PCCP

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

Journal Name

ARTICLE

[60]Fullerene-Porphyrin [*n*]Pseudorotaxanes: Self-Assembly, Photophysics and Third-order NLO responses

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

L. Đorđević,[a] T. Marangoni,[a] F. De Leo,[b] I. Papagiannouli,[c,d] P. Aloukos,[c,d] S. Couris,*[c,d] E. Pavoni,[e] F. Monti,[e] N. Armaroli,*[e] M. Prato[a] and D. Bonifazi*[a,b]

By means of different spectroscopic techniques, we investigate a novel series of free base porphyrin derivatives (H_2TPP), connected to dibenzo-24-crown-8 (DB24C8) moieties, which undergo self-assembly with different methano[60]fullerene units bearing dibenzylammonium (DBA) cations. The formation of both [*2*] and [*3*]pseudorotaxanes was proved by means of NMR, UV-Vis-NIR, absorption and emission spectroscopies. With the support of molecular modelling studies, spectroscopic investigations showed the presence of a secondary interaction between the porphyrin and the C_{60} chromophores leading to the formation of different types of "face-to-face" assemblies. Remarkably, investigations of the Non-Linear Optical (NLO) response of these supramolecular systems showed that individual porphyrin and fullerene derivatives exhibit significantly lower second hyperpolarizability values when compared to their pseudorotaxanes functionalised counterparts. This proves that this class of supramolecular materials possesses relevant NLO response, which strongly depends on the structural arrangement of the chromophores in solution.

Introduction

In the last decades, extensive research efforts have been made to develop organic materials that exhibit large and fast third-order optical nonlinearities[1-6] being potential candidates for optical data storage technologies.[7-9] Among the different families of π-conjugated scaffolds showing fast non-linear optical (NLO) output,[6,10-14] fullerenes[8,15-17] and porphyrins[18-20] – along with their hybrid conjugates – are excellent candidates due to their large excited-state absorption cross sections. Furthermore, both fullerene and porphyrin derivatives can be easily functionalised with other electron-donating and -withdrawing groups, offering the ability to finely tune the NLO response of the final donor-acceptor system.[21-23] Although a vast number of elegant studies on the photophysical properties of fullerene-porphyrin systems has been reported,[16,17,24-34] physical studies about third-order optical nonlinearity to elucidate NLO characteristics have been made only to a limited extent.

In that respect, we have reported the preparation and investigation of the NLO properties of a library of donor-acceptor systems featuring a [60]fullerene (C_{60}) core covalently linked, through a flexible triethylene glycol chain, to a porphyrin or a ferrocenyl donor moiety.[22,23] All dyads were found to display an increased third-order NLO response when compared to individual reference methano[60]fullerene or porphyrin derivatives. In particular, the porphyrin-[60]fullerene dyad showed a 20-fold enhancement of its hyperpolarizability as compared to pristine C_{60}.[22,23] Similar results have been also reported with other covalent fullerene-containing dyads,[35-40] however, to the best of our knowledge, the effect of non-covalent[41-46] linkages on the third-order NLO responses is yet unknown for such fullerene-based systems. Diverse crown ethers have been employed in C_{60} recognition processes[47-61] and the construction of [*n*]pseudorotaxane motifs is certainly one of the most versatile approaches to assemble molecular chromophores. Therefore, the formation of dibenzyl ammonium (DBA) cation and a dibenzo-24-crown-8 (DB24C8) ether macrocycle is one of the leading methods which could be exploited to prepare a porphyrin-[60]fullerene [*2*]pseudorotaxanes.[62-67]

---

[a] *Department of Chemical and Pharmaceutical Sciences, INSTM UdR Trieste, University of Trieste, Piazzale Europa 1, 34127 Trieste, Italy.*

[b] *Namur Research College (NARC) and Department of Chemistry, University of Namur, Rue de Bruxelles 61, 5000 Namur, Belgium. E-mail: davide.bonifazi@unamur.be*

[c] *Institute of Chemical Engineering Sciences, Foundation for Research and Technology-Hellas (FORTH), 26504 Patras, Greece.*

[d] *Department of Physics, University of Patras, 26504 Patras, Greece. E-mail: couris@iceht.forth.gr.*

[e] *Istituto per la Sintesi Organica e la Fotoreattività, Consiglio Nazionale delle Ricerche (CNR-ISOF), Via Gobetti 101, 40129 Bologna, Italy. E-mail: nicola.armaroli@isof.cnr.it*

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

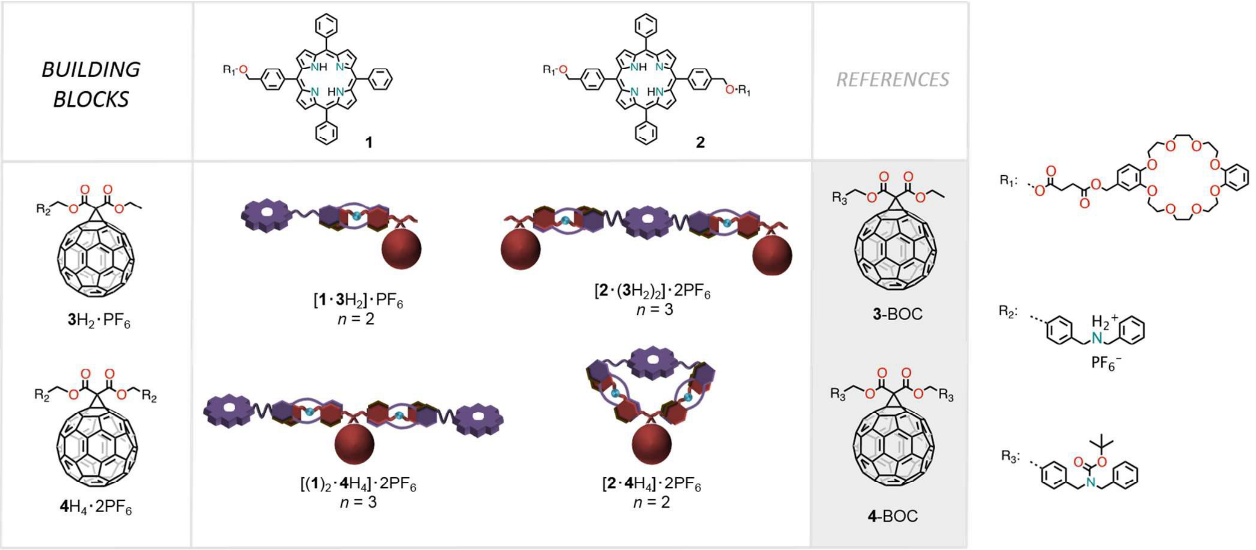


Figure 1. Library of the porphyrin- (**1** and **2**) and fullerene-based (**3**$H_2\cdot PF_6$ and **4**$H_4\cdot 2PF_6$) components for preparing [*2*]pseudorotaxanes [**1**·**3**H_2]·PF_6 and [**2**·**4**H_4]·$2PF_6$ and [*3*]pseudorotaxanes [(**1**)$_2$·**4**H_4]·$2PF_6$ and [**2**·(**3**H_2)$_2$]·$2PF_6$. The latter are sketched as cartoons; reference compounds **3**-BOC and **4**-BOC are highlighted in grey.

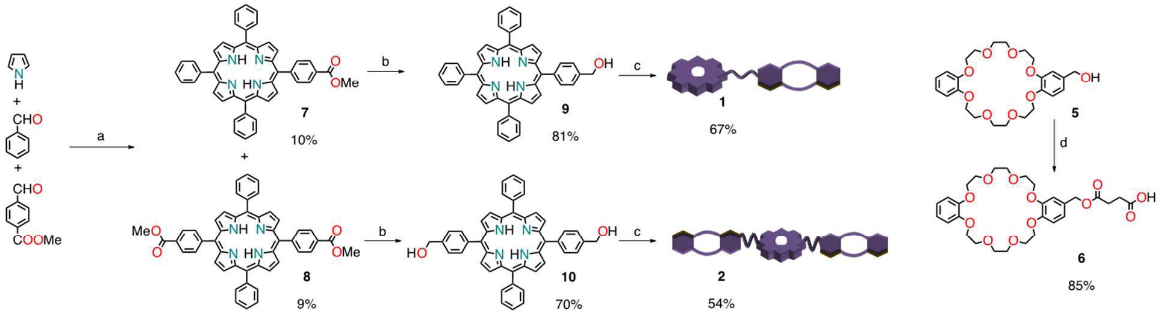
Herein we report the preparation of a library of non-covalent fullerene-porphyrin ensembles obtained by the combination of tetraphenylporphyrin (H_2TPP) and [60]fullerene derivatives, which bear one or two DBA or DB24C8 moieties, respectively (see the [*2*] and [*3*]pseudorotaxanes depicted in Figure 1). The self-assembly of the [*n*]pseudorotaxanes was studied by NMR (^{1}H-NMR and Diffusion Ordered Spectroscopy) and mass (HR-MALDI) spectroscopies. The absorption and Vis-NIR luminescence properties of the adducts were studied and the NLO responses of the [*n*]pseudorotaxane complexes in solution were investigated by means of the Z-scan technique. It is shown that the spectroscopic properties are strongly affected by intramolecular interactions with a strong enhancement of the third-order response, when compared to the non-threaded and reference individual components.

