Supramolecular click chemistry for the self-assembly of a stable Zn(II)–porphyrin–C_{60} conjugate†

Ali Trabolsi,[a] Mourad Elhabiri,[a] Maxence Urbani,[bc] Juan Luis Delgado de la Cruz,[c] Fettah Ajamaa,[c] Nathalie Solladié,*[b] Anne-Marie Albrecht-Gary*[a] and Jean-François Nierengarten*[c]

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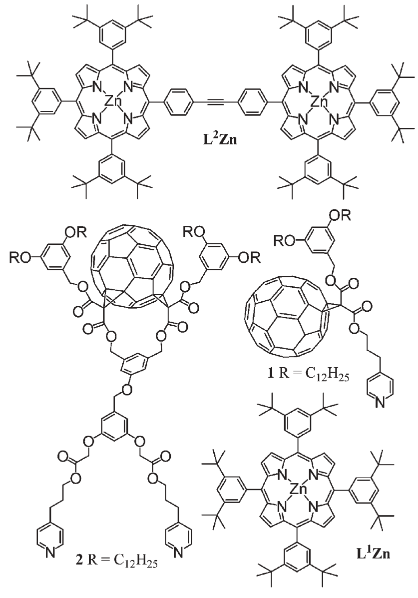
Owing to the complementarity between a bis-Zn(II)–porphyrin receptor and a fullerene ligand bearing two pyridine substituents, the substrate can be *clicked* onto the ditopic receptor, thus leading to a stable non-covalent macrocyclic 1 : 1 complex.

The use of non-covalent interactions to assemble molecular building blocks in a controlled manner is an attractive strategy to produce advanced functional materials with new optoelectronic properties.[1] However, self-assembled systems are not always very stable in solution, and the design of supramolecular ensembles with high binding constants remains an important challenge. As part of this research, we have recently developed the *supramolecular click chemistry* principle[2,3] as a new and powerful concept for the preparation of stable macrocyclic non-covalent arrays. Specifically, a supramolecular complex has been obtained from a bis-crown ether receptor and a bis-ammonium fullerene ligand. Owing to the complementarity of the two components, the bis-cationic substrate can be *clicked* onto the ditopic crown ether derivative, thus leading to a stable macrocyclic 1 : 1 complex. This new approach appears to be easily applicable to a wide range of functional groups for the preparation of new supramolecular architectures with tunable structural and electronic properties. In this paper, we now show that supramolecular click chemistry is perfectly suited for the preparation of a stable non-covalent fullerene–porphyrin hybrid system. Indeed, C_{60}–porphyrin dyads are interesting molecular devices in which photoinduced intramolecular processes such as electron and energy transfer are evident.[4] Furthermore, photovoltaic devices prepared from porphyrin–fullerene systems have shown promising energy conversion efficiencies.[5]

Non-covalent C_{60}–porphyrin derivatives can be easily obtained from C_{60} derivatives bearing a pyridine moiety and metalloporphyrins through coordination to the metal ion.[6] The binding constants are however rather low.[6] In order to improve the stability of such systems we have decided to apply the supramolecular click concept. The bis-Zn(II)–phorphyrinic receptor $\mathbf{L^2Zn}$ has been selected as a platform containing two equivalent Zn binding sites separated by about 20 Å. Substrate **2**, bearing two pyridine sub-units, has been designed to allow the assembly of a macrocyclic *clicked* edifice with the $\mathbf{L^2Zn}$ receptor. For the sake of comparison, binding studies have also been carried out with the reference compounds **1**, pyridine (**Py**) and $\mathbf{L^1Zn}$.



Compounds $\mathbf{L^1Zn}$ and $\mathbf{L^2Zn}$ have been prepared according to previously reported procedures.[7] The syntheses of compounds **1** and **2** are depicted in Scheme 1.

