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Synthesis of new luminescent supramolecular assemblies from fluorenyl porphyrins and polypyridyl isocyanurate-based spacers

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ABSTRACT

Two new dendrimeric supramolecular assemblies bearing twelve and twenty-four fluorenyl peripheral donor groups surrounding an organic core have been prepared and studied. These assemblies are composed of three zinc porphyrins possessing each four (**ZnTFP**) and eight fluorenyl chromophores (**ZnOOFP**) linked together by a central tris-pyridyl organic ligand. Due to efficient energy transfer between the fluorenyl arms, which act as antennas, and the Zn centres, which act as emitters; these assemblies behave as red emitters after selective UV or visible irradiation. The kinetic stability of these supramolecular assemblies and its impact on their photophysical properties are discussed.

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1. Introduction

Porphyrin systems present wide potential applications in different fields, such as, for instance, light-harvesting, Organic Light Emitting Diodes (OLEDs) or switches. For efficient solar energy harvesting, several chromophores are needed in order to collect light from the entire solar spectrum.¹ In this connection, the photosynthetic light-harvesting systems (I and II) consist of well organized porphyrin antennas in sophisticated three-dimensional structures.² As in nature, construction of multichromophoric systems is important to ensure maximum use of solar energy. Thus, the ability to design and construct (super- or supra-) molecular architectures in which the energy flow can be controlled constitutes a great (and timely) challenge.

We have previously reported the synthesis of porphyrins possessing several fluorenyl arms and focused on their photophysical properties,^{3–5} along with their possible use in OLEDs.⁶ Notably, a high fluorescence quantum yield (24%) was evidenced for **1**, demonstrating the good capacity of the fluorenyl units to enhance quantum yields by increasing the radiative deactivation process. By the fact that **1** exhibits good red chromaticity and enhanced emission efficiency, it is now interesting to incorporate the corresponding zinc complex **3** and the related zinc porphyrin **4** in oligomeric assemblies and to study their luminescence.

Arrays containing different kinds of dyes can be engineered in several ways: either by using covalent bonds or by self-assembly. On the one hand, star-shaped trimer structures in which the porphyrin building blocks are connected covalently by a purely organic spacer have been largely studied. In 1999, Osuka synthesized a model of benzene connected in the 1,3 and 5 positions to three zinc porphyrins.⁷ Other triangular spacers have been employed with the same 1,3,5 topology.⁸ Subsequently, a series of arrays containing three, four and six tetraphenylporphyrin (TPP) units were synthesized.9 For covalently bonded star-shaped pentamers, the use of (phenylethynyl)benzene spacers connected at the meso position of a central porphyrin unit has also been made by Lindsey and coworkers.¹⁰ Recently, Sanders reported a large scale synthesis of tripodal porphyrin arrays: in these assemblies, the three zinc porphyrins are covalently linked by an alkyne bridge to a tripodal unit.¹¹ On the other hand, supramolecular approaches offer an alternative way to assemble the nano-objects in a desired manner, like in the photosynthetic light-harvesting complexes. An interesting approach for mimicking these complicated systems is to design smallsized chromophores, which can self-organize into light-harvesting architectures. Supramolecular synthetic methods¹² have





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developed rapidly and porphyrins proved particularly useful for the design of robust architectures because of their rigid framework.¹³ One-, two-, and three-dimensional materials are now routinely accessible by synthetic strategies based on hierarchical organization of porphyrins. Thus, porphyrins are very useful not only as active molecular components for light-harvesting antenna systems, but also as rigid building blocks for the construction of variety of functional devices.¹⁴