Results and Discussion

Synthesis and Characterization

For the preparation of porphyrin crown ether conjugates **1** and **2** (Scheme 1), porphyrin methyl esters **7** and **8** were synthesized by acid-catalysed condensation reaction between pyrrole and a 1:1 mixture of benzaldehyde and methyl 4-formylbenzoate in the presence of BF_3·Et_2O, followed by oxidation with DDQ.[68] Subsequent reduction of esters **7** and **8** with $LiAlH_4$ yielded benzyl alcohols **9** and **10** in 81 and 70% yield, respectively. Esterification reaction of porphyrin alcohols **9** and **10** with DBC24C8-derived carboxylic acid **6** (synthesised from DB24C8-derived alcohol **5**[69] upon reaction with succinic anhydride in toluene at 110 °C) in the presence of EDC as coupling agent, afforded the final porphyrin crown ether conjugates **1** and **2** in 67 and 54% yield, respectively. Fullerene-derived ammonium salts **3**$H_2\cdot PF_6$ and **4**$H_4\cdot 2PF_6$ were synthesized according to previously reported synthetic protocols.[49,70,71]

At first, we evaluated the self-assembling abilities of porphyrin crown ether conjugates **1** and **2** to form a [*2*]pseudorotaxane and [*3*]pseudorotaxane-like complexes in a chloroform-*d*/acetonitrile-d_3 mixture ($CDCl_3/CD_3CN$, 9:1 *v/v*, c = 1.5 × 10^{-3} M). As previously observed for [60]fullerene-containing [*2*]pseudorotaxanes,[49,70] the ^{1}H-NMR spectrum of the appropriate stoichiometric mixture of porphyrin and [60]fullerene ammonium salt in $CDCl_3/CD_3CN$ (9:1 *v/v*, 298 K)



Scheme 1. Synthetic route towards porphyrin crown ether conjugates **1** and **2**; (a) BF_3·Et_2O, then DDQ, Et_3N, CH_2Cl_2, rt; (b) $LiAlH_4$, THF, 0˚C to rt; (c) **6**, EDC·HCl, DMAP, CH_2Cl_2, 0 ˚C to rt; (d) succinic anhydride, DMAP, toluene, reflux. Abbreviations: DDQ, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone; DMAP, 4-dimethylaminopyridine; EDC·HCl, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride.

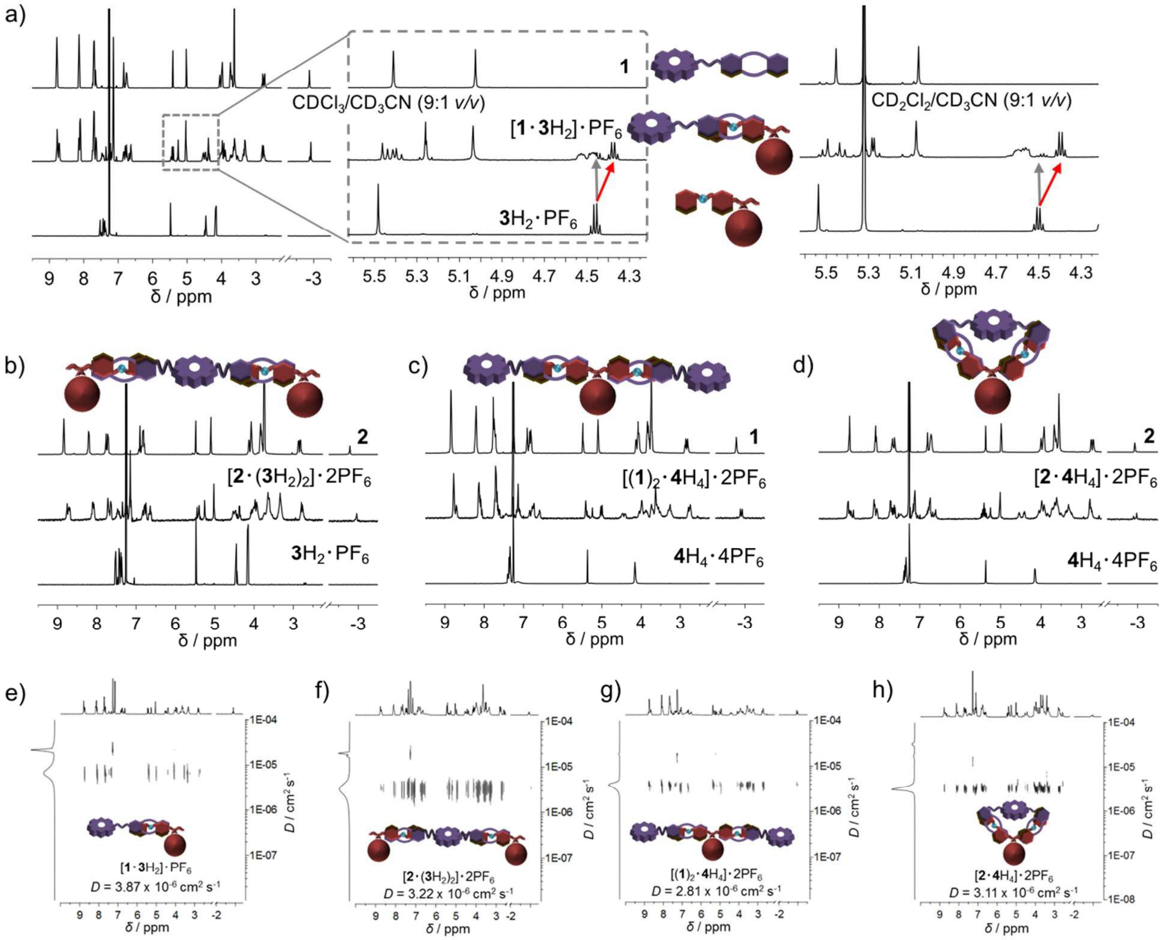


Figure 2. NMR characterisation (500 MHz, 298 K, c = 1.5 × 10^{-3} M) of [*2*]pseudorotaxane and [*3*]pseudorotaxane-like complexes after 60 minutes: (a) ^{1}H-NMR of **1** (top), [**1**·**3**H$_2$]·PF$_6$ and (middle) **3**H$_2$·PF$_6$ (bottom) in CDCl$_3$/CD$_3$CN (9:1 *v/v*, c = 3.0 × 10^{-3} M) (left) and in CD$_2$Cl$_2$/CD$_3$CN (9:1 *v/v*, c = 3.0 × 10^{-3} M) (right); (b) ^{1}H-NMR of [**2**·(**3**H$_2$)$_2$]·2PF$_6$;(c) ^{1}H-NMR of [(**1**)$_2$·**4**H$_4$]·2PF$_6$ and (d) ^{1}H-NMR of [**2**·**4**H$_4$]·2PF$_6$.Figures (e-h) are 2D-DOSY contour mode plots for the [*2*]pseudorotaxane and [*3*]pseudorotaxane-like complexes (500 MHz, 298 K, c = 6.0 × 10^{-3} M) with the corresponding diffusion values.

showed the appearance of a new pattern of proton resonances compared to those of the free molecular synthons, confirming the formation of the threaded complex (Figure 2a). In particular, the presence of the diagnostic multiple resonances around 4.5 ppm, typical of the -C*H*$_2$N- protons, were indicative of the threaded DBA moiety. The significant changes of chemical shifts of the *β*-proton and -NH- porphyrin resonances in the pseudorotaxane complexes suggested that the carbon cage is nested over the tetrapyrrolic macrocycle, indicating that the ‘tight’ or ‘face-to-face’ conformer is dominant, as also observed for other porphyrin-fullerene ensembles.[22,50,52,53,61,72,73] The same spectra have been also recorded in a CD$_2$Cl$_2$/CD$_3$CN mixture to avoid the presence of the acidic CHCl$_3$ and stabilizers (such as EtOH) that could disrupt the formation of the complex and affect both the NLO and photophysical investigations. Moreover, it is expected that the formation of the pseudorotaxane is stronger in CD$_2$Cl$_2$ than in CDCl$_3$.[61] The association constants (K_a) were obtained from measurements of the concentrations of the complexed and uncomplexed species and using the expression K_a = [**1**·**3**H$_2$·PF$_6$]/[**1**][**3**H$_2$·PF$_6$][62,63] (Figure 2a enlarged) and were 3950 M^{-1} and 8385 M^{-1} for CDCl$_3$/CD$_3$CN and CD$_2$Cl$_2$/CD$_3$CN, respectively. Next, the formation of [*3*]pseudorotaxanes [(**1**)$_2$·**4**H$_4$]·2PF$_6$ and [**2**·(**3**H$_2$)$_2$]·2PF$_6$ and [*2*]pseudorotaxane [**2**·**4**H$_4$]·2PF$_6$ was investigated. The ^{1}H-NMR spectra (CDCl$_3$/CD$_3$CN 9:1, c = 3.0 × 10^{-3} M, at 298 K) showed similar results to those observed for [**1**·**3**H$_2$]·PF$_6$ (Figures 2b-d). In all cases, upon addition of [60]fullerene ammonium salts **4**H$_4$·2PF$_6$ or **3**H$_2$·PF$_6$, the tetrapyrrolic-centered resonances for porphyrins **1** and **2** undergo dramatic spectral changes, yielding multiplets which suggest the formation of the [*2*]- and [*3*]pseudorotaxane complexes, respectively.

