Large photoactive supramolecular ensembles prepared from C_{60}–pyridine substrates and multi-Zn(II)–porphyrin receptors†

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Fullerene derivatives bearing a pyridine sub-unit have been prepared. Their ability to form self-assembled supramolecular structures with mono- and polytopic Zn(II)–porphyrin receptors has been first evidenced by UV-vis studies. These supramolecular complexes are multi-component photoactive devices, in which the emission of the porphyrinic receptor is dramatically quenched by the fullerene units. This new property, resulting from the association of the different molecular sub-units, also allowed us to investigate in detail the self-assembly process using fluorescence titrations. The binding studies revealed positive cooperative effects for the assembly of the C_{60}–pyridine derivatives with polytopic receptors as a result of intramolecular C_{60}–C_{60} interactions between the different guests assembled onto the multi-Zn(II)–porphyrin hosts.

Introduction

Self-assembly is an incredibly powerful concept in modern chemistry.[1] The ability of simple molecules to spontaneously assemble into discrete nanostructures offers unlimited possibilities for fundamental discoveries and practical applications. Furthermore, the self-assembly of carefully designed building blocks can generate new properties. In particular, this principle has been used to produce sophisticated photoactive supramolecular devices.[2,3] As part of this research, non-covalent fullerene–porphyrin conjugates have generated significant research efforts in the past few years.[4] In most cases, these supramolecular arrays have been obtained from a C_{60} derivative bearing a pyridyl moiety and a metalloporphyrin through coordination to the metal center.[5] However, the binding constants of such systems, initially developed by Diederich *et al.*[6] and D'Souza *et al.*,[7] are usually rather low. More recently, related supramolecular ensembles of improved stability have been obtained by designing systems with additional recognition elements,[8] or by applying the supramolecular click chemistry principle.[9] A few examples of structures resulting from the apical coordination of C_{60}–pyridine substrates to receptors appended with multiple Zn(II)–porphyrin sub-units have also been described.[10,11] Interestingly, photophysical investigations of such systems have revealed a more efficient electron transfer compared to simple porphyrin–fullerene supramolecular dyads.[10] Indeed, the larger number of C_{60} units enhances the probability of electron transfer from the Zn(II)–porphyrin units. In addition, efficient energy migration along the densely packed Zn(II) porphyrin array may also enhance the opportunity for this electron transfer. These considerations prompted us to study multi-component supramolecular edifices resulting from the self-assembly of fullerene–pyridine substrates onto multi-Zn(II)–porphyrin receptors. Interestingly, detailed spectrophotometric investigations revealed higher stability when the number of Zn(II)–porphyrin sub-units was increased. This can be explained by positive cooperative effects resulting from intramolecular C_{60}–C_{60} interactions between the different fullerene–pyridine guests assembled onto the multi-Zn(II)–porphyrin receptors. We thus show that an increase in the number of components within supramolecular fullerene–porphyrin conjugates is not only interesting from the photophysical point of view, but improves also the overall thermodynamic stability of the assembly.

Results and discussion

Synthesis

The porphyrinic building blocks used in this study are shown in Fig. 1. Compounds **LZn**,[12] **LZn_2**[12] and **LZn_6**[13] were prepared according to previously reported procedures. Their NMR spectra were identical to those described in the literature. In addition, mass spectrometry analysis confirmed their structures.

The synthesis of fullerene substrates **S1** and **S2** is depicted in Scheme 1. The synthetic approach to prepare compound **S1** relies upon the 1,3-dipolar cycloaddition of an azomethine