In the present contribution, the synthesis of the desired porphyrin trimer is based on the pyridine-to-metal coordination. Thus, porphyrins are connected by dative bonds to a new kind of organic bridge having three pyridine sites pointing at 120° from each other.¹⁵ This bridge consists of an original tripodal ligand (7), which was synthesized in a straightforward way from a readily available tris-alkynyl isocyanurate precursor, independently developed by some of us.¹⁵ Such a ligand is expected to exhibit a better transparency in the near UV and visible range, and therefore to impart a higher photostability to the supramolecular assembly than related 1,3,5-phenylene based derivatives. Two different porphyrins were used to test this approach: (i) the known monomeric zinc porphyrin 3 bearing four fluorenyl units rigidly held on the meso positions and (ii) a new zinc porphyrin mentioned above (4), bearing eight pendant fluorenyl units more flexibly connected to the same positions via methylene linkers. Following the synthesis of these new building blocks, we will describe the self-assembly and characterization of the desired porphyrin oligomers 5 and 6, respectively. Finally, the photophysical studies of the building blocks and related supermolecular systems will be reported and discussed.

2. Results and discussion

2.1. Synthesis

Zinc porphyrins **3** *and* **4**. The *meso*-tetrafluorenylporphyrin free base **1** was prepared as previously reported, ¹⁶ while the synthesis of the dendrimeric free base 2^{17} is based on the condensation reaction reported by Fréchet. The metallation of these porphyrin monomers by zinc acetate proceeds in dichloromethane at reflux, ¹⁸ to give the corresponding zinc porphyrins 3^5 and **4**, in 87% and 81% yield, respectively (Scheme 1). The new complex **4** was fully characterized by means of NMR spectroscopy, microanalysis and high resolution mass spectrometry.

New tris-pyridyl spacer **7**. This new isocyanurate-based ligand was obtained in one step from the corresponding triyne **8**,¹⁵ and 4-bromopyridine (**9**) following a Sonogashira coupling protocol in DMF (Scheme 2). After purification, **7** is obtained as a beige solid in 51% yield. This new ligand was also fully characterized by usual means. Its high symmetry allows monitoring the progress of the catalytical coupling reaction, in a straightforward way, by ¹H NMR.

Supramolecular assemblies **5** and **6**. To a solution of 3 equiv of **3** or **4** in CH₂Cl₂, 1 equiv of tris-pyridyl ligand **7** is added (Scheme 3). After 1 h, the desired porphyrin trimers **5** or **6** can be isolated, as deep violet powders. These new products were characterized by usual solution spectroscopies (NMR, UV–vis and IR) and microanalysis, but proved too fragile to be characterized by mass spectrometry, since only the constitutive fragments were detected by LSI-MS.

Ligation of pyridyl rings to zinc porphyrins is intrinsically weak (association constant, ca. $1 \times 10^3 \text{ M}^{-1}$) and relatively labile; thus, in solution, coordination oligomers are generally in equilibrium with the monomers.¹⁹ For these supramolecular systems, stability in (dilute) solution is therefore a key question. The stability of the supramolecular assemblies **5** and **6** in CH₂Cl₂ solution was thus checked by a combination of ¹H NMR, UV–vis absorption and spectrofluorimetric measurements.

The ¹H NMR signals obtained in deuterated chloroform for zinc complexes **3** and **4** are fine and well resolved. A clear difference in shift is observed for the bridging tripodal ligand **7** when free and in the corresponding assemblies **5** and **6** (Figs. 1 and 2). The latter is induced by axial coordination of **7** to zinc porphyrin units. In both cases, H–H polarization transfer studies (COSY) allowed to assign the various signals detected, the integration of the signals revealed that adducts **5** and **6** have the correct stoichiometry.

For example, the ¹H NMR spectrum of **5** reveals the two ¹H resonances of the pyridine units, H_A and H_B, significantly upfield of their positions in **7**, as expected for protons located within the shielding cone of a porphyrin (Fig. 2).^{19,20} This effect decreases gradually as the proton distance from the shielding macrocycles increases, with $\Delta\delta$ =-3.0 and $\Delta\delta$ =-0.8 for H_A and H_B, respectively. These signals are also broader and less resolved, in line with the highly fluxional nature of the ligand at ambient temperature. In addition, we can notice that all the twelve peripheral protons on the porphyrin *meso*-fluorene arms are equivalent. Similar statements hold for the larger assembly **6**, except that H_A is not observed at 25 °C, in reason of its strong fluxionality.