Additionally, diffusion ordered spectroscopy (DOSY-NMR) was used to study the diffusion behaviour, and thus the molecular hydrodynamic radii in solution, of free molecules **1**-**4** and of [*n*]pseudorotaxanes (Figures 2e-h). This technique unequivocally confirmed the formation of a stable complex for all pseudorotaxanes mixtures if compared to the free molecular components (for example, diffusion values *D* are 3.87 × 10^{-6} cm^2 s^{-1}, 4.14 × 10^{-6} cm^2 s^{-1} and 4.93 × 10^{-6} cm^2 s^{-1} for

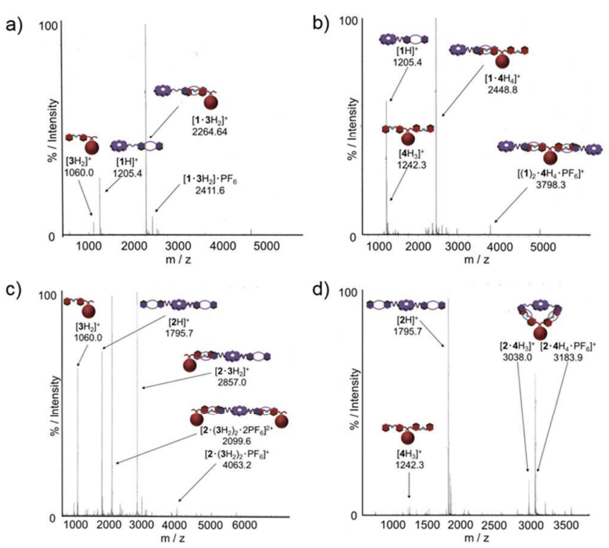


Figure 3. High-resolution (HR) MALDI-TOF mass spectrum of (a) $[\mathbf{1}\cdot\mathbf{3}H_2]\cdot PF_6$, (b) $[\mathbf{2}\cdot(\mathbf{3}H_2)_2]\cdot 2PF_6$, (c) $[(\mathbf{1})_2\cdot\mathbf{4}H_4]\cdot 2PF_6$ and (d) $[\mathbf{2}\cdot\mathbf{4}H_4]\cdot 2PF_6$.

$[\mathbf{1}\cdot\mathbf{3}H_2]\cdot PF_6$, **1** and $\mathbf{3}H_2\cdot PF_6$, respectively). Notably, DOSY confirmed the formation of a [*2*]pseudorotaxane over a supramolecular polymer assembly for $[\mathbf{2}\cdot\mathbf{4}H_4]\cdot 2PF_6$. The diffusion study showed that the complex-centered proton resonances have, within the experimental error, similar diffusion coefficients to porphyrin **2** alone, a value consistent with a folded conformation (3.11×10^{-6} cm^2 s^{-1}; see also the Supporting Info, Diffusion Measurements, Figures S5-S12).

Unambiguous proofs for the formation of the different complexes were also obtained by HR-MALDI-TOF mass spectrometric analysis of the threaded complexes. In particular, the main peaks corresponding to the supramolecular ions of the pseudorotaxane complexes were observed for all the non-covalent ensembles (Figure 3a-d and Supporting Info, Figures S13-S16). Peaks corresponding to the molecular ions of the constituting fullerene ammonium salts and the porphyrin crown ether conjugates are also apparent in the spectra (with and without PF_6^-). Notably, for the sample containing a 1:1 mixture of crown ether **2** and [60]fullerene bisammonium salt $\mathbf{4}H_4\cdot 2PF_6$, the MALDI-TOF spectrum displayed only the dimeric species, thus supporting the hypothesis for which a cyclic structure for the [*3*]pseudorotaxane $[\mathbf{2}\cdot\mathbf{4}H_4]\cdot 2PF_6$ is likely formed through an intramolecular threading process.[74]

Photophysical properties

The absorption and emission spectra, along with luminescence data and excited-state lifetimes of the individual compounds **1**, **2**, $\mathbf{3}H_2\cdot PF_6$ and $\mathbf{4}H_4\cdot 2PF_6$ in CH_3CN at 298 K have been measured and are reported in Figure 1 and Table 4.

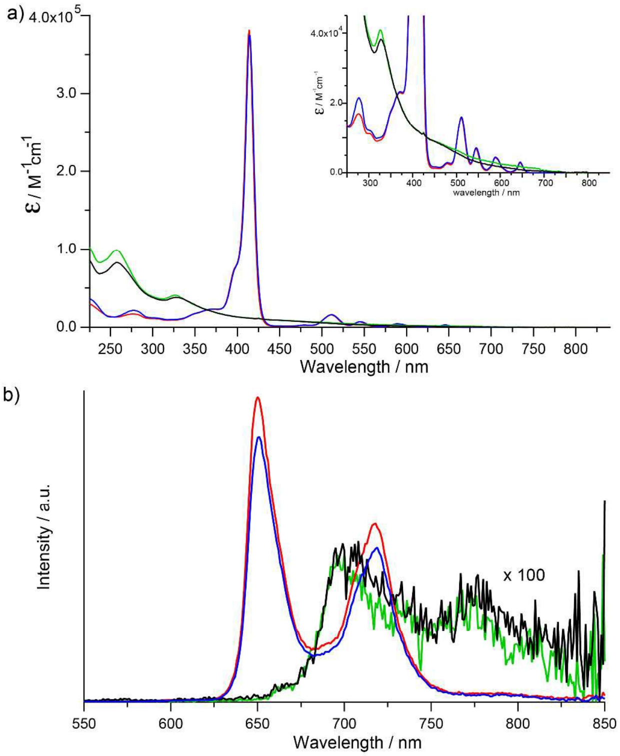


Figure 4. (a) Absorption and (b) luminescence spectra in acetonitrile at 298 K of **1** (red), **2** (blue), $\mathbf{3}H_2\cdot PF_6$ (green) and $\mathbf{4}H_4\cdot 2PF_6$ (black). λ_{exc} = 414 nm for **1** and **2** and λ_{exc} = 330 nm for $\mathbf{3}H_2\cdot PF_6$ and $\mathbf{4}H_4\cdot 2PF_6$).

Table1. Luminescence data and excited state lifetimes in acetonitrile at 298 K.

	$\lambda_{max}$$^{(a)}$ / nm	$\Phi^{(b)}$ / %	$\tau^{(c)}$/ ns
1	650	7.1	9.3
2	650	7.4	9.5
$\mathbf{3}H_2\cdot PF_6$	700	0.08	1.3
$\mathbf{4}H_4\cdot 2PF_6$	704	0.09	1.5

(a) Highest energy feature of the luminescence bands, at λ_{exc} = 414 for **1** and **2** nm and λ_{ex} = 330 nm for $\mathbf{3}H_2\cdot PF_6$ and $\mathbf{4}H_4\cdot 2PF_6$; (b) Calculated using $[Ru(bpy)_3]^{2+}$ as standard; (c) From time correlated single photon counting (TCSPC) apparatus using λ_{exc} = 331 nm.

The UV/Vis absorption spectra of **1** and **2** show the narrow and intense Soret band centred at 414 nm and the weaker Q-bands from about 500 nm up to 675 nm. As expected for porphyrin derivatives,[75] **1** and **2** are relatively good fluorophores with emission quantum yields around 7%. Methanofullerenes $\mathbf{3}H_2\cdot PF_6$ and $\mathbf{4}H_4\cdot 2PF_6$ absorb throughout the UV/Vis spectral region and exhibit weak fluorescence with emission quantum yields below 0.1%. Overall, no remarkable differences are found between reference compounds **1** and **2** and between $\mathbf{3}H_2\cdot PF_6$ and $\mathbf{4}H_4\cdot 2PF_6$ both in absorption and luminescence properties.

