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Porphyrins with fluorenyl and fluorenone pendant arms

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Abstract—Porphyrins with fluorenyl and fluorenone groups at the *meso*-positions have been synthesized and characterized, and the fluorescence of these compounds has been studied. Following selective excitation of the pendant arms with UV light, we show that the energy is transferred to the porphyrin core and reemitted as red light. In comparison to tetraphenylporphyrin, the luminescence properties are markedly improved. The fluorescence quantum yields of tetrafluorenylporphyrin **1** and tetrafluorenoneporphyrin **2** are 0.22 and 0.25, respectively.
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Pure organic species like organic light-emitting diodes (OLEDs) have attracted considerable scientific and industrial attention[1] due to their potential application in large area flat-panel displays.[2] For full-color applications, it is necessary to have a set of red, green, and blue emitters with sufficiently high luminous efficiency and proper chromaticity. Actually, organic materials for green and blue OLEDs with high luminescence have largely been developed.[3] Polyfluorenes are leading candidates for blue OLEDs[4] and are expected to be part of the full-color polymer displays. The corresponding organic materials for red electroluminescence (EL) are still rare.[5] Red light emission is usually achieved by doping red dyes into host materials with a large gap.[6] Red dyes, such as porphyrins, are organic molecules with reasonable fluorescence efficiency and good thermal stability. For instance, a conjugated polymer like poly(9,9-dioctylfluorene), doped with tetraphenylporphyrin dispersed into host matrix, has been successfully used as a light-emitting diode.[7] A series of star-shaped porphyrins bearing pendant oligofluorene, recently reported by Bo et al., offer another possibility.[8] In this example, the porphyrin and the polyfluorene groups are conjugated in order to achieve through-bond energy transfer between the fluorene and the porphyrin core. The rate of through-bond energy transfer is normally a 100 times

faster than that of through-space energy transfer (Főrster).[9,10] In this contribution, we have considered the design of new building blocks based on simpler tetrafluorenylporphyrins with the idea to obtain red emitting organic materials after polymerization. Indeed, we have previously shown that a free macrocycle possessing four pendant fluorene arms at the *meso*-positions could lead to an original polymeric material after electro-polymerization, which constituted a very efficient catalyst for 2,3-sigmatropic reactions or for classic cyclopropanation reactions.[11–13] As a first step, we focus here on the photophysical properties of these new porphyrins-based building blocks, bearing fluorene and fluorenone arms.

meso-Tetrafluorenylporphyrin **1** (**H₂TFP**) was prepared by condensation of pyrrole and 2-fluorenecarboxaldehyde as previously reported (Fig. 1).[11] Compound **2** was synthesized by adding macrocycle **1** to a mixture of heptane and a very basic water solution (NaOH) in the presence of a phase-transfer reagent (Aliquat 336). Oxidation gave the tetrafluorenone macrocycle (**H₂TFOP**) **2** with a good yield (68%) (Fig. 1). The new compound **2** was isolated using column chromatography and characterized by usual methods (see Supplementary data).

In the visible spectrum (Fig. 2), the macrocycle **1** exhibits an intense B(0,0) band, together with four weak Q-bands between 500 and 700 nm, and we can observe an additional broad band corresponding to the fluorene absorption in the UV range (268 nm). The UV–vis