Scheme 1. Synthesis of zinc complexes 3 and 4.



Scheme 2. Synthesis of ligand 7.

2.2. Photophysical properties

2.2.1. Electronic spectra. The absorption spectra of Zn(II) porphyrins display a single Q band absorption, which is a combination of the Q_X and Q_Y bands due to the D_{4h} symmetry of metal porphyrins [instead of the D_{2h} symmetry of free base porphyrins], with two discernible sub-bands (Q(0,1) and Q(0,0)).^{21–23} Thus, the zinc complexes **3** and **4** exhibit an intense B band (Soret band), together with two weak Q-bands in the visible range (Fig. 3 and Table 1). An additional broad band is also observed in UV range, which corresponds to $\pi - \pi^*$

absorption of the fluorene chromophores. This UV absorption is stronger for the zinc complex **4** due to the larger number (eight vs four) of fluorene groups in the *meso* arms.

The free tris-pyridine ligand **7** in CH_2Cl_2 displays two bands: a strong one at 285 nm and a weak one at 302 nm (Fig. 3a and Table 1). Upon apical binding of a pyridyl ligand to a zinc porphyrin, a red shift of 2–10 nm of the characteristic absorptions observed for the free porphyrin is expected, due to the stabilisation of the corresponding excited-states in the pyridyl-Zn adduct.¹⁹ Actually, these red shifts are observed for both **5** (Fig. 3b) and **6** (see



Scheme 3. Synthesis of supramolecular assemblies 5 and 6.



Fig. 1. Hydrogen and carbon atom-labelling for the porphyrin complexes 3, 4 and ligand 7.

Supplementary data S1), but only at relatively high concentrations (10^{-3} M) . At lower concentrations, due to the labile coordination of the pyridine to the zinc centres, the complex is more dissociated. As a result, the free ligand 7 and corresponding porphyrin dominate in solution over the adduct, resulting in no apparent bathochromic shift. Appreciable spectral changes, indicative of dissociation, are observed upon dilution to 1.0×10^{-6} M. Under these high dilutions conditions (10^{-6} M) , axial dissociation takes place, as shown mainly by a blue shift in absorption and for fluorescence (as we shall see below), the absorption peaks shifting back to the values observed for porphyrins 3 and 4. The Soret band in the absorption spectra of the self-assembled systems 5 and 6 can thus be usefully used to determine the concentrations at which these labile systems predominate in solution over their constituents $(1.0 \times 10^{-3} \text{ M})$. Notably, less marked shifts take place with the other absorption bands detected, such as the fluorene band near 300 nm or these characteristics of the apical ligand 7 near 285 nm.

2.2.2. Luminescence studies. The fluorescence spectra at 25 $^{\circ}$ C of the zinc(II) complexes **3** and **4** (Fig. 4) consist of three sub-bands

assigned to a vibronic progression from a Q state: the very weak band near 720 nm is assigned as Q(2,0) and actually appears as an extended tail on the Q(1,0) band. The major difference between them, compared to their corresponding free-bases (**1** and **2**), is the remarkable hypsochromic shift of ~50 nm for the strongest emission band Q(1,0) and ~70 nm for the second Q(0,0), due to the metal coordination.⁵

We then studied the photophysical properties of supramolecular assemblies **5** and **6**. At concentrations around 10^{-3} M and using a front-face (FF) fluorescence detection setup instead of a classical right-angle (RA) detection setup, we could observe a characteristic red shift (Fig. 4) for the emission spectra recalling that previously observed for **3** ($\Delta\gamma$ (Q1)=4) or **4** ($\Delta\gamma$ =5 nm for Q(1,0) and $\Delta\gamma$ =5 nm for the Q(0,0)). This red shift, already observed in absorption between **3** and **5** (respectively **4** and **6**), is characteristic of the apical coordination of the pyridine ligand to the metal (Table 2). Notably, when the fluorescence spectra are recorded for more dilute solutions, no difference can be stated compared to the corresponding monomer **3** (respectively **4**). These results clearly indicate that supramolecular assemblies **5** and **6** are mainly dissociated at



Fig. 2. NMR spectra of zinc complex 5.

concentrations required by the classical right-angle detection $(10^{-6}-10^{-7} \text{ M})$, (Fig. 5).