The C_s-symmetrical fullerene bis-adduct precursor **3** was obtained in eight steps as already described.[8] Reaction of dicarboxylic acid **3** with an excess of alcohol **4** in CH_2Cl_2 under esterification conditions using *N*,*N*′-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) gave **2** in 60% yield. Compound **1** was prepared in two steps from alcohol **4**. Esterification with acid **5**[8] (DCC, DMAP) followed by reaction of the resulting malonate with C_{60}, I_2 and diazabicyclo[5.4.0]undec-7-ene (DBU) under Bingel conditions[9] afforded methanofullerene **1**. The ^{1}H- and ^{13}C-NMR spectra of both **1** and **2** were in full agreement with their C_s-symmetrical structures. Compounds **1** and **2** were also characterized by FAB mass spectrometry. In both cases, the expected molecular ion peak was observed (**1**: m/z = 1400.3 $[M+H]^+$, calc. for $C_{102}H_{66}NO_6$ = 1400.49; **2**: m/z = 2436.1 $[M+H]^+$, calc. for $C_{163}H_{147}N_2O_{19}$ = 2436.06).

The ability of bis-porphyrin $\mathbf{L^2Zn}$ to form a supramolecular complex with bis-pyridine **2** was first evidenced by ^{1}H-NMR

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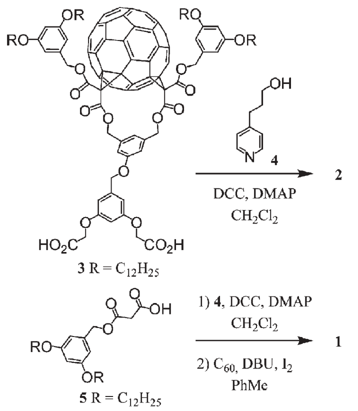
[a] *Laboratoire de Physico-Chimie Bioinorganique, UMR 7509 du CNRS, ECPM, ULP, 25 rue Becquerel, 67200, Strasbourg, France. E-mail: amalbre@chimie.u-strasbg.fr; Fax: +33 (0) 3 90 24 26 39; Tel: +33 (0) 3 90 24 26 38*
[b] *Groupe de Synthèse de Systèmes Porphyriniques, Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077, Toulouse Cedex 4, France. E-mail: solladie@lcc-toulouse.fr; Fax: +33 (0) 5 61 55 30 03; Tel: +33 (0) 5 61 33 31 00*
[c] *Groupe de Chimie des Fullerènes et des Systèmes Conjugués, Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077, Toulouse Cedex 4, France. E-mail: jfnierengarten@lcc-toulouse.fr; Fax: +33 (0) 5 61 55 30 03; Tel: +33 (0) 5 61 33 31 00*

† Electronic supplementary information (ESI) available: UV-vis and luminescence spectrophotometric titration of $\mathbf{L^1Zn}$ and $\mathbf{L^2Zn}$; F_0/F at 600 nm *vs.* concentration of **1** plot. See DOI: 10.1039/b510782b



Scheme 1 Preparation of compounds **1** and **2**.

binding studies performed at 298 K in $CDCl_3$. Complexation-induced changes in chemical shifts were observed upon addition of 1 equiv. of $\mathbf{L^2Zn}$ to a solution of **2**. In particular, dramatic upfield shifts were seen for the chemical shifts of the protons belonging to the pyridine moieties ($\Delta\delta > 4.5$ ppm). When coordination of the Zn(II) ions takes place, the pyridine moieties of **2** are located above the porphyrin cores, and the important chemical shift changes are a result of the ring current effect of the porphyrin macrocycles. Importantly, changes in the chemical shift were also evident for all the protons of the spacer moiety between the two pyridine units of **2** ($\Delta\delta = 0.2$ to 0.6 ppm). The latter observation suggests that all these protons must be close to the π-conjugated system of $\mathbf{L^2Zn}$ in the associate, which is in good agreement with the formation of a macrocyclic 1 : 1 supramolecular complex (Fig. 1).