The self-assembly of porphyrin crown ethers **1** and **2** with the [60]fullerene ammonium compounds $\mathbf{3}H_2\cdot PF_6$ and $\mathbf{4}H_4\cdot 2PF_6$ leading to pseudorotaxane-like complexes were investigated with UV-Vis-NIR absorption and luminescence spectroscopy in

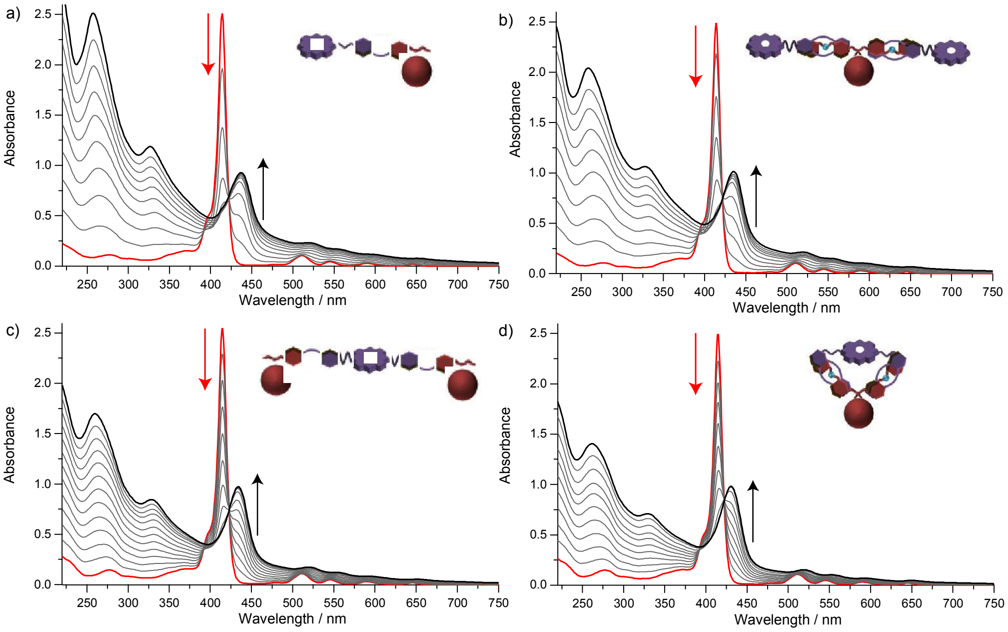


Figure 5. Absorption spectra of **1** and **2** in Et_2O/CH_3CN (98:2 *v/v*, 298 K, c = 5.5 × 10^{-6} M) upon addition of increasing amounts of fullerene derivatives; **1** (top, red line) + up to 4 eq. of fullerenes **3**$H_2 \cdot PF_6$ (a) and **4**$H_4 \cdot 2PF_6$ (b); **2** (bottom, red line) + up to 3 eq. of fullerenes **3**$H_2 \cdot PF_6$ (c) and **4**$H_4 \cdot 2PF_6$ (d).

a Et_2O/CH_3CN solution (98:2 *v/v*). The choice of the solvent is crucial in order to obtain strong porphyrin-fullerene interactions, particularly when working at low concentrations (10^{-5}–10^{-6} M), as necessary for photophysical investigations. In particular, a series of titration experiments were made to explore all the combinations between the individual moieties. The porphyrin crown ether **1** was mixed with both [60]fullerene ammonium salts **3**$H_2 \cdot PF_6$ and **4**$H_4 \cdot 2PF_6$ to form a [*2*]pseudorotaxane-like [**1**·**3**H_2]·PF_6 and a [*3*]pseudorotaxane [(**1**)$_2$·**4**H_4]·$2PF_6$complexes. Similarly, [60]fullerene ammonium salts were added to compound **2** to form [*3*]pseudorotaxane [**2**·(**3**H_2)$_2$]·$2PF_6$ and [*2*]pseudorotaxane [**2**·**4**H_4]·$2PF_6$.

The absorption spectra of porphyrin crown ethers **1** and **2** (Et_2O/CH_3CN, 98:2 *v/v* 5.5, × 10^{-6} M) were monitored upon addition of increasing amounts of [60]fullerene ammonium compounds (Figure 5). The number of fullerene equivalents added to the porphyrin solutions depends on the nature of the individual moieties. The formation of pseudorotaxanes [**1**·**3**H_2]·PF_6 and [(**1**)$_2$·**4**H_4]·$2PF_6$ is virtually complete after the addition of about four equivalents of **3**$H_2 \cdot PF_6$ and **4**$H_4 \cdot 2PF_6$, respectively, to a solution of **1**. Similarly, for the porphyrin **2**, the titration experiments are completed upon addition of three equivalents of fullerenes **3**$H_2 \cdot PF_6$ or **4**$H_4 \cdot 2PF_6$. The absorption profiles of all pseudorotaxanes exhibit a decreased Soret band and the appearance of a weaker, broader and bathochromically-shifted band. Notably, a neat isosbestic point is found at 420 nm, as the concentration of fullerene increases. In agreement with previous findings, these observations suggest the occurrence of strong porphyrin-fullerene interactions, most likely related to face-to-face arrangements.[22]

The self-assembly of porphyrin crown ethers **1** or **2** and [60]fullerene ammonium molecules **3**$H_2 \cdot PF_6$ and **4**$H_4 \cdot 2PF_6$ has been also traced by luminescence spectroscopy in Et_2O/CH_3CN (98:2 *v/v*, c = 5.5 × 10^{-6} M). Emission spectra were recorded by adding increasing aliquots of fullerene derivatives and exciting at the isosbestic point (420 nm), operating at the same concentrations employed in the absorption studies; both UV-Vis (Supporting Info, Figure S17) and IR (Figure 6) detectors were used. A progressive quenching of the porphyrin-centred fluorescence, together with the formation of a broad band around 950 nm, is found. The latter band can be attributed to a porphyrin → fullerene charge-transfer state (CT) between the units in a "tight" non-covalent ensemble, in line with earlier studies on tightly-folded fullerene-porphyrin conjugates.[72,76-80] The lifetime associated to this state is found to be about 3.5 ns (Table 2).

Table 2. Luminescence data and excited state lifetimes of the CT band in Et_2O/CH_3CN (98/2 *v/v*) at 298 K.

	λ_{max} / nm	τ/ ns
[**1**·**3**H_2]·PF_6	924	3.5
[(**1**)$_2$·**4**H_4]·$2PF_6$	922	3.3
[**2**·(**3**H_2)$_2$]·$2PF_6$	921	3.5
[**2**·**4**H_4]·$2PF_6$	922	3.4

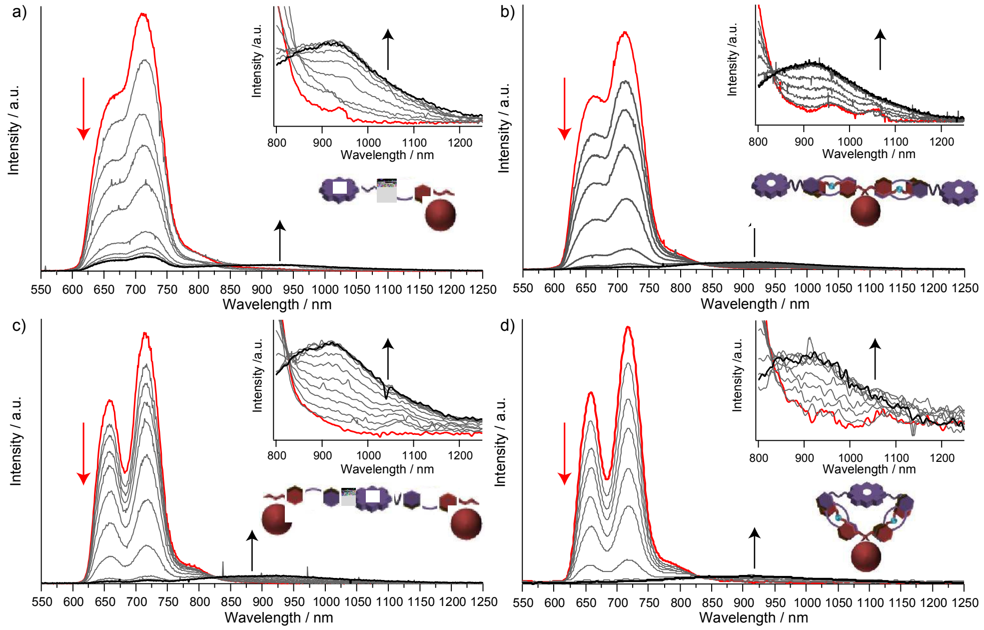


Figure 7. Luminescence spectra recorded with λ_{ex} = 420 nm and using an IR-sensitive detector in Et_2O/CH_3CN (98:2 *v/v*, 298 K, c = 5.5 × 10^{-6} M) (λ_{exc} = 420 nm): **1** (top, red line) + up to 4 eq. of fullerene **3**$H_2 \cdot PF_6$ (a) and **4**$H_4 \cdot 2PF_6$ (b); **2** (bottom, red line) + up to 3 eq. of fullerene **3**$H_2 \cdot PF_6$ (c) and **4**$H_4 \cdot 2PF_6$ (d). The insets show the charge transfer emission bands in the infrared region.

The photophysical characterization of all the pseudorotaxanes was also performed in the same conditions used to study the third order optical nonlinearity (*vide infra*). Namely, in a mixture of CH_2Cl_2/CH_3CN (9:1 *v/v,* c = 2.5 × 10^{-4} M) and using different ratios between the components (Figure 7 and Supporting Info, Figure S18). However, under these conditions, the CT emission bands in the NIR region were not observed. This is attributed to the greater polarity of this solvent mixture (CH_2Cl_2/CH_3CN, 9:1 *v/v*) compared to that used in the first set of experiments (Et_2O/CH_3CN, 98:2 *v/v*). In fact, it has been already demonstrated that, by increasing polarity, the CT emission band moves progressively to lower energy, decreasing its intensity until disappearance.[77] In particular, faint emission is detected in THF and no emission in benzonitrile, with CH_2Cl_2 (present case) showing intermediate dielectric constant.[77] However, clue of non-covalent porphyrin-fullerene interactions can be inferred by the dramatic quenching of the porphyrin fluorescence (Supporting Info, Figure S18).