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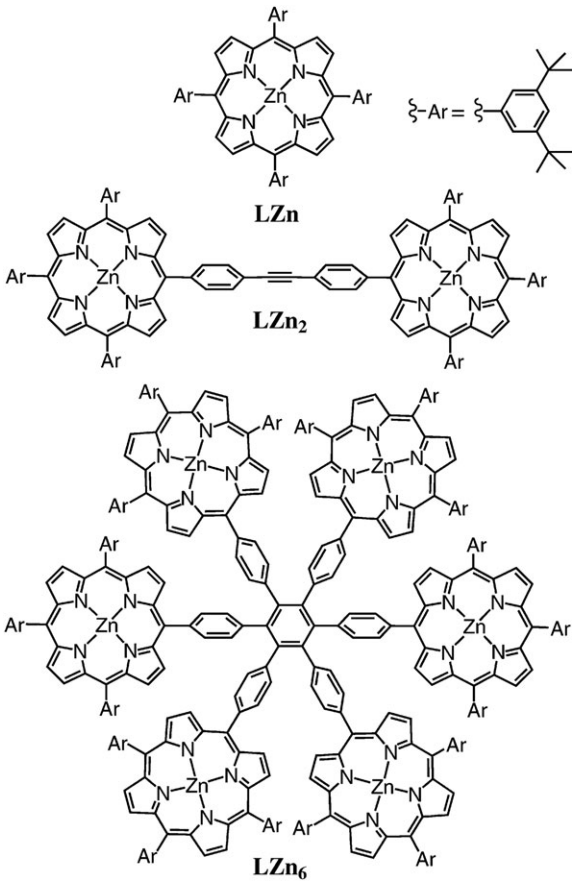
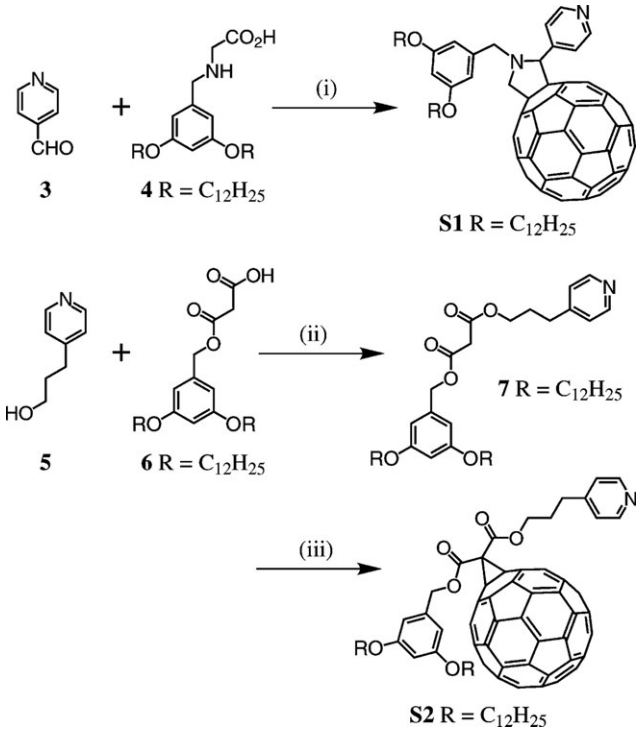


Fig. 1 Chemical structures of the porphyrin derivatives used in this study.

ylide generated *in situ* from 4-pyridinecarboxaldehyde (**3**) and a *N*-alkylglycine derivative. This methodology has proven to be a powerful procedure for the functionalization of C_{60} due to its versatility and the ready availability of the starting materials.[14] In the present study, we decided to use *N*-(3,5-didodecyloxybenzyl) glycine (**4**)[15] rather than the more commonly used *N*-methylglycine. Indeed, the 3,5-didodecyloxybenzyl group has proven to be a good solubilizing group for fullerene derivatives[16] and should prevent solubility problems in the target pyrrolidinofullerene. Thus, the reaction of aldehyde **3** with **4** and C_{60} in refluxing *ortho*-dichlorobenzene (ODCB) gave **S1** in 47% isolated yield after column chromatography on silica gel. Fullerene substrate **S2** was obtained by taking advantage of the versatile cyclopropanation reaction developed by Bingel.[17] To this end, malonate **7** was prepared by the reaction of alcohol **5** with acid **6**[18] under esterification conditions using *N*,*N*′-dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (HOBt) and 4-dimethylaminopyridine (DMAP). The reaction of C_{60} with compound **7**, iodine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under Bingel conditions[17,19] then gave methanofullerene **S2** in 47% yield.

Owing to the presence of the 3,5-didodecyloxybenzyl unit, compounds **S1** and **S2** are very soluble in common organic solvents such as toluene, CH_2Cl_2, $CHCl_3$ and THF, and complete spectroscopic characterization was easily achieved. The structures of both **S1** and **S2** were further confirmed by



Scheme 1 *Reagents and conditions*: (i) C_{60}, ODCB, Δ (47%); (ii) DCC, DMAP, HOBt, CH_2Cl_2, 0 °C to r.t. (91%); (iii) C_{60}, I_2, DBU, PhMe, r.t. (47%).

mass spectrometry. The expected molecular ion peaks were observed at *m*/*z* 1299.5 for **S1** ($[M]^+$, calc. for $C_{98}H_{62}N_2O_2$ 1299.58) and *m*/*z* 1401.4 for **S2** ($[M + H]^+$, calc. for $C_{102}H_{66}NO_6$ 1401.65).

Absorption and emission binding studies

The association of **LZn** with fullerene substrates **S1** and **S2** was studied in CH_2Cl_2 at 25 °C by UV-vis binding studies. The addition of **S1** or **S2** to **LZn** resulted in a bathochromic shift of the Zn(II)–porphyrin absorption bands, in agreement with the axial ligation of the pyridyl moieties (Fig. 2).[5] Luminescence titrations were also carried out. Indeed, a strong quenching of the porphyrin emission was observed upon addition of the C_{60}–pyridine derivatives to CH_2Cl_2 solutions of **LZn** (Fig. 2). At this point, it must be emphasized that both intramolecular and intermolecular (collisions and re-absorption events) quenching processes can occur. In order to obtain a suitable reference, all the investigations on mixtures of **LZn** and **S1** or **S2** were carried out in parallel with mixtures of the porphyrin receptor and model fullerene derivative **8** (Fig. 3), which is unable to form a supramolecular complex with Zn(II)–porphyrins (*i.e.* a C_{60} derivative with no pyridine unit).[6,9] Since a comparison with the reference solution is always made, the intermolecular quenching processes can be ignored, and the difference in emission intensity between the two solutions only accounts for intramolecular quenching. The titrations were performed at constant concentration of porphyrin **LZn**. The spectral changes observed in the emission spectra upon addition of **S1** or **S2** were recorded. Excitation occurred at an isosbestic point, at a wavelength where both complexed and uncomplexed species exhibit the same molar absorption

