

New tetra-aryl and bi-aryl porphyrins bearing 5,15-related fluorenyl pendants: the influence of arylation on fluorescence

Christine O. Paul-Roth,^{a,*} J. A. Gareth Williams,^{b,*} Julien Letessier^a and G. Simonneaux^a

^aGroupe Ingénierie Chimique et Molécules pour le Vivant, UMR CNRS 6226, Université de Rennes I, 35042 Rennes Cedex, France

^bDepartment of Chemistry, University of Durham, Durham DH1 3LE, UK

Received 4 April 2007; revised 20 April 2007; accepted 24 April 2007

Available online 27 April 2007

Abstract—The new tetra-aryl *trans*-A₂B₂-porphyrin with two fluorene-2-yl and two phenyl groups at the *meso*-positions has been synthesized and characterized, together with the analogous bi-aryl *trans*-A₂-porphyrin incorporating only the fluorenyl groups. The photophysical properties of these new compounds in solution are reported. The two additional phenyl groups in the A₂B₂ porphyrin stabilize the first excited singlet state by approximately 500 cm⁻¹ compared to the A₂ system, as revealed by the red-shift of the absorption Q bands and of the fluorescence emission bands. Both compounds display enhanced emission quantum yields compared to tetraphenylporphyrin: the augmentation is higher for the tetra-aryl than for the bi-aryl system, although not as high as for tetrafluorenylporphyrin. Fluorescence lifetime measurements of the series of four compounds suggest that the trends can be interpreted in terms of the larger influence of fluorenyl over phenyl groups in increasing the fluorescence radiative rate constant of the porphyrin, *k_f*.

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Organic and polymeric light-emitting devices (OLEDs and PLEDs) are attracting intense interest for flat-panel display screen technology.^{1–8} These applied developments have led to a concomitant increase in fundamental investigations aimed at better understanding the electro- and photoluminescence properties of various classes of molecules, and particularly of the factors that determine their luminescence efficiencies. Porphyrins are potentially attractive compounds for use as red emitting materials in OLEDs and PLEDs, owing to their high chemical and thermal stability and well-defined emission properties.⁷ In particular, whilst emitting in the red region where efficient emitters are relatively scarce, they typically display narrow emission linewidths, thereby offering good color purity for devices, and without the loss of efficiency that occurs for broader-band emitters whose emission tails into the near-IR. For example, tetraphenylporphyrin (**TPP**, **1**) has an emission maximum around 650 nm in solution, with a reasonably good fluorescence quantum yield ($\Phi_f = 0.11$ in benzene⁹). Energy transfer from blue to red has been demonstrated by Bradley and co-workers for **TPP** doped into a

poly(9,9-dioctylfluorene) host.¹⁰ More recently, Bo and co-workers have investigated the potential of porphyrins bearing covalently attached, pendent oligofluorene arms in such applications.^{11,12} The conjugated chemical connection between the polyfluorenes (host) and the porphyrin core (guest) leads to through bond energy transfer.

On our side, we have synthesized and studied several tetra-aryl porphyrins in the course of investigations aimed in the first instance at the development of porphyrin-based heterogeneous catalysts.^{13–16} Notably, of relevance to OLED applications, we have previously reported the synthesis of a porphyrin possessing four pendant fluorene arms at the *meso*-positions (**TFP**, **4**),¹³ and we subsequently demonstrated that the photophysical properties of this simple porphyrin were quite different from those of the well-known tetraphenyl analogue (**TPP**) (Fig. 1).¹⁷ The first excited state of **TFP** can be populated efficiently by irradiating at a lower wavelength than for **TPP** and, more importantly, the resulting red fluorescence occurs with a substantially enhanced quantum yield ($\Phi_f = 0.22$ for **4** in toluene¹⁷), almost the double of that displayed by **TPP**. This behavior is evidently a very promising and significant result for the elaboration of porphyrin-based fluorescent molecular devices and for possible display applications,

Keywords: Porphyrins; Fluorene; Luminescence; Quantum yield.