2.2.3. Fluorescence quantum yields. The fluorescence quantum yields $\Phi_{\rm F}$ of these compounds were determined by comparing with proper calibration standards²⁶ (Table 1). By comparison with the fluorescence quantum yield of the reference zinc complex of tetraphenylporphyrin **ZnTPP** ($\Phi_{\rm F}$ =3.3%), we found that compound **3** presents an unusually high luminescence quantum yield of 8.5%. Compound **4** presents a fair luminescence quantum yield of 3.4%, which is quite similar to that of **ZnTPP**. The fluorescence quantum yield of the pure organic linker **7** is much lower ($\Phi_{\rm F}$ =0.3%).

2.2.4. Energy transfer studies. The emission spectra of **3** and **4** presently used as supramolecular building blocks suggest that the fluorenyl donor transfers energy with high efficiency to the porphyrin acceptor. Indeed, excitation for both zinc complexes at 300 nm (i.e., in the fluorene band) results in the characteristic red emission of porphyrins (Fig. 4a). As a result, the blue fluorenyl emission is almost completely quenched for both compounds, and emission is seen predominantly from the porphyrin ring. Similar effect could also be observed for the assemblies **5** and **6**, with an emission also coming quasi-exclusively from the porphyrins (Fig. 4b).

3. Conclusions

We have synthesized and characterized two new threefold symmetric architectures from two porphyrins bearing numerous fluorenyl pendant arms and an original isocyanurate tris-pyridyl tripodal ligand **7**. The goal was to obtain luminescent soluble super-molecular architectures by combining simple and highly luminescent porphyrin building blocks with very transparent and stable bridging ligands. These new compounds along with the new porphyrin monomer **4** and the new ligand **7**, were fully characterized and their luminescence was studied. While **7** is essentially non luminescent in the free state, **4** proved to exhibit properties similar to **3**. It emits dominantly red light after selective UV or visible irradiation. Actually, in case of UV irradiation, such systems comprising a central zinc porphyrin core linked to peripheral photon-harvesting fluorene moieties have been shown to act as efficient relays between the antennas and the Zn atom. For these compounds, the red luminescence can be obtained from a large range of excitation wavelengths from UV to red.

We next attempted to compare the photophysical properties of **5** and **6** to these of the starting porphyrin monomers **3** and **4**. However, due to weak coordination of the pyridine end-groups of **7** to the Zn centres, the new assemblies **5** and **6** are quite labile in solution and exist mostly in the form of their dissociated components at concentrations where fluorescence studies are usually made. This frustrated us from the quantitative determination of the fluorescence yield of these fascinating assemblies. Nevertheless, at higher concentrations these assemblies are more stable and present distinct properties from their constitutive monomers, as evidenced by UV–vis and luminescence studies using a front-face detection setup. We are now planning to investigate their potential directly in the solid state, by using them directly as active layers (after deposition or spin coating from very concentrated solutions) in OLED or related devices.

4. Experimental section

4.1. General procedures

All reactions were performed under argon (with magnetic stirring). Solvents were distilled from appropriate drying agent prior to use, CH₂Cl₂ from CaH₂, CHCl₃ from P₂O₅ and all other solvents were HPLC grade. Commercially available reagents were used without further purification unless otherwise stated. 5,10,15,20-Tetra-9*H*fluoren-2-yl-21*H*,23*H*-porphine **1 (TFP)** was prepared as described in our earlier report.¹⁶

All reactions were monitored by thin layer chromatography (TLC) with Merck pre-coated aluminium foil sheets (Silica gel 60