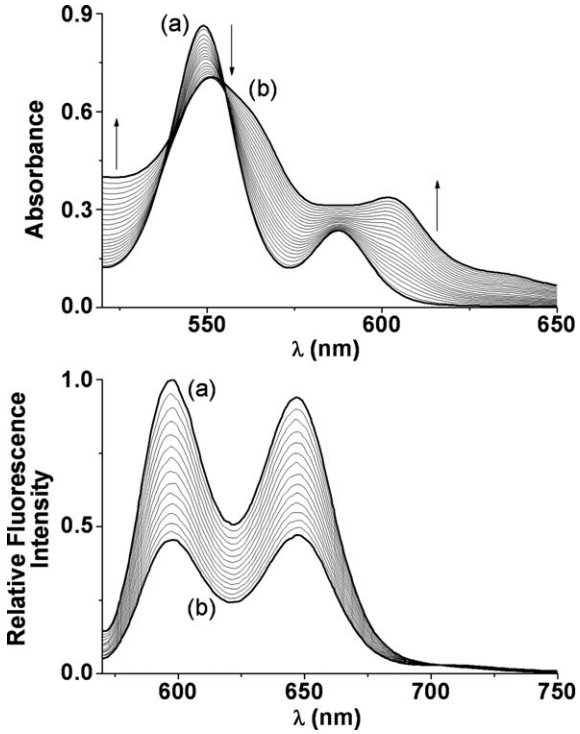


Fig. 2 Top: UV-vis absorption spectrophotometric titration of **LZn** with **S1**: l = 0.2 cm (l: optical cell pathlength); (a) $[\mathbf{LZn}]_{tot}$ = 1.85 × 10^{-4} M, (b) $[\mathbf{S1}]_{tot}/[\mathbf{LZn}]_{tot}$ = 6.8. Bottom: Luminescence spectrophotometric titration of **LZn** with **S1**; λ_{exc} = 559 nm, emission and excitation slit widths 15 and 20 nm, respectively; (a) $[\mathbf{LZn}]_{tot}$ = 1.79 × 10^{-6} M, (b) $[\mathbf{S1}]_{tot}/[\mathbf{LZn}]_{tot}$ = 63; solvent CH_2Cl_2, T = 25.0(2) °C.

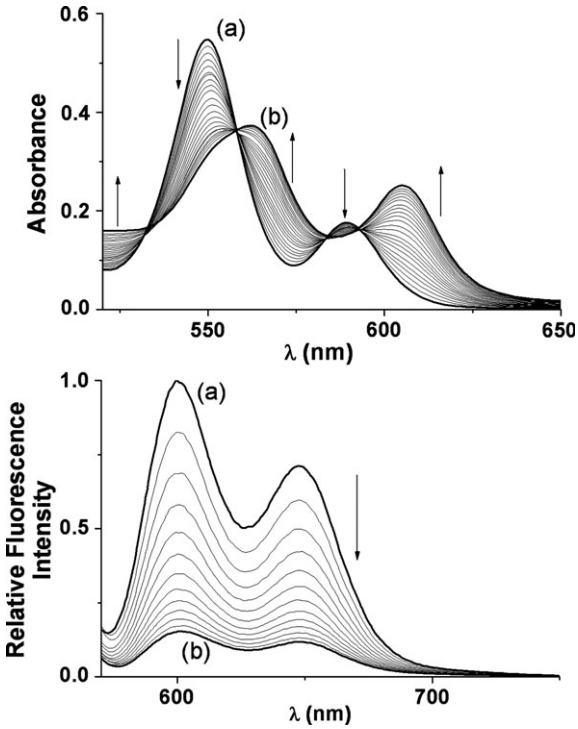
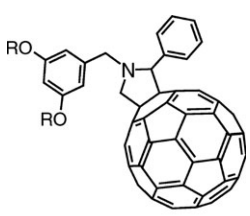


Fig. 4 Top: UV-vis absorption spectrophotometric titration of $\mathbf{LZn_2}$ with **S2**; l = 0.2 cm; (a) $[\mathbf{LZn_2}]_{tot}$ = 5.65 × 10^{-5} M; (b) $[\mathbf{S2}]_{tot}/[\mathbf{LZn_2}]_{tot}$ = 5.5. Bottom: Luminescence spectrophotometric titration of $\mathbf{LZn_2}$ with **S2**. λ_{exc} = 557 nm; emission and excitation slit widths 15 nm and 20 nm, respectively; (a) $[\mathbf{LZn_2}]_{tot}$ = 1.16 × 10^{-6} M; (b) $[\mathbf{S2}]_{tot}/[\mathbf{LZn_2}]_{tot}$ = 46.8. Solvent: CH_2Cl_2; T = 25.0(2) °C.