* Corresponding authors. Tel.: +33 02 23 23 63 72; fax: +33 02 23 23 56 37 (C.O.P.-R.); e-mail: christine.paul@univ-rennes1.fr

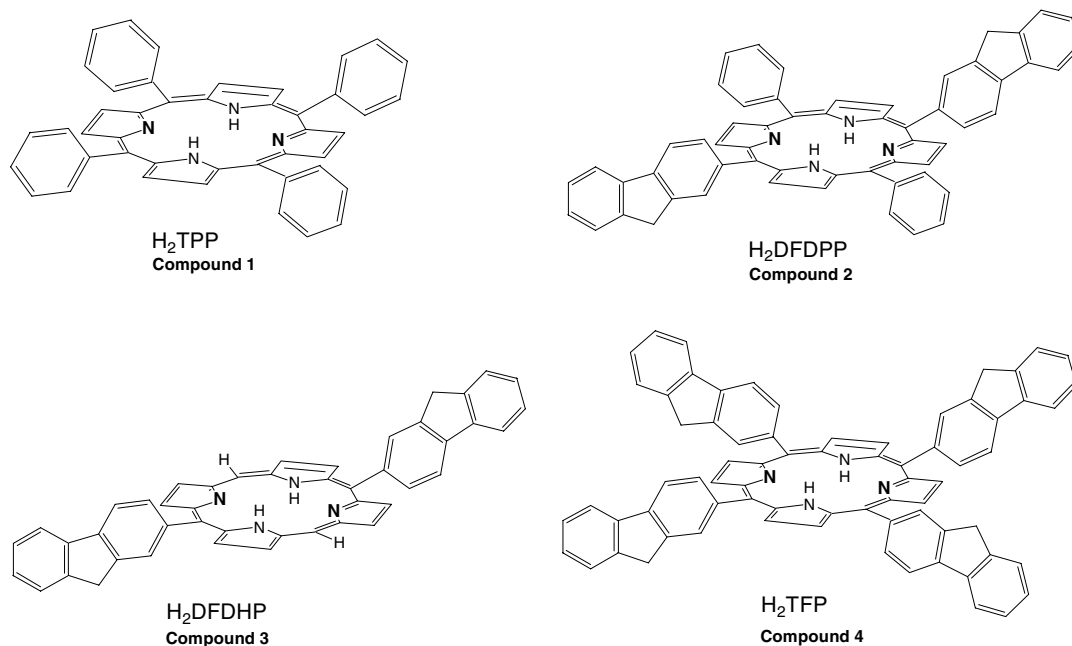


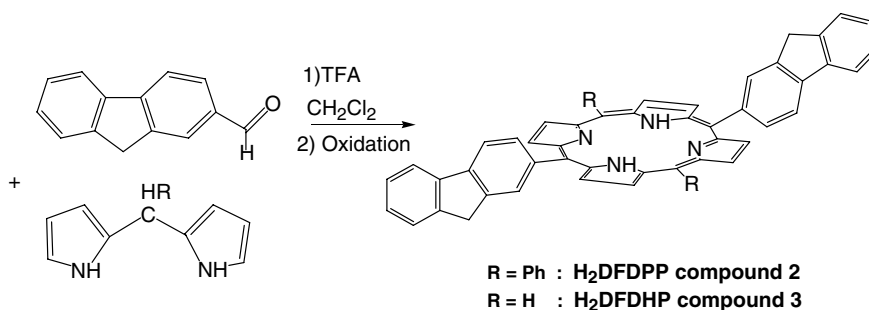
Figure 1. Porphyrins **1**, **2**, **3**, and **4**.

but the origins of the influence of the fluorenyl groups remained unclear. In order to get additional evidence for the decisive role of *meso*-fluorenyl units on the fluorescence of porphyrins like **4**, we have now synthesized and studied porphyrin **2** with two fluorenyl and two phenyl arms on opposite *meso*-positions (5,15-difluorenyldiphenylporphyrin, **DFDPP**), and a bi-aryl analogue **3** that lacks the two phenyl groups (**DFDHP**) (Fig. 1). We report here the synthesis and characterization of the new porphyrins, and the study of their fluorescence properties in solution, which will be discussed in the light of the corresponding data for model compounds **1** and **4**.

