Conjugated Macrocycles

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All-or-Nothing Cooperative Self-Assembly of an Annulene Sandwich**

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Large π-conjugated macrocycles and annulenes are intriguing compounds for testing theories of electronic structure because of their high symmetry, lack of end-group effects, strain, and distorted π overlap.[1–7] Some of these features lead to extraordinary linear and nonlinear optical properties[5] as well as unusual host–guest chemistry based on interactions of curved π surfaces.[6] With increasing ring size, these unique properties disappear because the rings become so flexible that they adopt polymer-like random-coil conformations.[2b,c] We recently introduced Vernier templating as a strategy for the synthesis of large monodisperse π-conjugated macrocycles, such as the [12]porphyrin nanoring ***c*-P12** (Figure 1 a).[4c] Structural rigidification of such macrocycles by coordination to radial templates becomes challenging because of the inaccessibility of large rigid templates. Linear conjugated porphyrin oligomers bind bidentate ligands, such as 1,4-diazabicyclo[2.2.2]octane (DABCO) and 4,4′-bipyridine, to form rigid, self-supported double strands.[8] Planarization of the π systems in these ladder complexes enhances the two-photon absorption and the charge-carrier mobilities.[9] Here we show that double-strand formation can also be used to lock the conformations of large π-conjugated macrocycles, as illustrated for ***c*-P12** in Figure 1.

The two simplest geometries providing complete π conjugation around an annulene are those in which the p orbitals are radial (as in carbon nanotubes)[3] or axial (as in classical aromatic molecules).[7] In principle, the formation of a double-strand complex offers a unique opportunity to switch between these two geometries, without altering the covalent structure.

Recent STM imaging experiments indicated that porphyrin nanoring ***c*-P12** lies flat on a gold(111) surface, with the porphyrin macrocycles parallel to the substrate,[4c] in the correct conformation to assemble a double-strand sandwich. Encouraged by this result, we tested the formation of (***c*-P12**)$_2$·(DABCO)$_{12}$ by adding DABCO to ***c*-P12**. When following this process by ^{1}H NMR spectroscopy, we observed the appearance of a new species of lower symmetry which is in slow exchange with ***c*-P12** (Figure 2). The most evident sign of complex formation is the resonance at $\delta_H = -4.1$ ppm corresponding to DABCO molecules bound between two porphyrin rings.[8] When a 12:2 stoichiometry is reached, the transformation is complete and further addition of DABCO only results in the growth of a broad signal corresponding to free DABCO at $\delta_H = 2.7$ ppm, which is in slow exchange with the signal at $\delta_H = -4.1$ ppm.

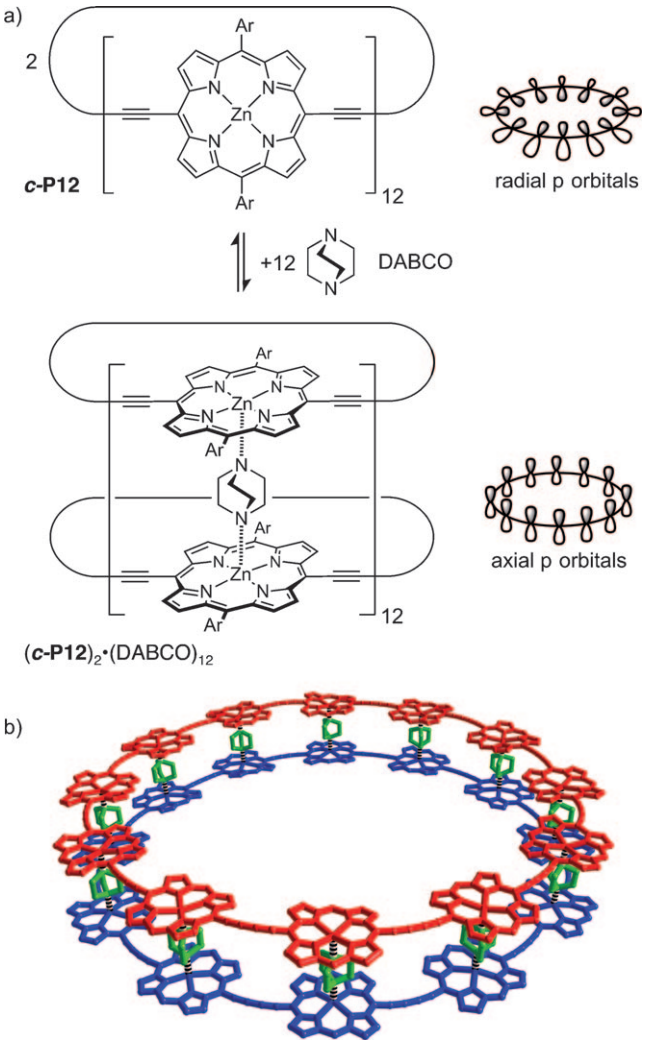

Figure 1. a) Formation of (***c*-P12**)$_2$·(DABCO)$_{12}$ from ***c*-P12** and DABCO (Ar = 3,5-dioctyloxyphenyl) with schematic representations indicating the orientation of porphyrin p orbitals. b) Calculated structure of the sandwich complex (MM+ force field, HyperChem; aryl side groups and hydrogen atoms are omitted for clarity, but were present during the calculation).

