Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron
ELSEVIER
Tetrahedron 62 (2006) 1979–1987

Supramolecular complexes obtained from porphyrin–crown ether conjugates and a fullerene derivative bearing an ammonium unit

Nathalie Solladié,[a,*] Mathieu E. Walther,[a] Haiko Herschbach,[b] Emmanuelle Leize,[b] Alain Van Dorsselaer,[b,*] Teresa M. Figueira Duarte[c] and Jean-François Nierengarten[c,*]

[a]*Groupe de Synthèse de Systèmes Porphyriniques, Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex 4, France*
[b]*Laboratoire de Spectrométrie de Masse Bio-organique, Ecole de Chimie, Polymères et Matériaux (ECPM), Université Louis Pasteur and CNRS, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France*
[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*

Received 8 April 2005; revised 26 April 2005; accepted 30 April 2005

Available online 14 November 2005

Abstract—A methanofullerene derivative with an ammonium subunit (**1**) has been prepared and its ability to form a supramolecular complex with a porphyrin–crown ether conjugate evidenced by NMR, UV–vis, electrospray mass spectrometry (ES-MS) and luminescence experiments. Interestingly, in addition to the ammonium–crown ether recognition, intramolecular stacking of the fullerene moiety and the porphyrin subunit has been evidenced. Due to this additional recognition element, the association constant for the supramolecular complex is increased by two orders of magnitude when compared to the K_a values found for the complexation of **1** with benzo-18-crown-6. Finally, non-covalent systems resulting from the association of cation **1** with porphyrin derivatives bearing two crown ether subunits have been investigated. Intramolecular C_{60}–porphyrin interactions have also been evidenced within these supramolecular complexes. As a result, the 2:1 complexes are very stable as shown by the ES-MS studies.

1. Introduction

Owing to their particular electrochemical and electronic properties, C_{60} and porphyrins are interesting building blocks for the construction of new photochemical molecular devices.[1] Indeed, the synthesis of covalently linked porphyrin–fullerene hybrids have generated significant research efforts in the last few years.[2,3] Their photophysical properties have been studied in details and intramolecular processes such as electron and energy transfer evidenced in such multicomponent hybrid systems.[2,3] Importantly, excited-state dynamic investigations on C_{60}–porphyrin conjugates have revealed that the fullerene sphere is a particularly interesting electron acceptor in artificial photosynthetic models.[4] The characteristics of C_{60} are effectively in stark contrast with those of common acceptors with smaller size such as benzoquinone. Actually, accelerated charge separation and decelerated charge recombination has been observed in a fullerene-based acceptor–donor system when compared to the equivalent benzoquinone-based system.[4] This has been interpreted by the smaller reorganization energy (λ) of C_{60} compared with those of small acceptors: the smaller reorganization energy of C_{60} positions the photoinduced charge separation rate upward along the normal region of the Marcus parabolic curve, while forcing the charge recombination rate downward in the inverted region. The efficient photogeneration of long lived charge-separated states by photoinduced electron transfer is of particular interest for solar energy conversion and photovoltaic devices prepared from porphyrin–fullerene systems have shown promising energy conversion efficiencies.[5]

Whereas research focused on covalently bound C_{60}–porphyrin derivatives has received considerable attention, only a few related examples of non-covalent assemblies have been described so far.[6,7] In most cases, these non-covalent assemblies have been obtained from a C_{60} derivative bearing a pyridyl moiety and a metalloporphyrin through coordination to the metal ion.[6] Due to the apical

Keywords: Binding studies; Crown ether; Fullerene; Porphyrin; Supramolecular chemistry.
* Corresponding authors. Tel.: +33 561 33 31 00; fax: +33 561 55 30 03; e-mail addresses: solladie@lcc-toulose.fr; vandors@chimie.u-strasbg.fr; jfnierengarten@lcc-toulouse.fr

0040–4020/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2005.07.120

binding on the porphyrin subunit, the attractive van der Waals interaction of the fullerene sphere with the planar π-surface of the porphyrin seen for several covalent C_{60}–porphyrin derivatives[8] or in the solid state structures of porphyrin–fullerene co-crystals[9] is not possible in such arrays. It can also be mentioned here that the π–π stacking between C_{60} and porphyrin moieties is capable of enhancing the efficiency of the end-capping reactions of pseudo-rotaxanes and C_{60} thus leading to [2]-rotaxanes in higher yields.[10] As part of this research, we have recently shown that π-stacking of the two chromophores can have a dramatic effect on the recognition interactions in non-covalent C_{60}–porphyrin ensembles.[7] Specifically, a supramolecular complex has been obtained from porphyrin–crown ether conjugate **2** and methanofullerene derivative **1** bearing an ammonium function (Fig. 1). In addition to the ammonium–crown ether interaction, intramolecular stacking of the fullerene moiety and the porphyrin subunit has been evidenced in the supramolecular system. Due to this additional recognition element, the association constant (K_a) for the complex obtained from **1** and **2** is increased by two orders of magnitude when compared to K_a values previously found for the complexation of **1** with other crown ether derivatives. In this paper, we now report a full account on this work. In addition, we also show that more complex supramolecular systems are easily accessible by using similar interactions as illustrated by the association of cation **1** with porphyrin derivatives **3** and **4** bearing two crown ether subunits (Fig. 1).

2. Results and discussion

2.1. Synthesis

The synthesis of the functionalized methanofullerene derivative **1** is depicted in Scheme 1. Commercially available methyl 4-(aminomethyl)benzoate hydrochloride was converted to its *t*-butylcarbonyl (Boc) derivative **5** as previously reported.[11] $LiAlH_4$ reduction of compound **5** afforded compound **6** in 93% yield. Reaction of acid **7**[12] with benzylic alcohol **6** under esterification conditions using *N*,*N*′-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) led to malonic ester **8** in 78% yield. The functionalization of C_{60} with **8** is based on the Bingel reaction.[13] Nucleophilic addition of a stabilized α-halocarbanion to the C_{60} core, followed by an intramolecular nucleophilic substitution, leads to clean cyclopropanation of C_{60}.[14] It has been shown that the α-halomalonate can be generated in situ, and direct treatment of C_{60} with malonates in the presence of I_2 under basic conditions affords the corresponding methanofullerenes in good yields.[15] Treatment of C_{60} with **8**, iodine and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) in toluene at room temperature afforded methanofullerene **9** in 57% yield. Finally, removal of the Boc group with CF_3CO_2H afforded the targeted derivative **1** as its trifluoroacetate salt in a quantitative yield.