Fig. 3. (a) UV–vis absorption spectra in 10-mm path length cells of compounds **3** (black line), **7** (blue line) in CH₂Cl₂ at 25 °C at a concentration of ca. 10^{-6} M, of a mixture solution of 3 equiv of **3** and 1 equiv of **7** at ~ 10^{-6} M concentration (red line) and theoretical absorption spectrum resulting from the additive contribution of 3 equiv of **7** (dashed line). (b) Absorption spectra in 1-mm path length cell of compounds **3** and **5** in CH₂Cl₂ at 25 °C at higher concentration (1.5×10^{-3} M).

with fluorescent indicator UV₂₅₄). Compounds were visualized with ultra-violet light at 254 and 365 nm. Column chromatography was carried out using silica gel from Merck (0.063–0.200 mm). ¹H NMR and ¹³C NMR in CDCl₃ were recorded using Bruker 200

Table 1

Photophysical properties of the zinc fluorenyl porphyrins 3 and 4 and of ligand 7, in CH_2Cl_2 solution at 298 K ($\sim 10^{-6}$ M)

Compound	$\lambda_{max2}^{abs} \ ^{a} [nm]$	$\begin{bmatrix} \epsilon_{max2} & b \\ [cm^{-1}] & M^{-1} \end{bmatrix}$	$\lambda_{max1}^{abs} \ ^{a} [nm]$	ε _{max1} b [cm ⁻¹ M ⁻¹]	λ ^{em} _{max} c [nm]	Φ^{d}
Tripod 7	285	102,000	302	93,000	316	0.003 ^e
ZnTFP (3)	264	76,000	428	535,000	608, 657	0.085 ^f
ZnOOFP (4)	269	216,000	425	519,000	602, 650	0.034 ^f

^a Experimental absorption maxima.

^b Molar extinction coefficients.

^c Experimental emission maxima.

^d Fluorescence quantum yield.

^e Determined relative to anthracene in EtOH ($\Phi_{\rm F}=0.27^{24}$).

^f Determined relative to tetraphenyl-porphine in toluene ($\Phi_{\rm F}$ =0.12²⁵).

DPX, 300 DPX and 500 DPX spectrometers. The chemical shifts are referenced to internal tetramethylsilane (TMS) and coupling constants are in hertz. The assignments were performed by 2D NMR experiments: COSY (Correlation Spectroscopy), HMBC (Heteronuclear Multiple Bond Correlation) and HMQC (Heteronuclear Multiple Quantum Coherence). For Hydrogen and/or carbon atom-labelling for the porphyrin complexes **3**, **4** and for the tripodal ligand **7**, see Fig. 1. High-resolution mass spectra were recorded on a ZabSpec TOF Micromass spectrometer in FAB mode or ESI positive mode at the CRMPO. IR spectra were recorded on Bruker IFS 28, using KBr pellets or in dichloromethane solution. UV–vis spectra were recorded on UVIKON XL from Biotek instruments.

4.2. Synthesis of [5,10,15,20-tetra-9H-fluoren-2-yl-21H,23H-porphinato(2-)]zinc(II) (3)

Free base porphyrin **1** (100 mg, 0.10 mmol) was dissolved in 20 mL of distilled dichloromethane. Zinc acetate dihydrate (108 mg, 0.49 mmol) was added in one portion to the stirred solution. The



Fig. 4. (a) Photoluminescence spectra of compound **4** at different excitation wavelengths. (b) Photoluminescence spectra of compound **4** and of supramolecular assembly **6** (1.5 10^{-3} M) in CH₂Cl₂ at 25 °C (excitation at 430 nm).