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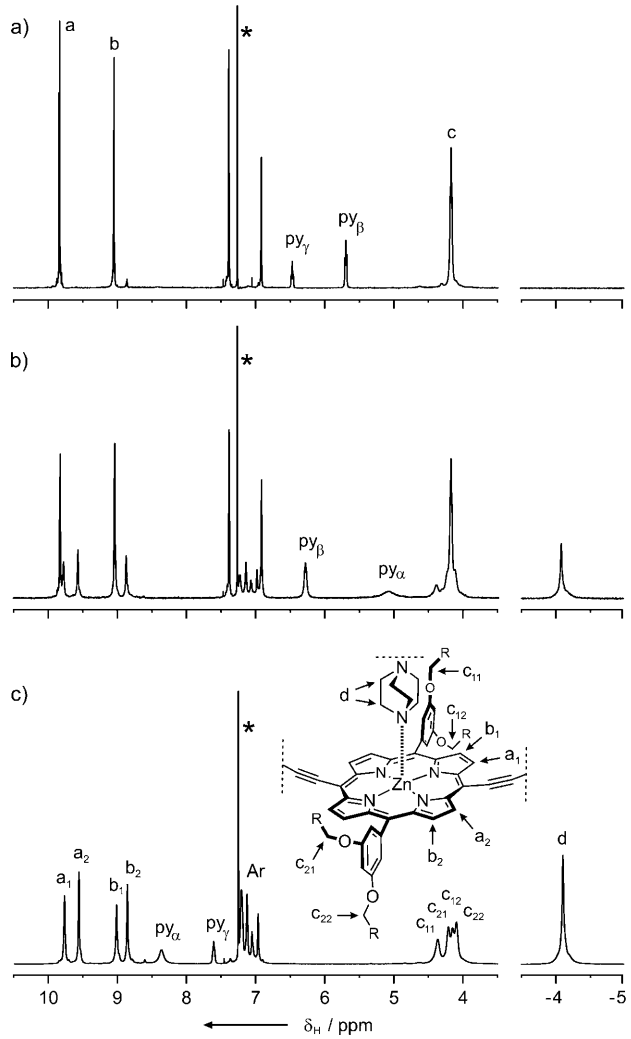

Figure 2. ^{1}H NMR titration of DABCO into ***c*-P12** ($CDCl_3$, 298 K, 500 MHz) and assignment of signals. a) 0 equivalents DABCO, b) 3 equivalents DABCO, and c) 6 equivalents DABCO. Signals labeled as py are due to the presence of 12 equivalents of pyridine initially bound to ***c*-P12** and displaced by DABCO in the course of the titration. The asterisks mark the solvent signal ($CHCl_3$).

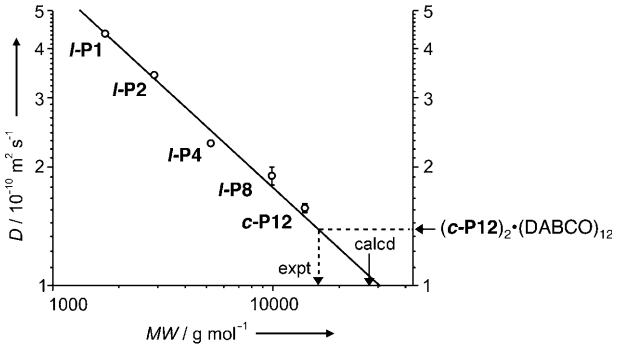

Figure 3. Diffusion coefficients (D) of linear oligomers (***l*-P1**–***l*-P8**) and ***c*-P12** (circles), all as pyridine complexes, plotted against their molecular weights (M). An exponential decay fitted to data from linear oligomers (black line, $D = 203 \times 10^{-10}\ M^{-0.51}$) was used to estimate the molecular weight of (***c*-P12**)$_2$·(DABCO)$_{12}$ (dotted arrow) from its diffusion coefficient (black arrow). The vertical black arrow marks the calculated molecular mass. Error bars are not shown for ***l*-P1**, ***l*-P2**, and ***l*-P4** because they are smaller than the corresponding data points.