coefficient. In any case, the porphyrin emission bands were quenched and red-shifted with successive addition of **S1** or **S2** to **LZn**. Finally, for the sake of comparison and to emphasize the role of the fullerene units in the final conjugates, the binding properties of pyridine (**Py**) were also examined. In all of these cases, the titrations allowed the characterization of a single supramolecular complex: $[\mathbf{LZn \cdot py}]$ ($\log K_1$ = 3.55(4)), $[\mathbf{LZn \cdot S1}]$ ($\log K_1$ = 3.50(8)) and $[\mathbf{LZn \cdot S2}]$ ($\log K_1$ = 3.66(8)). The binding constants were not strongly dependent on the nature of the substrate, thus pointing out the absence of additional interactions between the porphyrinic π-system and the C_{60} unit within the supermolecules obtained from **S1** and **S2**.

The binding behavior of **Py**, **S1** and **S2** to bis-metalloporphyrin $\mathbf{LZn_2}$ was also investigated by UV-vis absorption and luminescence in CH_2Cl_2. The results of the thermodynamic studies of $\mathbf{LZn_2}$ with the different substrates are summarized in Table 1. As a typical example, the UV-vis and luminescence spectrophotometric titrations of $\mathbf{LZn_2}$ with substrate **S2** are shown in Fig. 4.



8 R = $C_{12}H_{25}$

Fig. 3 Model compound **8**.

Both the UV-vis and luminescence studies of $\mathbf{LZn_2}$ with substrate **Py** showed the presence of two complexes: $[\mathbf{LZn_2 \cdot Py}]$ and $[\mathbf{LZn_2 \cdot Py_2}]$. In contrast, only the global stability constants of complexes $[\mathbf{LZn_2 \cdot S1_2}]$ and $[\mathbf{LZn_2 \cdot S2_2}]$ were deduced from the UV-vis titrations, suggesting that the 1 : 1 complexes are minor species under our experimental conditions. This observation is a first indication of positively-cooperative interactions in the 1 : 2 associates. Processing of the luminescence data allowed us to precisely determine the successive stability constants (K_1 and K_2), defined by equilibria (1) and (2).

$$\mathbf{LZn_2} + \mathbf{Sn} \overset{K_1}{\rightleftharpoons} [\mathbf{LZn_2 \cdot Sn}] \quad K_1 = \frac{[\mathbf{LZn_2 \cdot Sn}]}{[\mathbf{LZn_2}] \times [\mathbf{Sn}]} \qquad (1)$$

$$[\mathbf{LZn_2 \cdot Sn}] + \mathbf{Sn} \overset{K_2}{\rightleftharpoons} [\mathbf{LZn_2 \cdot Sn_2}]$$
$$K_2 = \frac{[\mathbf{LZn_2 \cdot Sn_2}]}{[\mathbf{LZn_2}] \times [\mathbf{LZn_2 \cdot Sn}]} \qquad (2)$$

A thorough examination of these thermodynamic parameters thus confirmed the strong positive cooperativity in the self-assembly of the 1 : 2 ensembles. Indeed, the K_2/K_1 ratio provides a criterion to quantify the interactions between the two identical and independent binding sites.[20] For the binding of **S1** and **S2** to $\mathbf{LZn_2}$, the K_2/K_1 values summarized in Table 1

Table 1 Stability constants determined for $\mathbf{LZn_2}$ and substrates **S1**, **S2** and **Py** by UV-vis and luminescence binding studies[a]

Substrate	log K_1	log K_2	log β_2	K_2/K_1
Py	4.1(1)[b]	3.4(3)[b]	7.4(3)[b]	0.3(1)
	4.1(3)[c]	3.6(9)[c]	7.7 (9)[c]	
S1	—	—	8.4(5)[b]	3.2(7)
	4.02(2)[c]	4.5(2)[c]	8.5(2)[c]	
S2	—	—	8.6(1)[b]	10.0(3.3)
	3.7(3)[c]	4.7(3)[c]	8.4(3)[c]	

[a] Solvent CH_2Cl_2, T = 25.0(2) °C, error = 3σ. [b] Determined from the UV-vis absorption titration. [c] Determined from the luminescence titration (σ: standard deviation; β_2: global stability constant).

are significantly larger than 0.25, which is the value expected for a statistical model, clearly indicating positive intramolecular interactions in the 1 : 2 associates. The observed cooperativity may be ascribed to strong intramolecular fullerene–fullerene interactions between the two guests within $[\mathbf{LZn_2} \cdot \mathbf{S1}_2]$ and $[\mathbf{LZn_2} \cdot \mathbf{S2}_2]$ (Fig. 5). This hypothesis is in line with previous observations made on supramolecular C_{60}–oligophenylenevinylene conjugates,[21] and is further supported by the absence of any positive interactions for the 2 : 1 complex obtained from $\mathbf{LZn_2}$ and **Py**, for which the K_2/K_1 ratio ≈ 0.3(1). It is also important to highlight that the K_2/K_1 ratio is significantly greater for substrate **S2** than **S1**. Indeed, the chain connecting the C_{60} moiety to the pyridine binding unit in **S2** gives a larger degree of flexibility, thus allowing optimization of the contacts between the two C_{60} spheres in the 1 : 2 complex.