mixture was stirred 2 h at reflux. Reaction progress is monitored by TLC, spotting directly from the organic layer. Then, the solvent was removed, and the black red residue was chromatographed on silica gel column with a MeOH/CH₂Cl₂ mixture (2 %–10 % MeOH). Compound **3**, was obtained as a dark red colour powder in a yield of 87%. This porphyrin complex (**3**) was already described earlier.⁵ For clarity, the ¹H NMR data are however reported below. ¹H NMR (500 MHz, CDCl₃, δ in ppm): 8.97 (s, 8H, H_{β-pyrrolic}), 8.42 (s, 4H, H_{1'}), 8.28 (d, ³J_{H,H}=8.2 Hz, 4H, H_{3'}), 8.20 (d, ³J_{H,H}=7.6 Hz, 4H, H_{4'}), 8.10 (d, ³J_{H,H}=6.6 Hz, 4H, H_{5'}), 7.72 (d, ³J_{H,H}=6.8 Hz, 4H, H_{8'}), 7.56 (t, ³J_{H,H}=5.7 Hz, 4H, H_{6'}), 7.46 (t, ³J_{H,H}=6.8 Hz, 4H, H_{7'}), 4.23 (s, 8H, H_{9'} and H_{9'}).

4.3. Synthesis of [5,10,15,20-tetrakis[3,5-bis(9*H*-fluoren-2-ylmethoxy)phenyl]-21*H*,23*H*-porphinato(2-)]zinc(II) (4)

To a solution of free base porphyrin 2 (60 mg, 28 μ mol) in CH₂Cl₂ (15 mL) was added $Zn(OAc)_2 \cdot 2H_2O$ (30 mg, 140 µmol) in methanol (7 mL) and the mixture was stirred 2 h at reflux. When metallation was complete (TLC checking), the reaction mixture was washed with water, dried over MgSO₄ and purified by column chromatography (CH_2Cl_2) to afford 50 mg of a pink solid **ZnOOFP** (81%). ¹H NMR (500 MHz, CDCl₃, δ in ppm): 8.94 (s, 8H, H_{β-pyrrolic}), 7.68 (d, 8H, ${}^{3}J_{H,H}=8$ Hz, 8H, H₄'), 7.64 (d, ${}^{3}J_{H,H}=8$ Hz, 8H, H₅'), 7.46 (s, 8H, H₁'), 7.45 (d, ${}^{3}I_{H,H}=7$ Hz, 8H, H₈'), 7.41 (s, 8H, H_B), 7.32 (d, ${}^{3}I_{H,H}=7$ Hz, 8H, $H_{3'}$), 7.28 (t, ${}^{3}J_{H,H}$ =7 Hz, 8H, $H_{6'}$), 7.25 (t, ${}^{3}J_{H,H}$ =7 Hz, 8H, $H_{7'}$), 6.85 (s, 4H, H_E), 5.02 (s, 16H, OCH₂), 3.75 (s, 16H, H_{9'} and H_{9"}). 13 C NMR (125 MHz, CDCl₃, δ in ppm): 157.6 (C_C), 149.9 (C₁₋₄₋₆₋₉₋₁₁₋₁₄₋₁₆₋₁₉), 144.6 (C_A), 143.5 (C_{1"}), 143.3 (C_{8"}), 141.6 (C_{4"}), 141.2 (C_{5"}), 135.1 (C_{2'}), 132.0 $(C_{2-3-7-8-12-13-17-18})$, 126.8 $(C_{6'})$, 126.7 $(C_{7'})$, 126.5 $(C_{3'})$, 125.0 (C_{8'}), 124.5 (C_{1'}), 120.7 (C_{4'}), 119.9 (C_{5'}), 119.8 (C₅₋₁₀₋₁₅₋₂₀), 115.3 (C_B), 102.2 (C_D), 70.6 (C_H), 36.8 (C_{9'}). UV-vis (λ max, CH₂Cl₂, nm): 270, 292 and 303 (fluorene), 425 (Soret band), 551 (Q band), 596 (Q band). Anal. Calcd (%) for C₁₅₆H₁₀₈N₄O₈Zn · H₂O: C, 83.28; H, 4.93; N, 2.49. Found: C, 82.86; H, 4.88; N, 2.36. MS (ESI-CH₂Cl₂/ CH₃COCH₃: 90/10): calcd for C₁₅₆H₁₀₈N₄O₈NaZn: 2251.73508 [MNa]⁺. Found 2251.73500 [MNa]⁺.