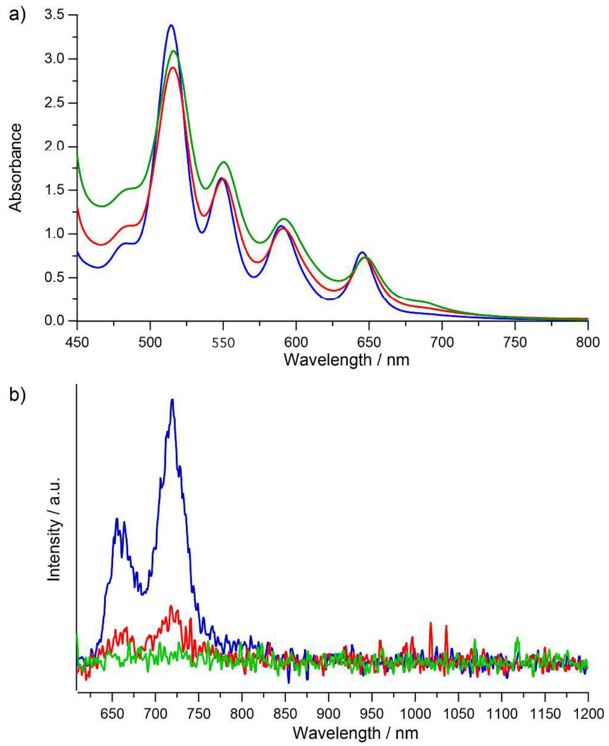


Figure 6. (a) Absorption and (b) emission spectra in CH_2Cl_2/CH_3CN (9:1) of **1** (0.25 mM) upon addition of 0.5 (blue), 1 (red), 2 (green) equivalents of **3**$H_2 \cdot PF_6$. λ_{exc} 600 nm, IR detector.

Molecular Modelling

The characterization of the supramolecular species in solution, which evidenced strong fullerene-porphyrin interaction, was further complemented by the molecular models built for the [*n*]pseudorotaxane complexes (Figure 8 and Supporting Info, Molecular Modelling part). By performing geometry optimization on each derivative alone and in complex (PM6 semi-empirical level of theory, vacuum) it was possible to compute their molecular volumes, together with the hydrodynamic radius of an ideal sphere that included the molecules. Subsequently, the calculated (r_{calc}) hydrodynamic radius was compared with the experimental one (r_{exp}) as calculated from the DOSY-NMR experiments (values reported in Figure 8, under the molecular models). The geometry optimizations, in all cases, showed the presence of 'face-to-

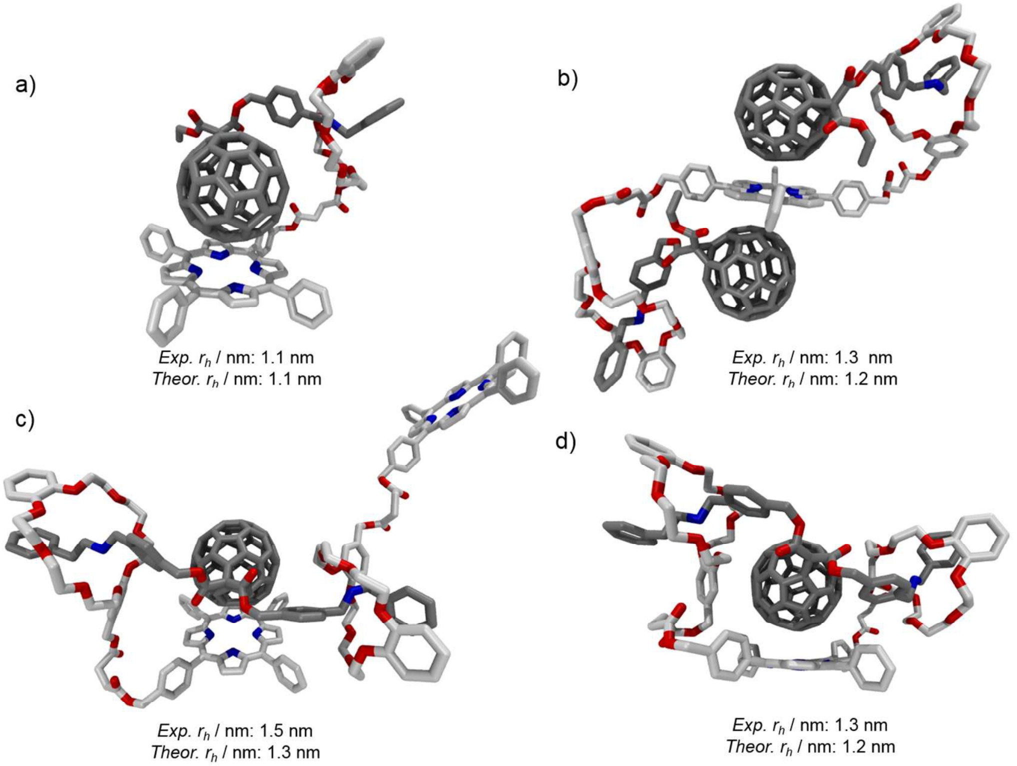


Figure 8. Optimised geometries obtained for the pseudorotaxanes (a) [**1**·**3**H_2]·PF_6, (b) [**2**·(**3**H_2)$_2$]·2PF_6, (c) [(**1**)$_2$·**4**H_4]·2PF_6 and (d) [**2**·**4**H_4]·2PF_6 in the vacuum at the PM6 level of theory.

face' conformations. The porphyrin and the fullerene are in a close contact with a distance of about 3.2 Å, as a result of the π-π intramolecular interaction (Figure 8a). The optimised geometry of the [**2**·(**3**H_2)$_2$]·2PF_6 complex showed a "sandwiched" complex, in which the two fullerene moieties are both 'stacking' in a 'face-to-face" fashion at a distance of 3.4 Å from the two opposite π-faces of the porphyrin macrocycle (Figure 8b). On the contrary, in the case of [(**1**)$_2$·**4**H_4]·2PF_6, whose ratio among the chromophores is inverted, the situation is substantially different, with only one of the porphyrin units being in close contact with the fullerene sphere. Finally, the hydrodynamic radius as calculated from the optimised geometry of [**2**·**4**H_4]·2PF_6 (1.2 nm) proved to be in good agreement with the experimental hydrodynamic value of 1.3 nm (calculated from the diffusion coefficient in DOSY-NMR experiment through the Stokes-Einstein equation). This further corroborates the formation of the complexes.

Third-Order non-linear optical (NLO) properties

The third-order NLO properties of all the pseudorotaxanes and the molecular references (*i.e.*, C_{60}, fullerenes **3**-BOC, **4**-BOC, **3**H_2 and **4**H_4, porphyrins **1** and **2**, 1:1 mixtures of **1**/**3**-Boc, **2**/**3**-Boc, **1**/**4**-Boc and **2**/**4**-Boc) have been investigated in CH_2Cl_2/CH_3CN (9:1 *v*/*v*, c = 2.5 × 10^{-4} M) solutions by means of the Z-scan technique[81,82] under 35 ps, 532 nm laser excitation. By performing measurements on different concentrations under various incident laser excitation energies, the nonlinear absorption coefficient, β, and the nonlinear refractive index parameter, γ', have been determined. Some characteristic "open" and "divided" Z-scans of pseudorotaxanes solutions are present in Figure 9. Then, the third-order susceptibility $\chi^{(3)}$ and the second hyperpolarizability γ have been deduced (the details are given in the Supporting Info, NLO part). Among these NLO parameters, the value of the second hyperpolarizability γ, being concentration independent, can be regarded as a molecular property, allowing the direct comparison of the NLO response of different molecules. The determined values of the second hyperpolarizability γ of the studied molecules are listed in Table 3 (which also contains the data obtained after the Et_3N addition, see also Table S1-S2). As shown, the values of the hyperpolarizability of the pseudorotaxanes were found to be larger than the sum of the hyperpolarizabilities of the reference porphyrin and the respective [60]fullerene derivative, suggesting a underlying operational mechanism leading to some synergistic action. Specifically, the enhancement of the NLO response of the pseudorotaxanes compared to the sum of the individual NLO responses of the constituents' molecular entities becomes comprehensible considering the presence of an efficiently formed CT state. In fact, such CT states are characteristic features of the [60]fullerene-porphyrin assemblies, whose contribution is known to be favoured by the present excitation conditions (*i.e.*, under 532 nm laser excitation).[83-86] Similar enhancement of the NLO response of other fullerene-based systems has been observed and reported in the literature previously.[22,23,87-89] Another interesting observation is the