Upon addition of **Py**, the UV-vis spectrum of $\mathbf{LZn_6}$ changed substantially, and the observed bathochromic shifts of the B and Q bands were in full agreement with the apical coordination of the **Py** substrate to the Zn(II)–porphyrin moieties of $\mathbf{LZn_6}$. As shown in Fig. 6, Job's plot[22] revealed a 1 : 6 stoichiometry for the complex of **Py** with $\mathbf{LZn_6}$. The UV-vis titration results are also presented in Fig. 6. Interestingly, clear isosbestic points are observed. This result may reflect the fact that the Zn(II)–porphyrin units in $\mathbf{LZn_6}$ behave as independent binding sites. Indeed, the absorption and emission spectra of $\mathbf{LZn_6}$ were similar to those of **LZn** and $\mathbf{LZn_2}$, thus providing further evidence that the porphyrin sub-units behave independently in $\mathbf{LZn_6}$.

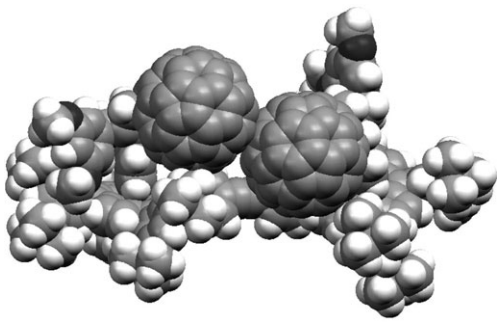


Fig. 5 Calculated structure of the supramolecular complex $[\mathbf{LZn_2} \cdot \mathbf{S1}_2]$ showing the intramolecular fullerene–fullerene interactions (the dodecyl chains have been replaced by methyl groups in the calculations.

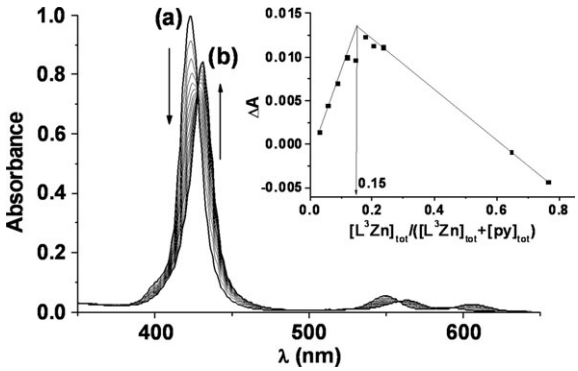


Fig. 6 UV-vis spectrophotometric titration of $\mathbf{LZn_6}$ with substrate **Py**; l = 0.5 cm; (a) $[\mathbf{LZn_6}]_{tot} = 1.17 \times 10^{-6}$ M; (b) $[\mathbf{Py}]_{tot}/[\mathbf{LZn_6}]_{tot}$ = 735; solvent CH_2Cl_2, T = 25.0(2) °C. Inset: Job's plots ($\Delta A/\Delta A_{max}$ at 564 nm) upon mixing $\mathbf{LZn_6}$ and **Py**; $([\mathbf{LZn_6}]_{tot} + [\mathbf{Py}]_{tot}) = 3.0 \times 10^{-5}$ M.

Table 2 Apparent successive stability constants (log K*) determined for $\mathbf{LZn_6}$ and substrates **Py**, **S1** and **S2** by UV-vis and luminescence binding studies[a]

Py	**1**	**2**
3.7(3)[b]	4.1(2)[b]	4.5(5)[b]
4.11(8)[c]	5.0(1)[c]	5.49(9)[c]

[a] Solvent CH_2Cl_2, T = 25.0(2) °C, error = 3σ. [b] Determined from the UV-vis absorption titration. [c] Determined from the luminescence titration.

The same studies were carried out with compounds **S1** and **S2**. In both cases, a Job's plot provided evidence for 1 : 6 complex formation, and the UV-vis titrations were closely similar to that discussed for **Py**. The apparent association constants,[11] deduced from the spectrophotometric titrations of $\mathbf{LZn_6}$ with **Py**, **S1** and **S2**, are summarized in Table 2. The complexation of $\mathbf{LZn_6}$ with ligands **Py**, **S1** and **S2** was further investigated by luminescence experiments. As a typical example, the luminescence spectrophotometric titration of $\mathbf{LZn_6}$ with substrate **S2** is shown in Fig. 7. The apparent association constants derived from the emission data (Table 2) are higher by about one order of magnitude for the fullerene-substituted ligands **S1** and **S2** compared to those obtained from the