4.4. Synthesis of tripod 7

In a Schlenk tube under argon containing a mixture of starting trivne¹⁵ **8** (0.50 g, 1.16 mmol), 4-bromopyridine hydrochloride **9** (1.36 g, 7 mmol, 6 equiv), CuI (18 mg, 0.09 mmol, 0.08 equiv) and PdCl₂(PPh₃)₂ (33 mg, 0.047 mmol, 0.04 equiv) were added dry DMF (40 mL) and distilled triethylamine (10 mL). After 2 days of stirring at 70 °C and cooling to room temperature, the solvents were removed by cryoscopic transfer. The reaction mixture was extracted with CH₂Cl₂, washed with water and dried over MgSO₄. After filtration and evaporation to dryness, the crude product was purified by column chromatography on neutral aluminium oxide eluting with pure ethyl acetate first and then a mixture of ethyl acetate/ methanol (95/5), to afford the corresponding product 7 as a beige solid (0.39 g, 51%). ¹H NMR (200 MHz, CD_2Cl_2 , δ in ppm): 8.66 (d, ${}^{3}J_{\text{H,H}}$ =6 Hz, 6H), 7.78 (d, ${}^{3}J_{\text{H,H}}$ =9 Hz, 6H), 7.52–7.45 (m, 12H). ${}^{13}\text{C}$ NMR (50 MHz, CD₂Cl₂): 150.3, 148.6, 134.5, 133.3, 131.1, 129.2, 125.9, 124.0, 92.6, 88.4. IR (KBr, cm⁻¹): 2224 (m, $\nu_C \equiv_C$), 1778 (vw, C=O),



Fig. 5. Dissociation of supramolecular systems 5 and 6.

Table 2

Photophysical properties of the zinc fluorenyl porphyrins **3** and **4**, and of the supramolecular systems **5** and **6** at 1.5×10^{-3} M in CH₂Cl₂ solution at 298 K

Compound	$\lambda_{\max}^{abs} a [nm]$	$\lambda_{\max}^{em} a [nm]$
ZnTFP (3)	556, 598	621, 660
(ZnTFP) ₃ -tripod (5)	562, 605	620, 664
ZnOOFP (4)	553, 594	604, 654
(ZnOOFP) ₃ -tripod (6)	558, 599	609, 659

^a Experimental absorption and emission maxima

1717 (vs, C=O). HRMS-ESI: calcd for C₄₂H₂₅N₆O₃ 661.1988 [M+H]⁺. Found 661.1981.

4.5. Synthesis of supramolecular assembly 5

To a solution of zinc complex ZnTFP (3) (50 mg, 49 µmol) in CH₂Cl₂ (15 mL) was added the ligand 7 (10 mg, 15 µmol). The reaction mixture was stirred at room temperature under argon. After 1 h (TLC checking), the reaction mixture was concentrated and precipitated with pentane to afford 51 mg (91%) of the desired supramolecular assembly **5** as a purple solid. ¹H NMR (500 MHz, CDCl₃, δ in ppm): 8.98 (s, 24H, H_{β -pyrrolic}), 8.40 (large s, 12H, H_{1'}), 8.26 (large d, ${}^{3}J_{H,H}=7$ Hz, 12H, H_{3'}), 8.13 (d, ${}^{3}J_{H,H}=7$ Hz, 12H, H_{4'}), 8.05 (d, ${}^{3}J_{H,H}$ =8 Hz, 12H, H₅'), 7.68 (d, ${}^{3}J_{HH}$ =7 Hz, 12H, H₈'), 7.52 (t, ${}^{3}J_{HH}$ =6 Hz, 12H, H₆'), 7.42 (t, ${}^{3}J_{HH}$ =6 Hz, 12H, H₇'), 7.34 (d, ${}^{3}J_{HH}$ =8 Hz, 6H, H_{phenyl}), 7.21 (d, ${}^{3}J_{HH}$ =8 Hz, 6H, H_{phenyl}), 6.55 (large d, ${}^{3}J_{HH}$ =5 Hz, 6H, H_B), 5.71 (v large d, 6H, H_A), 4.20 (s, 24H, H_{9'}, CH_{2fluorene}). UV-vis (λ max, CH₂Cl₂, nm): 263 (fluorene), 303 (ligand 7), 428 (Soret band), 554 (Q band), 596 (Q band). FT-IR (KBr, cm⁻¹): 2221 (m, $\nu_C \equiv_C$), 1740 (s, $\nu_C \equiv_0$). Anal. Calcd (%) for C258H156N18O3Zn3·3CH2Cl2: C, 78.23; H, 4.07; N, 6.29. Found: C, 78.97; H, 4.38; N, 6.23.