The synthesis of the porphyrin–crown ether derivatives **2**, **3**, and **4** is depicted in Scheme 2. Porphyrin **2** was obtained

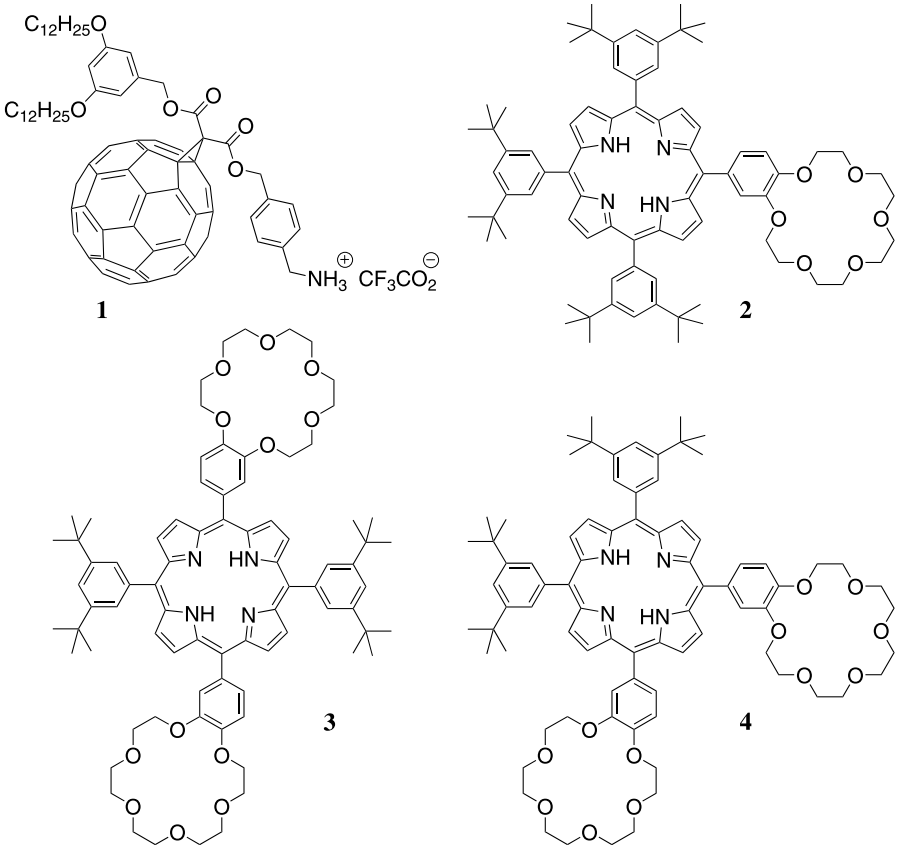
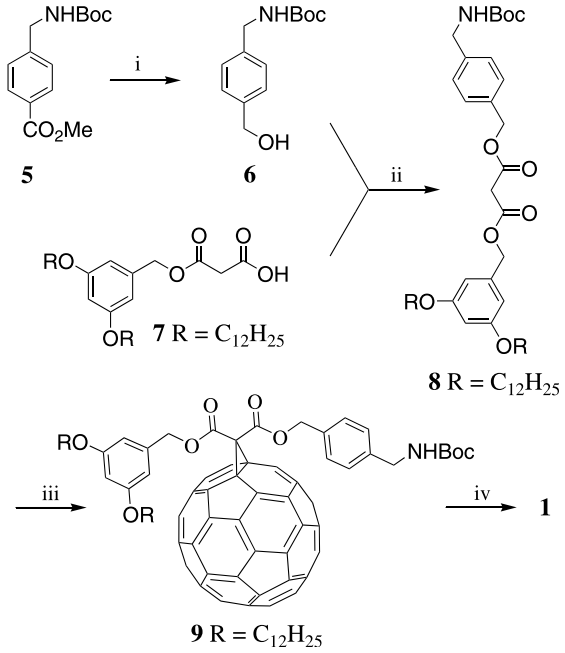
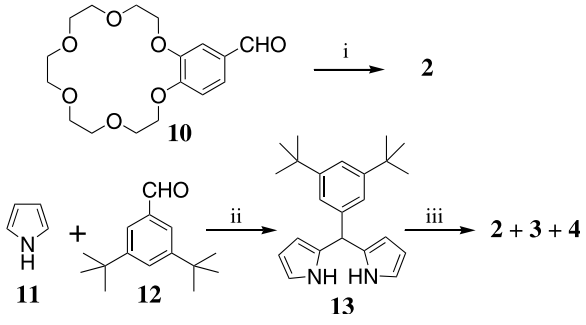


Figure 1. Compounds **1**–**4**.



Scheme 1. Reagents and conditions: (i) $LiAlH_4$, THF, 0 °C (93%); (ii) DCC, DMAP, CH_2Cl_2, 0 °C to rt (78%); (iii) C_{60}, I_2, DBU, toluene, rt (57%); (iv) CF_3CO_2H, CH_2Cl_2, rt (99%).

under the classical conditions developed by Lindsey.[16] Condensation of aldehydes **10**[17] (1 equiv) and **12** (3 equiv) with pyrrole (4 equiv) in $CHCl_3$ in the presence of $BF_3{\cdot}Et_2O$ as catalyst was followed by the oxidation of the porphyrinogens by *p*-chloranil. Compound **2** was thus obtained in 13% yield after purification.



Scheme 2. Reagents and conditions: (i) **12** (3 equiv), **11** (4 equiv), $BF_3{\cdot}Et_2O$, $CHCl_3$, rt then *p*-chloranil, Δ (13%); (ii) $BF_3{\cdot}Et_2O$, rt (69%); (iii) **10**, $BF_3{\cdot}Et_2O$, $CHCl_3$, rt then *p*-chloranil, Δ (**2**: 14%; **3**: 11%; **4**: 12%)

The selective preparation of *trans*-A_2B_2 porphyrin **3** was attempted by the condensation of dipyrromethane **13** and aldehyde **10**. Compound **13** was obtained in a good yield by acid catalyzed condensation of aldehyde **12** with an excess pyrrole in solvent free conditions. Treatment of dipyrromethane **13** with aldehyde **10** in $CHCl_3$ in the presence of a catalytic amount of $BF_3{\cdot}Et_2O$ yielded a mixture of porphyrins **2**, **3**, and **4**. Indeed, under these conditions, polypyrrolic rearrangement reactions took place as often observed during the condensation of aldehydes with 5-substituted dipyrromethane derivatives containing an unhired aryl substituent (lacking β-substituents).[18] As a result of this scrambling process, the desired *trans*-A_2B_2 porphyrin **3** was obtained together with other porphyrin derivatives. Indeed, compounds **2**, **3**, and **4** were isolated after tedious chromatographic purifications.

2.2. Binding studies

The ability of the fullerene derivative **1** to form supramolecular complexes with crown ether derivatives was first investigated with commercially available benzo-18-crown-6 (**14**) by NMR studies. As shown in Figure 2, the ^1H NMR spectra of **1** in $CDCl_3$ showed dramatic changes upon successive addition of **14**. The complexation-induced changes in chemical shifts were particularly important for the aromatic protons of the 4-(aminomethyl)benzyl moiety in **1** (H_c and H_d). Indeed, the signal of H_{c-d} in **1** was shifted upfield when benzo-18-crown-6 (**14**) was added. The latter observation maybe ascribed to the proximity of the aromatic unit of guest **14** within the supramolecular complex [(**1**)·(**14**)] in good agreement with the proposed structure. The association constant for the 1:1 complex based on the H_b chemical shifts of **1** was determined as $K_a = 2100 \pm 100\ M^{-1}$, corresponding to a Gibbs free energy of complexation $\Delta G^0 = -4.5$ kcal/mol. Identical results within the error range were obtained when the complexation-induced changes in chemical shifts were monitored for the other protons of **1**.