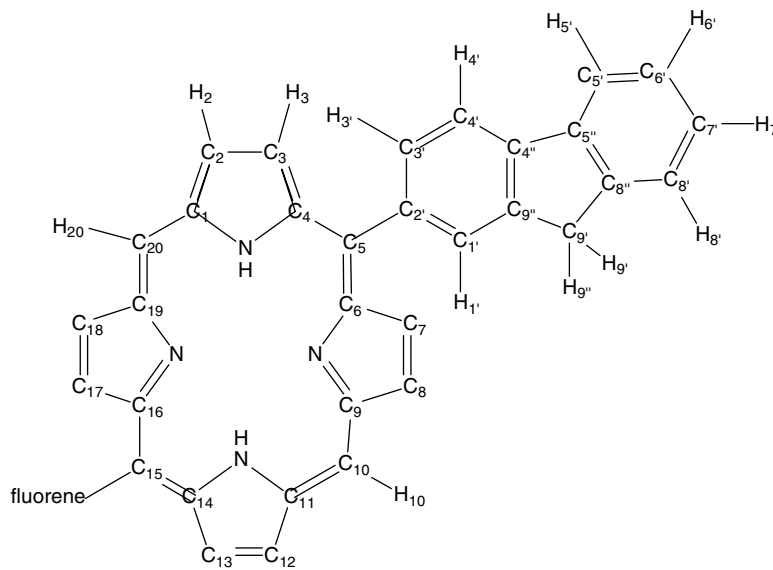
The desired 5,15-*meso*-difluorenyldiphenylporphyrin **2** was prepared in two steps by condensation from 5-phenyldipyrromethane¹⁸ and 2-fluorencarboxaldehyde¹⁸ and 2-fluorencarboxaldehyde, according to the classical TFA-catalyzed procedure developed by Manka and Lawrence,¹⁹ followed by oxidation with chloranil (Scheme 1). However, the final isolated yield of **2**^{20a} is quite low (14%) owing to the competitive formation of isomers resulting from the scrambling of various *meso*-aryl substituents. The 5,15-*meso*-difluorenylporphyrin **3** was similarly prepared by

condensation from dipyrromethane and 2-fluorencarboxaldehyde (Scheme 1).^{20b} Compound **3** was isolated with a substantially higher yield than **2** (22%). Obviously, the dipyrromethane is much less subject to scrambling than was the 5-phenyldipyrromethane during the synthesis of **2**.²¹

The photophysical measurements of fluorenyl porphyrins **2–4** were done in dilute CH₂Cl₂ solution at 298 K.^{22a} The UV–vis absorption spectra of the four porphyrins in solution are dominated in each case by the Soret band (B band) at around 400 nm (Fig. 3) and a weaker set of four Q bands at lower energy (Fig. 4). In addition, the fluorenyl-containing porphyrins **2–4** display bands in the far-UV [~265 and 300 nm], due to π – π^* transitions associated specifically with the fluorenyl groups, that are absent from the spectrum of **TPP**, **1** (normalized full-range spectra are provided in the Supplementary data). Within the series of *tetra*-aryl porphyrins **TPP**, **DFDPP**, **TFP** (**1**, **2**, and **4**), the Soret band is progressively red-shifted with increasing number of fluorenyl substituents: $\lambda_1 < \lambda_2 < \lambda_4$ (Table 1 and Fig. 3). On the other hand, the corresponding band for the *bi*-aryl porphyrin **DFDHP**, **3**, is blue-



Scheme 1. Synthesis of 5,15-difluorenyl-10,20-diphenylporphyrin **DFDPP**, **2**, and 5,15-difluorenylporphyrin, **DFDHP**, **3**.



