Inclusion of C_{60} into an adjustable porphyrin dimer generated by dynamic disulfide chemistry†

Amy L. Kieran, Sofia I. Pascu, Thibaut Jarrosson and Jeremy K. M. Sanders*

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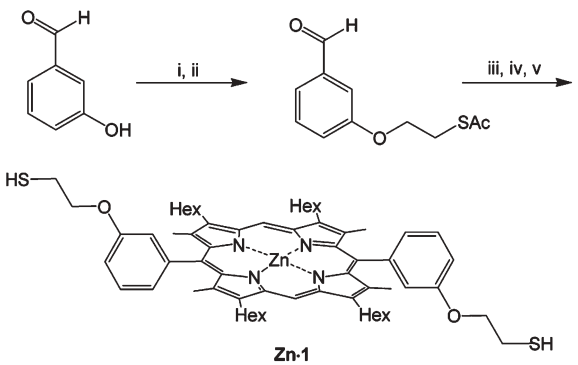
A new, highly flexible porphyrin dimer was isolated in preparative scale from a dynamic disulfide library; this receptor adjusts to fit guests with a wide range of steric requirements and, whilst C_{60} proved to be an unsuitable template for this library, a new C_{60}-porphyrin complex was isolated and characterised.

Since the discovery of fullerenes,[1] there has been increasing interest in their supramolecular chemistry because of their potential applications in chemistry, biology and materials science.[2,3] Fullerenes fit into appropriate preorganised cavities to form stable complexes.[4,5] After the first report of a co-crystallisation of C_{60} with a porphyrin monomer, the search for a highly selective receptor has intensified. Successful co-crystallisations of C_{60} and C_{70} with tetraarylporphyrins and octaethylporphyrin revealed a zigzag arrangement of porphyrins with fullerenes sandwiched in the cleft.[6–10] There is an unexpectedly strong interaction between the curved π surface of C_{60} and the flat π surface of porphyrins, which is largely van der Waals in origin (the $C_{fullerene}$-to-porphyrin plane distance is *ca.* 2.7 Å).[7] Based on those observations, many jaw-like bis-porphyrin systems have been designed to minimise the reorganisation required for binding.[11–13]

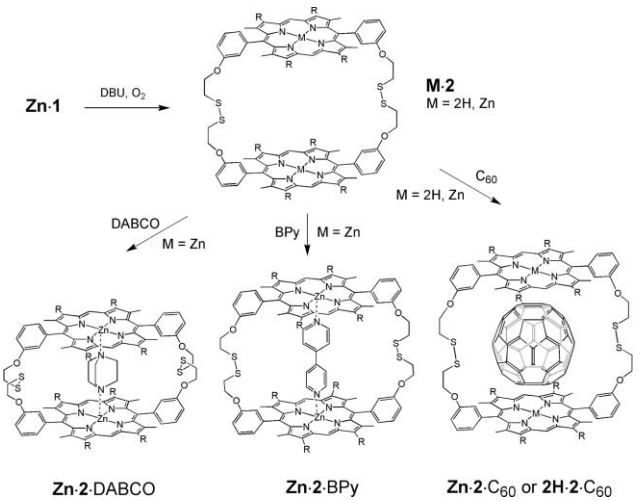
We have recently described the use of a bis-benzylthiol substituted porphyrin as a building block in a dynamic library, which led, upon binding to DABCO, to the exclusive formation of dimer as a result of the excellent geometrical fit of this template.[14] We report here the dynamic synthesis of a flexible new porphyrin dimer which is an effective receptor for C_{60}.

The new monomer Zn-1 was synthesised in five steps according to Scheme 1. In order to obtain the desired flexible dimer by dynamic chemistry, initiation of exchange was carried out with 5 mM solutions of Zn-1 in $CHCl_3$, and 0.2 equiv. DBU. Thermodynamic equilibrium was reached in 3 days, as judged by HPLC analysis. The composition of the library in the absence of guests was found to be 94 : 5 : 1 dimer : trimer : tetramer. When a small template 1,4-diazabicyclo(2.2.2)octane (DABCO) or a larger one 4,4′-Bipyridine (BPy) was added to monomer Zn-1, the equilibrium composition changed to 98 : 2 dimer : trimer for both DABCO and BPy, demonstrating the accordion-like features of the new receptor (Scheme 2).‡ On chromatography over alumina the guest remained encapsulated in the dimer cavity, bound between the two porphyrin faces. When use of C_{60} as template was attempted it was apparent that this began to decompose under the library conditions. This is due to the instability of C_{60} with respect to thiols under basic conditions, leading to C_{60}^{2-} as shown by Kadish *et al.*[15]