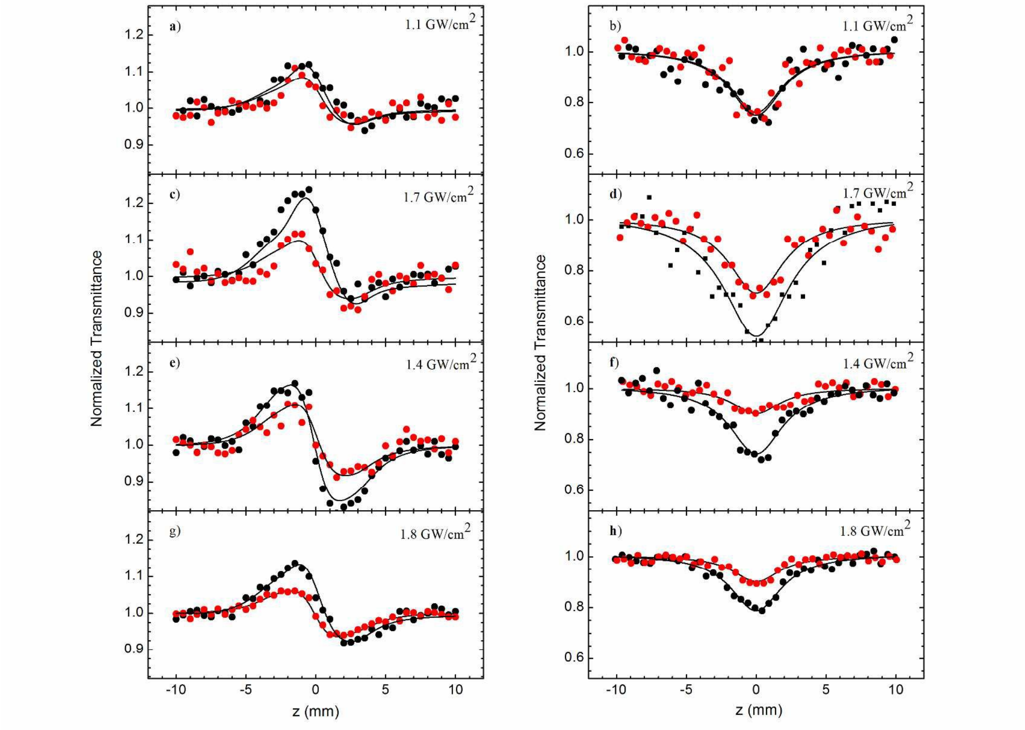


Figure 9. (a, c, e, g) "Divided" and (b, d, f, h) "open-aperture" Z-scans of solutions of the pseudorotaxanes assemblies $[\mathbf{1}\cdot\mathbf{3}\mathrm{H}_2]\cdot\mathrm{PF}_6$, $[(\mathbf{1})_2\cdot\mathbf{4}\mathrm{H}_4]\cdot2\mathrm{PF}_6$, $[\mathbf{2}\cdot(\mathbf{3}\mathrm{H}_2)_2]\cdot2\mathrm{PF}_6$ and $[\mathbf{2}\cdot\mathbf{4}\mathrm{H}_4]\cdot2\mathrm{PF}_6$ (from top to bottom) in CH_2Cl_2/CH_3CN (9:1 v/v) without (black lines, c = 7.0, 7.0, 8.3 and 9.8 × 10^{-4} M, respectively) and with Et_3N (red lines, c = 6.0, 6.5, 7.2 and 9.0 × 10^{-4} M, respectively). The solid lines correspond to the best numerical fits of the experimental data points and were used for the determination of the NLO parameters.

strong dependence of the hyperpolarizability on the number of electron-accepting fullerene appends, as pseudorotaxanes $[\mathbf{1}\cdot\mathbf{3}\mathrm{H}_2]\cdot\mathrm{PF}_6$ and $[(\mathbf{1})_2\cdot\mathbf{4}\mathrm{H}_4]\cdot2\mathrm{PF}_6$ (Figure 9 and Table 3) were found to exhibit a modest increase of γ, whereas stronger enhancements was observed for pseudorotaxane $[\mathbf{2}\cdot(\mathbf{3}\mathrm{H}_2)_2]\cdot2\mathrm{PF}_6$, with two [60]fullerene units. Notably, larger γ values were also found for cyclic pseudorotaxane $[\mathbf{2}\cdot\mathbf{4}\mathrm{H}_4]\cdot2\mathrm{PF}_6$. Presumably, the presence of different conformations is reflected on the CT mechanism, namely when going from the "tight" conformation to the "loose" one, the electron transfer process could change, with substantial changes of the hyperpolarizability values of the molecular assembly. Therefore, molecular systems in which the fullerene and the porphyrin are mostly in a folded conformation, as in the case of the pseudorotaxane assemblies $[\mathbf{2}\cdot\mathbf{4}\mathrm{H}_4]\cdot2\mathrm{PF}_6$ and $[\mathbf{2}\cdot(\mathbf{3}\mathrm{H}_2)_2]\cdot2\mathrm{PF}_6$, display more efficient charge transfer than for the assemblies $[\mathbf{1}\cdot\mathbf{3}\mathrm{H}_2]\cdot\mathrm{PF}_6$ and $[(\mathbf{1})_2\cdot\mathbf{4}\mathrm{H}_4]\cdot2\mathrm{PF}_6$, and thus higher NLO responses.

Additionaly, 1.8 equivalents of a base (Et_3N) were added and the sum of the second hyperpolarizability γ values of the non-threaded components was observed to recover (Figure 9 and Table 3, entries 6, 8, 10 and 12), thus further supporting our hypothesis according to which the ground-state fullerene-porphyrin interchromophoric interaction is the key requirement for enhancing the hyperpolarizability. As expected, this behaviour is more pronounced for the tightly-bonded pseudorotaxane assemblies $[(\mathbf{1})_2\cdot\mathbf{4}\mathrm{H}_4]\cdot2\mathrm{PF}_6$, $[\mathbf{2}\cdot(\mathbf{3}\mathrm{H}_2)_2]\cdot2\mathrm{PF}_6$ and $[\mathbf{2}\cdot\mathbf{4}\mathrm{H}_4]\cdot2\mathrm{PF}_6$, while it is weaker for complex $[\mathbf{1}\cdot\mathbf{3}\mathrm{H}_2]\cdot\mathrm{PF}_6$. The values of NLO parameters of several donor-acceptor systems from the literature are included in Table S3 (see Supporting Information) for comparison purposes. As one can notice, the pseudorotaxanes reported in the present study exhibit remarkably enhanced NLO response if compared to similar dyads. As anticipated in the introductory section, these studies include porphyrin- and ferrocene-fullerene derivatives.[16,17,22-34,87-98] Among others, previous works by our groups clearly showed a dramatic effect of the functionalization on the NLO response,[22,38,97] further proving the existence of the charge-transfer event.[99,100] For instance, when studying the NLO properties of two fullerene derivatives in various chemical environments under 35 ps, 532 nm using Z-scan technique, the presence of an electron donor moiety causes an enhancement of the NLO response by almost a factor of two,[38] with the porphyrin moieties displaying the highest response (see Table S3 in the SI).[22] It should be mentioned that two types of charge-transfer interactions are generally present between an electron donor (e.g. a porphyrin unit) and an electron acceptor (e.g. a fullerene unit). The first is covalent contribution, also known as "through-bond" interactions where the electrons charge transfer is realized through an intermediate chain linking the donor with the acceptor. The second is a non-covalent or "through-space" interactions where the electron charge transfer is succeeded by the contiguity of the donor and acceptor units in space.[101,102] Most of the aforementioned hybrids belong in the first category (*i.e.*, covalent linkages), in contrast to the fullerene-porphyrin pseudorotaxanes (*i.e.* non-covalent linkages). This work therefore demonstrated the superiority of the charge transfer through space systems, highlighting their capability of reversing the charge transfer effect (as has been shown by the addition of Et$_3$N) and subsequently their potentials in term of on-off NLO performance.

Conclusions

Exploiting the versatile crown-ether ammonium recognition motif, we have reported the preparation of a series of [60]fullerene-porphyrin [*n*]pseudorotaxanes, allowing the [60]fullerene acceptor and the porphyrin donor to adopt a folded conformation, in which the two moieties get in tight contact. The non- covalent donor-acceptor systems reveal a strong enhancement of the third-order NLO response as measured by the Z-scan technique, which is significantly different from the corresponding response of the individual species. This is ascribed to the threading process that brings in close proximity the fullerene and the porphyrin moieties, allowing the formation of a polar charge-transfer state. Notably, addition of a base capable of deprotonating the ammonium allows a reversible suppression of the NLO responses as a consequence of the dethreading process. By describing the construction of supramolecular fullerene materials whose NLO properties can be tuned by external stimuli, this work provides yet another example for the technological potential of organic materials displaying high versatility and ease of construction.

Acknowledgements

DB gratefully acknowledges the EU through the ERC Starting Grant “COLORLANDS” project, the FRS-FNRS (FRFC contracts n° 2.4.550.09), the Science Policy Office of the Belgian Federal Government (BELSPO-IAP 7/05 project), the “TINTIN” ARC project (09/14-023), the MIUR through the FIRB “Futuro in Ricerca” (“SUPRACARBON”, contract n° RBFR10DAK6). LĐ thanks the University of Trieste for his doctoral fellowship. MP acknowledges funding from the Italian Ministry of Education MIUR (cofin Prot. 2010N3T9M4). Access to the computational resources supplied by CINECA in agreement with the University of Trieste is gratefully acknowledged. NA thanks Consiglio Nazionale delle Ricerche (MACOL PM. P04. 010 and Progetto Bandiera N-CHEM) and MIUR (PRIN 2010 INFO-CHEM-CX2TLM). IP, PA and SC acknowledge partial support by the European Union (European Social Fund–ESF) and Greek national funds through the Operational Program ‘Education and Lifelong Learning’ of the National Strategic Reference Framework (NSRF)-Research Funding Program: HERACLEITUS II and THALIS (ISEPUMA): Investing in knowledge society through the European Social Fund. DB thanks Prof. François Diederich for the synthesis and the research project.