Compound 3

Figure 2. 5,15-Difluorenylporphyrin, DFDHP, 3.

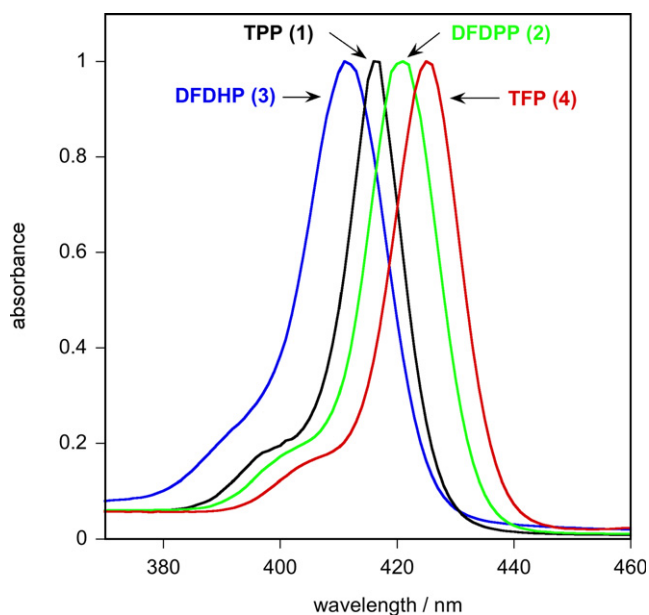
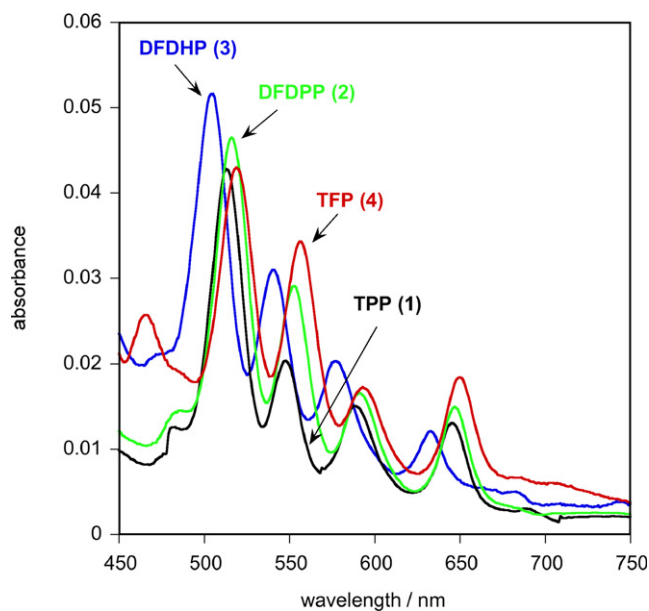
Figure 3. Normalized UV-vis absorption spectra in the Soret region for compounds 1 (black line), 2 (green), 3 (blue), and 4 (red), in CH_2Cl_2 solution at 298 K.

Figure 4. UV-vis absorption spectra in the Q-band region for compounds 1, 2, 3, and 4; scale, conditions and color coding as for Figure 3.

shifted compared to **TPP 1**, as are the Q bands also. Thus, the two additional phenyl groups in **DFDPP**, **2**, apparently stabilize the excited state by some 500 cm^{-1} compared to **3**.

