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Porphyrin, Phthalocyanine and Porphyrazine Derivatives with Multifluorenyl Substituents as Efficient Deep-Red Emitters

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Abstract: The synthesis and photophysical properties are described for a series of porphyrin, phthalocyanine and pyrazinoporphyrazine derivatives which bear four or eight peripheral fluorenyl substituents as antennae. Representative examples are 5,10,15,20-tetra(9,9-dihexyl-9*H*-fluoren-2-yl)porphyrin (**2**), 5,10,15,20-tetrakis[4-(9,9-dihexyl-9*H*-fluoren-2-yl)phenyl]porphyrin (**3**), 2,3,9,10,16,17,23,24-octakis(9,9-dihexyl-9*H*-fluoren-2-yl)-29*H*,31*H*-phthalocyanine (**8**) and 2,3,9,10,16,17,-23,24-octakis[4-(9,9-dihexyl-9*H*-fluoren-2-yl)phenyl]-29*H*,31*H*-tetrapyrazinoporphyrazine (**9**). Palladium-mediated Suzuki–Miyaura cross-coupling reactions have been key steps for attaching the substituents. The compounds are deep-red emitters: λ_{max}(em) = 659 (**3**), 737 (**8**) and 684 nm (**9**). Their absorption and emission spectra, their fluorescence lifetimes and quantum yields are correlated with the structures of the macrocycles and the substituents. The solution fluorescence quantum yields of porphyrin derivatives substituted with fluorene (**2**–**4**) and terphenyl substituents (**7**) (Φ_f = 0.21–0.23) are approximately twice that of tetraphenylporphyrin. For phthalocyanine derivative **8**, Φ_f was very high (0.88). Specific excitation of the fluorene units of **8** produced emission from both of them (λ_{max} = 480 nm) and also from the phthalocyanine core (λ_{max} = 750 nm), indicating a competitive rate of energy transfer and radiative decay of the fluorenes. Organic light-emitting devices (OLEDs) were made by spin-coating techniques by using a polyspirobifluorene (PSBF) copolymer as the host blended with **3** (5 wt.%) in the configuration ITO/PEDOT:PSS/PSBF copolymer:**3**/Ca/Al. Deep-red emission (λ_{max} = 663 nm; CIE coordinates $x = 0.70$, $y = 0.27$) was observed with an external quantum efficiency of 2.5% (photons/electron) (at 7.5 mA cm^{-2}), a low turn-on voltage and high emission intensity (luminance) of 5500 cd m^{-2} (at 250 mA/m^2).

Keywords: fluorene · fluorescence · phthalocyanines · porphyrazine · porphyrinoids

Introduction

The array of optoelectronic and coordination properties displayed by porphyrins,[1] phthalocyanines[2] and related macrocycles, for example, porpyrazines (tetraazaporphyrins), has ensured that there is continued interest in the synthesis of new functionalised derivatives which are of academic and industrial importance. These macrocycles exhibit high chemical and thermal stability, and their well-defined optical absorption and emission properties have led to many applications in materials science. For example, tetraphenylporphyrin is a red emitter with reasonable fluorescence efficiency ($\Phi_f = 0.11$)[3] which has been used as a dopant in a host polyfluorene matrix to give red organic light-emitting devices (OLEDs).[4] The narrow emission linewidth of porphyrins makes them attractive materials in this regard. Porphyrin[5] and phthalocyanine[6] derivatives with peripheral substituents have been used as probes of intramolecular charge-transport phenomena (through-bond and/or through-space) which can modulate fluorescence of the macrocycle. Many of the properties of these macrocycles are highly dependent on the extent of intermolecular π–π stacking interactions,

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Supporting information for this article contains experimental details and characterisation data for **4**–**7**, **11**, **13** and **17**–**19**, general experimental details for photophysical and OLED measurements, the excitation/emission matrix for compound **8**, the X-ray molecular structure of **18** and calculated minimum-energy conformations for **3** and **8**. This information is available on the WWW under http://www.chemeurj.org/ or from the author.

with strong interactions between neighbours (for example, face-to-face dimerisation), leading to fluorescence quenching. Bulky peripheral substituents can reduce self-quenching and enhance fluorescence intensity. In a complementary approach, axial substituents on a metallophthalocyanine (for example, attached to the central Si atom) can similarly reduce intermolecular stacking. For these systems, intramolecular interactions between the axial substituents and the macrocyclic π-system can be examined.[7]

The aim of the present work was to synthesize a series of porphyrin, phthalocyanine and pyrazinoporphyrazine derivatives functionalised with peripheral 9,9-dialkylfluorenyl substituents and to explore the energy transfer between the fluorenyl units and the macrocyclic core. Fluorene was chosen as a substituent for this study as it is a thermally very stable unit which can act as an antenna to harvest and transfer energy efficiently to longer wavelength emitters in blends or composite structures.[8] Furthermore, we have shown that small molecules (namely, iridium complexes) substituted with multifluorene units have good structural compatibility when used as dopants in a host poly(fluorene) matrix for OLED applications.[9] The present work has furnished a series of deep-red emitters with good solubility in organic solvents, high stability and interesting photophysical properties, including a new porphyrin material for efficient red OLEDs. Related porphyrin systems reported during the course of our studies are: an analogue of **3** with octyl chains on the fluorene moieties,[10] a porphyrin substituted with four truxene units[11] and a platinum tetraphenylporphyrin derivative with eight peripheral carbazole units.[12] The latter system was used to obtain saturated red electroluminescence from a multilayer OLED.

