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Molecular recognition of La@C_{82} endohedral metallofullerene by an isophthaloyl-bridged porphyrin dimer

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ABSTRACT

La@C_{82} is recognized by an isophthaloyl-bridged porphyrin dimer forming a stable 1:1 supramolecular complex with an association constant $K_{assoc} = (67.3 \pm 3.2) \times 10^3\ M^{-1}$.

Endohedral metallofullerenes (EMFs) have captured the interest of the scientific community not only because of their unique structures, but also due to their novel electronic properties and the metal-to-cage electron transfer that occurs.[1] La@C_{82}, in which lanthanum donates three valence electrons to the carbon sphere, was the first EMF isolated,[2] and probably the most studied. EMFs offer a diverse range of applications spanning from materials science to medicine. For example, gadolinium-encapsulated EMFs have been widely studied because of their magnetic contrast-enhancing properties,[3] while other metallofullerenes, due to their low HOMO-LUMO gap, have been exploited in molecular electronics and in electron donor-acceptor dyads.[4]

Receptors with open cavities, the so-called molecular tweezers, are able to host materials through non-specific interactions, such as hydrogen bonding, metal coordination, π–π and/or van der Waals interactions.[5,6] In this context, porphyrins have already been exploited as active components to recognize complex fullerene spheres.[7] On the other hand, isophthalic esters have been utilized to bridge extended tetrathiafulvalenes (extTTF) and for constructing some novel receptors for fullerenes based on concave–convex complementarity.[8] However, as far as EMFs are concerned, to the best of our knowledge, their molecular recognition[9] is based on supramolecular host-guest complexation with azacrown ethers,[10] unsaturated thiacrown ethers,[11] and spin-site exchange systems with organic electron donors.[12] Moreover, there is a specific affinity demonstrated by aniline, pyridine, and *N*,*N*-dimethylformamide toward the extraction of EMF from soot,[13] which is believed to occur via interactions of the solvent nitrogen atoms with the EMF.

In this Letter, we report an isophthaloyl-bridged porphyrin dimer–La@C_{82} supramolecular complex (Scheme 1). The complexation is based on cooperative non-covalent forces developed between the tweezer-type porphyrin dimer **1** as well as the N-atoms of **1** and La@C_{82}, and spectroscopically justified with UV–vis titration experiments complemented with photoluminescence, EPR, and electrochemistry. It is worth noting that any electronic interactions in the form of charge-transfer from the photoexcited porphyrin units to the EMF, either in the ground and/or excited states, that may stabilize or even enhance the association constant between **1** and La@C_{82}, are missing.

For the purpose of the current study, La@C_{82} with C_{2v} molecular symmetry (isomer **I**) was used. Briefly, La@C_{82} (**I**) was prepared by the direct current arc discharge method of La-doped graphite composite rods. The resulting soot was collected under totally anaerobic conditions to avoid any degradation due to air during the collection procedure and high-performance liquid chromatography was performed for separation of the lanthanum EMF. The purity of La@C_{82} (**I**) (>99%) was confirmed by both positive and negative laser-desorption time-of-flight (LD-TOF) mass spectrometry.

Porphyrin dimer **1** was synthesized via a condensation reaction between 5-(4-aminophenyl)-10,15,20-triphenyl-21,23*H*-porphyrin and isophthaloyl chloride in 94% yield, and characterized by ^1H and ^{13}C NMR, UV–vis, ATR-IR, and mass spectrometry (Supplementary data, Figs. S1–S5).