4.6. Synthesis of supramolecular assembly 6

To a solution of zinc complex ZnOOFP (4) (50 mg, 22 µmol) in CH₂Cl₂ (15 mL) was added ligand tripod 7 (5 mg, 7 µmol). The reaction mixture was stirred at room temperature under argon. After 1 h (TLC checking), the reaction mixture was concentrated and precipitated with pentane to afford 48 mg (96%) of desired supramolecular assembly **6**, as a purple solid. ¹H NMR (500 MHz, CDCl₃, δ in ppm): 8.94 (s, 24H, H_{β-pyrrolic}), 7.76 (d, ${}^{3}J_{H,H}$ =8 Hz, 24H, H_{4'}), 7.75 (d, ${}^{3}J_{H,H}$ =8 Hz, 24H, H_{5'}), 7.66 (s, 24H, H_{1'}), 7.54 (s, 24H, H_B), 7.51 (d, ${}^{3}J_{H,H}$ =7 Hz, 24H, H_{8'}), 7.47 (d, ${}^{3}J_{H,H}$ =7 Hz, 24H, H_{3'}), 7.34 (t, ${}^{3}J_{H,H}=7$ Hz, 24H, H₆'), 7.27 (t, ${}^{3}J_{H,H}=7$ Hz, 24H, H₇'), 7.16 (d, ${}^{3}J_{H,H}=8$ Hz, 6H, H_{phenyl}), 7.12 (s, 12H, H_E), 7.01 (d, ${}^{3}J_{H,H}=8$ Hz, 6H, H_{phenyl}), 5.90 (large s, 6H, H_{pyridine}), 5.26 (s, 48H, OCH₂), 3.86 (s, 48H, H_{9'} and H_{9''}). UV-vis (λ max, CH₂Cl₂, nm): 270 (fluorene), 304 (ligand 7), 425 (Soret band), 551 (Q band), 591 (Q band). FT-IR (KBr, cm⁻¹): 2223 (m, $\nu_{C} \equiv_{C}$), 1740 (s, $\nu_{C} \equiv_{O}$). Anal. Calcd (%) for C510H348N18O27Zn3·3CHCl3: C, 79.87; H, 4.59; N, 3.27. Found: C, 78.82; H, 5.36; N, 3.09.

4.7. Photophysical methods

All photophysical properties measurements have been performed at room temperature (298 K). UV-vis absorption spectra were recorded on a Jasco V-570 spectrophotometer, using 10-mm or 1-mm path length quartz cells, depending on the concentration of the solution. Fluorescence measurements on dilute solutions $(10^{-6} \text{ M}, \text{ optical density } < 0.1)$ were performed using a right-angle detection setup in standard 10-mm guartz cuvettes on an Edinburgh Instruments (FLS920) spectrometer equipped with a 450 W Xenon lamp and a Peltier-cooled Hamamatsu R928P photomultiplier tube in photon-counting mode. Fully corrected emission spectra were obtained, for each compound, at $\lambda_{ex} = \lambda_{max}^{abs}$ with an optical density at λ_{ex} < 0.1 to minimize internal absorption. Fluorescence quantum yields were measured according to literature procedures.^{24,26} Fluorescence measurements at higher concentrations (10⁻³ M) were performed using a front-face detection setup in 1-mm path length quartz cells on a Horiba Jobin-Yvon Fluorolog-3 spectrometer equipped with 450 W Xenon lamp an a Hamamatsu R928P photomultiplier tube.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.10.081.

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