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COMMUNICATION

A BPTTF-based self-assembled electron-donating triangle capable of C₆₀ binding†‡

Sébastien Goeb, Sébastien Bivaud, Paul Ionut Dron, Jean-Yves Balandier, Marcos Chas and Marc Sallé*

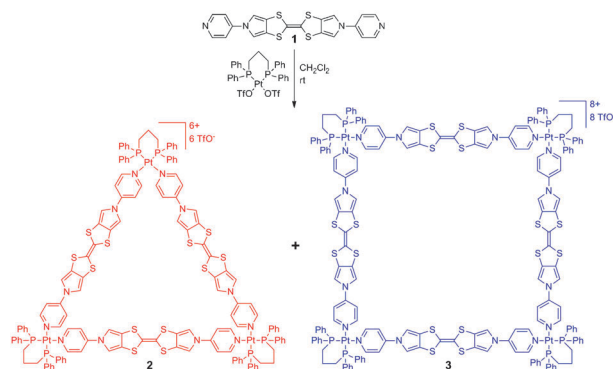
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A kinetically stable self-assembled redox-active triangle is isolated. The resulting electron-donating cavity, which incorporates three BPTTF units, exhibits a remarkable binding ability for electron-deficient C₆₀, supported by a favorable combination of structural and electronic features.

The designing of artificial receptors is the subject of a continuous intense interest, with a special emphasis in recent years towards preorganized macrocyclic¹ or acyclic² hosts able to bind neutral guests such as fullerenes derivatives. The synthesis of covalent macrocyclic receptors is often challenging, and many recent examples have instead taken advantage of the straightforward metal-driven self-assembly methodology.³ In the course of our studies related to the designing of new electron-rich receptors incorporating the tetrathiafulvalene unit,⁴ we recently investigated the preparation of molecular square **3**,⁵ built from self-assembly of a BPTTF-based electron-rich bis-pyridyl ligand with a *cis*-blocked square-planar (*dppp*)Pt(OTf)₂ complex (BPTTF: bis(pyrrolo)tetrathiafulvalene).⁶ Self-assembled molecular squares are expected to be formed from linear rigid bis-pyridyl ligands and square planar metallic centers (M = Pd, Pt), as in the case of the prototypical 4,4'-dipyridyl molecule.⁷ Nevertheless, they are often accompanied by triangle homologues, in particular when longer and/or less rigid bridging bis-pyridyl ligands are used.⁸ Both supramolecular polygons generally exist as an equilibrium mixture that is difficult to separate/isolate. Their characterization is often puzzling and needs a combination of spectroscopic tools (*i.e.* ¹H, ³¹P, and diffusion-ordered NMR spectroscopies, mass spectrometry). On this ground, we report here that triangle **2** and square **3** can be separately isolated, and that they show remarkably distinctive coulometric and fullerene binding properties.

The reaction of ligand **1** with an equimolar amount of *dppp*Pt(OTf)₂ in methylene chloride (Scheme 1) leads to the rapid dissolution of the ligand, and the subsequent precipitation



Scheme 1 Polygons obtained by metal-mediated self-assembly of ligand **1**.

of the square system **3** in a 31% yield after filtration.⁵ Interestingly, we could also recently isolate the triangle analogue **2** in 60% yields from the remaining solution through evaporation of the solvent. The latter shows a good kinetic stability and was characterized by various analytical tools (Fig. 1). Multinuclear NMR (¹H, ³¹P, ¹⁹F) analyses of **2** in acetone-*d*₆ are illustrative of the formation of a discrete supramolecule. Only two AA'XX' signals are observed on the ¹H-NMR spectrum for pyridyl protons (H_α = 8.86 ppm, H_β = 7.31 ppm) in accordance with pyridine units coordinated to Pt.⁹ Metal binding is confirmed by a downfield shift of the CH₂P signal (3.46 ppm) in **2** relative to the *dppp*Pt(OTf)₂ complex (3.25 ppm). The ¹⁹F and ³¹P NMR analyses are consistent with the occurrence of a single discrete structure. ¹H-DOSY experiments were run from each polygon species **2** and **3** in acetone for comparison (Fig. 1 and Fig. S1, ESI†). In both cases, a single alignment of signals was observed, as expected from a single discrete structure. Moreover, it is known that a correlation can be established between the diffusion coefficient *D* and the size of the species under study, assimilated to spherical entities, and recent reviews have detailed the scope of this issue¹⁰ through the use of the Stokes–Einstein equation ($D = k_B T / 6\pi\eta r_H$).¹¹ On this basis, square **3** presents a lower experimental diffusion coefficient ($D_S = 4.78 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) than the smaller triangle **2** ($D_T = 5.56 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$).¹² From these data, a ratio of 0.80 is found between the square and the triangle experimental radii, in excellent agreement with the theoretical value obtained from geometrical