The binding behavior of ammonium **1** to porphyrin **2** was also investigated by ^1H NMR titration in $CDCl_3$ at 298 K. As depicted in Figure 3A, the comparison between the ^1H NMR spectra of **1**, **2** and mixtures of both components revealed the apparition of new sets of signals as well as complexation-induced changes in chemical shifts. This is particularly visible for the pyrrolic protons of the porphyrin moiety and the signals arising from the crown ether subunit. The latter observations suggest the existence of two conformers for the supramolecular complex obtained upon association of the two components, one being in fast exchange with uncomplexed **1** and **2** on the NMR time-scale, the other one in slow exchange as shown in Figure 3B. On the one hand, the initial ammonium–crown ether association leading to conformer **A** is responsible for the observed complexation-induced changes in chemical shifts upon addition of ammonium **1** to solutions of **2**. In principle, association of the two molecular units should be possible by π-stacking of the two chromophores only. However, no significant changes in chemical shifts were observed in the ^1H NMR spectrum of **1** upon addition of compound **9** thus showing that the C_{60}–porphyrin interaction does not take place in the absence of ammonium–crown ether recognition. On the other hand, the new sets of signals seen in the ^1H NMR spectra correspond to conformer **B**. The dramatic upfield shift observed for the pyrrolic protons in **B** must be the result of the close proximity of the fullerene sphere suggesting that supramolecule [(**1**)·(**2**)] adopts a conformation in which the C_{60} subunit is located atop the porphyrin macrocycle. Further evidence for C_{60}–porphyrin interactions came from UV–vis measurements. Addition of increasing amount of **1** to a CH_2Cl_2 solution of **2** causes a red shift of the Soret band, no further spectral changes being observed beyond the addition of ca. 5 equiv of **1** ($\lambda_{max} = 421$ and 427 nm before and after addition of **1**, respectively). The latter observation confirmed the existence of the C_{60}–porphyrin interactions in [(**1**)·(**2**)]. Effectively, red shifts in

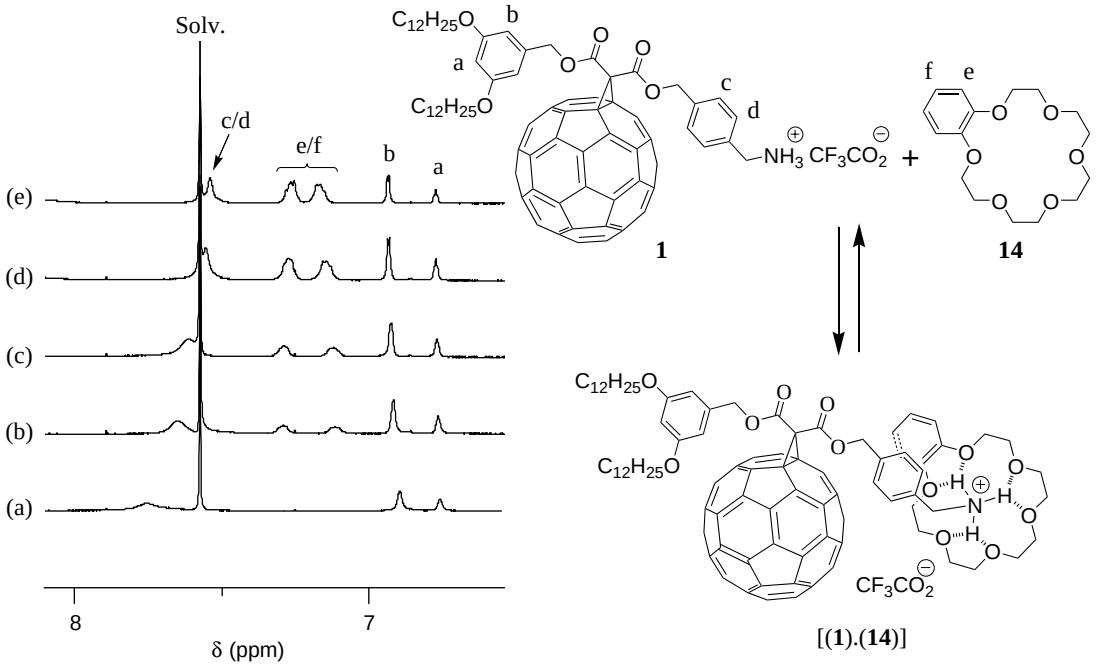


Figure 2. ^{1}H NMR spectra (300 MHz, $CDCl_3$, 298 K) of **1** with 0 (a), 0.25 (b), 0.5 (c), 1.25 (d) and 2 equiv (e) of **14**.

the Soret band have been observed for covalent C_{60}–porphyrin conjugates due to intramolecular π-stacking of the two chromophores.[8] As reported in detail in the preliminary communication,[7] the K_a value for the binding of **1** to **2** was determined by a fluorescence titration. A surprisingly high value for the association constant K_a = 375,000 M^{-1} was obtained. Effectively, the association constant between porphyrin **2** and fullerene **1** is unexpectedly increased by two orders of magnitude when compared to the K_a value found for the complexation of **1** with crown ether **14**. Such a stabilization of the supramolecular complex formed between **1** and **2**, which can be attributed to an additional intramolecular interaction, provides further evidence for the π-stacking of the fullerene moiety and the porphyrin subunit in [(**1**)·(**2**)] suggested by the NMR studies.

The binding behavior of **1** to porphyrins **3** and **4** was also investigated by ^{1}H NMR in $CDCl_3$ at 298 K. As discussed for the NMR binding studies of **1** to **2**, apparition of new sets of signals and complexation-induced changes in chemical shifts were observed in the ^{1}H NMR spectra of **3** and **4** upon addition of ammonium **1** revealing the effective formation of supramolecular structures. However, the interpretation of the NMR spectra appeared difficult due to the possible formation of 1:1 and 2:1 complexes. It must, however, be noted that, as in the case of [(**1**)·(**2**)], intramolecular C_{60}–porphyrin interactions were evidenced for the supramolecular complexes obtained from the association of both **3** and **4** with ammonium **1**. Effectively, some signals corresponding to the pyrrolic protons were dramatically up-field shifted in the ^{1}H NMR spectra of **3** and **4** upon addition of methanofullerene **1**. Furthermore, by adding increasing amount of **1** to CH_2Cl_2 solutions of **3** and **4**, the characteristic red shift of the Soret band due to the C_{60}–porphyrin interactions was observed in the UV–vis spectra.