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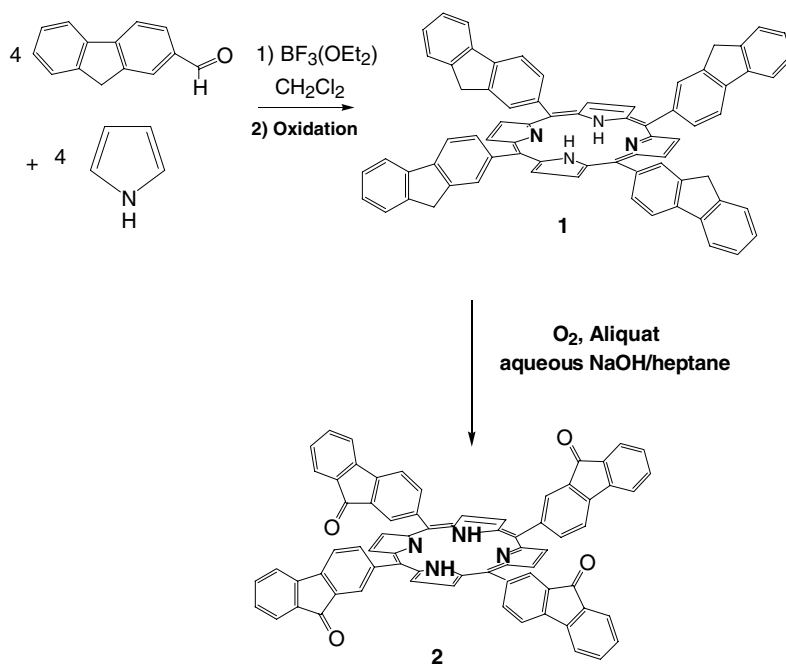
Figure 1. Synthesis of tetrafluorenylporphyrin **1** and tetrafluorenoneporphyrin **2**.
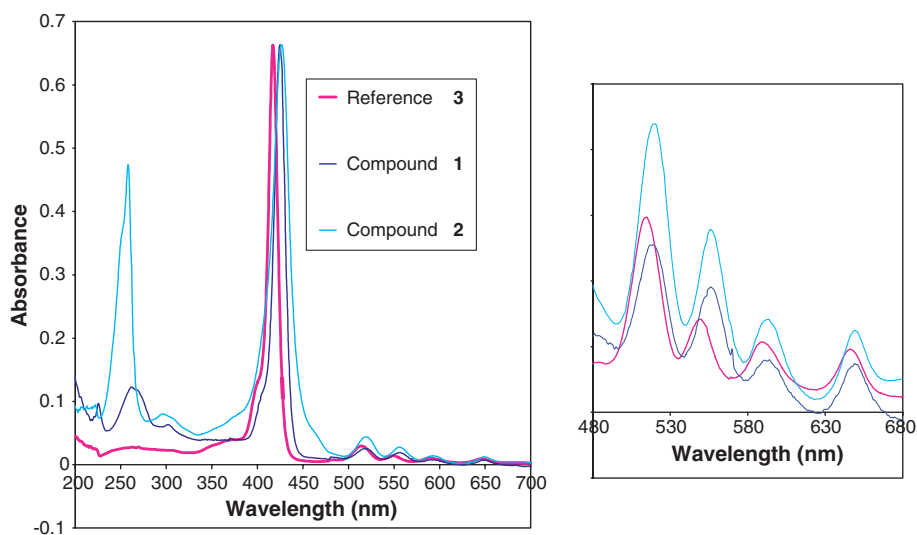

Figure 2. UV–vis absorption spectra for compounds **1**, **2**, and **3**, in CH_2Cl_2 at 25 °C (2.6×10^{-6} M for **1** and normalized to the same absorbance for **2** and **3**).

spectrum of **2** exhibits an intense Soret band with a maximum absorption around 427 nm (Fig. 2). The fluorenone arms absorb in the UV range with a maximum absorption peak at 258 nm; this peak is remarkably sharper and stronger than the corresponding fluorene absorption peak. The very strong π–π^* absorption in the UV range, due to the presence of fluorene or fluorenone arms, is clearly apparent. Both Soret bands of **1** and **2** are slightly red shifted compared to tetraphenylporphyrin (compound **3**) as well as the Q bands. Notably, for compound **2** the Soret band is broadened in comparison to that of compound **1** and contains a significant shoulder. The presence of the electronegative

oxygen atoms at the 9 position might be at the origin of these changes.