The formation of (***c*-P12**)$_2$·(DABCO)$_{12}$ holds the edges of the porphyrin rings in different environments. The top and bottom face of the porphyrins become inequivalent, as do the inside and outside (near and far from the center of the nanoring). This results in the observation of four signals for aryl alkoxy protons H_c, whereas only one signal is observed in the conformationally flexible unbound nanoring ***c*-P12**. The ^{1}H NMR spectrum of (***c*-P12**)$_2$·(DABCO)$_{12}$ was fully assigned by using NOESY and COSY NMR techniques.[10]

To confirm formation of a discrete double-strand complex, rather than a mixture of oligomeric assemblies, we measured the diffusion coefficient (D) by diffusion-ordered NMR spectroscopy. Molecular weights of unknown assemblies can be estimated from their diffusion coefficients using a calibration curve created from a series of structurally similar compounds.[11] We established such a calibration using linear analogues of ***c*-P12** (monomer ***l*-P1**, dimer ***l*-P2**, tetramer ***l*-P4**, and octamer ***l*-P8**) and found that ***c*-P12** fitted well on this curve, thus confirming the validity of the calibration (Figure 3). The measured diffusion coefficient of (***c*-P12**)$_2$·(DABCO)$_{12}$ of $(1.39 \pm 0.04) \times 10^{-10}$ m^{2}s^{-1} corresponds to an apparent molecular weight of 16.2 kDa, which is significantly less than the expected value of 27.4 kDa. The low apparent molecular weight of the sandwich complex reflects its compactness (see calculated models in the Supporting Information).[12] This result shows that large polymeric assembles are not formed.

UV/Vis/NIR titrations provided more insight into the self-assembly process. Titration of ***c*-P12** with DABCO gave an abrupt end-point at six equivalents of DABCO, thus confirming the 12:2 stoichiometry, but the binding curve was too square to provide a measure of the formation constant K_f (see the Supporting Information). A large excess of DABCO (about 10^4 equivalents) resulted in a second spectroscopic change, corresponding to disassembly of the sandwich complex (Figure 4a). Both these processes can be understood by considering a general thermodynamic cycle (Figure 5).[4,8,13] Both phases of the titration have several isosbestic points, which indicates that the processes behave as two-state equilibria and that the only four species that build up to significant concentrations are A (the receptor, ***c*-P12**), B (the ligand, DABCO), A_2B_N (the sandwich complex), and AB_N (the ligand-saturated receptor). The isotherm for breaking up a double-strand complex of a receptor with N binding sites by adding excess ligand is given by Equation (1), where $[A]_0$ and

$$\theta = \frac{[AB_N]}{[A]_0} = \frac{-K_b[B]_0^N + \sqrt{K_b^2[B]_0^{2N} + 8K_b[B]_0^N[A]_0}}{4[A]_0} \qquad (1)$$

$[B]_0$ are the total concentrations of A and B.[14]

Thus, a plot of the extent of denaturation (θ) against $[B]_0$ (Figure 4b) provides information on the number of binding sites N and the equilibrium constant K_b. In Figure 4b, the experimental data are fitted to the calculated curves for $N = 8$,

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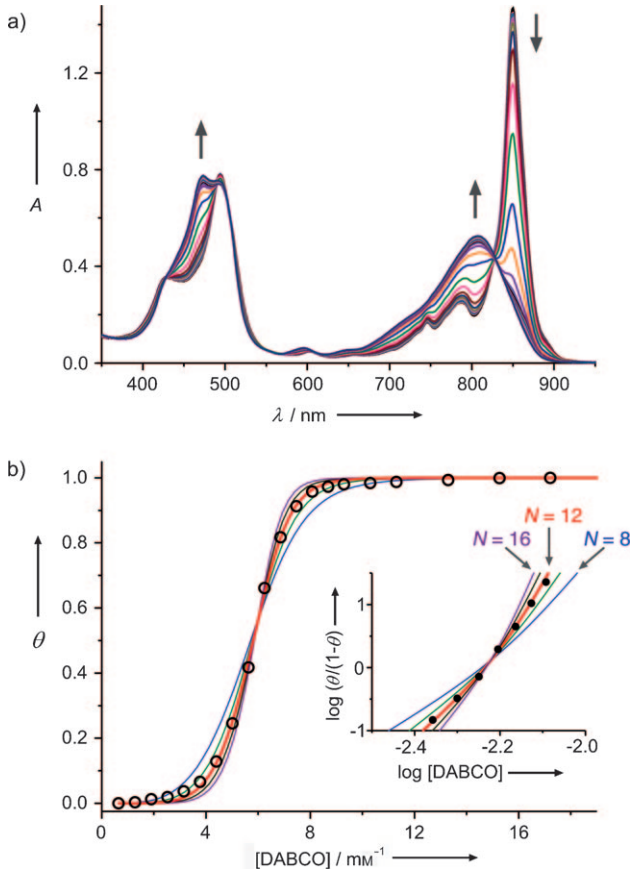

Figure 4. UV/Vis/NIR titration of DABCO into (***c*-P12**)$_2$·(DABCO)$_{12}$ ($c = 0.34$ μM, $CHCl_3$, 298 K). a) Absorption spectra in the course of the titration. Arrows indicate the change in the spectrum with increasing DABCO concentration. b) Extent of denaturation of (***c*-P12**)$_2$·(DABCO)$_{12}$ (θ) derived from the absorption at 850 nm (black dots) fitted to the calculated curves for $N = 8$ (blue line), 10 (green line), 12 (red line), 14 (gray line), and 16 (purple line) binding sites. The inset shows the Hill plot with fits for the same values of N.