2.3. Mass spectrometric characterization

The supramolecular complexes obtained from fullerene derivative **1** and the porphyrin–crown ether conjugate **2**–**4** were further characterized in the gas phase by electrospray mass spectrometry (ES-MS). Unlike other mass spectrometric methods, ES-MS allows pre-existing ions in solution to be transferred to the gas phase without fragmentation. This soft ionization technique, mainly developed by Fenn and co-workers,[19] is now commonly applied to the study of large non-covalent assemblies[20] and appears as ideally suited to characterize the non-covalent complexes formed from **1** and **2**–**4**. The positive ES mass spectrum (Fig. 4) recorded from a 1:1 mixture of **1** and **2** displayed a singly charged ion peak at m/z=2587.2, which can be assigned to the 1:1 complex after loss of the trifluoroacetate counteranion (calculated m/z=2587.24).

As shown in Figure 5, the positive ES mass spectrum obtained under mild conditions (extracting cone voltage V_c=50 V) from a 2:1 mixture of **1** and **4** is characterized by a doubly charged ion peak at m/z=2055.2, which can be assigned to the 2:1 complex after loss of the two trifluoroacetate counteranions (calculated m/z=2055.45). The peak corresponding to the 1:1 complex could almost not be detected under these conditions thus suggesting that the self-assembled array [(**1**)·(**3**)$_2$] is the most abundant species in the analysed solution.

ES-MS analysis of a 2:1 mixture of **1** and **3** gave similar results. At low V_c, only the signal corresponding to the supramolecular complex [(**1**)·(**3**)$_2$] was observed (Fig. 6). Under more brutal conditions (V_c=180 V), the spectrum was still dominated by the doubly charged ion peak at m/z=2055.6 but a singly charged ion peak attributed to the 1:1 complex was also observed at m/z=2709.6 (calculated m/z=2709.28). The intensity of the latter signal is increased

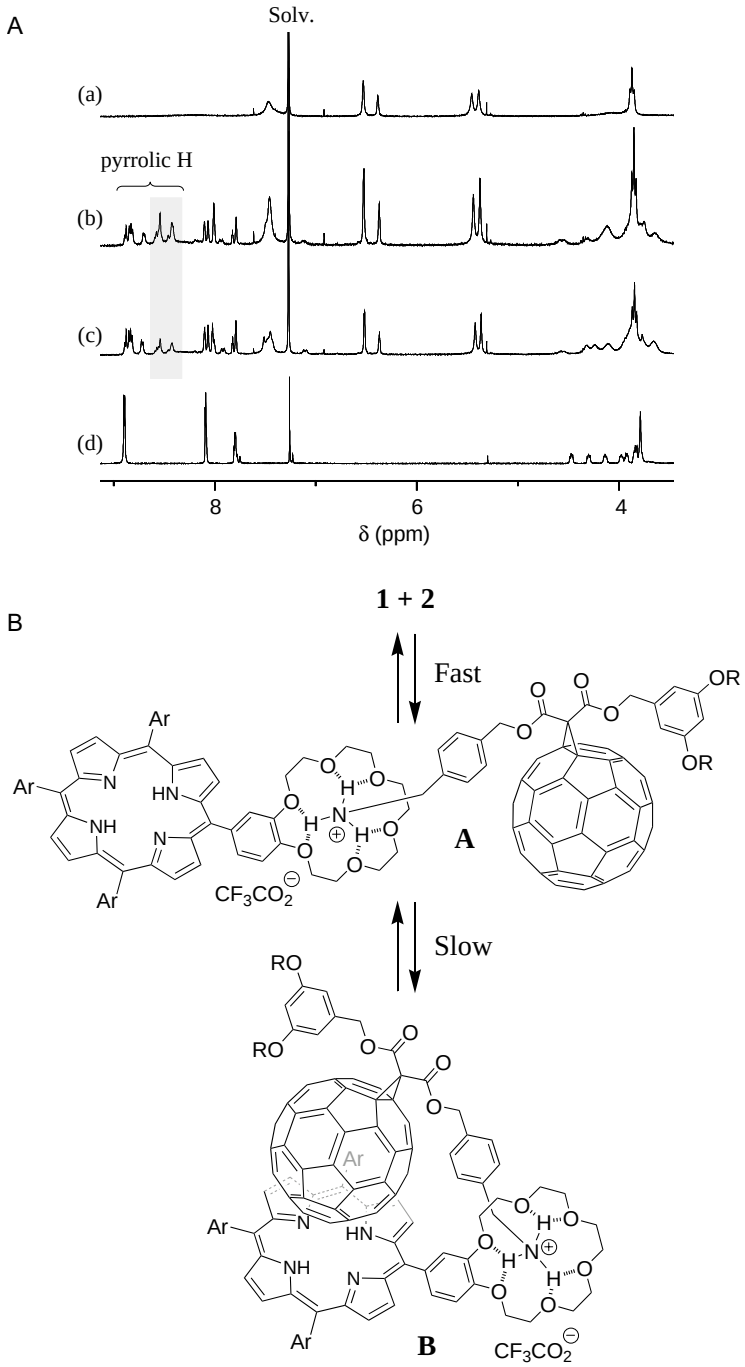


Figure 3. (A) ^{1}H NMR spectra ($CDCl_3$, 300 MHz, 298 K) of **1** (a), **2** (d), a 2:1 mixture of **1** and **2** (b) and a 1:1 mixture of **1** and **2** (c); the signals of the pyrrolic protons of **B** are highlighted. (B) Schematic representation of the two conformers of the supramolecular complex obtained upon association of **1** and **2**. **A** is in fast exchange with uncomplexed **1** and **2** on the NMR time-scale and **B** in slow exchange.

as the V_c value is increased, thus the peak corresponding to [(**1**)·(**3**)] must result from the fragmentation of the 2:1 supramolecular complex [(**1**)·(**3**)$_2$] initially present in solution. A similar behavior was also observed for the ES mass spectra of the 2:1 mixture of **1** and **4** recorded at various V_c values. In both cases, the fragmentation is still limited thus showing the high stability of the non-covalent arrays [(**1**)·(**3**)$_2$] and [(**1**)·(**4**)$_2$]. This observation further corroborates the existence of intramolecular stacking interactions between the fullerene moiety and the porphyrin subunit in [(**1**)·(**3**)$_2$] and [(**1**)·(**4**)$_2$] as suggested by the NMR and UV–vis data.