Results and Discussion

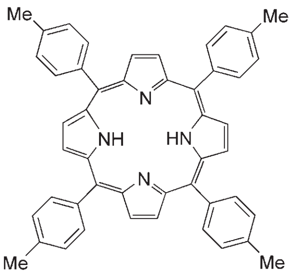
Synthesis: 5,10,15,20-Tetra-*para*-tolylporphyrin (**1**) was synthesised as a known model compound following a standard route[13] from pyrrole and *para*-tolualdehyde in refluxing propionic acid. The tetrakis(fluorenyl) derivative **2** was obtained from pyrrole and 9,9-dihexyl-9*H*-fluorene-2-carbaldehyde (**11**)[14] in 13 % yield under standard Lindsey condensation conditions (Scheme 1).[15] The *n*-hexyl chains at C(9) of the fluorene units ensured good solubility of the product in organic solvents. The analogue **3** containing a phenyl spacer between the porphyrin core and each of the fluorene units was obtained by using different methodology (Scheme 2). The efficient four-fold Suzuki–Miyaura cross-coupling of 5,10,15,20-tetrakis(4-bromophenyl)porphyrin (**12**)[16] with **13**[17] gave **3** in 72 % yield. The octakis(N-carbazolyl) derivative **4** was similarly isolated in 52 % yield from the corresponding boronate ester reagent **14**. The zinc derivatives of **3** and **4** (for example, complexes **5** and **6**, respectively) were obtained upon reaction with zinc acetate by using standard procedures.[18] For comparative purposes, analogue **7** containing branched terphenyl substituents was synthesized (14 % yield) by the reaction of pyrrole with 3,5-diphenylbenzaldehyde **15** (obtained in turn from 3,5-dibromobenzaldehyde and phenylboronic acid) (Scheme 3).

To explore the effect of changing the macrocyclic core while retaining peripheral fluorenyl substituents, the phthalocyanine and pyrazinoporphyrazine derivatives **8** (Schemes 4 and 5, respectively) and **9** were synthesized by tetramerisation of the precursor dinitrile derivatives **17** and **19**, respectively. The model porphyrazine **10** was obtained from 5,6-di-*p*-tolylpyrazine-2,3-dicarbonitrile following literature procedures.[19]

Optimised geometries: The calculated optimised geometries (Hyperchem V6.03) for porphyrin derivative **3** and pyrazinoporphyrazine derivative **8** are shown in Figures 1 and 2, respectively. For structure **3**, the phenyl substituents are substantially twisted out of the plane of the porphyrin ring system, as observed in crystal structures of other 5,10,15,20-tetraphenylporphyrin derivatives.[20] For **8**, the macrocyclic core is essentially planar; the calculated torsion angles for the diphenylpyrazine subunits in **8** were very similar ($\pm<1^\circ$) to those observed in the X-ray molecular structure of precursor **18** (see the Supporting Information).

Photophysical studies: The photophysical data for compounds **1**–**10** in dichloromethane solution are collated in Table 1. The free-base porphyrins **2**, **3** and **7** display similar absorption and emission profiles to the model compound **1**. Dilute solutions were used (10^{-6} M) to minimize any tendency for aggregation. The UV-visible absorption spectra were characterized by a sharp intense Soret band at $\lambda_{max}=425$ nm approximately, with four weak Q-bands in the range of 500–660 nm[21] (Figure 3). The Soret bands of **2**, **3**, **4** and **7** were slightly red-shifted compared to **1**. These compounds all exhibit intense deep-red emission (Figure 4) with two main peaks ($\lambda_{max}=660$ and 725 nm approximately), which are again consistently red-shifted compared to **1** (by 3–4 nm) due to the conjugated fluorenyl substituents in **2**, **3** and **4**: no significant red shift is observed in the less-conjugated terphenyl compound **7**. Compared to **2**, increasing the conjugation in the substituents with an additional phenyl group (derivative **3**) has no appreciable effect on the fluorescence properties.

The fluorescence quantum yield obtained for tetra-*para*-tolyl compound **1** ($\Phi_f=0.11$) is in agreement with the literature values for **1** and the tetraphenyl analogue ($\Phi_f=0.11$–0.13).[3,22] The Φ_f values for the fluorenyl derivatives **2**–**4** ($\Phi_f=0.21$) and the terphenyl derivative **7** ($\Phi_f=0.23$) are substantially increased compared to compound **1** and are high for the porphyrin derivatives. The very high literature value for 5,10,15,20-tetra[3,5-di(4-*tert*-butylphenyl)benzyl]-porphyrin ($\Phi_f=0.66$ in dichloromethane) can be attributed to reduced aggregation due to the four bulky *tert*-butyl groups.[23] The fluorescence lifetime we observed for **1** ($\tau_f=8.6$ ns) is similar to the literature value of 9.40 ns obtained in a different solvent mixture.[22] The substituents in **2**–**4** and **7** do not significantly effect the lifetimes ($\tau_f=7.3$–8.4 ns) which are long and indicative of a small non-radiative decay



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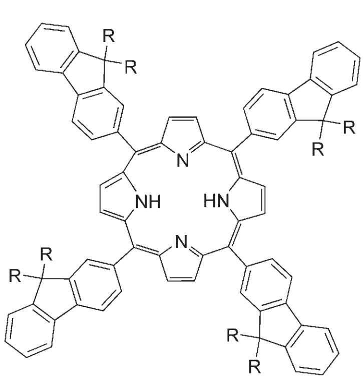
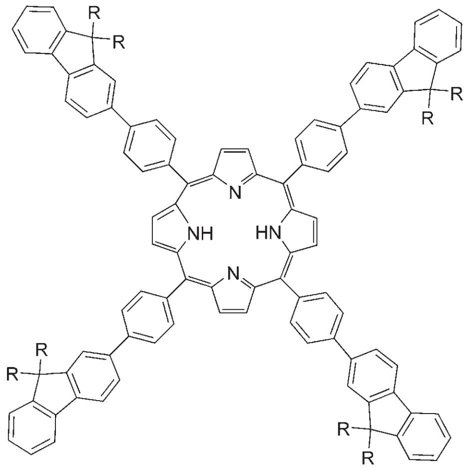
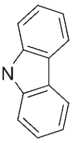