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† Dedicated to Dr Hubert Le Bozec on the occasion of his 60th birthday.
‡ Electronic supplementary information (ESI) available: Detailed synthesis protocol, experimental method and additional spectroscopic data. See DOI: 10.1039/c2cc00065b

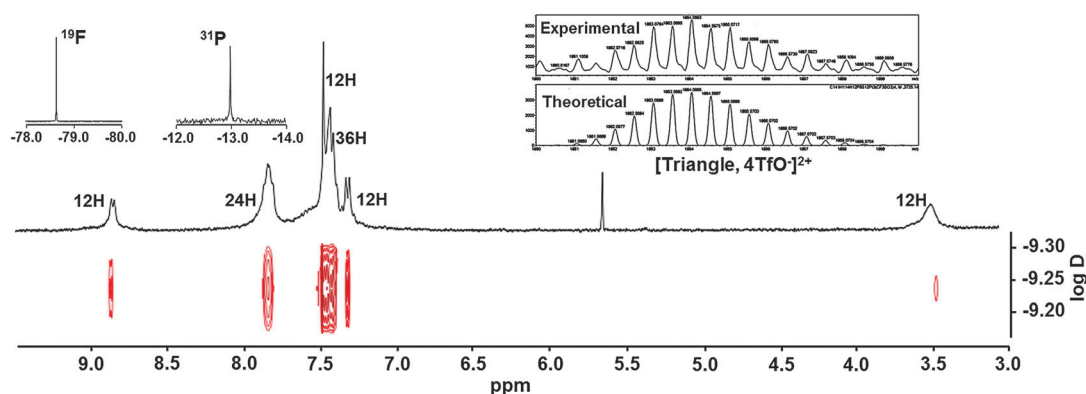


Fig. 1 Analytical data for triangle 2.

considerations (0.82)¹³ (Fig. S2, ESI†). The molecular structure of triangle 2 was confirmed by ESI analysis led in acetonitrile, with an experimental isotopic pattern centered on the m/z 1864 peak. The comparison with a theoretical isotopic distribution calculated for a dicharged species ($\Delta m = 0.5$ u) confirms the transfer into the gas-phase of the molecular triangle structure $[(1\text{-Pt}dppp)_3\text{4TfO}]^{2+}$.

Cyclic voltammetry of compound 2 was carried out in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1/1 v/v) (Bu_4NPF_6 0.1 M), and two redox waves assigned to the two successive reversible oxidations usually observed with BPTTF moieties are found ($E_{\text{ox}}^1 = 700$ mV, $E_{\text{ox}}^2 = 998$ mV) (Fig. 2). The electrochemical reversibility of triangle 2, which remains unchanged upon recurrent scanning of the potentials between 0.3 and 1.2 V vs. Ag/AgCl, illustrates the stability of this self-assembled structure, regardless of the oxidation state of the redox-active BPTTF unit. A CV experiment was led from a mixture of ligand 1 and three equivalents of ferrocene, used as an internal coulometric reference. As observed from the deconvoluted CV (Fig. 2), the intensity for the two reversible redox waves corresponding to BPTTF units is similar to the ferrocene ones. This finding confirms that each of the three BPTTF units behaves independently through two successive one electron reversible oxidation processes, similarly to what we observed previously from a model corner complex.¹⁴ Therefore, full oxidation of triangle 2 produces stable $2^{3(+)}$ and 2^{6+} species and, importantly, allows a reversible control over the charge state of the cavity. The same electrochemical study was extended to

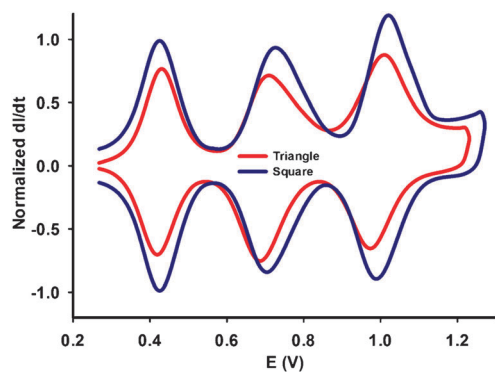


Fig. 2 Deconvoluted cyclic voltammograms of triangle 2 (0.5 mM) and square 3 (0.5 mM) in the presence of ferrocene (3 equiv. and 4 equiv., respectively) $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1/1 v/v) (Bu_4NPF_6 0.1 M), vs. Ag/AgCl.

the square derivative 3 containing four BPTTF units. In this case, four equivalents of ferrocene were introduced, and a similar observation as for 2 can be done (Fig. 2), which in this case signifies the generation of $3^{4(+)}$ and 3^{8+} species upon oxidation. Such electrochemical behavior is also compatible with recent observations made from a self-assembled macrocycle incorporating vinylous tetrathiafulvalene units (ref. 15).