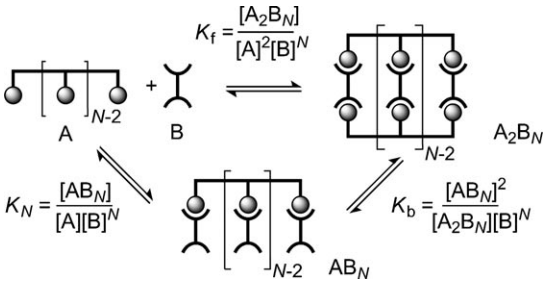

Figure 5. Generic thermodynamic cycle for the formation of a double-strand complex. (In the case studied here, N is 12, A is ***c*-P12**, and B is DABCO.)

10, 12, 14, and 16. The best fit is obtained for $N = 12$. The Hill plot (insert in Figure 4b) shows that the Hill coefficient increases with N and that the observed value ($n_H = 9.5$) matches that predicted for $N = 12$. Although this is the expected result, the quality of the fit is amazingly good, indicating that this is a remarkably clean all-or-nothing two-state process, probably because of the lack of end-group effects; a linear duplex is expected to fray more easily than a cyclic one.

From fitting the titration data we obtained the break-up constant $K_b = (4.6 \pm 0.2) \times 10^{20}\,M^{-11}$. According to the thermodynamic cycle in Figure 5, this value implies a formation constant $\log K_f = 131 \pm 1$ (see the Supporting Information).[15]

Molecular mechanics calculations confirm that (***c*-P12**)$_2$·(DABCO)$_{12}$ adopts a conformation in which all 12 porphyrin moieties of each ring are locked in a coplanar geometry, with axially aligned p orbitals (Figure 1b). Planarization of ***c*-P12** results in dramatic changes in the absorption and emission spectra (Figure 4a and see the Supporting Information). Whilst the spectra of the free-nanoring ***c*-P12** are similar to those of the linear polymer (***l*-PN**, $N \approx 40$), there is a significant red-shift of the Q absorption band in (***c*-P12**)$_2$·(DABCO)$_{12}$, as a consequence of increased conjugation ($\Delta E = 78$ meV). The rigid symmetric geometry of the complex, compared to the single-strand ring, is reflected by its sharper Q band (full width of half maximum height (FWHM) = 46 meV and 195 meV, respectively) and smaller Stokes shift (21 meV and 95 meV, respectively).

In conclusion, we have used NMR titrations, diffusion-ordered NMR spectroscopy, and UV/Vis/NIR titrations to show that [12]porphyrin nanoring ***c*-P12** forms a remarkably stable 2:12 sandwich complex with DABCO. Addition of a large excess of DABCO results in disassembly of the sandwich, in a highly cooperative all-or-nothing process. The sharp NIR absorption band of the double-strand complex indicates that its π system is locked into a regular planar conformation. It appears likely that this strategy could be used to lock the geometries of even larger rings, by using readily available ligands. We are currently exploring the effect of planarization on exciton delocalization in these large nanorings.

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[10] For the sake of clarity in Figure 2, we assume that the protons nearer the center of the nanoring (a_1, b_1, c_{11}, c_{12}) are more deshielded than those on the outside (a_2, b_2, c_{21}, c_{22}), because of their closer proximity of the other porphyrin units.

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[12] Molecular mechanics calculations confirm that ***c*-P12** and (***c*-P12**)$_2$·(DABCO)$_{12}$ have similar radii of gyration and solvent-accessible volumes. Analysis by gel-permeation chromatography (GPC) confirmed the monodispersity of (***c*-P12**)$_2$·(DABCO)$_{12}$ (see the Supporting Information).

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[14] The derivation of Equation (1) assumes that the K_f value is so high that the concentration of the free receptor is negligible (i.e. $[A] \approx 0$) and it makes the approximation $[B] \approx [B]_0$, which is valid when $[B]_0 \gg [A]_0$, as in the titration in Figure 4.

[15] The value for K_f has the unit M^{-13}. The concentration at which 50% of the complex is dissociated upon dilution is $c_{50} = (8.2 \pm 0.4) \times 10^{-12}$ M.

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