The influence of *meso* aryl groups in red-shifting the electronic absorption spectra of porphyrins has been known for many years,²³ yet the origins of the effect remain controversial, recent work having concluded that a major reassessment is required.²⁴ Whilst sterically demanding substituents probably exert their effect primarily by inducing out-of-plane distortion of the por-

phyrin ring, less encumbered groups, such as simple aryl pendants, may do so predominantly through in-plane nuclear reorganization (INPR).^{23,24} The effect of the substituent is then to draw the *meso* carbon (C_m) away from the porphyrin core, leading to a contracted $C_\alpha C_m C_\alpha$ angle, rather than to distort the ring significantly away from planarity (C_α = pyrrolic 2-carbon). The interpretation is reinforced by TDDFT calculations, which reveal that a consequence of INPR is an increase in the HOMO energy with little effect on the LUMO, and hence a red-shift.²⁵ The present work supports the notion that the steric effect is not the

Table 1. Photophysical properties of the fluorenyl porphyrins **2**, **3**, and **4** in dilute CH₂Cl₂ solution at 298 K, and of **TFP**, **1**, under the same conditions for comparison

Porphyrin	DFDHP (3)	TPP (1)	DFDPP (2)	TFP (4)
$\lambda_{\text{max}}/\text{nm}^{\text{a}}$ Soret band	411	417	421	426
$\lambda_{\text{max}}/\text{nm}^{\text{a}}$ Q bands	505, 541, 577, 633	513, 548, 589, 646	516, 553, 591, 647	519, 557, 593, 649
$\lambda_{\text{em}}/\text{nm}$	640, 704	650, 714	657, 722	661, 725
$\Phi_{\text{f}}^{\text{b}}$	0.14	0.13	0.17	0.24
$\tau/\text{ns}^{\text{c}}$	8.3	8.6	8.3	8.0
$k_{\text{f}}/10^7 \text{ s}^{-1\text{d}}$	1.70	1.51	2.05	3.00
$\sum k_{\text{nr}}/10^7 \text{ s}^{-1\text{d}}$	10.4	10.1	10.0	9.50

^a Wavelengths of the absorption maxima in the Soret or B band region (400–450 nm range), and in the Q band region (500–700 nm range).

^b Fluorescence quantum yields in degassed solution, using **TFP** in benzene as standard, following excitation into the Soret bands; estimated uncertainty in absolute values ± 0.02 , in relative values $< \pm 0.01$.

^c Fluorescence lifetimes using pulsed excitation at 374 nm; estimated uncertainty ± 0.1 ns.

^d k_{f} and $\sum k_{\text{nr}}$ are the fluorescence radiative rate constant and the sum of non-radiative decay constants, respectively, and are estimated from Φ_{f} and τ as described in the text.

determining factor, since fluorenyl and phenyl would be expected to have a similar steric demand at C_m, yet the fluorenyl groups are seen to exert a greater stabilizing influence on the excited state. It is possible that enhanced conjugation in this case leads to greater INPR. On the other hand, we can also conclude that the net effect of two fluorenyl substituents is not as large as that of four phenyl groups, since $\lambda_{\text{DFDHP}} < \lambda_{\text{TFP}}$.

Excitation of the new porphyrins in the Soret band leads to strong fluorescence in the red region, with two sharp bands in the emission spectrum (Fig. 5 and Table 1). The trends in energies that are observed in absorption are also observed in emission. Thus, the emission of **DFDPP**, **2** ($\lambda_{\text{em}}^{\text{max}} = 657$ nm) is slightly red-shifted compared to **TFP**, **1** (650 nm), but not quite to the same extent as that of **TFP**, **4** (661 nm). In contrast, the emission of the bi-aryl system **DFDHP**, **3** is blue-shifted to 640 nm. It may also be noted that the relative intensity

of the lower-energy emission band decreases on going from **3** through **2** to **4** (note that the spectra shown are corrected for the wavelength dependence of the spectrometer).