2.4. Preliminary fluorescence studies

The complexation between **1** and **2**–**4** was finally investigated in CH_2Cl_2 by luminescence studies. A large decrease in intensity of the characteristic porphyrin emission was observed when the fullerene ammonium salt **1** was added to a CH_2Cl_2 solution of **2**, **3** or **4**. This decrease can be attributed, at least in part, to the reabsorption of the porphyrin luminescence by the fullerene derivative **1**. However, experiments carried out in parallel with mixtures of **2**, **3** or **4** and methanofullerene **9**, which are not able to form a supramolecular complex show that the decrease in

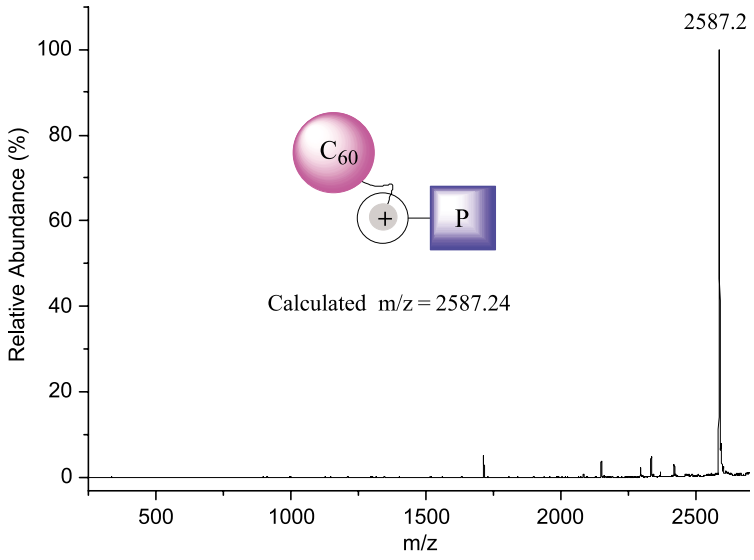


Figure 4. ES mass spectrum (V_c = 20 V) recorded from an equimolar mixture (10^{-5} M) of **1** and **2** in CH_2Cl_2.

luminescence intensity could mainly originate from an intramolecular photoinduced process in the supramolecular C_{60}–porphyrin conjugates. Further evidence for an intramolecular quenching of the porphyrin excited-state by the fullerene moiety in [(**1**)·(**2**)], [(**1**)·(**3**)$_2$] and [(**1**)·(**4**)$_2$] was obtained from the following experiments. Addition of DBU to mixtures of **1** and **2**, **3** or **4** in CH_2Cl_2 causes an increase of the porphyrin emission. Actually, the fluorescence intensity of the resulting solution was found to be similar to that of the reference solution containing **9** and **2**, **3** or **4**. In other words, the treatment with a base deprotonates the ammonium moiety of **1** and, thereby, disrupts the non-covalent bonding interactions that brought the components together. Addition of trifluoroacetic acid to the CH_2Cl_2 solution regenerates the ammonium center, thus allowing the formation of the supramolecular complexes, and the luminescence intensity of final solution is the same as that of the starting mixture of **1** and **2**, **3** or **4**. The observed decrease in luminescence intensity originates from either energy or electron transfer from the photoexcited porphyrin to the C_{60} acceptor in the supramolecular complexes. Steady state measurements are not sufficient to determine the nature of the quenching because the residual porphyrin emission overlaps the much weaker fullerene emission, thus prohibiting clean excitation spectroscopy. Detailed photophysical studies are currently under investigation and will be reported in due time.

3. Conclusions

A methanofullerene derivative bearing an ammonium unit (**1**) was synthesized. Its ability to form supramolecular complexes with crown ether derivatives was first evidenced with commercially available benzo-18-crown-6 (**14**) by NMR studies. The value found for the association constant is quite low (2100 M^{-1} in $CDCl_3$ at 298 K) but consistent with association constants already reported for supramolecular associates resulting from ammonium–crown ether interactions.[20d,21] The assembly of the C_{60}–ammonium

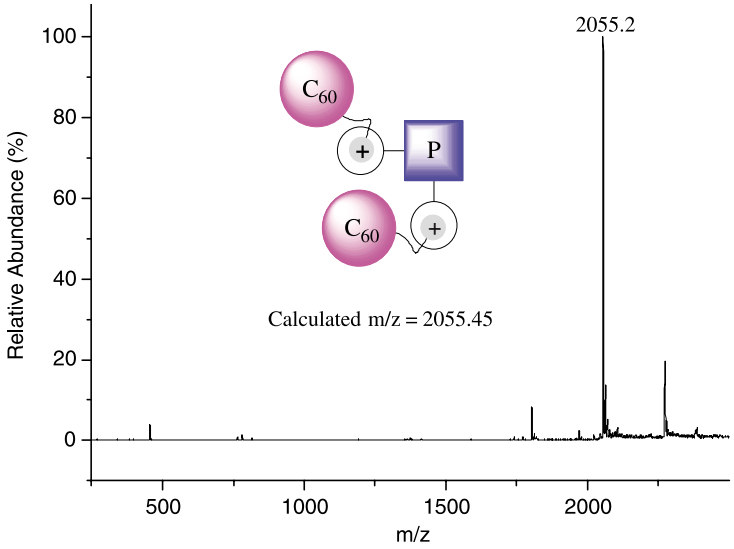


Figure 5. ES mass spectrum (V_c = 50 V) recorded from a 2:1 mixture of **1** and **4** in CH_2Cl_2.

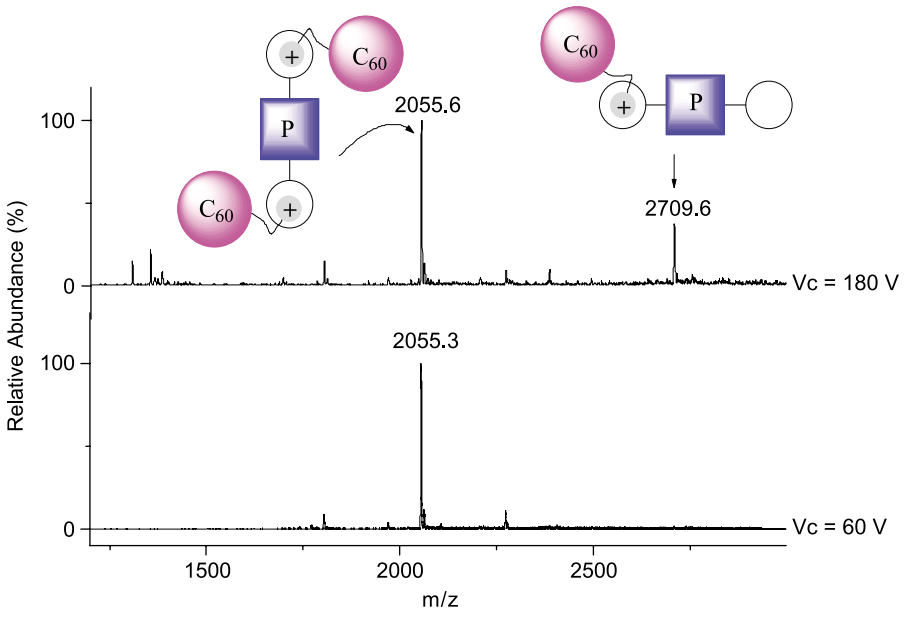


Figure 6. ES mass spectra recorded at different V_c from a 2:1 mixture of **1** and **3** in CH_2Cl_2.

cation **1** with a porphyrin derivative bearing one crown ether moiety (**2**) was also investigated. The NMR and UV–vis binding studies revealed an interesting behavior. Effectively, in addition to the ammonium–crown ether recognition, intramolecular stacking of the fullerene moiety and the porphyrin subunit has been evidenced. Due to this additional recognition element, the association constant for the supramolecular complex is increased by two orders of magnitude when compared to the K_a values found for the complexation of **1** with crown ether **14**. Finally, more complex non-covalent systems resulting from the association of cation **1** with porphyrin derivatives **3** and **4** bearing two crown ether subunits were investigated. Intramolecular C_{60}–porphyrin interactions have also been evidenced within the resulting supramolecular complexes. As a result, the 2:1 complexes are very stable as shown by the ES-MS studies. These supramolecular arrays containing two fullerene subunits appear to be particularly interesting candidates for photophysical studies. Effectively, the beneficial effect resulting from the presence of a second fullerene moiety on the properties of C_{60}-dumbbells has been recently highlighted by Martin and co-workers.[22]

In conclusion, this work paves the way toward the construction of new stable non-covalent supramolecular arrays combining porphyrin and fullerene units. Upon a suitable choice of the molecular components, new supramolecular architectures displaying interesting photoinduced intercomponent processes can be envisaged. Work in this direction is under progress in our laboratories.