In order to determine the binding affinity of La@C_{82} to **1**, a UV–vis spectroscopic titration was carried out in CH_2Cl_2/CS_2 under ambient conditions. The electronic absorption spectrum of **1** (2×10^{-6} M in CH_2Cl_2), showing the characteristic Soret band at 419 nm and Q-bands at 515, 550, 590, and 646 nm (Supplementary data, Fig. S3) was changed upon addition of La@C_{82} (4×10^{-5} M in CS_2). This strongly suggests, that (i) depletion of the absorption maximum at 419 nm, and (ii) the red-shift of the absorption band, leading to the formation of clear isosbestic points at 414 and 424 nm (Fig. 1a) occurred. These changes are indicative of complexation between tweezer-type porphyrin dimer **1** and endohedral metallofullerene La@C_{82}. On the other hand, careful

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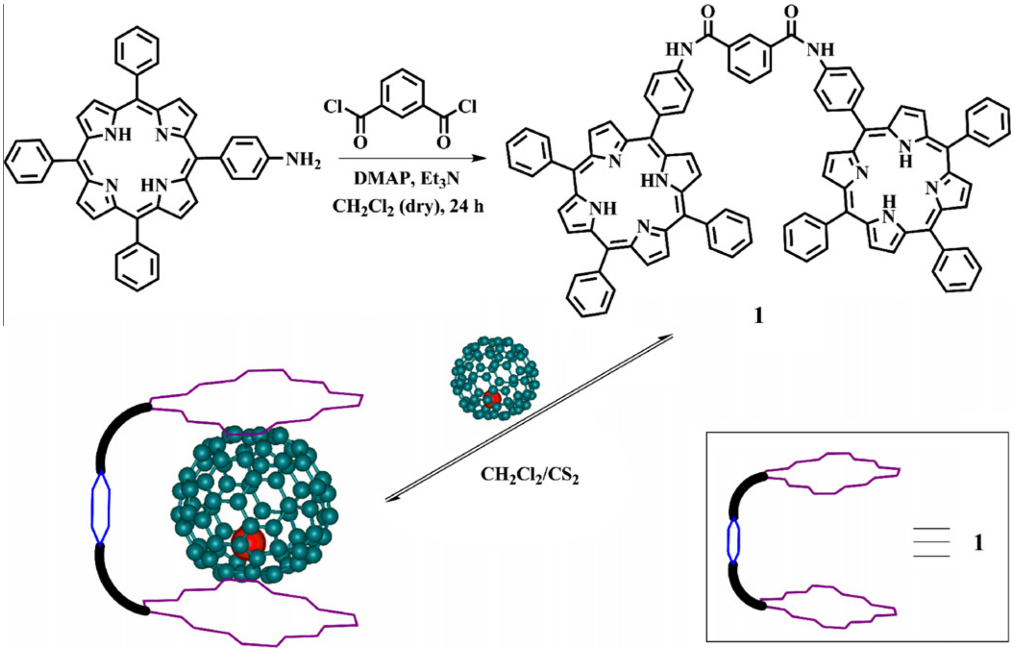

Scheme 1. Synthesis of isophthaloyl-bridged porphyrin dimer **1** and complex formation between **1** and La@C_{82}.

inspection of the near infrared (NIR) region showed that the characteristic absorption of La@C_{82} at 1010 nm is retained throughout the titration experiments, suggesting a lack of anion formation (i.e., fingerprint absorption at around 930 nm[14]), and thus appreciable intracomplex electronic communication between **1** and La@C_{82} in the ground state.