2 R = n-C_6H_{13}

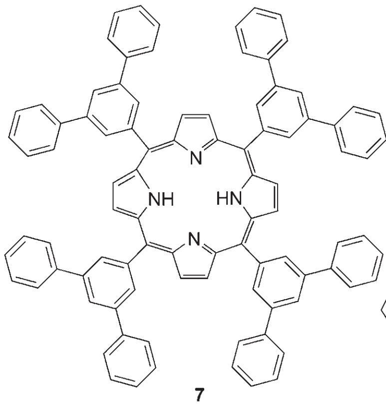


3 R = n-C_6H_{13}

4 R = — $(CH_2)_6$ —N



5 = **3** – Zn complex
6 = **4** – Zn complex



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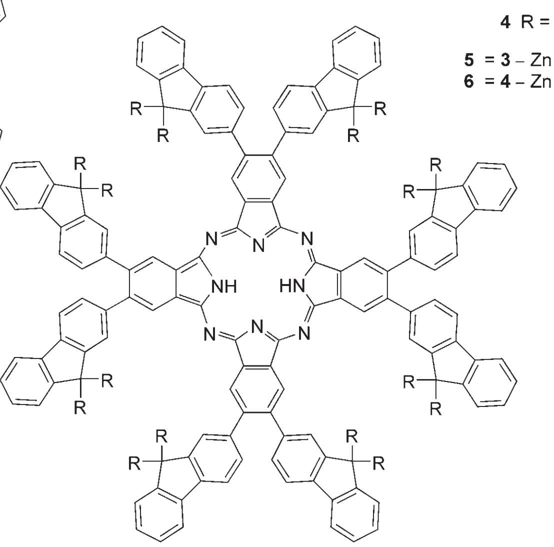
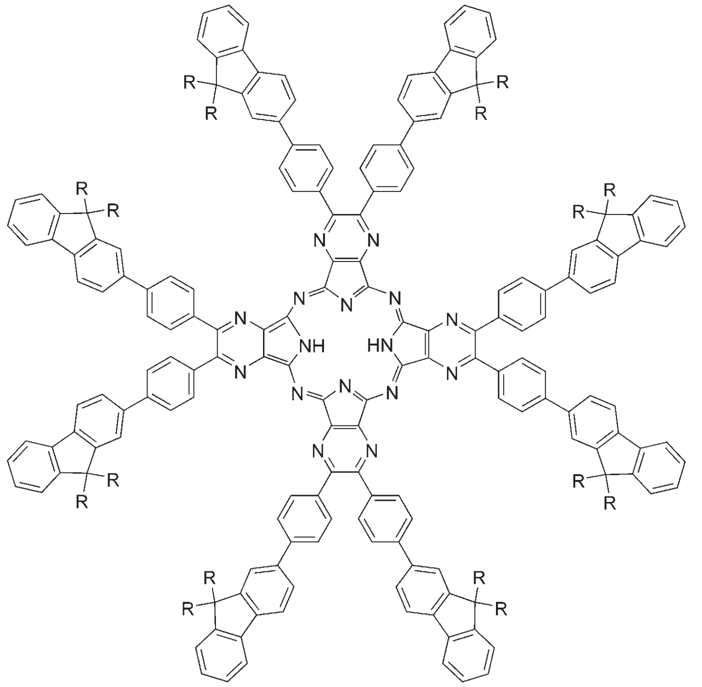
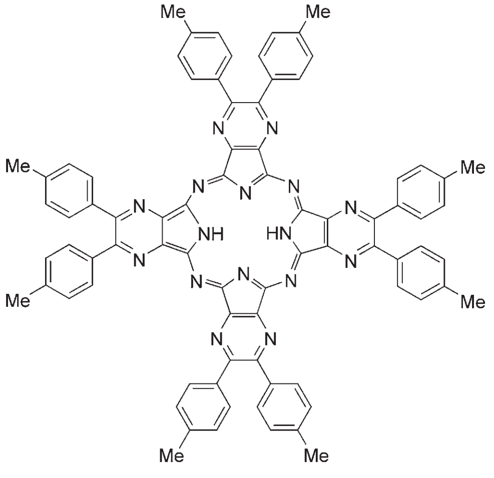


8 R = n-C_6H_{13}



9 R = n-C_6H_{13}



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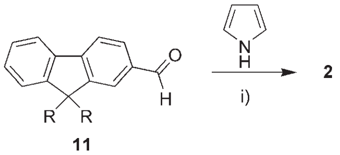
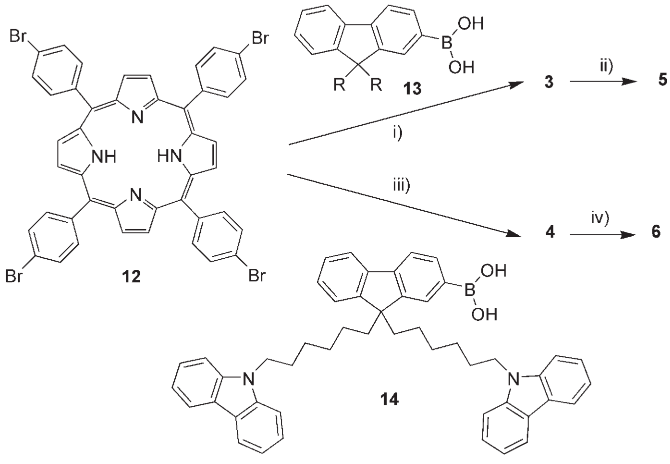
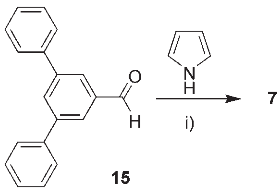


Scheme 1. i) Trifluoroacetic acid, $CHCl_3$, 61 °C, 3 h; then DDQ, 20 °C, 10 h, NEt_3 (13 % yield). DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