4. Experimental

4.1. General

Reagents and solvents were purchased as reagent grade and used without further purification. THF was distilled over sodium benzophenone ketyl. Compounds **5**,[11] **7**,[12] and **10**[17] were prepared as previously reported. All reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration were done at water aspirator pressure and drying in vacuo at 10^{-2} Torr. Column chromatography: silica gel 60 (230–400 mesh, 0.040–0.063 mm) was purchased from Merck. Thin-layer chromatography (TLC) was performed on glass sheets coated with silica gel 60 F_{254} purchased from Merck, visualization by UV light. UV–vis spectra were recorded on a Hitachi U-3000 spectrophotometer. NMR spectra were recorded on a Bruker AC 300 with solvent peaks as reference. Elemental analyses were performed by the analytical service at the Institut Charles Sadron, Strasbourg.

4.1.1. Compound 6. A 1 M $LiAlH_4$ solution in dry THF (4 mL, 4.0 mmol) was added dropwise to a stirred solution of **5** (0.9 g, 3.39 mmol) in dry THF (100 mL) at 0 °C. The resulting mixture was stirred for 5 h at 0 °C, then MeOH was carefully added. The resulting mixture was filtered (Celite) and evaporated. Column chromatography (SiO_2, CH_2Cl_2/2% MeOH) yielded **6** (0.75 g, 93%) as a colorless glassy product. ^{1}H NMR (300 MHz, $CDCl_3$): 7.31 (AB, J=7 Hz, 4H), 4.83 (broad s, 1H), 4.69 (d, J=6 Hz, 2H), 4.31 (d, J=6 Hz, 2H), 1.67 (broad s, 1H), 1.46 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): 155.9, 140.0, 138.2, 127.6, 127.2, 79.5, 64.9, 44.3, 28.3. Anal. Calcd for $C_{13}H_{19}O_3N$: C 65.80, H 8.07, N 5.90. Found: C 66.52, H 8.18, N 6.03.

4.1.2. Compound 8. DCC (2.57 g, 12.6 mmol) was added to a stirred solution of **6** (0.745 g, 3.14 mmol), **7** (1.94 g, 3.45 mmol) and DMAP (0.153 g, 1.26 mmol) in CH_2Cl_2 (100 mL) at 0 °C. After 1 h, the mixture was allowed to slowly warm to room temperature (within 1 h), then stirred for 12 h, filtered and evaporated to dryness. Column chromatography (SiO_2, CH_2Cl_2/hexane 4:1) yielded **8** (1.93 g, 78%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): 7.28 (AB, J=7 Hz, 4H), 6.46 (d, J=2 Hz, 2H), 6.41 (t, J=2 Hz, 1H), 5.16 (s, 2H), 5.09 (s, 2H), 4.84 (broad s, 1H), 4.31 (d, J=6 Hz, 2H), 3.91 (t, J=7 Hz, 4H), 3.47 (s,

2H), 1.75 (m, 4H), 1.44 (s, 9H), 1.30 (m, 36H), 0.88 (t, J= 7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 166.2, 160.4, 155.8, 139.3, 137.1, 134.3, 128.6, 127.6, 106.4, 101.1, 79.5, 68.1, 67.2, 66.9, 44.3, 41.5, 31.9, 29.65, 29.6, 29.5, 29.4, 29.3, 29.2, 28.4, 26.0, 22.7, 14.1.

4.1.3. Compound 9. DBU (0.16 mL, 1.04 mmol) was added to a stirred solution of C_{60} (300 mg, 0.41 mmol), I_2 (116 mg, 0.45 mmol) and **8** (326 mg, 0.41 mmol) in toluene (500 mL) at room temperature. The solution was stirred for 12 h at room temperature, filtered through a short plug of SiO_2 (toluene) and evaporated. Column chromatography (SiO_2, CH_2Cl_2/hexane 7:3) yielded **9** (0.71 g, 57%) as a dark brown solid. UV–vis (CH_2Cl_2): 256 (125,500), 325 (35,900), 425 (3300), 688 (190); ^{1}H NMR (300 MHz, $CDCl_3$): 7.35 (AB, J=7 Hz, 4H), 6.56 (d, J=2 Hz, 2H), 6.42 (t, J=2 Hz, 1H), 5.47 (s, 2H), 5.39 (s, 2H), 4.87 (broad s, 1H), 4.32 (d, J= 6 Hz, 2H), 3.89 (t, J=7 Hz, 4H), 1.75 (m, 4H), 1.43 (s, 9H), 1.30 (m, 36H), 0.88 (t, J=7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 163.3, 163.2, 160.4, 155.8, 145.1, 145.05, 145.0, 144.95, 144.85, 144.8, 144.6, 144.5, 144.4, 143.8, 143.7, 143.0, 142.9, 142.8, 142.1, 141.8, 141.7, 140.8, 140.7, 139.6, 139.1, 138.8, 136.4, 133.6, 129.1, 127.7, 107.0, 101.6, 79.5, 71.3, 68.8, 68.5, 68.1, 51.7, 44.3, 31.9, 29.7, 29.6, 29.4, 29.3, 29.2, 28.4, 26.1, 22.7, 14.1. Anal. Calcd for $C_{107}H_{73}O_8N$: C 85.64, H 4.90, N 0.93. Found: C 85.41, H 4.90, N 0.84.

4.1.4. Compound 1. A solution of **9** (393 mg, 0.26 mmol) and CF_3CO_2H (20 mL) in CH_2Cl_2 (40 mL) was stirred at room temperature for 4 h. The mixture was then washed with water, dried ($MgSO_4$), filtered and evaporated to dryness. Recrystallization from CH_2Cl_2/hexane yielded **1** (397 mg, 99%) as a dark brown solid. UV–vis (CH_2Cl_2): 257 (130,200), 326 (36,900), 425 (3200), 687 (180); ^{1}H NMR (300 MHz, $CDCl_3$): 7.46 (AB, J=8 Hz, 4H), 6.51 (d, J=2 Hz, 2H), 6.37 (t, J=2 Hz, 1H), 5.46 (s, 2H), 5.37 (s, 2H), 4.16 (s, 2H), 3.86 (t, J=7 Hz, 4H), 1.67 (m, 4H), 1.25 (m, 36H), 0.87 (t, J=7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 163.4, 163.3, 160.4, 145.2, 145.1, 144.9, 144.6, 144.4, 143.8, 142.9, 142.1, 141.8, 141.7, 140.9, 140.8, 139.3, 138.6, 136.4, 136.1, 129.4, 129.1, 107.3, 101.8, 71.2, 69.0, 68.2, 51.6, 31.9, 29.7, 29.5, 29.4, 29.3, 26.2, 22.7, 14.2; FAB-MS: 1401.5 ($[M-CF_3CO_2^-]^+$, calcd for $C_{102}H_{66}O_6N$: 1401.6). Anal. Calcd for $C_{104}H_{66}O_8NF_3\cdot 0.8\ CH_2Cl_2$: C 79.54, H 4.31, N 0.89. Found: C 79.74, H 4.35, N 0.83.