Excitation of **2** and **3** into the fluorenyl absorption bands at 265 nm also results in the characteristic porphyrin emission bands. However, in contrast to **4**, the porphyrin bands are now accompanied by a very weak emission band around 320–330 nm, attributable to residual emission from the fluorenyl chromophores (see ESI, Fig. 2): apparently, energy transfer to the porphyrin, though evidently fast given the predominance of the porphyrin emission, is not quite fast enough to completely quench the radiative decay of the fluorenyl groups. Bo and co-workers have also noted simultaneous fluorene and porphyrin-based emission in their oligofluorene-appended systems, although in that case, significant fluorene emission is more likely to be anticipated, since the pendants incorporate several (3–6) fluorene units.¹²

The fluorescence quantum yields of the new porphyrins were determined in dichloromethane solution at 298 K, together with those of **TFP** and **TPP** under the same conditions (Table 1).^{22b} Previously, we demonstrated that the fluorescence quantum yield of **TFP** was enhanced by a factor of almost 2 compared to **TPP**.¹⁷ The present work reveals that the introduction of just two fluorenyl groups into the tetra-aryl system leads to an enhancement that is approximately half that observed with four fluorenes ($\Phi_{\text{f}} = 0.24$, 0.17, and 0.13 for **4**, **2**, and **1**, respectively, in CH₂Cl₂); thus, the effect of the fluorenyl pendants appears to be approximately additive. Interestingly, the fluorescence quantum yield of **3** ($\Phi_{\text{f}} = 0.14$) is also slightly enhanced compared to **1**, even though its excited state energy is raised rather than lowered.

In an attempt to determine the origin of the enhancement in emission efficiency accompanying fluorenyl substitution, in particular, whether it is due to an increase in the radiative rate constant or to reduced non-radiative decay, the fluorescence lifetimes of the compounds in dichloromethane solution were measured. Time-correlated single-photon counting using pulsed laser excita-

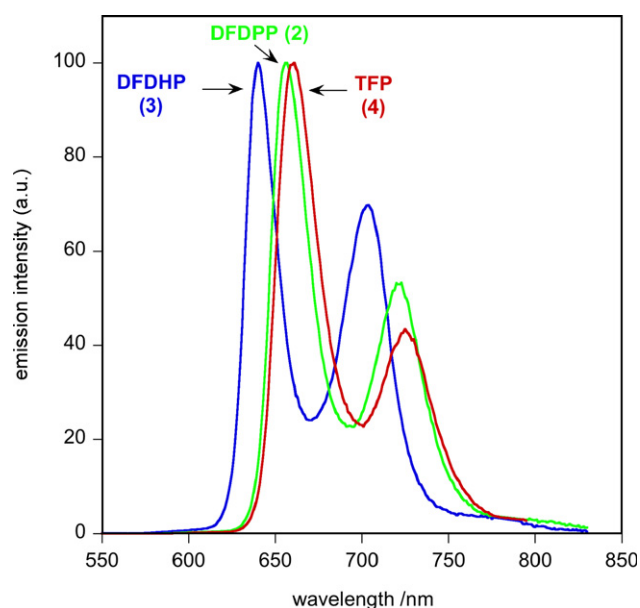


Figure 5. Normalized corrected fluorescence emission spectra of the fluorenyl-containing porphyrins **2** (green line), **3** (blue), and **4** (red) in CH₂Cl₂ solution at 298 K, upon excitation into the Soret band; excitation and emission band passes = 2 nm.

tion at 374 nm was employed; the values obtained are given in Table 1 and a representative decay and fit are shown in Figure 6. The observed lifetimes were found to decrease slightly as the number of fluorenyl arms increases: $\tau_1 > \tau_2 \sim \tau_3 > \tau_4$. Assuming that the emissive state is formed with unitary efficiency in each case when excited directly into the porphyrin at this wavelength, then