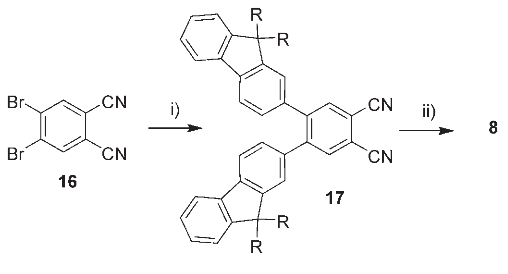


Scheme 2. i) $Pd(PPh_3)_4$, Na_2CO_3, THF, toluene, H_2O, 105 °C, 24 h (72 % yield); ii) $Zn(OAc)_2$, $CHCl_3$, 62 °C, 4 h (95 % yield); iii) $Pd(PPh_3)_4$, Na_2CO_3, THF, toluene, H_2O, 105 °C (52 % yield); iv) $Zn(OAc)_2$, $CHCl_3$, 62 °C, 4 h (95 % yield).

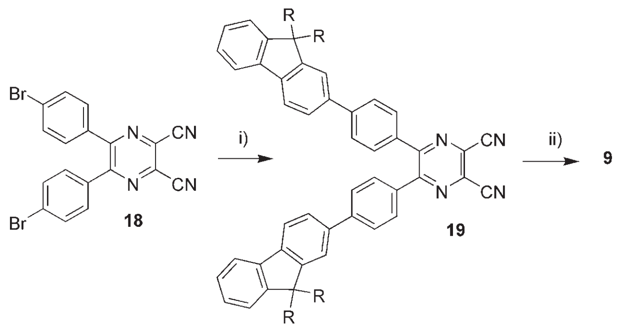


Scheme 3. i) Trifluoroacetic acid, $CHCl_3$, 50 °C, 2 h; then DDQ, 20 °C, 2.5 h, NEt_3 (14 % yield).

constant. A comparison of **3** with **4** and **5** with **6** (Table 1) shows that the carbazolyl units of **4** and **6** do not have any significant influence on the photophysical properties of the free bases or the zinc complexes. We had envisaged that the flexible N-hexyl spacers could enable some of the electron-rich carbazolyl units to be oriented in such a way that porphyrin fluorescence might be quenched by intramolecular through-space transfer. However, this effect is not observed.



Scheme 4. i) $Pd(PPh_3)_4$, Na_2CO_3, THF, toluene, H_2O, 110 °C, 96 h (87 % yield); ii) Li, $n\text{-}C_5H_{11}OH$, 125 °C, 2 h, HCl (11 % yield).



Scheme 5. i) **13**, $Pd(PPh_3)_4$, Na_2CO_3, THF, toluene, H_2O, 105 °C, 72 h (59 % yield); ii) Li, $n\text{-}C_5H_{11}OH$, 1,4-dioxane, 105 °C, 12 h, AcOH (23 % yield).

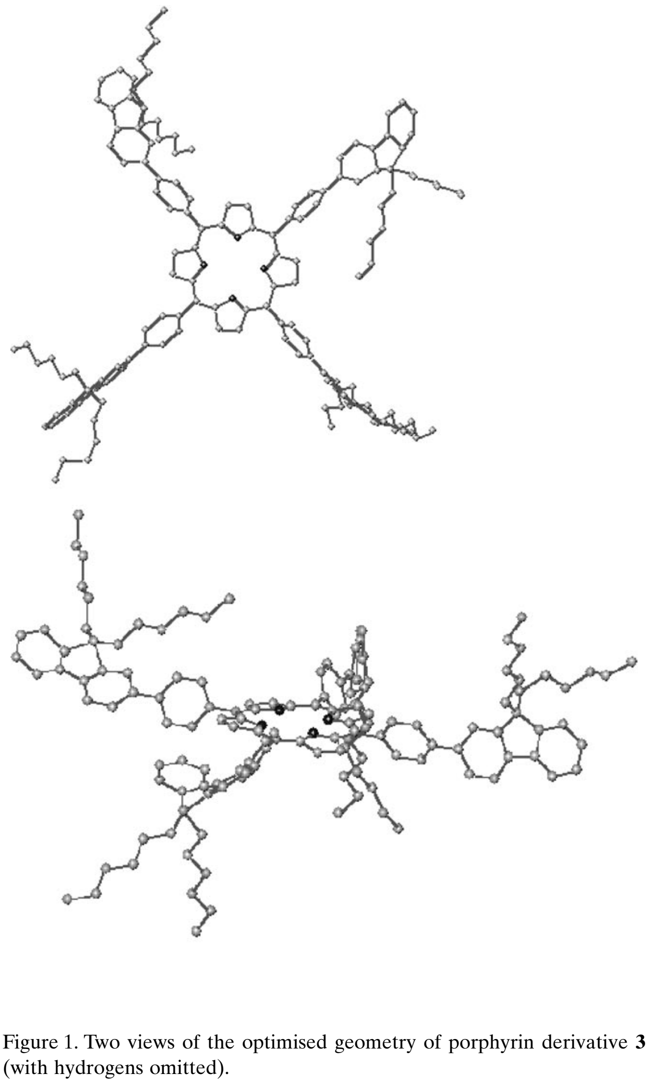


Figure 1. Two views of the optimised geometry of porphyrin derivative **3** (with hydrogens omitted).