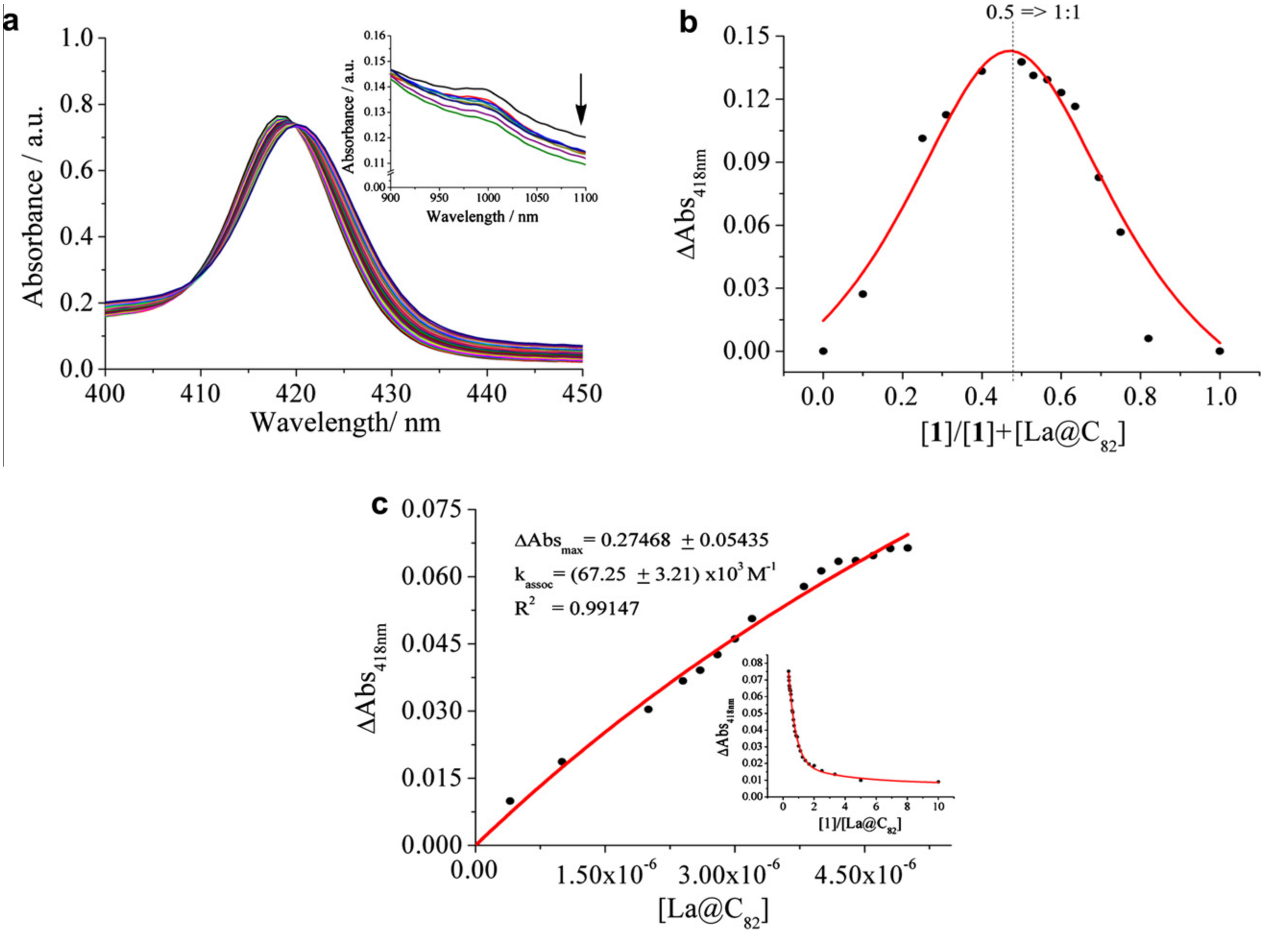

Figure 1. (a) UV–vis spectra of **1** (CH_2Cl_2, 2×10^{-6} M) upon successive addition of La@C_{82} (CS_2, 4×10^{-5} M). Inset: NIR region. (b) Job plot for **1** upon increasing the molar fraction of La@C_{82} in CH_2Cl_2/CS_2 at a fixed overall concentration of 4×10^{-6} M. (c) Fitting curve of ΔAbs (418 nm) with the Hill equation. Inset: Titration plots at 418 nm.