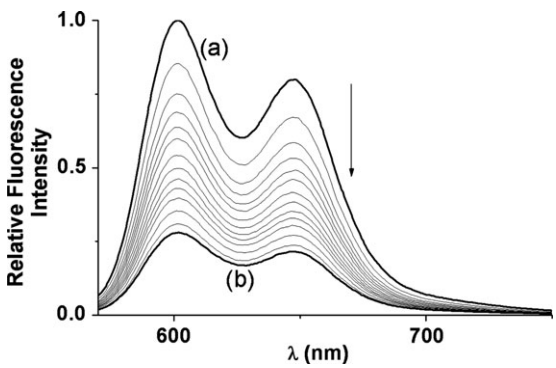


Fig. 7 Luminescence titration of $\mathbf{LZn_6}$ with **S2**. Solvent CH_2Cl_2, T = 25.0(2) °C, λ_{ex} = 428 nm, emission and excitation slit widths 15 and 20 nm, respectively; (a) $[\mathbf{LZn_6}]_{tot} = 4.91 \times 10^{-8}$ M; (b) $[\mathbf{S2}]/[\mathbf{LZn_6}]_{tot}$ = 277.

UV-vis titrations. These differences may be ascribed to the partial quenching of the emission of free Zn(II)–porphyrin units in **LZn$_6$** upon binding of the first fullerene ligand. However, the binding studies clearly revealed a significant increase in the binding constants for the fullerene-functionalized substrates relative to **Py**. As discussed for **LZn$_2$** (*vide supra*), the latter observation can be rationalized by the existence of intramolecular π–π interactions between the different fullerene sub-units within the complexes, resulting from the association of **LZn$_6$** with **S1** or **S2**. This positive cooperative effect is more pronounced for substrate **S2**. As seen for binding to the ditopic receptor **LZn$_2$**, the spacer connecting the C_{60} unit to the pyridine moiety in **S2** brings sufficient flexibility to optimize the fullerene–fullerene interactions.

Conclusion

Fullerene derivatives bearing a pyridine sub-unit have been prepared. Their ability to form self-assembled supramolecular structures with mono- and polytopic Zn(II)–porphyrin receptors has been first evidenced by UV-vis studies. Further binding studies were easily carried out in solution thanks to efficient intramolecular quenching of the emission of the Zn(II)–porphyrin receptors by the C_{60} acceptor within the non-covalent arrays. The presence of the fullerene sub-unit in the guests is not only important for their ability to act as energy and/or electron acceptors in photoactive assemblies, but is also of significant importance in the increased stability of the 2 : 1 and 6 : 1 complexes containing C_{60}–pyridine derivatives, and the polytopic receptors **LZn$_2$** and **LZn$_6$**, respectively, due to positive cooperative interactions. The results reported in this paper demonstrate that increasing the number of building blocks does not constitute a severe limitation in the self-assembly of large supramolecular architectures. However, it shows that the largest assemblies are strengthened due to increasing numbers of secondary interactions (π–π stacking, hydrophobic interactions) within the self-assembled photoactive devices.

Experimental

General methods

Reagents and solvents were purchased as reagent grade and used without further purification. Compounds **LZn**,[12] **LZn$_2$**,[12] **LZn$_6$**,[13] **4**[15] and **6**[18] were prepared according to previously reported procedures. All reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration were performed at water aspirator pressure with drying *in vacuo* at 10^{-2} Torr. Column chromatography: Silica gel 60 (230–400 mesh, 0.040–0.063 mm) was purchased from E. Merck. Thin Layer Chromatography (TLC) was performed on glass sheets coated with silica gel 60 F254 purchased from E. Merck, visualized by UV light. NMR spectra were recorded on a Bruker AM 300 (300 MHz) instrument with solvent peaks as a reference. FAB mass spectra (MS) were obtained on a ZA HF instrument with 4-nitrobenzyl alcohol as the matrix. Elemental analyses were performed by the analytical service at the Laboratoire de Chimie de Coordination, Toulouse.

Synthesis

Compound S1. A solution of **3** (45 mg, 0.42 mmol), C_{60} (300 mg, 0.42 mmol) and **4** (333 mg, 0.63 mmol) in ODCB (60 mL) was refluxed for 12 h. The mixture was cooled to r.t., filtered and evaporated to dryness under reduced pressure. Column chromatography (SiO_2, CH_2Cl_2/MeOH 95 : 5) yielded brown glassy product **S1** (256 mg, 47%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (t, J = 7 Hz, 6 H), 1.30–1.43 (m, 32 H), 1.58 (m, 4 H), 1.79 (m, 4 H), 3.62 (d, J = 13.5 Hz, 1 H), 4.01 (m, 4 H), 4.19 (d, J = 9.5 Hz, 1 H), 4.43 (d, J = 13.5 Hz, 1 H), 4.92 (d, J = 9.5 Hz, 1 H), 5.20 (s, 1 H), 6.49 (t, J = 2 Hz, 1 H), 6.80 (d, J = 2 Hz, 2 H), 7.89 (br s, 2 H) and 8.72 (d, J = 6 Hz, 2 H). FAB-MS: m/z 1299.5 ($[M]^+$, calc. for $C_{98}H_{62}N_2O_2$ 1299.58). Elemental analysis calc. for $C_{98}H_{62}N_2O_2 \cdot$ MeOH: C, 89.30; H, 5.00; N, 2.10; found C, 88.90; H, 5.04; N, 2.24%.