As recently reviewed,^{1a} the search for molecular receptors able to bind electron-deficient fullerenes is the subject of intense interest, and their chemical recognition is supported by an unusual combination of structural and electronic parameters. In such receptors, van der Waals and π - π interactions, which are in essence dependent on the available surface area, prominently contribute to the C_{60} sphere recognition, besides other interactions such as electrostatic accounting for the electron deficient character of C_{60} .¹⁶ On this ground, pristine TTF, though being known as a strong electron-donating system, but which suffers from a moderate π -extension surface, generates relatively small interactions with fullerene guests,¹⁷ unlike π -extended analogues such as the so-called *ex*TTF in which two 1,3-dithiole rings are conjugated through a bent anthracene unit,^{1a,18} or calix[4]pyrrole conjugates.¹⁹ The binding affinity of triangle 2 for C_{60} was studied by UV-visible titration in a $\text{CS}_2/\text{CH}_2\text{Cl}_2$ (8/2 v/v) solution. The titration curve (Fig. S3, ESI†) shows a decrease in the contribution of receptor 2 at 408 nm, the appearance of a tiny charge-transfer band in the 500 nm region, and an isosbestic point at ca. 455 nm, which are assigned to the binding of C_{60} by triangle 2. This result is confirmed by a Job's plot analysis (Fig. 3) from which a 1 : 1 stoichiometry is determined. A binding constant of $\log K_a = 4.2$ is found, based on the Benesi-Hildebrand equation for 1 : 1 complexes, which corresponds, as far as we know, to the highest value ever described for a BPTTF-based receptor. The fact that C_{60} is bound by host 2 is therefore ascribed to the favorable rigid preorganized structure of the latter which inner cavity size (13 Å) matches with the fullerene size, allowing a cooperative contribution of the three BPTTF units. In addition, the electron-donating ability of the latter appears to favorably compensate their moderate π -extension surface. From this point of view, it is worth noting that no evidence of C_{60} binding could be determined from the similar UV-vis titration experiment with square derivative 3.⁵ Regarding this issue, the comparison of the cavity size between triangle 2 and square 3 is particularly informative since a value

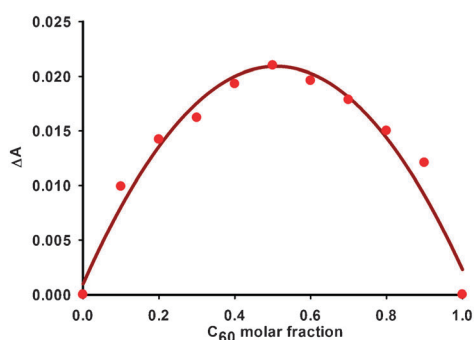


Fig. 3 A Job's plot at 407 nm, triangle **2** (1.3×10^{-5} M) vs. C_{60} (1.3×10^{-5} M) at rt in CS_2/CH_2Cl_2 (8/2 v/v).

of 22 Å is observed for the plane to plane distance between facing BPTTF units in the latter case (Fig. S2, ESI[†]), far too large to bind one C_{60} unit in a cooperative way.

In summary, we report here that a metalla-assembled redox-active triangle **2** can be isolated and that this system presents well-defined electrochemical properties, providing a full control over the charge state of the cavity and opening promising perspectives in terms of binding control for a given guest. From this point of view, whereas several metalla-assembled cages able to bind C_{60} have been produced,²⁰ receptor **2** constitutes the first example of a self-assembled polygon able to bind efficiently a C_{60} molecule. In addition to validate the use of electron-donating BPTTF ligands on one hand and the macrocyclic approach already recently developed in the covalent series on the other hand,^{18a,b} this result contributes to underline the efficiency of the Pt-driven self-assembly methodology for a straightforward access to macrocyclic receptors. On this basis, extension of this strategy to electron-rich cages is underway.

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- T is the absolute temperature, k_B the Boltzmann constant, r_H the hydrodynamic radius, and η the solvent viscosity at temperature T .
- The experimentally determined values of r_H are, as usually observed with polygons, smaller than the calculated ones. This is assigned, when applying the Stokes–Einstein equation, to the initial geometrical approximation of polygons complexes as spherical ones and to the occurrence of a cavity within the complex, which may reduce the effective diffusion coefficient additionally.
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