The zinc-centred derivatives **5** and **6** display significantly blue-shifted emission as well as greatly reduced Φ_f and τ_f values compared to their free-base precursors **3** and **4**, respectively. These values are characteristic of zinc porphyrins in general[24] and demonstrate the effective reduction of

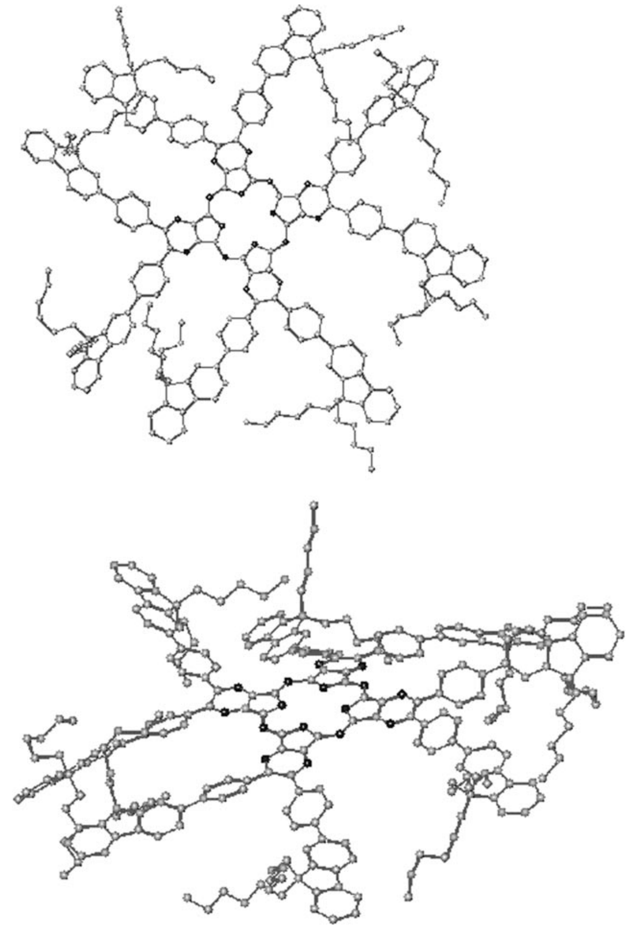


Figure 2. Two views of the optimised geometry of pyrazinoporphyrazine derivative **8** (with hydrogens omitted).

Table 1. Solution photophysical data obtained in dichloromethane solution (10^{-4}–10^{-7} M).

Compound	λ_{max}(abs) [nm]	λ_{max}(em) [nm]	Φ_f[a]	τ_{f1} [ns][b]	τ_{f2} [ns][b]
1	420	656 (721)	0.11	8.6	–
2	427	660.5 (725)	0.21	8.2	–
3	426	659 (724)	0.21	8.3	–
4	427	659.5 (725)	0.21	8.4	–
5	427	603.5 (651)	0.088	1.6	–
6	427	603 (650.5)	0.088	1.6	–
7	424	657 (715.5 br)	0.23	7.3	–
8	696, 729	737	0.88	4.7	–
9	654, 681	684	0.019	4.0 (60%)	1.5 (40%)
10	669	676.5	0.022	7.0 (75%)	3.6 (25%)

[a] ±10%; $\lambda_{ex}=430$ nm (615 nm for **8**–**10**), $\lambda_{em}=600$–850 nm (525–815 nm for **5**–**6**, 630–850 nm for **8**–**10**), 293 K, in dichloromethane. [b] ±10%; for **1**–**7**, ±0.1 ns, $\lambda_{ex}=400$ nm (635 nm for **8**–**10**), $\lambda_{em}=655$–700 nm (600–650 nm for **5**–**6**, 690 nm for **8**–**10**), 293 K, in dichloromethane.

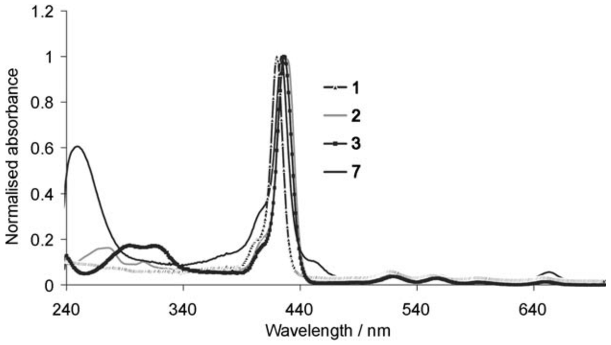


Figure 3. Normalised absorption spectra of porphyrins **1**, **2**, **3** and **7** in dichloromethane at 298 K.

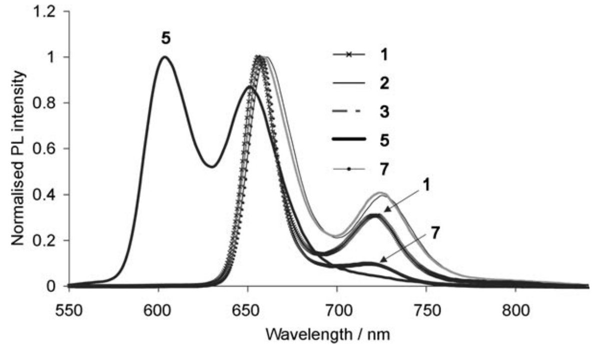


Figure 4. Normalised emission spectra of porphyrins **1**, **2**, **3**, **5** and **7** in dichloromethane at 298 K.

fluorescence from the porphyrin by inter-system crossing to the excited triplet state.

Phthalocyanine derivative **8** displays an extremely high fluorescence quantum yield ($\Phi_f=0.88$); PLQY values of this magnitude have been observed in other highly conjugated peripherally substituted free-base phthalocyanines.[25] The fluorescence lifetime for **8** ($\lambda_{ex}=615$ nm, $\tau_f=4.8$ ns) is consistent with values for derivatives bearing peripheral alkoxy substituents,[26] demonstrating that τ_f is relatively insensitive to the substituents at the periphery of the phthalocyanine core.