Compound 7. DCC (2.90 mg, 14.19 mmol) and DMAP (173 mg, 1.42 mmol) were added to a solution of alcohol **5** (536 mg, 3.91 mmol) and acid **6** (2.0 g, 3.55 mmol) in CH_2Cl_2 stabilized by amylene (100 mL) at 0 °C under argon. After 1 h, the cooling bath was removed. The mixture was allowed to slowly warm to r.t. After 24 h, the mixture was filtered and the solvent removed under reduced pressure. Column chromatography (SiO_2, CH_2Cl_2/MeOH 95 : 5) afforded **7** (2.20 mg, 91%) as a colorless, glassy product. IR (KBr, cm^{-1}): 1749 (C═O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.87 (t, J = 7 Hz, 6 H), 1.27 (m, 36 H), 1.67 (m, 4 H), 2.02 (m, 2 H), 2.71 (t, J = 6 Hz, 2 H), 3.69 (s, 2 H), 3.88 (t, J = 6.5 Hz, 4 H), 4.26 (t, J = 6 Hz, 2 H), 5.07 (s, 2 H), 6.42 (m, 3 H), 7.23 (m, 2 H) and 8.56 (m, 2 H).

Compound S2. DBU (0.2 mL, 1.39 mmol) was added to a solution of C_{60} (400 mg, 0.56 mmol), compound **7** (378 mg, 0.56 mmol) and iodine (155 mg, 0.61 mmol) in toluene (600 mL) under argon. After 12 h, the mixture was filtered over SiO_2 (CH_2Cl_2 then CH_2Cl_2/MeOH 95 : 5) and the solvent removed under reduced pressure. Purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 95 : 5) afforded **S2** (545 mg, 47%) as a dark red, glassy product. IR (KBr, cm^{-1}): 1752 (C═O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.87 (t, J = 7 Hz, 6 H), 1.27 (m, 36 H), 1.67 (m, 4 H), 2.05 (m, 2 H), 2.75 (t, J = 6 Hz, 2 H), 3.88 (t, J = 6.5 Hz, 4 H), 4.35 (t, J = 6 Hz, 2 H), 5.44 (s, 2 H), 6.35 (t, J = 1.5 Hz, 1 H), 6.52 (d, J = 1.5 Hz, 2 H), 7.15 (m, 2 H) and 8.47 (m, 2 H). FAB-MS: m/z 1401.4 ($[M + H]^+$, calc. for $C_{102}H_{66}NO_6$ 1401.65). Elemental analysis calc. for $C_{102}H_{65}NO_6 \cdot H_2O$: C, 86.36; H, 4.76; N, 2.10; found C, 86.14; H, 4.77; N, 0.99%.

Compound 8. As described for **S1**, with benzaldehyde (59 mg, 0.56 mmol), C_{60} (400 mg, 0.56 mmol) and **4** (333 mg, 0.63 mmol) in ODCB (100 mL). Column chromatography (SiO_2, hexane/CH_2Cl_2 8 : 2) yielded **8** (327 mg, 45%) as a brown, glassy product. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (t, J = 7 Hz, 6 H), 1.30–1.43 (m, 32 H), 1.58 (m, 4 H), 1,79 (m, 4 H), 3.61 (d, J = 13.5 Hz, 1 H), 3.96 (m, 4 H), 4.15 (d, J = 9.5 Hz, 1 H), 4.43 (d, J = 13.5 Hz, 1 H), 4.92 (d, J = 9.5 Hz, 1 H), 5.21 (s, 1 H), 6.45 (t, J = 2 Hz, 1 H), 6.76 (d, J = 2 Hz, 2 H), 7.40 (m, 1 H), 7.48 (m, 2 H) and 7.85 (m, 2 H). FAB-MS: m/z 1299.5 ($[M + H]^+$, calc. for $C_{99}H_{64}NO_2$ 1299.60). Elemental

analysis calc. for $C_{99}H_{63}NO_2 \cdot H_2O$: C, 90.25; H, 5.05; N, 1.06; found C, 90.38; H, 5.01; N, 1.21%.

Binding studies

All the binding studies were carried out with spectroscopic grade CH_2Cl_2 (E. Merck, 99.9% for spectroscopy). To prevent any photochemical degradation, all the solutions were protected from daylight exposure. All stock solutions were prepared using an AG 245 Mettler Toledo analytical balance (precision 0.01 mg), and complete dissolution in CH_2Cl_2 was achieved using an ultrasonic bath. The concentrations of stock solutions of the receptors and substrates ($\approx 10^{-4}$ M) were calculated by the quantitative dissolution of solid samples in CH_2Cl_2.