Notes and references

1 P. Chen, X. Wu, X. Sun, J. Lin, W. Ji and K. Tan, *Phys. Rev. Lett.*, 1999, **82**, 2548–2551.
2 O. R. Evans and W. Lin, *Acc. Chem. Res.*, 2002, **35**, 511–522.
3 R. L. Sutherland, Handbook of Nonlinear Optics, Mercel Dekker, New York, 2003.
4 C. Sanchez, B. Lebeau, F. Chaput and J. P. Boilot, *Adv. Mater.*, 2003, **15**, 1969–1994.
5 J. M. Wessels, H. G. Nothofer, W. E. Ford, F. von Wrochem, F. Scholz, T. Vossmeyer, A. Schroedter, H. Weller and A. Yasuda, *J. Am. Chem. Soc.*, 2004, **126**, 3349–3356.
6 S. R. Marder, *Chem. Commun.*, 2006, 131–134.
7 D. R. Kanis, M. A. Ratner and T. J. Marks, *Chem. Rev.*, 1994, **94**, 195–242.
8 P. Innocenzi and B. Lebeau, *J. Mater. Chem.*, 2005, **15**, 3821–3831.
9 P. G. Lacroix, Eur. *J. Inorg. Chem.*, 2001, **2001**, 339–348.
10 T. Kaino and S. Tomaru, *Adv. Mater.*, 1993, **5**, 172–178.
11 H. S. Nalwa, *Adv. Mater.*, 1993, **5**, 341–358.
12 W. Nie, *Adv. Mater.*, 1993, **5**, 520–545.
13 N. J. Long, *Angew. Chem. Int. Ed.*, 1995, **34**, 21–38.
14 S. Kato and F. Diederich, *Chem. Commun.*, 2010, **46**, 1994–2006.
15 P. Innocenzi and G. Brusatin, *Chem. Mater.*, 2001, **13**, 3126–3139.
16 D. M. Guldi, B. M. Illescas, C. M. Atienza, M. Wielopolski and N. Martín, *Chem. Soc. Rev.*, 2009, **38**, 1587–1597.
17 G. Accorsi and N. Armaroli, *J. Phys. Chem. C*, 2010, **114**, 1385–1403.
18 M. O. Senge, M. Fazekas, E. G. A. Notaras, W. J. Blau, M. Zawadzka, O. B. Locos and E. M. N. Mhuircheartaigh, *Adv. Mater.*, 2007, **19**, 2737–2774.
19 N. Aratani, D. Kim and A. Osuka, Chem. Asian J., 2009, **4**, 1172–1182.
20 M. Pawlicki, H. A. Collins, R. G. Denning and H. L. Anderson, *Angew. Chem. Int. Ed.*, 2009, **48**, 3244–3266.
21 M. Prato, *J. Mater. Chem.*, 1997, **7**, 1097–1109.
22 E. Xenogiannopoulou, M. Medved, K. Iliopoulos, S. Couris, M. G. Papadopoulos, D. Bonifazi, C. Sooambar, A. Mateo-Alonso and M. Prato, *ChemPhysChem*, 2007, **8**, 1056–1064.
23 P. Aloukos, K. Iliopoulos, S. Couris, D. M. Guldi, C. Sooambar, A. Mateo-Alonso, P. G. Nagaswaran, D. Bonifazi and M. Prato, *J. Mater. Chem.*, 2011, **21**, 2524–2534.
24 H. Imahori and Y. Sakata, *Eur. J. Org. Chem.*, 1999, **1999**, 2445–2457.
25 D. M. Guldi, *Chem. Soc. Rev.*, 2001, **31**, 22–36.
26 H. Imahori and S. Fukuzumi, *Adv. Funct. Mater.*, 2004, **14**, 525–536.
27 H. Imahori, *Org. Biomol. Chem.*, 2004, **2**, 1425–1433.
28 J. N. Clifford, G. Accorsi, F. Cardinali, J.-F. Nierengarten and N. Armaroli, *C. R. Chimie*, 2006, **9**, 1005–1013.
29 E. M. Pérez and N. Martín, *Chem. Soc. Rev.*, 2008, **37**, 1512–1519.
30 S. Fukuzumi, *Phys. Chem. Chem. Phys.*, 2008, **10**, 2283–2297.
31 F. D'Souza and O. Ito, *Chem. Commun.*, 2009, 4913.
32 F. D'Souza and O. Ito, *Chem. Soc. Rev.*, 2012, **41**, 86–96.
33 E. M. Pérez and N. Martín, *Chem. Soc. Rev.*, 2015, **44**, 6425–6433.
34 C. Schubert, J. T. Margraf, T. Clark and D. M. Guldi, *Chem. Soc. Rev.*, 2015, **44**, 988–998.
35 S. Couris, E. Koudoumas, A. A. Ruth and S. Leach, *J. Phys. B*, 1995, **28**, 4537–4554.
36 Y. P. Sun, G. E. Lawson, J. E. Riggs, B. Ma, N. Wang and D. K. Moton, *J. Phys. Chem. A*, 1998, **102**, 5520–5528.
37 E. Koudoumas, M. Konstantaki, A. Mavromanolakis, S. Couris, M. Fanti, F. Zerbetto, K. Kordatos and M. Prato, *Chem. Eur. J.*, 2003, **9**, 1529–1534.
38 A. Mateo-Alonso, K. Iliopoulos, S. Couris and M. Prato, *J. Am. Chem. Soc.*, 2008, **130**, 1534–1535.
39 O. Loboda, R. Zaleśny, A. Avramopoulos, J. M. Luis, B. Kirtman, N. Tagmatarchis, H. Reis and M. G. Papadopoulos, *J. Phys. Chem. A*, 2009, **113**, 1159–1170.
40 S. Urnikaite, T. Malinauskas, V. Gaidelis, R. Maldzius, V. Jankauskas and V. Getautis, *Carbon*, 2011, **49**, 320–325.
41 J.-M. Lehn, *Angew. Chem. Int. Ed.*, 1990, **29**, 1304–1319.
42 J.-M. Lehn, *Proc. Natl. Acad. Sci. U.S.A.*, 2002, **99**, 4763–4768.
43 C. A. Schalley, A. Lützen and M. Albrecht, *Chem. Eur. J.*, 2004, **10**, 1072–1080.
44 F. J. Hoeben, P. Jonkheijm, E. W. Meijer and A. P. Schenning, *Chem. Rev.*, 2005, **105**, 1491–1546.
45 G. V. Oshovsky, D. N. Reinhoudt and W. Verboom, *Angew. Chem. Int. Ed.*, 2007, **46**, 2366–2393.
46 S. Yagai and A. Kitamura, *Chem. Soc. Rev.*, 2008, **37**, 1520–1529.

47 J.-P. Bourgeois, L. Echegoyen, M. Fibbioli, E. Pretsch and F. Diederich, *Angew. Chem. Int. Ed.*, 1998, **37**, 2118–2121.

48 D. M. Guldi, J. Ramey and M. V. Martínez-Díaz, *Chem. Commun.*, 2002, 2774–2775.

49 M. V. Martínez-Díaz, N. S. Fender, M. S. Rodríguez-Morgade, M. Gómez-López, F. Diederich, L. Echegoyen, J. F. Stoddart and T. Torres, *J. Mater. Chem.*, 2002, **12**, 2095–2099.

50 N. Solladié, M. E. Walther, M. Gross, T. M. Figueira-Duarte, C. Bourgogne and J.-F. Nierengarten, *Chem. Commun.*, 2003, 2412–2413.

51 F. Marotti, D. Bonifazi, R. Gehrig, J.-L. Gallani and F. Diederich, *Isr. J. Chem.*, 2005, **45**, 303–319.

52 N. Solladié, M. E. Walther, H. Herschbach, E. Leize, A. Van Dorsselaer, T. M. Figueira-Duarte and J.-F. Nierengarten, *Tetrahedron*, 2006, **62**, 1979–1987.

53 J.-F. Nierengarten, U. Hahn, T. M. Figueira-Duarte, F. Cardinali, N. Solladié, M. E. Walther, A. Van Dorsselaer, H. Herschbach, E. Leize, A.-M. Albrecht-Gary, A. Trabolsi and M. Elhabiri, *C. R. Chimie*, 2006, **9**, 1022–1030.

54 D. M. Guldi, J. F. Stoddart, M. C. Díaz, B. M. Illescas, M. A. Canales, J. Jiménez-Barbero and G. Sarova, *Tetrahedron*, 2006, **62**, 1998–2002.

55 B. M. Illescas, J. Santos, M. C. Díaz, N. Martín, C. M. Atienza and D. M. Guldi, *Eur. J. Org. Chem.*, 2007, **2007**, 5027–5037.

56 F. D'Souza, E. Maligaspe, A. S. Sandanayaka, N. K. Subbaiyan, P. A. Karr, T. Hasobe and O. Ito, *J. Phys. Chem. A*, 2010, **114**, 10951–10959.

57 E. Maligaspe and F. D'Souza, *Org. Lett.*, 2010, **12**, 624–627.

58 S. K. Dey, F. Beuerle, M. A. Olson and J. F. Stoddart, *Chem. Commun.*, 2011, **47**, 1425–1427.

59 J. Iehl, J. F. Stoddart, M. Frasconi, H.-P. Jacquot de Rouville, N. Renaud, S. M. Dyar, N. L. Strutt, R. Carmieli, M. R. Wasielewski, M. A. Ratner and J.-F. Nierengarten, *Chem. Sci.*, 2013, **4**, 1462–1469.