Excitation of **8** at 300 nm produced a second component to the fluorescence lifetime, corresponding to an emission at $\lambda_{em}\approx 500$ nm. When excitation spectra were run with monitoring at both $\lambda_{em}=500$ and 760 nm, it was clear that this emission band was due entirely to the fluorene units. Specific excitation of the fluorene units produced emission from them and also from the phthalocyanine core (Figures S5 and S6 in the Supporting Information). Thus, we conclude that following excitation, the fluorene units decay by two pathways: either by direct luminescence giving rise to the band at $\lambda_{max}=480$ nm, or by energy transfer to the Pc core, leading to red emission at $\lambda_{max}=750$ nm. This indicates that the rate of energy transfer from the peripheral fluorene groups to the core is competing with the radiative decay of the fluorenes and hence energy transfer is not as rapid as might be expected for a closely coupled system, which in turn may be due to the poor spectral overlap between the fluorene emission and the B1/B2 absorption bands of the Pc.

The spectra of pyrazinoporphyrazine derivatives **9** and **10** show small Stokes shifts, indicating very little molecular rearrangement in the excited state, as observed for other octasubstituted derivatives.[27] The emission maximum for **9** is red-shifted (by 7.5 nm) compared with **10**. For **9**, the π–π* absorption band in the 300–400 nm region originated from the peripheral fluorenyl-substituents.[28] Several excitation spectra were run at varying emission wavelengths (Figure 5), confirming that the majority of energy is absorbed by the peripheral substituents and then transferred to the macrocyclic core. The reason for the low Φ_f values for **9** and **10** is unclear at present.

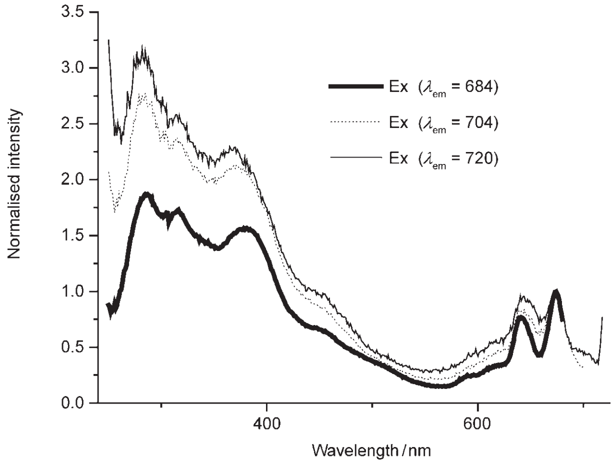


Figure 5. Excitation spectra of **9** in dichloromethane at 298 K.

Both **9** and **10** displayed a large secondary component to the fluorescence lifetime, which may be the result of electron transfer within the molecule. The absorption spectrum of **9** was essentially unchanged after storing a solution in dichloromethane in direct sunlight for five days (Figure S4 in the Supporting Information). Moreover, MALDI-TOF analysis of the solution showed only a single peak due to the $[M]^+$ ion with no evidence of decomposition.

OLED studies: Bradley et al. demonstrated energy transfer from blue to red in an OLED by doping tetraphenylporphyrin into a poly(9,9-dioctylfluorene) host: an external quantum efficiency (EQE) of 0.9% (photons/electron) and a luminance of 90 cd m^{-2} was obtained.[4] Other workers[10,11,12] have noted the potential of functionalised porphyrins to serve as emitters in OLEDs. In a complementary approach, Cao et al. reported saturated red emission from copolymers comprising 9,9-dioctylfluorene and 4,7-di(4-hexylthieny-2-yl)-2,1,3-benzothiadiazole (DHTBT) units (for example, units with a wide and narrow HOMO–LUMO gap, respectively), utilising efficient intramolecular energy transfer from the former (blue) to the latter (red) units.[29]

We have tested compound **3** in an OLED with the following configuration: ITO/PEDOT:PSS/PSBF copolymer:**3**/Ba/Al, in which the emissive layer is **3** as a blend (5 weight%) in a polyspirobifluorene copolymer host.[30] Compound **3** was chosen from among the available derivatives due to its good processability and the high-quality blend films which were formed. The structure of the copolymer is shown in Figure S7 in the Supporting Information. These unoptimised devices showed significantly improved efficiencies and stability compared to tetraphenylporphyrin devices.[4] A major factor here is likely to be that the phenyl-fluorenyl units of **3** increase the compatibility of the small-molecule guest with the polymer host. Hence, a more homogeneous blend is formed with a reduced tendency for phase segregation which would lead to a decay of efficiency with increasing current density.[31] Figure 6 shows the normalised electroluminescence (EL) spectra of devices containing solely the PSBF copolymer and the PSBF copolymer device doped with compound **3**. The EL spectrum of the device (λ_{max} = 665, 730 nm) is very similar to the solution PL spectrum of **3** (λ_{max} = 659, 724 nm). The emission spectrum (CIE coordinates $x = 0.70$, $y = 0.27$) represents a very deep red, as shown on a colour CIE diagram in Figure S8 in the Supporting Information.

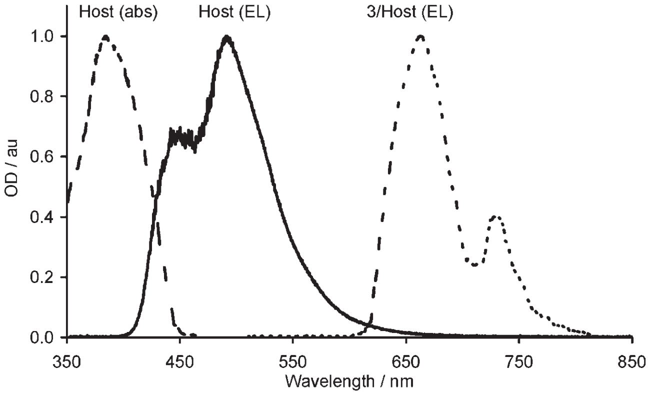


Figure 6. Normalised thin-film absorbance of the PSBF copolymer host and electroluminescence spectra of devices ITO/PEDOT:PSS/PSBF copolymer/Ba/Al and ITO/PEDOT:PSS/PSBF copolymer:**3**/Ba/Al (5% by weight of **3** in the blend).