The emission spectrum of compound **1**, after excitation in the fluorene absorption (262 nm), in the Soret band (425 nm) or in the highest $Q_y(0, 1)$ transition (519 nm) reveals a strong red fluorescence with a peak maximum at 662 nm and a weak shoulder at 726 nm (Fig. 3). A supplementary broad emission at about 450 nm is also observed due to the porphyrin. There is apparently a good energy transfer between fluorene and porphyrin, since almost no residual emission of the fluorene around 300 nm is observed in comparison to that of the porphy-
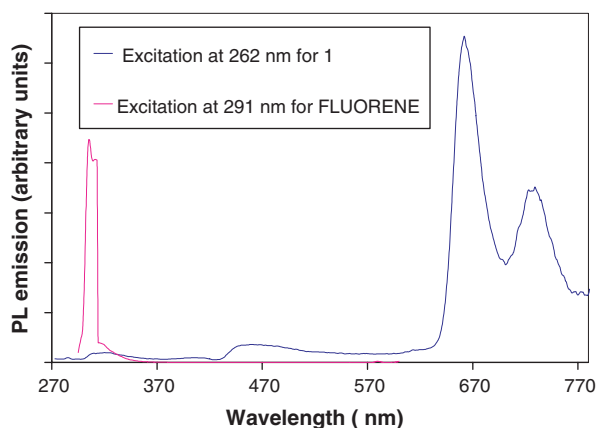
Figure 3. Photoluminescence spectrum of free ligand **1** $(3.6 \times 10^{-7}$ M) compared to commercial fluorene $(1.1 \times 10^{-7}$ M) in CH_2Cl_2 solution. The emission spectrum was cut above 770 nm for clarity (strong loss of sensitivity of our apparatus at ca. 800 nm).

rin. Thus, almost all the absorbed energy by the *antennae* is reemitted by the porphyrin chromophore. For comparison, the emission spectrum of free fluorene is shown on the same graph to demonstrate how the emission from an unbound fluorene proceeds. The ET efficiency can also be estimated by comparing the absorption (Fig. 2) and the excitation spectra (see Supplementary data). Indeed, the excitation spectrum obtained after exciting in the strongest emission band at 661 nm reveals the Soret band, the three first Q bands $(Q_y(0,1)$, $Q_y(0,0)$, and $Q_x(0,1))$, and the fluorene band. This indicates that excitation over all the 200–650 nm region leads to the population of the fluorescent excited state of the porphyrin.

The emission spectrum of compound **2** is very similar. After excitation in the fluorenone arms (258 nm), in the Soret band (427 nm) or in the highest energy $Q_y(0,1)$ transition (519 nm), a strong red light emission is observed. Again, an efficient energy transfer between *antennae* and porphyrin takes place for compound **2**, and almost no residual emission of the fluorenone units ($\sim$300 nm) is detected. We have also verified for these compounds that the irradiation could be modulated in a large range of excitation wavelengths, to finally obtain the desired red emission (see Supplementary data).

The fluorescence quantum yields of these compounds were next determined by comparing with a calibration standard of compound **3** in degassed toluene solution presenting a fluorescence quantum yield of 0.12.[14] All measurements were made under an argon atmosphere to limit photo-oxidative degradation (Table 1). Compound **1** presents a luminescence quantum yield (22%),

which is roughly twice that of reference **3** (12%). Compound **2** also possesses a comparable quantum yield (25%), slightly higher than the parent compound **1**. Considering the very similar steric interactions of the *meso*-fluorene substituents with the porphyrin core in comparison to *meso*-phenyl ones in **3**, this cannot be explained by a conformation less favorable to the energy transfer process in **3**[15] relative to **1** and **2** and must therefore be essentially related to the electronic influence of the *meso*-substituents.

In summary, we have synthesized and characterized here a new porphyrin **H₂TFOP**, bearing fluorenone pendant arms at the *meso*-positions starting from the previously reported tetrafluorenylporphyrin **1** (**H₂TFP**). Both porphyrins **1** and **2** were shown to emit red light after UV–vis irradiation. In addition, this study suggests that the energy transfer process from the *meso*-substituents to the porphyrin cycle is more efficient than for **3**. Remarkably, the fluorescence quantum yields values presently found for **1** and **2** are much higher than these usually observed for many other porphyrins.[15] Accordingly, **1** and **2** constitute therefore promising candidates to access luminescent materials after electro-polymerization.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.03.031.

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Table 1. Quantum yield[a] (%) of free macrocycles **1**, **2**, and **3** measured in toluene, degassed and excited at the same wavelength ($\lambda = 420$ nm)

Compounds	H₂TPP (3)	H₂TFP (1)	H₂TFOP (2)
λ_{ex} (nm)	420	427	431
λ_{em} (nm)	653 and 721	661 and 726	661 and 727
Quantum yield (%)	12	22	25

[a] Measured in degassed toluene, at 298 K.

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