4.1.5. Compound 2. A 3.2 M solution of $BF_3\cdot OEt_2$ (200 μL) in $CHCl_3$ was added to a stirred solution of **10** (170 mg, 0.50 mmol), **11** (140 μL, 2.02 mmol) and **12** (331 mg, 1.51 mmol) in $CHCl_3$ (200 mL) at room temperature under argon. The resulting solution was stirred for 1 h and *p*-chloranil (382 mg, 1.56 mmol) added. The mixture was then refluxed for 1 h and evaporated. Column chromatography (SiO_2, CH_2Cl_2/MeOH 90:10) gave **2** (75 mg, 13%) as a dark purple solid. UV–vis (CH_2Cl_2): 421 (455,000), 517 (16,500), 553 (9800), 592 (5300), 648 (5300); ^{1}H NMR ($CDCl_3$, 300 MHz): 8.90 (s, 8H), 8.09 (d, J=2 Hz, 4H), 8.08 (d, J=2 Hz, 2H), 7.80 (t, J=2 Hz, 2H), 7.79 (d, J=2 Hz, 1H), 7.78 (t, J=2 Hz, 1H), 7.76 (dd, J=7, 2 Hz, 1H), 7.24 (d, J=7 Hz, 1H), 4.47 (t, J=6 Hz, 2H), 4.30 (t, J=6 Hz, 2H), 4.14 (t, J=6 Hz, 2H), 3.98 (t, J= 6 Hz, 2H), 3.93 (m, 2H), 3.85 (m, 4H), 3.79 (m, 6H), 1.54 (s, 36H), 1.53 (s, 18H), −2.69 (broad s, 2H).

4.1.6. Compound 13. A 3.2 M solution of $BF_3\cdot OEt_2$ (0.28 mL) in $CHCl_3$ was added to a stirred mixture of **12** (804 mg, 3.68 mmol) and pyrrole (10 mL, 36.6 mmol) at room temperature under argon. After 2 h, the resulting dark brown solution was evaporated. The residue was dissolved in CH_2Cl_2, washed with a 1 M aqueous NaOH solution (2×) and evaporated. Column chromatography (SiO_2, hexane/ CH_2Cl_2/Et_3N 94:5:1) gave **13** (848 mg, 69%) as a brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.87 (broad s, 2H), 7.49 (t, J= 2 Hz, 1H), 7.22 (d, J=2 Hz, 2H), 6.73 (m, 2H), 6.29 (m, 2H), 6.06 (m, 2H), 5.52 (s, 1H), 1.46 (s, 18H).

4.1.7. Compounds 2, 3, and 4. A 3.2 M solution of $BF_3\cdot OEt_2$ (0.2 mL) in $CHCl_3$ was added to a stirred solution of **13** (334 mg, 1 mmol) and **10** (340 mg, 1 mmol) in $CHCl_3$ (200 mL) at room temperature under argon. The resulting dark red solution was stirred for 1 h and *p*-chloranil (367 mg, 1.5 mmol) added. The mixture was then refluxed for 1 h and evaporated. Column chromatography (SiO_2) gave **2** (eluent: CH_2Cl_2/MeOH 90:10, 54 mg, 14%), **3** (eluent: CH_2Cl_2/MeOH 88:12, 73 mg, 11%), **4** (eluent: CH_2Cl_2/MeOH 85:15, 80 mg, 12%).

Compound **3**. Dark purple solid. UV–vis (CH_2Cl_2): 422 (230,000), 519 (10,700), 546 (7300), 594 (6500), 645 (6600); ^{1}H NMR ($CDCl_3$, 300 MHz): 8.88 (s, 8H), 8.07 (d, J=2 Hz, 4H), 7.80 (t, J=2 Hz, 2H), 7.77 (broad s, 2H), 7.74 (broad d, J=7 Hz, 2H), 7.23 (d, J=7 Hz, 2H), 4.46 (t, J=6 Hz, 4H), 4.29 (t, J=6 Hz, 4H), 4.13 (t, J=6 Hz, 4H), 3.97 (t, J=6 Hz, 4H), 3.93 (m, 4H), 3.81 (m, 8H), 3.78 (m, 12H), 1.53 (s, 36H), −2.74 (broad s, 2H).

Compound **4**. Dark purple solid. UV–vis (CH_2Cl_2): 422 (280,000), 520 (19,400), 552 (14,300), 594 (9700), 646 (9500); ^{1}H NMR ($CDCl_3$, 300 MHz): 8.88 (m, 8H), 8.08 (d, J=2 Hz, 2H), 8.07 (d, J=2 Hz, 2H), 7.81 (t, J=2 Hz, 1H), 7.80 (t, J=2 Hz, 1H), 7.78 (m, 2H), 7.74 (m, 2H), 7.23 (m, 2H), 4.46 (m, 4H), 4.29 (m, 4H), 4.12 (m, 4H), 3.97 (m, 4H), 3.90 (m, 4H), 3.82 (m, 8H), 3.78 (m, 12H), 1.54 (s, 18H), 1.53 (s, 18H), −2.73 (broad s, 2H).

4.2. ES-MS

Samples for ES-MS were prepared from stock solutions of **1**, **2**, **3**, and **4** in CH_2Cl_2 to achieve a concentration of 10^{-5} M. Positive ES mass spectra were obtained on an ES triple quadrupole mass spectrometer Quattro II with a mass-to-charge (m/z) ratio range extended to 8000 (Micromass, Altrincham, UK). The electrospray source was heated to 40 °C. Sample solutions were introduced into the mass spectrometer source with a syringe pump (Harvard type 55 1111: Harvard Apparatus Inc., South Natick, MA, USA) with a flow rate of 3 μL min^{-1}. The extraction cone voltage (V_c) was systematically changed from 20 to 180 V. Calibration was performed using protonated horse myoglobin. Scanning was performed in the MCA (Multi Channel Analyzer) mode, and several scans were summed to obtain the final spectrum.