60 L. Moreira, J. Calbo, R. M. K. Calderon, J. Santos, B. M. Illescas, J. Aragó, J.-F. Nierengarten, D. M. Guldi, E. Ortí and N. Martín, *Chem. Sci.*, 2015, **6**, 4426–4432.

61 L. Moreira, J. Calbo, B. M. Illescas, J. Arago, I. Nierengarten, B. Delavaux-Nicot, E. Orti, N. Martin and J.-F. Nierengarten, *Angew. Chem. Int. Ed.*, 2015, **54**, 1255–1260.

62 P. R. Ashton, E. Chrystal and P. T. Glink, *Chem. Eur. J.*, 1996, **2**, 709–728.

63 P. R. Ashton, P. T. Glink, M. V. Martínez-Díaz, J. F. Stoddart, A. J. P. White and D. J. Williams, *Angew. Chem. Int. Ed.*, 1996, **35**, 1930–1933.

64 P. T. Glink, J. F. Stoddart, C. Schiavo and D. J. Williams, *Chem. Commun.*, 1996, 1483–1490.

65 P. R. Aston, P. T. Glink, J. F. Stoddart, P. A. Tasker, A. J. P. White and D. J. Williams, *Chem. Eur. J.*, 1996, **2**, 729–736.

66 B. Zheng, F. Wang, S. Dong and F. Huang, *Chem. Soc. Rev.*, 2012, **41**, 1621–1636.

67 M. Xue, Y. Yang, X. Chi, X. Yan and F. Huang, Chem. Rev., 2015, **115**, 7398–7501.

68 J. S. Lindsey, I. C. Schreiman, H. C. Hsu, P. C. Kearney and A. M. Marguerettaz, *J. Org. Chem.*, 1987, **52**, 827–836.

69 X. Wang, V. Ervithayasuporn, Y. Zhang and Y. Kawakami, *Chem. Commun.*, 2011, **47**, 1282–1284.

70 F. Diederich, L Echegoyen, M Gome-Lopez, R. Kessinger and J. F. Stoddart, *J. Chem. Soc., Perkin Trans.*, 1999, **2**, 1577–1586.

71 H. W. Gibson, A. Farcas, J. W. Jones, Z. Ge, F. Huang, M. Vergne and D. M. Hercules, *J. Polym. Sci. A Polym. Chem.*, 2009, **47**, 3518–3543.

72 N. Armaroli, G. Marconi, L. Echegoyen, J. Bourgeois and F. Diederich, *Chem. Eur. J.*, 2000, **6**, 1629–1645.

73 R. M. K. Calderon, J. Valero, B. Grimm, J. de Mendoza and D. M. Guldi, *J. Am. Chem. Soc.*, 2014, **136**, 11436–11443.

74 W. Jiang, K. Nowosinski, N. L. Löw, E. V. Dzyuba, F. Klautzsch, A. Schäfer, J. Huuskonen, K. Rissanen and C. A. Schalley, *J. Am. Chem. Soc.*, 2012, **134**, 1860–1868.

75 B. Ventura, L. Flamigni, G. Marconi, F. Lodato and D. L. Officer, *New J. Chem.*, 2008, **32**, 166–178.

76 N. Armaroli, F. Diederich, L. Echegoyen, T. Habicher, L. Flamigni, G. Marconi and J.-F. Nierengarten, *New J. Chem.*, 1999, **23**, 77–83.

77 N. Armaroli, G. Accorsi, F. Song, A. Palkar, L. Echegoyen, D. Bonifazi and F. Diederich, *ChemPhysChem*, 2005, **6**, 732–743.

78 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.

79 A. Hosseini, Steven Taylor, G. Accorsi, N. Armaroli, C. A. Reed and P. D. W. Boyd, *J. Am. Chem. Soc.*, 2006, **128**, 15903–15913.

80 F. D'Souza, R. Chitta, S. Gadde, L. M. Rogers, P. A. Karr, M. E. Zandler, A. S. D. Sandanayaka, Y. Araki and O. Ito, *Chem. Eur. J.*, 2007, **13**, 916–922.

81 M. S. Bahae, A. Said, T. Wei, D. Hagan and V. Stryland, *IEEE J. Quantum Electron.*, 1990, **26**, 760.

82 P. Aloukos, G. Chatzikyriakos, I. Papagiannouli, N. Liaros and S. Couris, *Chem. Phys. Lett.*, 2010, **495**, 245–250.

83 D. M. Guldi and P. V. Kamat, eds. K. M. Kadish and R. S. Ruoff, Wiley Interscience, New York, 2000, pp. 225–282.

84 N. Armaroli, in Fullerenes: From Synthesis to Optoelectronic Properties, eds. D. M. Guldi and N. Martín, Kluwer Academic Publishers, Dordrecht, 2008, pp. 137–162.

85 N. Tsuboya, R. Hamasaki, M. Ito, M. Mitsuishi, T. Miyashita and Y. Yamamoto, *J. Mater. Chem.*, 2003, **13**, 511–513.

86 H. Kanato, K. Takimiya, T. Otsubo, Y. Aso, T. Nakamura, Y. Araki and O. Ito, *J. Org. Chem.*, 2004, **69**, 7183–7189.

87 V. Filidou, G. Chatzikyriakos, K. Iliopoulos, S. Couris and D. Bonifazi, *AIP Conf. Proc.*, 2010, **1288**, 188–191.

88 W.-S. Zhang, D. Wang, H. Cao and H. Yang, *Tetrahedron*, 2014, **70**, 573–577.

89 W. Y. Wang, L. Wang, N. N. Ma, C. L. Zhu and Y. Q. Qiu, *Dalton Trans.*, 2015, **44**, 10078–10088.

90 S.V. Kirnen, D. Arteaga, C. Henkel, J.T. Margraf, N. Alegret, K. Ohkubo, B. Insuasty, A. Díaz, N. Martín, L. Echegoyen, S. Fukuzumi, T. Clark, D.M. Guldi, *Chem. Sci*, 2015, **6**, 5994-6007.

91 F. D'Souza, E. Maligaspe, P.A Karr, A.L. Schumacher, M.El Ojaimi, C.P. Gros, J. Barbe, K. Ohkubo, S. Fukuzumi, *Chem. Eur. J.*, 2008, **14**, 674-681.

92 H. Imahori, Y. Sekiguchi, Y. Kashiwagi, T. Sato, Y. Araki, O. Ito, H. Yamada, S. Fukuzumi, *Chem. Eur. J.*, 2004, **10**, 3184-3196.

93 R. Zalesny, O. Loboda, K. Iliopoulos, G. Chatzikyriakos, S. Couris, G. Rotas, N. Tagmatarchis, A. Avramopoulos, *Phys Chem. Chem. Phys.* 2010, **12**, 373-381.

94 Y. Cheng, H. Hao, H. Xiao, S. Zhu, *J. Phys. B: At. Mol. Opt. Phys.*, 2009, **42**, 235401-235406.

95 Y. Cheng, T. He, H. Hao, S. Zhu, H. Xiao, H. *Opt. Commun.*, 2009, **282**, 4271-4275.

96 Y.L. Mao, Y.G. Cheng, J.H. Liu, B.C. Lin, Y.P. Huo, H.P. Zeng, *Chin. Phys. Lett.*, 2007, **24**, 950-953.

97 R. Zalesny, O. Loboda, K. Iliopoulos, G. Chatzikyriakos, S. Couris, G. Rotas, N. Tagmatarchis, A. Avramopoulos, *Phys. Chem. Chem. Phys.*, 2010, **12**, 373-381.

98 O.B. Mavritsky, A.N. Egorov, A.N. Petrovsky, K.V. Yakubovsky, W.J. Blau, D.N. Weldon, F.Z. Henary, *Proc. SPIE*, 1996, **2854**, 254-265.

99 B. Sahraoui, I.V. Kityk, J. Bielieninik, P. Hudhomme, A. Gorgues, *Opt. Mater.*, 1999, **13**, 349-353.

100 B. Sahraoui, I. Fuks-Janczarek, S. Bartkiewicz, K. Matczyszyn, J. Mysliwiec, I.V. Kityk, J. Berdowski, E. Allard, J. Cousseau, *Chem. Phys. Lett.*, 2002, **365**, 327-332.

101 M.M. Alam, M. Chattopadhyaya, S. Chakrabarti, K. Ruud, *J. Phys. Chem. Lett.*, 2012, **3**, 961-966.

102 J. Zyss, I. Ledoux, S. Volkov, V. Chernyak, S. Mukamel, G.P. Bartholomew, G.C. Bazau, *J. Am. Chem. Soc.* 2000, **122**, 11956-11962.

[60]Fullerene-Porphyrin [*n*]Pseudorotaxanes: Self-Assembly, Photophysics and Third-order NLO responses

L. Đorđević, T. Marangoni, F. De Leo, I. Papagiannouli, P. Aloukos, S. Couris,* E. Pavoni, F. Monti, N. Armaroli,* M. Prato and D. Bonifazi*