To quantify the interactions between $\mathbf{L^2Zn}$ and **2**, the complexation was further studied in CH_2Cl_2 by UV-vis and fluorescence binding studies. For comparison purposes, the association of $\mathbf{L^1Zn}$ and **1**, $\mathbf{L^1Zn}$ and **Py**, and $\mathbf{L^2Zn}$ and **Py** were also investigated. Addition of ligand **1** to $\mathbf{L^1Zn}$ in CH_2Cl_2 resulted in bathochromic shifting of the Q bands (see ESI†). The processing[10] of the titration data allowed the characterization of a single supramolecular complex [($\mathbf{L^1Zn}$)·(**1**)] in solution (log $K_1 = 3.54 \pm 0.08$).‡ The binding constant of [($\mathbf{L^1Zn}$)·(**1**)] is similar to that found for [($\mathbf{L^1Zn}$)·(**Py**)] (log $K_1 = 3.56 \pm 0.03$) and in good agreement with values already reported in the literature for related systems involving pyridyl-substituted fullerene derivatives and Zn(II)-porphyrins.[6] The spectrophotometric studies of the bis-porphyrinic receptor $\mathbf{L^2Zn}$ with **Py** as substrate revealed the presence of two complexes: [($\mathbf{L^2Zn}$)·(**Py**)] (log $K_1 = 4.0 \pm 0.1$) and [($\mathbf{L^2Zn}$)·$(\mathbf{Py})_2$] (log $K_2 = 3.4 \pm 0.3$). Assuming that the two metalloporphyrins in $\mathbf{L^2Zn}$ are identical and independent, the K_2/K_1 ratio therefore provides a criterion to quantify the interactions between the two binding sites.[11] The ratio K_2/K_1 is close to 0.25, which is the value expected for a statistical model. The binding behavior of bis-pyridine **2** to bis-metalloporphyrin $\mathbf{L^2Zn}$ was also investigated by UV-vis absorption in CH_2Cl_2. As depicted in Fig. 2, upon addition of increasing amounts of **2** to a solution of $\mathbf{L^2Zn}$, the Q and Soret bands of the metalloporphyrins experienced bathochromic shifts, as already observed for the two axially-bonded pyridyl ligands in [($\mathbf{L^2Zn}$)·$(\mathbf{Py})_2$].

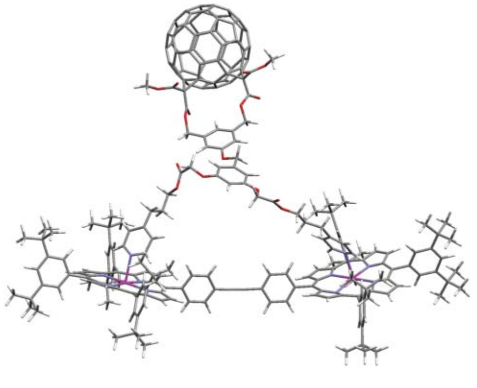


Fig. 1 Calculated structure of the macrocyclic supramolecular complex [($\mathbf{L^2Zn}$)·(**2**)] (molecular modelling performed with Spartan, the 3,5-didodecyloxybenzyl units have been replaced by methyl groups in the calculations).

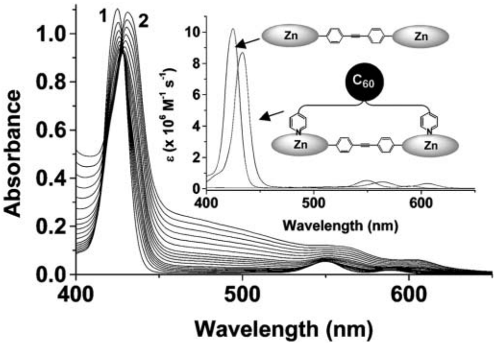


Fig. 2 UV-visible absorption spectrophotometric titration of $\mathbf{L^2Zn}$ with substrate **2**. $l = 2$ cm; (1) $[\mathbf{L^2Zn}]_{tot} = 5.4 \times 10^{-7}$ M, (2) $[\mathbf{2}]_{tot}/[\mathbf{L^2Zn}]_{tot} = 57.2$. Inset: absorption electronic spectra of $\mathbf{L^2Zn}$ and [($\mathbf{L^2Zn}$)·(**2**)]. Solvent: CH_2Cl_2; $T = 25.0 \pm 0.2$ °C.