4.3. Determination of the association constant K_a by NMR titration

The ^{1}H NMR binding studies were performed at 298 K in $CDCl_3$. The concentration of **1** was kept constant (0.5 mM). Increasing amounts of **14** were added (0.2–2 mM; 12 data points) and the chemical shift (δ) of the aromatic protons in **1** were observed. The complexation-induced variation of the chemical shift ($\Delta\delta$) was plotted against the concentration of **14**. The complexation data (K_a, ΔG^0, $\Delta\delta_{sat}$) were obtained by iteration using a nonlinear regression analysis curve-fitting software developed in the laboratories of Prof. François Diederich.[23] The experiment was performed in duplicate.

Acknowledgements

This work was supported by the CNRS and the French Ministry of Research (*ACI Jeunes Chercheurs* to N.S.).

References and notes

1. (a) Martín, N.; Sánchez, L.; Illescas, B.; Pérez, I. *Chem. Rev.* **1998**, *98*, 2527–2547. (b) Nierengarten, J.-F. *Sol. Energy Mater. Sol. Cells* **2004**, *83*, 187–199. (c) Segura, J. L.; Martín, N.; Guldi, D. M. *Chem. Soc. Rev.* **2005**, *34*, 31–47. (d) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Soc. Rev.* **2004**, *104*, 4891–4945. (e) Nierengarten, J.-F. *New J. Chem.* **2004**, *28*, 1177–1191.
2. Guldi, D. M. *Chem. Soc. Rev.* **2002**, *31*, 22–36 and references therein.
3. (a) Imahori, H.; Sakata, Y. *Eur. J. Org. Chem.* **1999**, 2445–2457. (b) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40–48. (c) Imahori, H. *J. Phys. Chem. B* **2004**, *108*, 6130–6143. (d) Imahori, H. *Org. Biomol. Chem.* **2004**, *2*, 1425–1433.
4. Imahori, H.; Hagiwara, K.; Akiyama, T.; Aoki, M.; Taniguchi, S.; Okada, T.; Shirakawa, M.; Sakata, Y. *Chem. Phys. Lett.* **1996**, *263*, 545–550.
5. Imahori, H.; Fukuzumi, S. *Adv. Funct. Mater.* **2004**, *14*, 525–536 and references therein.
6. (a) Armaroli, N.; Diederich, F.; Echegoyen, L.; Habicher, T.; Flamigni, L.; Marconi, G.; Nierengarten, J.-F. *New J. Chem.* **1999**, *23*, 77–83. (b) D'Souza, F.; Deviprasad, G. R.; Rahman, M. S.; Choi, J.-P. *Inorg. Chem.* **1999**, *38*, 2157–2160. (c) Da Ros, T.; Prato, M.; Guldi, D. M.; Alessio, E.; Ruzzi, M.; Pasimeni, L. *Chem. Commun.* **1999**, 635–636. (d) Guldi, D. M.; Da Ros, T.; Braiuca, P.; Prato, M.; Alessio, E. *J. Mater. Chem.* **2002**, *12*, 2001–2008. (e) Wilson, S. R.; MacMahon, S.; Tat, F. T.; Jarowski, P. D.; Schuster, D. I. *Chem. Commun.* **2003**, 226–227.
7. Solladié, N.; Walther, M. E.; Gross, M.; Figueira Duarte, T. M.; Bourgogne, C.; Nierengarten, J.-F. *Chem. Commun.* **2003**, 2412–2413.
8. (a) Schuster, D. I.; Jarowski, P. D.; Kirschner, A. N.; Wilson, S. R. *J. Mater. Chem.* **2002**, *12*, 2041–2047. (b) Armaroli, N.; Marconi, G.; Echegoyen, L.; Bourgeois, J.-P.; Diederich, F. *Chem. Eur. J.* **2000**, *6*, 1629–1645.
9. Boyd, P. D. W.; Reed, C. A. *Acc. Chem. Res.* **2005**, *38*, 235–242 and references therein.
10. Sasabe, H.; Kihara, N.; Furusho, Y.; Mizuno, K.; Ogawa, A.; Takata, T. *Org. Lett.* **2004**, *6*, 3957–3960.
11. Zistler, A.; Kock, S.; Schlüter, A. D. *J. Chem. Soc., Perkin Trans 1* **1999**, 501–508.
12. Felder, D.; Gutiérrez Nava, M.; del Pilar Carreon, M.; Eckert, J.-F.; Luccisano, M.; Schall, C.; Masson, P.; Gallani, J.-L.; Heinrich, B.; Guillon, D.; Nierengarten, J.-F. *Helv. Chim. Acta* **2002**, *85*, 288–319.
13. Bingel, C. *Chem. Ber.* **1993**, *126*, 1957–1959.
14. Nierengarten, J.-F. In *Fullerenes: from Synthesis to Optoelectronic Applications*; Guldi, D. M., Martin, N., Eds.; Kluwer Academic: Dordrecht (The Netherlands), 2002; pp 51–79.
15. Nierengarten, J.-F.; Gramlich, V.; Cardullo, F.; Diederich, F. *Angew. Chem., Int. Ed.* **1996**, *35*, 2101–2103.
16. Lindsey, J. S.; Wagner, R. W. *J. Org. Chem.* **1989**, *54*, 828.
17. Handyside, T. M.; Lockhart, J. C.; McDonnell, M. B.; Rao, P. V. S. *J. Chem. Soc., Dalton Trans.* **1982**, 2331–2336.
18. (a) Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864–2872. (b) Geier, G. R., III,; Littler, B. J.; Lindsey, J. S. *J. Chem. Soc., Perkin Trans. 2* **2001**, 701–711.
19. Fenn, J. B.; Mann, M.; Meng, C. K.; Wong, S. F.; Whitehouse, C. M. *Science* **1989**, *246*, 64–66.
20. (a) Nierengarten, H.; Rojo, J.; Leize, E.; Lehn, J.-M.; Van Dorsselaer, A. *Eur. J. Inorg. Chem.* **2002**, 573–579. (b) Rogniaux, H.; Van Dorsselaer, A.; Barth, P.; Biellmann, J.-F.; Barbanton, J.; van Zandt, M.; Chevrier, B.; Howard, E.; Mitschler, A.; Potier, N.; Urzhumtseva, L.; Moras, D.; Poodjarny, A. *J. Am. Soc. Mass Spectrom.* **1999**, *10*, 209–212. (c) Gutiérrez-Nava, M.; Jaeggy, M.; Nierengarten, H.; Masson, P.; Guillon, D.; Van Dorsselaer, A.; Nierengarten, J.-F. *Tetrahedron Lett.* **2003**, *44*, 3039–3042. (d) Gutiérrez-Nava, M.; Nierengarten, H.; Masson, P.; Van Dorsselaer, A.; Nierengarten, J.-F. *Tetrahedron Lett.* **2003**, *44*, 3043–3046. (e) Schalley, C. A. *Int. J. Mass Spectrom.* **2000**, *194*, 11–39.
21. Lehn, J.-M. *Supramolecular Chemistry, Concepts and Perspectives*; VCH: Weinheim, Germany, 1995.
22. Sanchez, L.; Herrantz, A.; Martin, N. *J. Mater. Chem.* **2005**, *15*, 1409–1421.
23. Peterson, B. Associate V.1.6, Ph.D. Thesis, University of California, Los Angeles, 1994.