^{1}H NMR spectroscopy revealed that the complexes share similar features and symmetry, with the ligands in slow bound-free exchange. Dimer Zn-2 can be easily demetallated by treatment with acid to give 2H-2 and then remetallated following a standard procedure. Addition of 1 equiv. DABCO to a solution of BPy-encapsulated dimer results in the quantitative displacement of BPy. Thermodynamic measurements by isothermal microcalorimetry



Scheme 1 *Reagents and conditions*: (i) 1,2-dibromoethane, K_2CO_3, DMF, 60 °C, 40%; (ii) KSAc, Toluene, 110 °C, 95%; (iii) 5,5′-dibenzyloxycarbonyl-3,3′-dihexyl-4,4′-dimethyl-2,2′-dihydropyrrin, Pd/C, THF with 2% NEt_3 and 2% MeOH; TFA, 0 °C, 53%; (iv) $Zn(OAc)_2{\cdot}2H_2O$, $CHCl_3$, 50 °C, 100%; (v) $NH_2NH_2{\cdot}H_2O$, CH_2Cl_2, 25 °C, 100%.



Scheme 2 Binding of guests inside the adjustable receptors M-2.

† Electronic supplementary information (ESI) available: details of the instrumentation used and the synthetic procedures. See http://www.rsc.org/suppdata/cc/b4/b417951j/

*jkms@cam.ac.uk

Table 1 ITC results for Zn-2 with DABCO and Bpy in $CHCl_3$ (0.4 mM ligand titrated into *ca.* 0.04 mM porphyrin dimer). ITC data for the titration of M-2 with C_{60} were not obtained due to the low solubility of the C_{60} complex in $CHCl_3$

Dimer	K_{ITC}/ $10^6 \times M^{-1}$	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	$\Delta G°$/ kJ mol^{-1}
DABCO	7.75	−80.8	−41.4	−39.3
BPy	0.50	−68.8	−36.3	−32.5

(ITC) indicate a smaller favourable enthalpy of binding for BPy, as expected for an aromatic amine compared to an aliphatic one (Table 1). The same order of magnitude was found for $T\Delta S$ in both BPy and DABCO adducts, suggesting that the entropic contributions are dominated by the restriction in conformational freedom induced by complexation.

^{1}H NMR (293 K, $CDCl_3$, 500 MHz) showed that the *meso* signals of the free porphyrin host can be found between 8.5 and 9.5 ppm as broad signals, due to an off-set π–π stacking and the presence of a variety of conformations.[16–18] Binding to DABCO or BPy led to the 'freezing' of the host into a single conformation, and consequently a clearer region in ^{1}H NMR: *meso*-hydrogens resonate at 10 ppm (BPy complex) or 9.5 ppm (DABCO complex) as sharp singlets.

^{1}H NMR spectroscopy (293 K, 500 MHz, CS_2 : $CDCl_3$ 9 : 1) was used to monitor titration of C_{60} into solutions of dimers.

Changes in the aromatic region were observed. For 2H-2, a single sharp *meso*-H was seen at 9.88 ppm, and the aromatic region was simplified with respect to the spectrum of the free host. This indicates an increase in the rigidity of the system upon C_{60} complexation. It can only be assumed that the inner *ortho*-H vicinal to the alkyl chain (7.03 ppm) points into the cavity as it has been shown to do in the case of BPy (7.36 ppm) or DABCO (7.49 ppm) binding. This upfield shift indicates that the proton falls into a strongly shielding region of the guest, in contrast to the binding of DABCO or BPy, where deshielding by the porphyrin ring current was observed. A similar upfield shift is seen for the –OC*H*$_2$C*H*$_2$S– linker protons, which again points towards C_{60} encapsulation within the dimer. Whilst the ^{1}H spectrum suggests that the complex adopts one conformation, it gives no indication about the rate of exchange of the host and guest. However, attempts to monitor the binding by ^{13}C NMR (293 K, $CDCl_3$, 125 MHz) suggested that it was in fast exchange on the NMR timescale. Signal averaging resulted in just one signal for C_{60} being observed at 142.3 ppm due to the rapid exchange of complexed and free fullerene on the NMR timescale (*N.B.* δ for free C_{60} in $CDCl_3$ 143.1 ppm).