Under our experimental conditions, the statistical processing of the spectrophotometric data revealed the formation of a single complex [($\mathbf{L^2Zn}$)·(**2**)] with log $K_1 = 5.09 \pm 0.07$. The sizeable increase of stability compared to that of the compounds [($\mathbf{L^1Zn}$)·(**1**)], [($\mathbf{L^1Zn}$)·(**Py**)], [($\mathbf{L^2Zn}$)·(**Py**)] or [($\mathbf{L^2Zn}$)·$(\mathbf{Py})_2$] emphasized the peculiar structure of [($\mathbf{L^2Zn}$)·(**2**)], in which the bis-pyridyl fullerene substrate **2** is *clicked* onto the ditopic receptor $\mathbf{L^2Zn}$ (Fig. 1). Similar increases in the association constants have been reported by D'Souza and co-workers for supramolecular systems resulting from the axial coordination of the C_{60}–pyridine ligand to Zn(II)-porphyrins and possessing an additional recognition element.[12]

To further confirm the data derived from the absorption studies, the complexation of $\mathbf{L^1Zn}$ and $\mathbf{L^2Zn}$ with the pyridine ligands **1** and **2**, respectively, were also investigated by luminescence experiments. Indeed, a strong quenching of the porphyrin emission was observed upon addition of the C_{60}–pyridine derivatives to CH_2Cl_2 solutions of $\mathbf{L^1Zn}$ or $\mathbf{L^2Zn}$. At this point, it must be emphasized that both intramolecular and intermolecular (collisions and reabsorption events) quenching processes can occur.[6a] Indeed, in order to have a suitable reference, all the binding studies have been carried out in parallel with mixtures of the porphyrin receptor and a model fullerene derivative unable to form a supramolecular complex (*i.e.* a C_{60} derivative with no pyridine substituent).[6a] 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 therefore only accounts for the intramolecular quenching of the porphyrin excited state by the fullerene moiety in the supramolecular

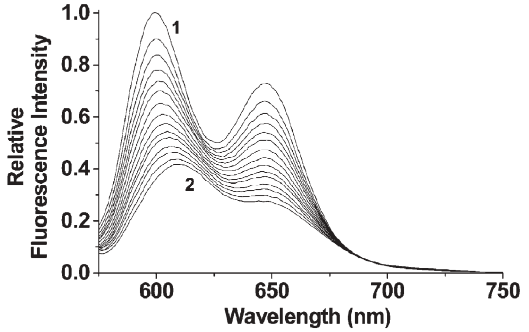


Fig. 3 Luminescence titration of $\mathbf{L^2Zn}$ by **2**. Solvent: CH_2Cl_2, $T = 25.0 \pm 0.2$ °C, $\lambda_{exc} = 559$ nm (isosbestic point), emission and excitation slit widths 15 and 20 nm, respectively; (1) $[\mathbf{L^2Zn}]_{tot} = 1.08 \times 10^{-6}$ M; (2) $[\mathbf{2}]/[\mathbf{L^2Zn}]_{tot} = 19$.

complex. The titrations were performed at constant concentration of porphyrin $\mathbf{L^1Zn}$ or $\mathbf{L^2Zn}$. The spectral changes observed in the emission spectrum upon addition of increasing amounts of **1** or **2** were recorded. The excitation occurred at an isosbestic point (559 nm), at a wavelength where both complexed and uncomplexed species exhibited the same molar absorption coefficient. As shown in Fig. 3, upon progressive addition of **2** to a solution containing $\mathbf{L^2Zn}$, the porphyrin emission bands centered at 599 and 648 nm were quenched and red-shifted. The processing of the luminescence data allowed us to identify the formation of a single species, the clicked complex, with a binding constant $\log K_1 = 5.05 \pm 0.09$. Similar studies were carried out with $\mathbf{L^1Zn}$ and **1**, leading to a binding constant $\log K_1 = 3.78 \pm 0.02$. The K values deduced from the emission data are in perfect agreement with those derived from the absorption studies and confirm the increased stability of the macrocyclic complex $[(\mathbf{L^2Zn})\cdot(\mathbf{2})]$ as a result of simultaneous coordination of the two Zn centers of $\mathbf{L^2Zn}$ by the two pyridine moieties of **2**.