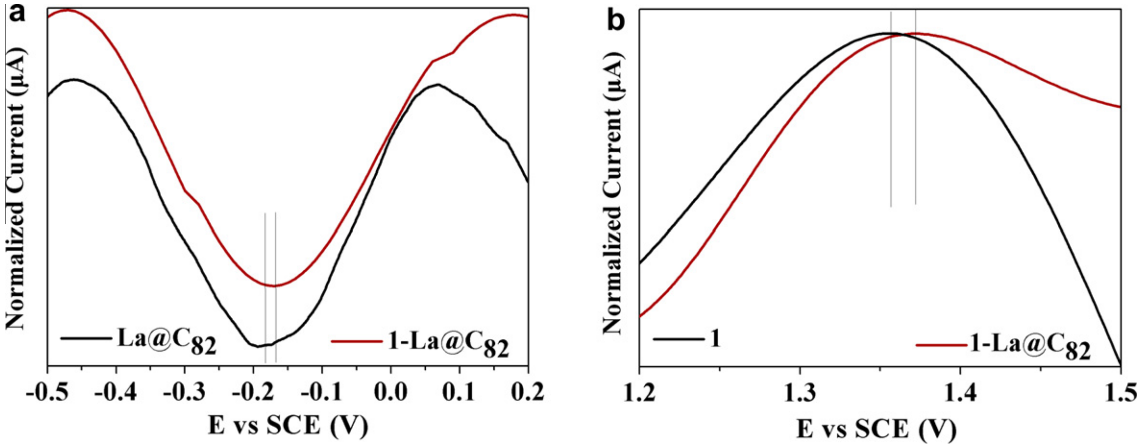

Figure 2. DPV (a) reduction of La@C_{82} (black) and **1**–La@C_{82} (red), and (b) oxidation of **1** (black) and **1**–La@C_{82} (red).

Table 1
Electrochemical data for **1**, La@C_{82} and **1**–La@C_{82}

	E_{ox}	E_{red}	ΔG
1	1.36 V	–	–
La@C_{82}	–	−0.18 V	–
1–La@C_{82}	1.37 V	−0.17 V	−1.28 eV

The continuous variation method, Job plot analysis, as presented in Figure 1b, giving a maximum value of 0.5, together with the spectroscopic titration results, demonstrates that **1** and La@C_{82} form a 1:1 complex. The association constant (K_{assoc}) for the 1:1 complex was determined to be $K_{assoc} = (67.3 \pm 3.2) \times 10^3\ M^{-1}$ by nonlinear curve fitting (Hill equation) analysis of the UV–vis titration curve, using the data obtained in CH_2Cl_2/CS_2, the general form of the Hill equation,

$$\Delta\text{Abs} = \Delta\text{Abs}_{\max}[\text{La@C}_{82}]^n K^n_{\text{assoc}}/(1 + K^n_{assoc}[\text{La@C}_{82}]^n) \qquad (1)$$

where n is the Hill coefficient.

Furthermore, the Hill coefficient of $n_H = 0.94 \pm 0.16$ combined with the fact that the variation in absorption at 424 nm, fits well to a 1:1 binding isotherm, thus strongly suggests the formation of a complex in which one La@C_{82} is entrapped by one porphyrin dimer unit. On the other hand, a complex, where the EMF sphere is sandwiched between two molecules of **1** but recognized by one of the two porphyrin units, where **1** takes a pseudo-planar configuration, is not favored to a great extent, not only because the Hill coefficient is <2,[15] but also because of the suggestive 1:1 binding isotherm (Fig. 1c).

Photoluminescence experiments with excitation at the isosbestic point (i.e., 424 nm) were carried out to complement the absorption titration measurements. In this context, the characteristic emission bands of **1** at 651 and 718 nm, were virtually retained upon addition of La@C_{82} (Supplementary data, Fig. S6). Notably, regardless of changing the solvent, from less polar toluene to polar *o*-dichlorobenzene and nitrobenzene, the emission bands were always the same. This occurs due to the lack of appreciable ground-state electronic interactions between **1** and La@C_{82}, thus intracomplex charge-transfer in the excited state is also missing. Therefore, it is postulated that La@C_{82} is only recognized by non-covalent structural-type supramolecular interactions stabilizing **1**–La@C_{82} complex formation. Contrary to our expectations, the lack of significant charge-transfer interactions does not result in even higher K_{assoc} values being recorded.