UV-vis titrations

The spectrophotometric titrations of **LZn**, **LZn$_2$** and **LZn$_6$** with **S1** ($[\mathbf{LZn}]_{tot} = 1.84 \times 10^{-4}$ M, $[\mathbf{LZn_2}]_{tot} = 5.65 \times 10^{-5}$ M, $[\mathbf{LZn_6}]_{tot} = 2.93 \times 10^{-6}$ M) and **S2** ($[\mathbf{LZn}]_{tot} = 5.82 \times 10^{-5}$ M, $[\mathbf{LZn_2}]_{tot} = 5.65 \times 10^{-5}$ M, $[\mathbf{LZn_6}]_{tot} = 3.04 \times 10^{-6}$ M) were carried out in a Hellma quartz optical cell (l = 0.2 cm). To evaluate the influence of the fullerene units on the binding constants, spectrophotometric titrations of the same receptors with **Py** were conducted under similar experimental conditions ($[\mathbf{LZn}]_{tot} = 1.79 \times 10^{-6}$ M, l = 1 cm; $[\mathbf{LZn_2}]_{tot} = 1.13 \times 10^{-6}$ M, l = 1 cm; $[\mathbf{LZn_6}]_{tot} = 1.17 \times 10^{-6}$ M, l = 0.5 cm). Microvolumes of a concentrated solution of **S1**, **S2** or **Py** were added to 2, 1 or 0.4 mL of **LZn**, **LZn$_2$** or **LZn$_6$** with μL Hamilton syringes (#710 and #750). The $[substrate]_{tot}/[receptor]_{tot}$ ratios were varied within ranges from 0 to 863 for **Py**, from 0 to 108 for **S1** and from 0 to 24.5 for **S2** (see the ESI for detailed conditions†). Special care was taken to ensure that complete equilibration was attained. The corresponding UV-vis spectra were recorded from 290 to 700 nm on a Cary 300 (Varian) spectrophotometer maintained at 25.0(2) °C by the flow of a Haake NB 22 thermostat. The spectrophotometric data were processed using the Specfit program,[23] which adjusts the stability constants and the corresponding extinction coefficients of the species formed at equilibrium. Specfit uses factor analyses to reduce the absorbance matrix and extract the eigenvalues prior to the multi-wavelength fit of the reduced data set according to the Marquardt algorithm.[24]

Luminescence titrations

Luminescence titrations were carried out on solutions of **LZn**, **LZn$_2$** and **LZn$_6$** with absorbances smaller than 0.1 at wavelengths $\geq \lambda_{exc}$ in order to avoid any errors due to the inner filter effect. The titrations of 2 mL of **LZn**, **LZn$_2$** and **LZn$_6$** with **Py** ($[\mathbf{LZn}]_{tot} = 1.79 \times 10^{-6}$ M; $[\mathbf{LZn_2}]_{tot} = 1.13 \times 10^{-6}$ M; $[\mathbf{LZn_6}]_{tot} = 1.17 \times 10^{-6}$ M), **S1** ($[\mathbf{LZn}]_{tot} = 1.79 \times 10^{-6}$ M; $[\mathbf{LZn_2}]_{tot} = 1.13 \times 10^{-6}$ M; $[\mathbf{LZn_6}]_{tot} = 4.91 \times 10^{-8}$ M) and **S2** ($[\mathbf{LZn}]_{tot} = 1.90 \times 10^{-6}$ M; $[\mathbf{LZn_2}]_{tot} = 1.16 \times 10^{-6}$ M; $[\mathbf{LZn_6}]_{tot} = 4.91 \times 10^{-8}$ M) were carried out in a 1 cm Hellma quartz optical cell by the addition of known microvolumes of solutions of **S1**, **S2** and **Py** with μL Hamilton syringes (#710 and #750). The $[substrate]_{tot}/[receptor]_{tot}$ ratios were varied within ranges from 0 to 531 for **Py**, from 0 to 220 for **S1** and from 0 to 277 for **S2** (see ESI for detailed conditions†). Special care was taken to ensure that complete equilibration was attained. The excitation wavelengths were set at 557(1) or 559(1) nm for **LZn**, at 557(1) or 559(1) nm for **LZn$_2$** and 558(1) or 428(1) nm for **LZn$_6$**, respectively, and correspond, in most of the cases, to the isosbestic points between the electronic spectra of the free Zn(II) porphyrinic receptors and the corresponding pentacoordinated complexes. The Zn(II) porphyrin-centered luminescence spectra were recorded from 500 to 800 nm on a Perkin-Elmer LS-50B instrument maintained at 25.0(2) °C by the flow of a Haake FJ thermostat. The slit widths were set at 15 and 20 nm for the emission and excitation, respectively. Luminescence titrations of **LZn**, **LZn$_2$** and **LZn$_6$** receptors were conducted under precise and identical experimental conditions using a model fullerene derivative that was unable to form complexes (C_{60} derivative with a phenyl group as a substitute for the pyridine unit) in order to separate the variation of the luminescence intensity that results from dynamic and re-absorption phenomena. For the **Py** substrate, the spectrofluorimetric data were processed with the Specfit program.[23] For guests **S1** and **S2**, the luminescence data sets were analyzed[25,26] with the Microcal Origin program.[27]

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