$$\Phi_f = k_f/k_{\text{obs}},$$

where

$$k_{\text{obs}} = (k_f + \sum k_{\text{nr}}) = \tau_{\text{obs}}^{-1},$$

allowing estimates of the radiative rate constant k_f and the sum of the non-radiative decay constants $\sum k_{\text{nr}}$ to be estimated from the measured lifetime τ_{obs} and the quantum yield Φ_f . The rate constants obtained in this way are collated in Table 1, whence it can be seen that the introduction of the fluorenyl groups has little effect on the rate of non-radiative decay processes, but increases the radiative rate constant. Indeed, k_f increases by a factor of 2 upon going from **1** to **4**, and by an intermediate factor for difluorenyl system **2**. A similar conclusion is also drawn for the difference between **TPP 1** and bi-aryl porphyrin **3**, where k_f is increased, again with apparently no significant difference in $\sum k_{\text{nr}}$. In all cases, therefore, the enhanced quantum yields observed can be attributed almost exclusively to an influence of the fluorenyl groups in increasing the oscillator strength of the radiative transition. The same trend in porphyrin-based emission lifetimes was observed upon excitation into the fluorenyl bands.^{22b}

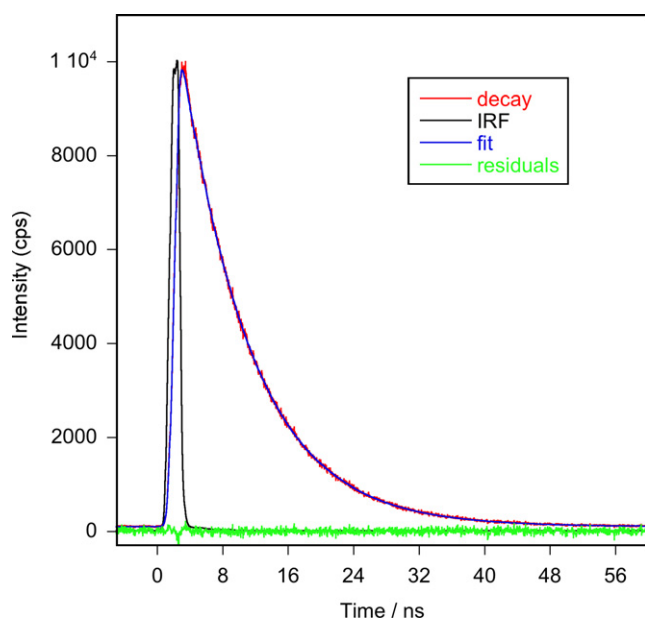


Figure 6. Representative fluorescence emission decay of **2** in CH_2Cl_2 solution at 298 K (red line) registered at 655 nm, following pulsed excitation at 374 nm (pulse length ca. 60 ps). The best-fit to a single exponential decay, after deconvolution of the instrument response function (IRF, black line), is shown in blue, and the residuals (difference between the data and the fit, scaled 20 \times) in green. Analogous data for **3** and **4** are provided in the Supplementary data.

In summary, we have synthesized and characterized two new porphyrins **DFDPP**, **2**, and **DFDHP**, **3**, bearing fluorenyl pendent arms at two trans-disposed *meso*-positions, with either phenyl substituents (**2**) or no substituents (**3**) at the other two *meso*-carbons. Both porphyrins show enhanced emission, in terms of solution-state fluorescence quantum yield, compared to tetraphenyl porphyrin, even though their emission energies are affected differently, **2** being red-shifted and **3** being blue-shifted compared to **TPP**. These results suggest that a judicious choice of *meso*-aryl substituents can allow the properties of porphyrins to be optimized for OLEDs, both in terms of efficiency and color tuning. In particular, these new compounds constitute interesting building blocks to access new emissive organic materials. Based on our recent results of anodic electropolymerization of **1** and **4**,²⁶ we expect to be able to obtain a polymeric wire-1D network after selective connections of the *trans*-fluorenyl pendant arms in **2** or **3**, or a polymeric 2D network after connection of the four arms in **2**.^{20a} This will allow control of the solid state architecture formed upon assembling, for materials applications.

Acknowledgments

The authors are grateful to S. Sinbandhit (CRMPO), S. Juillard, and P. Le Maux for their technical assistance and helpful discussions.

Supplementary data

Supplementary data (full-range UV–vis spectra, emission spectrum of **2** excited at 265 nm, and fluorescence decay curves for compounds **1**, **3**, and **4**) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.04.110.

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