Figure 7 shows that the blend devices reached an EQE of 2.5% at 7.5 mA cm^{-2}. The good stability of the EQE at high current densities is a notable feature of these devices. The devices had a low turn-on voltage (approximately 3 V) and recording the EL spectra at 6 V established that the time to half brightness was approximately 15 h under continuous operation with essentially no change in the spectral profile. This confirms the high chemical stability of the blend. Taking these data together with the high emission intensity (luminance) of 5500 cd m^{-2} (at 250 mA m^{-2}) (Figure 8) it has been established that compound **3** is a very promising material for OLED applications. Optimisation (with respect to layer thicknesses, doping concentration, use of encapsulation procedures, etc.) would be expected to enhance performance and durability.

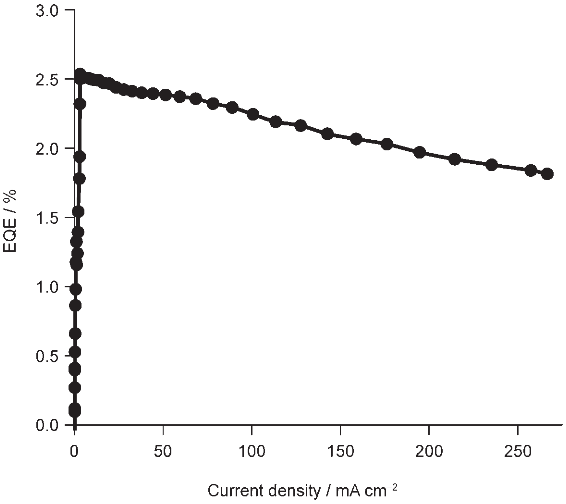


Figure 7. The external quantum efficiency (EQE) versus current density for the device ITO/PEDOT:PSS/PSBF copolymer:**3**/Ba/Al (5% by weight of **3** in the blend).

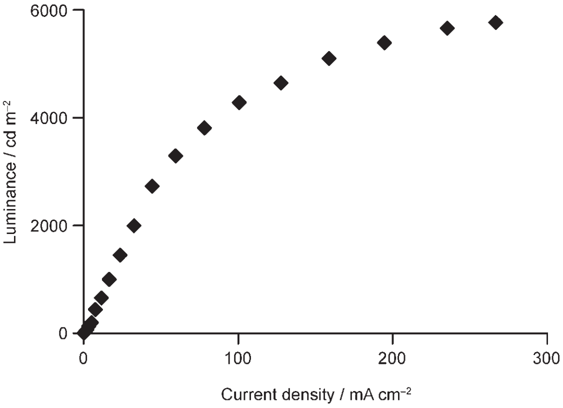


Figure 8. Luminance versus current density for the device ITO/PEDOT:PSS/PSBF copolymer:**3**/Ba/Al (5% by weight of **3** in the blend).

Conclusion

We have synthesized a series of porphyrin, phthalocyanine and pyrazinoporphyrazine derivatives which bear four or eight peripheral fluorenyl substituents. The compounds are deep-red emitters: for example, λ_{max}(em) = 659 (**3**), 737 (**8**) and 684 nm (**9**). A general feature of these systems is the fast and efficient energy transfer, which occurs from the fluorenyl substituents to the macrocyclic cores. The emission from the zinc-centred porphyrin derivatives **5** and **6** is significantly blue-shifted and the Φ_f and τ_f values are greatly reduced compared to their free-base precursors **3** and **4**, respectively, demonstrating the effective reduction of fluorescence from the porphyrin by inter-system crossing to the excited triplet state. These are promising OLED materials as demonstrated by a device using porphyrin-fluorene hybrid **3** blended into the blue polyspirobifluorene copolymer host. Deep-red emission (λ_{max} = 665 nm) was observed from the device with an EQE of 2.5% (at 7.5 mA cm^{-2}), a low turn-on voltage and emission intensity (luminance) of 5500 cd m^{-2} (at 250 mA m^{-2}). Future work will address new functionalisation modes at the periphery of the macrocyclic platforms to enable further tuning of the structural, optoelectronic and device properties of these interesting multifunctional materials.

Experimental Section

5,10,15,20-Tetra(9,9-dihexyl-9*H*-fluoren-2-yl)porphyrin (2): Trifluoroacetic acid (0.31 mL, 4.02 mmol) was added dropwise to a stirred solution of pyrrole (0.19 mL, 2.73 mmol) and **11**[14] (0.13 g, 2.73 mmol) in degassed anhydrous chloroform (20 mL) and the solution was stirred at 61 °C for 3 h. After allowing the solution to cool to room temperature, DDQ (0.62 g, 2.73 mmol) was added and stirring was then continued for a further 10 h. Triethylamine (0.56 mL, 4.02 mmol) was added dropwise and the reaction mixture was filtered through a short column (initial eluent: dichloromethane followed by ethyl acetate) giving a crude product after the removal of solvents in vacuo. Purification by column chromatography (eluent: 33% dichloromethane in hexane) gave **2** as a purple solid (145 mg, 13%). M.p. 276–278 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -1.50$ (2H, s; NH), 0.74 (24H, t, $^3J = 3.6$ Hz), 0.87–0.89 (16H, m), 1.13–1.15 (48H, m), 2.12–2.14 (16H, m), 7.43–7.50 (12H, m), 7.97 (4H, d, $^3J = 7.2$ Hz), 8.08 (4H, d, $^3J = 7.8$ Hz), 8.22 (8H, d, $^3J = 6.6$ Hz), 8.92 ppm (8H, d, $^3J = 13.8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.06$, 22.76, 24.02, 29.99, 31.99, 40.07, 55.95, 118.01, 120.03, 120.09, 123.76, 127.74, 127.88, 129.54, 141.43, 141.95, 149.26, 151.97 ppm; IR (Nujol): 3304, 3176, 2949, 2918, 2852, 2719, 2663, 1463, 1377, 1299, 1257, 1146, 1054, 1018, 965, 874, 799, 720 cm^{-1}; MS (MALDI-TOF): *m*/*z*: 1639.7 $[M]^+$; elemental analysis: calcd (%) for $C_{120}H_{142}N_4{\cdot}H_2O$: C 86.91, H 8.75, N 3.38; found: C 86.93, H 8.74, N 3.09.