The X-ray diffraction structure shows formation of the inclusion complex (Fig. 1).§ The porphyrin macrocycles are saddled in order to accommodate the convex C_{60}. A difference Fourier map suggested that C_{60} is rotationally disordered within the cavity (consistent with the ^{13}C NMR spectrum) and more than two atoms became necessary to model each of the C_{60} sites. Therefore, a 'smeared-out' electron density over the surface of the sphere provided an alternative model for C_{60} with a refined radius of 3.531(4) Å.[19] As a result, it could not be determined with precision which edge or face of the C_{60} has the closest approach to the porphyrin core. The hexyl side chains of the porphyrin dimer are folded around the C_{60}, creating a cage-like species. In Aida and co-workers' complexes,[20] a 5 : 6 ring-juncture of C_{60} was located above the central metal ion. In our case, the best-fit plane of the porphyrin–C_{60} outer shell distance was found to be 2.87 Å, significantly less than the sum of the van der Waals radii (3.09 Å).[21] This observation suggests the presence of a π interaction. The ethyloxydisulfide linkers of the dimer are folded to adjust the porphyrin–porphyrin distance in an asymmetric fashion. This results in a tilt angle between the porphyrin planes of 11°, much smaller that the angle reported by Reed *et al.* in their tweezer host (42°).[11]

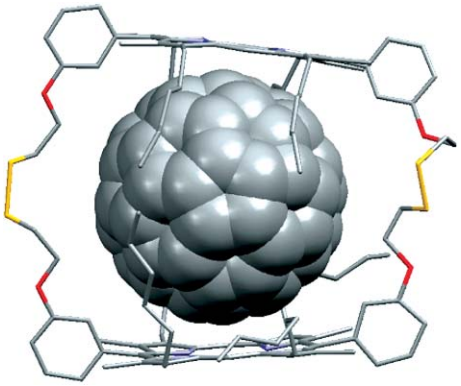


Fig. 1 Molecular structure of the inclusion complex between receptor 2H-2 and C_{60} (hydrogen atoms omitted for clarity).

In conclusion, we have developed a new porphyrin receptor for C_{60} through dynamic reversible chemistry. Use of an 'extendable' linker allowed the construction of the receptor with templates of differing steric requirements.

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Amy L. Kieran, Sofia I. Pascu, Thibaut Jarrosson and Jeremy K. M. Sanders*
Department of Chemistry, University of Cambridge, Lensfield Rd, Cambridge, UK CB2 1EW. E-mail: jkms@cam.ac.uk; Fax: +44 1223 336017; Tel: +44 1223 336411

Notes and references

‡ Use of extended tripyridyl templates leads to efficient templated synthesis of the trimer.

§ Layering of a concentrated solution of the 2H-2·C_{60} complex ($CDCl_3$: CS_2 1 : 9) with hexane yielded small deep red triangular-shaped crystals. Crystallographic data were collected using the synchrotron radiation source at Station 9.8, Daresbury SRS, UK, on a Bruker SMART CCD diffractometer. The structures were solved by direct methods using the program programs SIR92[22] The refinement (on *F*) and graphical calculations were performed using the CRYSTALS[23] program suite. Crystal data: $C_{128}H_{168}N_8O_4S_4$ C_{60}, M = 2731.72, Z = 4, monoclinic, space group $P2_1/n$, a = 20.3893(19) Å, b = 29.840(3) Å, c = 23.181(2) Å, β = 90.746(2)°, U = 14103(2) Å^3, T = 150 (2) K, μ = 0.133 mm^{-1}, synchrotron radiation λ = 0.68920 Å. Of 26067 reflections measured, 11009 were independent (*R*int = 0.03). Final R = 0.1651 (3780 reflections with $I > 3\sigma(I)$) and wR = 0.1776. CCDC 256714. See http://www.rsc.org/suppdata/cc/b4/b417951j/ for crystallographic data in .cif or other electronic format.

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