it was cooled to room temperature, the reaction mixture was extracted with dichloromethane (3 × 50 mL), and the organic layer was washed with H2O and brine, then dried with anhydrous MgSO4 and evaporated. The crude product was purified by column chromatography using dichloromethane as eluent to afford a deep yellow solid. Recrystallization from a mixture of CHCl3–methanol (2:1) gave 4a (128 mg, 65%) as colourless needles. M.p. 335 °C.

IR: νmax (KBr)/cm⁻¹: 3422.5, 2961.0, 2366.6, 1593.2, 1496.6, 1363.8, 1252.8, 1177.6, 1070.3, 894.7, 762.3, 701.3, 626.1 and 483.1. 1H NMR (400 MHz, CDCl3): δ = 1.39 (s, 9H, tBu), 7.40–7.54 (m, 12H, Ar-H), 7.63–7.70 (m, 8H, Ar-H), 7.98 (s, 1H, pyrene-H), 8.16 (s, 2H, pyrene-H) and 8.29 (s, 2H, pyrene-H) ppm. 13C NMR (100 MHz, CDCl3): δ = 148.6, 141.4, 141.1, 139.8, 137.2, 130.6, 130.5, 130.1, 129.7, 128.4, 128.3, 127.4, 127.3, 127.2, 125.5, 124.5, 124.1, 35.4 and 31.6 ppm. FABMS: m/z: 562.28 [M⁺]. C39H14 (562.74): calc C 93.62, H 5.38; found C 93.25, H 5.25.

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7-tert-Butyl-1,3,5,9-tetraakis(4-methoxyphenyl)pyrene (4c). Yellow prisms (CHCl₃–methanol, 2:1) (144 mg, 62%). M.p. 244 °C. IR: 3058, 3032, 1600, 1486, 1442, 1071, 1034, 893, 790, 759, 740, 700, 620 and 475. 1H NMR (400 MHz, CDCl₃): δ = 1.37 (s, 9H, tBu), 2.22 (s, 4H, -CH₂OH), 5.17; 5.16 (s, 2H, pyrene-H), 8.08 (s, 1H, pyrene-H), 8.17 (s, 2H, pyrene-H) and 8.14 (d, J = 8 Hz, 2H, pyrene-H) ppm; 13C NMR (100 MHz, CDCl₃): δ = 147.5, 147.2, 142.7, 142.4, 136.8, 133.4, 129.9, 128.5, 128.1, 127.1, 126.4, 124.8, 122.4, 122.2, 121.9, 114.9, 116.0, 115.96, 109.4, 109.3, 33.0 and 29.0 ppm. FABMS: m/z: 662.31 [M⁺]. C₆₀H₆₂O₄ (662.31): calcd C 91.55, H 8.45; found: C 91.25, H 8.55.

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Notes

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5. Electronic Supplementary Information (ESI) available: 1H/13C NMR spectra of 4a-f, 5 and 6, the effect of different solvents on the fluorescence emission spectra of 4 and 5, etc. See DOI: 10.1039/b000000x

References

1. (a) P. Tyagi, A. Venkateswararao and K. R. J. Thomas, J. Org. Chem., 2011, 76, 4571–4581; (b) L. Schmidt-Mende, A. Fechtenkötter, K. 4072, 1009, 974, 943, 836, 730, 607, 568, 524 and 466. 1H NMR (400 MHz, CDCl₃): δ = 1.29 (s, 9H, tBu), 2.22 (s, 4H, OH), 7.34 (d, J = 8.0 Hz, 4H, Ar-H), 7.45 (d, J = 8.0 Hz, 4H, Ar-H), 7.53 (d, J = 8.0 Hz, 4H, Ar-H), 7.62, (s, 2H, pyrene-H), 7.66 (d, J = 8.0 Hz, 4H, Ar-H), 7.67 (s, 2H, -CH=N-H), 8.05 (s, 2H, -CH=N-H), 8.14 (d, J = 9.2 Hz, 2H, pyrene-H) and 8.24 (s, 2H, pyrene-H) ppm; 13C NMR (100 MHz, CDCl₃): δ = 115.02, 149.8, 143.3, 142.9, 140.7, 138.1, 133.9, 133.6, 131.9, 131.8, 131.5, 131.3, 130.0, 129.8, 128.3, 128.0, 127.9, 126.4, 125.7, 125.4, 122.7, 36.4 and 32.1 ppm. FABMS: m/z: 734.52 [M⁺]. calcd C₆₃H₅₈N₄O (734.84): C 78.45, H 5.21; found: C 78.20, H 5.25.

Synthesis of 1,3,5,9-tetraphenylpyrene (6). A mixture of 7-tert-butyl-1,3,5,9-tetraakis(4-hydroximino phenyl)pyrene 4a (50 mg, 0.09 [more s.f. needed] mmol), Nafion-H (50 mg), and 2 mL o-xylene were refluxed for 24 h, and then cooled to room temperature. The solid was removed in vacuo and the mother solution collected. The crude product was purified by column chromatography using dichloromethane–hexane (1:1) as eluent to afford a yellow solid. Recrystallization from a mixture of CH₂Cl₂–ethanol (2:1) gave 6 (23 mg, 51%) as light yellow prisms. M.p. 244 °C. IR: 3058, 3032, 1600, 1442, 1071, 1034, 893, 790, 759, 740, 700, 620 and 475. 1H NMR (400 MHz, CDCl₃): δ = 7.42–7.45 (m, 4H, Ar-H), 7.49–7.53 (m, 4H, Ar-H), 7.59–7.61 (m, 4H, Ar-H), 7.66–7.68 (m, 4H, Ar-H), 7.85–7.89 (m, 1H, pyrene-H), 8.00 (s, 1H, pyrene-H), 8.17 (s, 2H, pyrene-H) and 8.14 (d, J = 8 Hz, 2H, pyrene-H) ppm; 13C NMR (100 MHz, CDCl₃): δ = 141.2, 141.0, 139.6, 134.7, 130.7, 130.6, 130.1, 128.4, 128.3, 127.4, 123.7, 129.2, 125.7, 125.5 and 124.1 ppm. FABMS: m/z: 506.12 (M⁺). C₆₃H₅₈N₂O (506.20): calcd C 94.83, H 5.17; found: C 94.77, H 5.29.