5,10,15,20-Tetrakis[4-(9,9-dihexyl-9*H*-fluoren-2-yl)phenyl]porphyrin (3): Compound **12**[16] (93 mg, 0.1 mmol), **13**[17] (156 mg, 0.41 mmol), tetrakis(triphenylphosphine)palladium(0) (13.8 mg, 0.012 mmol) and sodium carbonate (53 mg, 0.5 mmol) were stirred together in a degassed solution of THF (12 mL), toluene (12 mL) and water (0.5 mL) at 105 °C for 24 h. The solution was allowed to cool to room temperature and the solvents were removed in vacuo. The residue was redissolved in dichloromethane (20 mL) and washed with water (30 mL) before being dried over anhydrous magnesium sulphate. After removal of the solvent in vacuo and purification by column chromatography (eluent: 50% dichloromethane in hexane), **3** was obtained as a dark-red powder (140 mg, 72%). M.p. 270–271 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -2.59$ (2H, s), 0.88–0.72 (56H, m), 1.19–1.07 (48H, m), 2.18–2.05 (16H, m), 7.43–7.33 (12H, m), 7.80 (4H, dd, $^3J = 7.2$, $^4J = 0.9$ Hz), 7.92–7.90 (12H, m), 8.10 (8H, d, $^3J = 8.4$ Hz), 8.36 (8H, d, $^3J = 8.4$ Hz), 9.03 ppm (8H, s); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 12.99$, 21.60, 22.85, 28.77, 30.53, 39.53, 54.30, 118.83, 119.01, 119.16, 120.53, 121.95, 124.40, 125.20, 125.84, 126.14, 134.14, 138.51, 139.79, 139.83, 139.86, 140.04, 150.06, 150.69 ppm; MS (MALDI-TOF): *m*/*z*: 1945.4 $[M+H]^+$; elemental analysis calcd (%) for $C_{144}H_{158}N_4{\cdot}H_2O$: C 88.11, H 8.22, N 2.85; found: C 87.89, H 8.24, N 2.83.

2,3,9,10,16,17,23,24-Octakis(9,9-dihexyl-9*H*-fluoren-2-yl)-29*H*,31*H*-phthalocyanine (8): Lithium (20 mg, 2.88 mmol) was added to a stirred solution of **17** (400 mg, 0.504 mmol) in degassed 1-pentanol (2 mL). The mixture was heated at 125 °C for 2 h and then allowed to cool to room temperature. The dark solution was acidified with 37% aq HCl (1 mL) and poured into methanol (100 mL) forming a bright green precipitate, which was then filtered to give a crude green solid (0.094 g). Purification by column chromatography (eluent: 40% dichloromethane in hexane) gave **8** as a green solid (42 mg, 11%). M.p. 325–327 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.58$ (32H, m), 0.68 (48H, t, $^3J = 6.6$ Hz), 0.97 (96H, m), 1.82 (32H, m), 7.30 (24H, m), 7.52 (8H, m), 7.64–7.77 (24H, m), 9.64 ppm (8H, br s), NH protons not observed; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 14.05, 22.32, 24.01, 29.97, 31.89, 40.33, 55.57, 120.01, 120.03, 123.57, 125.93, 126.04, 127.21, 127.85, 129.98, 136.11, 140.56, 141.23, 144.76, 151.85, 151.97 ppm; IR (Nujol): 3175, 2933, 2911, 2853, 2714, 2656, 2595, 1735, 1459, 1376, 1298, 1219, 1201, 1144, 1070, 946, 909, 873, 837, 759, 720, 511 cm^{-1}; MS (MALDI-TOF): *m*/*z*: 3173, 3174, 3175, 3176 $[M]^+$; elemental analysis calcd (%) for $C_{232}H_{274}N_8{\cdot}H_2O$: C 87.28, H 8.71, N 3.51; found: C 87.30, H 8.56, N 2.91.

2,3,9,10,16,17,23,24-Octakis[4-(9,9-dihexyl-9*H*-fluoren-2-yl)phenyl]-29*H*,31*H*-tetrapyrazinoporphyrazine (9): A freshly prepared lithium pentoxide solution in 1-pentanol (1.89 M, 5 mL) was added to a stirred solution of **19** (99.5 mg, 0.105 mmol) in degassed anhydrous 1,4-dioxane (2 mL) and the solution was stirred at 105 °C for 12 h. The solution was allowed to cool to room temperature and the solvent removed in vacuo. The black residue was redissolved in degassed anhydrous chloroform (2 mL), a solution of acetic acid (1 mL) in ethanol (30 mL) was added and the mixture was then stirred at 78 °C for 20 h. After cooling to room temperature, the mixture was placed in an ice bath for 1 h and then filtered to give a crude blue solid. Purification by flash chromatography (eluent: dichloromethane) gave **9** as a dark-blue solid (23 mg, 23 %). M.p. >400 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.71$ (96 H, m), 1.03 (80 H, m), 1.88 (32 H, m), 7.34 (32 H, m), 7.57–7.74 ppm (56 H, m), NH protons not observed; IR (Nujol): 3162, 2911, 2852, 2710, 2658, 2032, 1610, 1489, 1376, 1299, 1219, 1174, 1070, 986, 919, 873, 837, 759, 720, 511 cm^{-1}; MS (MALDI-TOF): *m*/*z*: 1924.3, 2862.9, 3793.5 $[M+2H]^+$.

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