Further support for the above conclusions arose from EPR experiments. La@C_{82} is a paramagnetic species due to the electron transfer from La to the cage, thus giving rise to a well-defined eight-line EPR spectrum with characteristic *hfcc* and g-factor parameters.[16] Addition of **1** (1 or even 2 equiv) to a degassed CS_2 solution of La@C_{82}, did not bring any changes in the EPR spectrum (Supplementary data, Fig. S7). Thus, overall it is concluded that any substantial electronic interactions between **1** and La@C_{82} are missing.

Finally, voltammetric studies, performed in *o*-dichlorobenzene/acetonitrile (5:1) under ambient conditions, supported the formation of a **1**–La@C_{82} complex. The redox potential values of **1**–La@C_{82} were determined with the aid of differential pulsed voltammetry (DPV) measurements, with Pt wire as the working electrode, standard Ag/$AgNO_3$ as the reference electrode and $n$$Bu_4NPF_6$ as the supporting electrolyte. As shown in Figure 2, **1**–La@C_{82} exhibits an oxidation peak at 1.37 V, slightly shifted compared with the oxidation of free porphyrin dimer **1** at 1.36 V. The reduction of La@C_{82} was observed at −182 mV versus SCE, while in the presence of **1** the reduction shifts to less negative potentials at −171 mV. Employing the Rehm–Weller equation yields the free energy ΔG at −1.28 eV, thus thermodynamically enabling complex formation of **1**–La@C_{82} via supramolecular means. These electrochemical data are collected in Table 1.

In conclusion, isophthaloyl-bridged porphyrin dimer **1**[16] forms a 1:1 complex with La@C_{82}. Despite the photoactive character of the porphyrin moiety, the association ability of **1** for La@C_{82} is based exclusively on cooperative supramolecular forces, namely structural non-covalent interactions of the porphyrin rings as well as of the nitrogen atoms present in **1** with La@C_{82}.

Acknowledgments

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Supplementary data

Supplementary data (experimental details and spectroscopic data) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.08.111.

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16. *Synthesis of isophthaloyl-bridged porphyrin dimer* **1**: To a solution of aminoporphyrin (0.01 g, 0.016 mmol) and 4-dimethylaminopyridine (0.001 g, 0.008 mmol) in 5 mL of CH_2Cl_2 (dry), a solution of isophthaloyl chloride (0.016 g, 0.08 mmol) in 10 mL of CH_2Cl_2 (dry) was added dropwise over a period of 2 h using an addition funnel. The resulting solution was allowed to stir at room temperature for 24 h and then concentrated under reduced pressure. The residue was taken in EtOAc (20 mL), and the organic layer washed with a saturated solution of NH_4Cl (2×10 mL), then with a saturated solution of $NaHCO_3$ (2×10 mL) dried over Na_2SO_4, and finally concentrated to afford 20 mg (94% yield) of the title compound. ^1H NMR (300 MHz, $CDCl_3$) δ: -2.76 (s, 4H), 7.74 (m, 20H), 8.32–8.14 (m, 20H), 8.60 (s, 2H), 8.92–8.78 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 118.60 (4C), 119.34 (1C), 120.18 (8C), 126.64 (16C), 129.61 (1C), 129.67 (8C), 130.84 (18C), 134.51 (16C), 135.10 (2C), 135.23 (8C), 135.49 (2C), 137.58 (2C), 138.65 (2C), 142.06 (6C), 165.33 (2C); UV–vis (CH_2Cl_2, λ/nm): 419, 515, 550, 590, 646. ATR-IR (cm^{-1}): 3317, 3053, 2954, 2922, 2850, 1720, 1598, 1517, 1278, 1072; ESI-MS: m/z calcd for [M^+] $C_{96}H_{64}N_{10}O_2$: 1389; found: 1389.