The efficiency of the intramolecular quenching process within the clicked supramolecular complex $[(\mathbf{L^2Zn})\cdot(\mathbf{2})]$ was deduced from the emission spectra depicted in Fig. 4.

The comparison of the emission intensity of $[(\mathbf{L^2Zn})\cdot(\mathbf{2})]$ with the one determined for $[(\mathbf{L^2Zn})\cdot(\mathbf{Py})_2]$ allowed us to estimate a quantum yield of 0.66 ± 0.07. In spite of the long distance between the photoactive units (*ca.* 18 to 20 Å, Fig. 1), the quenching of the lowest porphyrin singlet excited state by the fullerene unit remains quite efficient, suggesting that the initial energy transfer typically observed in Zn(II)–porphyrin–C_{60} conjugates[4] is still effective. Steady-state fluorescence measurements are, however, not sufficient to conclude whether an electron transfer from the lowest fullerene singlet excited state thus populated occurs in our supramolecular system. Effectively, the fluorescence of $\mathbf{L^2Zn}$ ($\Phi = 0.011$)§ strongly overlaps the weaker fullerene emission ($\Phi \approx 10^{-4}$ for **2**),§ thus preventing clean excitation spectroscopy. Further photophysical studies are under way to determine the effective excited state deactivation pathways in $[(\mathbf{L^2Zn})\cdot(\mathbf{2})]$ and will be reported in due time.

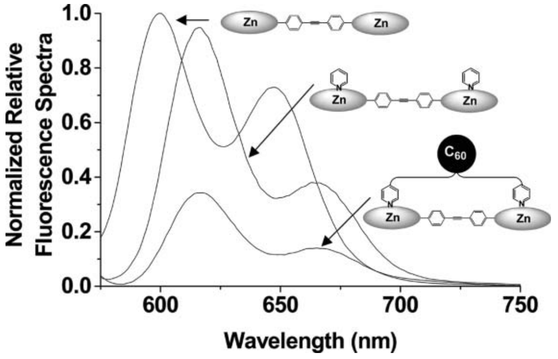


Fig. 4 Normalized relative fluorescence spectra of $\mathbf{L^2Zn}$, $[(\mathbf{L^2Zn})\cdot(\mathbf{Py})_2]$ and $[(\mathbf{L^2Zn})\cdot(\mathbf{2})]$. Solvent: CH_2Cl_2, $T = 25.0 \pm 0.2$ °C, $\lambda_{exc} = 557$ nm (excitation of the porphyrin unit in $[(\mathbf{L^2Zn})\cdot(\mathbf{Py})_2]$), $\lambda_{exc} = 559$ nm (excitation of the porphyrin unit in $[(\mathbf{L^2Zn})\cdot(\mathbf{2})]$).

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Notes and references

‡ The errors in the stability constants are given as 3σ, with σ = standard deviation.

§ Absolute quantum yields, errors = 10%.

1 For general references on supramolecular chemistry, see: (*a*) *Self-Assembling Architecture*, ed. J. E. Varner, Liss, New York, 1988; (*b*) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995, ch. 9; (*c*) D. Philp and J. F. Stoddart, *Angew. Chem.*, 1996, **108**, 1242–1286; (*d*) L. F. Lindoy and I. M. Atkinson, *Self-Assembly in Supramolecular Systems*, Royal Society of Chemistry, Cambridge, UK, 2000; (*e*) M. Fujita, in *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle and J.-M. Lehn, Pergamon Press, Oxford, 1996, vol. 9, pp. 253–282; (*f*) F. Vögtle, *Supramolecular Chemistry*, Wiley, Chichester, 1991; (*g*) J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, Wiley, Chichester, 2000.

2 U. Hahn, M. Elhabiri, A. Trabolsi, H. Herschbach, E. Leize, A. Van Dorsselaer, A.-M. Albrecht-Gary and J.-F. Nierengarten, *Angew. Chem., Int. Ed.*, 2005, **44**, 5338–5341.

3 The concept of "click chemistry" has been introduced by K. B. Sharpless, see: H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004–2021.

4 (*a*) D. M. Guldi, *Chem. Soc. Rev.*, 2002, **31**, 22–36; (*b*) H. Imahori and Y. Sakata, *Eur. J. Org. Chem.*, 1999, 2445–2457; (*c*) D. Gust, T. A. Moore and A. L. Moore, *Acc. Chem. Res.*, 2001, **34**, 40–48; (*d*) H. Imahori, *J. Phys. Chem. B*, 2004, **108**, 6130–6143; (*e*) H. Imahori, *Org. Biomol. Chem.*, 2004, **2**, 1425–1433.

5 H. Imahori and S. Fukuzumi, *Adv. Funct. Mater.*, 2004, **14**, 525–536 and references therein.

6 (*a*) N. Armaroli, F. Diederich, L. Echegoyen, T. Habicher, L. Flamigni, G. Marconi and J.-F. Nierengarten, *New J. Chem.*, 1999, **23**, 77–83; (*b*) F. D'Souza, G. R. Deviprasad, M. S. Rahman and J. Choi, *Inorg. Chem.*, 1999, **38**, 2157–2160; (*c*) T. Da Ros, M. Prato, D. M. Guldi, E. Alessio, M. Ruzzi and L. Pasimeni, *Chem. Commun.*, 1999, 635–636; (*d*) F. Hauke, A. Swartz, D. M. Guldi and A. Hirsch, *J. Mater. Chem.*, 2002, **12**, 2088–2094; (*e*) S. R. Wilson, S. MacMahon, F. T. Tat, P. D. Jarowski and D. I. Schuster, *Chem. Commun.*, 2003, 226–227.

7 M. Takase, R. Ismael, R. Murakami, M. Ikeda, D. Kim, H. Shinmori, H. Furuta and A. Osuka, *Tetrahedron Lett.*, 2002, **43**, 5157–5159.

8 D. Felder, M. Gutiérrez Nava, M. del Pilar Carreón, J.-F. Eckert, M. Luccisano, C. Schall, P. Masson, J.-L. Gallani, B. Heinrich, D. Guillon and J.-F. Nierengarten, *Helv. Chim. Acta*, 2002, **85**, 288–319.

9 C. Bingel, *Chem. Ber.*, 1993, **126**, 1957–1959.

10 (*a*) R. A. Binsteadt and A. D. Zuberbühler, *SPECFIT: A program for global least squares fitting of equilibrium and kinetics systems using factor analysis and Marquardt minimisation*, Version 2–11 C, Spectrum Software Associates, Chapel Hill, NC, USA, 1998; (*b*) H. Gampp, M. Maeder, C. J. Meyer and A. D. Zuberbühler, *Talanta*, 1985, **32**, 95–101; (*c*) H. Gampp, M. Maeder, C. J. Meyer and A. D. Zuberbühler, *Talanta*, 1985, **32**, 257–264; (*d*) H. Gampp, M. Maeder, C. J. Meyer and A. D. Zuberbühler, *Talanta*, 1986, **33**, 943–951.

11 (*a*) B. Perlmutter-Hayman, *Acc. Chem. Res.*, 1986, **19**, 90–96; (*b*) G. Ercolani, *J. Am. Chem. Soc.*, 2003, **125**, 16097–16103.

12 (*a*) F. D'Souza, S. Gadde, M. E. Zandler, M. Ito, Y. Araki and O. Ito, *Chem. Commun.*, 2004, 2276–2277; (*b*) F. D'Souza, R. Chitta, S. Gadde, M. E. Zandler, A. S. D. Sandanayaka, Y. Araki and O. Ito, *Chem. Commun.*, 2005, 1279–1281; (*c*) F. D'Souza, R. Chitta, S. Gadde, M. E. Zandler, A. L. McCarty, A. S. D. Sandanayaka, Y. Araki and O. Ito, *Chem.–Eur. J.*, 2005, **11**, 4416–4428.