The Self-Assembly of a 3-Component Complex: Solid-State Structure of a 1:1:1 *N,N'*-Di(hydroxyethoxyethoxy)pyromellitic Diimide/Dinaphtho-18-crown-6/Water Complex

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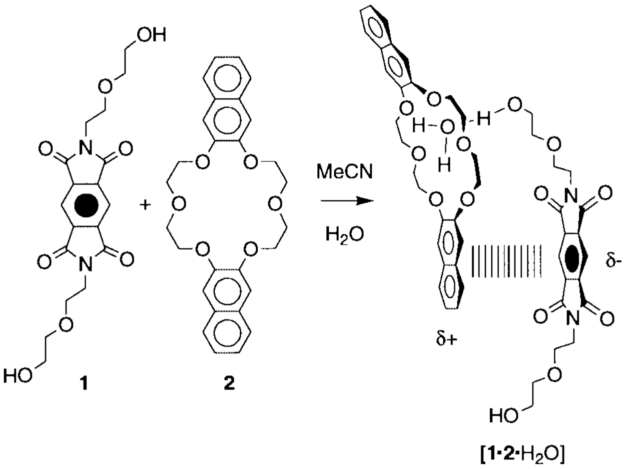
Dinaphtho-18-crown-6, which contains two π-electron rich dialkoxynaphthalene units, self-assembles with the π-electron deficient *N,N'*-di(hydroxyethoxyethoxy)pyromellitic diimide in solution to form 1:1 complexes that have the ability to undergo further self-organisation on crystallisation from MeCN/H_2O to form linear arrays.

Pedersen's discovery[1] that dibenzo-3*n*-crown-*n* form inclusion complexes with a wide range of metal cations provided the incentive for the initial development of host–guest and supramolecular chemistry.[2] Since that time, a variety of stable 1:1 complexes based on the interaction of such crown ethers with organic substrates bearing H-bond donors such as aliphatic ammonium salts[3,4] or aromatic substrates[5] which interact with the catechol units, have been determined. Our present interest in using substituted pyromellitimides (PMI) and naphthalene diimides (NDI) as a set of supramolecular components for the construction of new redox-active materials[6] and supramolecular polymers[7] led us to explore the nature and extent of the interactions between **1**[8] and DN18C6 **2**.[9] We expected that PMI **1** bearing a π-electron deficient aromatic diimide group tethered by an appropriately sized hydrogen bond donor, and DN18C6 **2,** bearing the π-electron rich naphthalene group and a crown ether hydrogen bond acceptor, would self-assemble using multiple interactions to form 1-dimensional arrays.[10] Here, we report on self-assembly of the 1:1:1 complex [**1**·**2**·H_2O] in the solid-state by X-ray crystallography and of the critical role played by water in the process.

When **1** is mixed progressively with more and more **2** in either MeCN or $CHCl_3$, a deep yellow coloured solution develops on account of the partial charge-transfer interactions between the π-electron rich and deficient units present in the two supramolecular components (Scheme 1). The nature of the superstructure present in either CD_3CN or $CDCl_3$ solution could not be accurately determined by ^1H NMR spectroscopy. Chemical shift changes ($\Delta\delta$) for selected probe protons in both components in uncomplexed and complexed forms for 3 mM solutions were very small (< 0.03 ppm) compared to other systems,[5] indicating a low association constant for the complex in solution. The K_a of this 1:1 complex[11] was estimated as < 100 M^{-1} using a spectroscopic titration method (at 400 nm) in $CHCl_3$.

Slow evaporation of a wet MeCN solution of a 1:1 mixture of **1** and **2** afforded single crystals that were suitable for X-ray crystallography.[12] Interestingly, the presence of water is essential to the self-assembly process. All attempts to induce appropriate crystallisation in the absence of water yields yellow powders under identical conditions. X-ray structural analysis shows the presence of a 1:1:1 complex in the solid-state in which a centrally included water molecule plays a pivotal role (Figure 1).[13] A characteristic feature of this assembly is the 118.5° angle subtended by the two naphthalene units of **2**. The water molecule spans the crown cavity and interacts by four short contacts (2.21-2.44 Å) between the two water hydrogens and the ether oxygens directly attached to the naphthalene rings, commensurate with [H···O] hydrogen bonding in a bifocated manner. The fact that**2** and the included water molecule create a convex surface allows for a very strong hydrogen bond between the alcohol group of **1** with the water oxygen (O–O distance 2.81 Å). There is also a proximal relationship (3.52 Å) between the pyromellitimide of **1** and naphthalene ring of **2**, indicating a degree of π–π stabilisation in this portion of the complex. The complexes interact to form an extended array aligned (Figure 1) along the crystallographic *b* direction. The distances between the sandwiched pyromellitimide in **1** and the naphthalene rings of **2** are similar (3.5 Å). The repeat separation between alternate water molecules within these arrays is 28.2 Å.



The need for water as a vital component to the self-assembly process prompted us to re-investigate the effect wet MeCN has on the formation of the complex in solution. To our amazement, the addition of ca. 5 µL of D_2O to a 42 mM solution of **1** and **2** in CD_3CN resulted in the deposition of X-ray quality crystals within the NMR tube after shaking (ca. 30 s). X-ray analysis showed that this unique self-assembly process gave rise to an identical structure to that illustrated in Figure 1. From this result we view the role of water as two-fold: (1) it acts as a vital structural member for the resulting array and, (2) the addition of water reduces the hydrophilic nature of the MeCN solution inducing crystallisation. The fact that PMI **1** and DN18C6 **2** self-assemble in the presence of water to form 1:1:1 complexes opens up the prospect of constructing, by self-assembly,[5] another family of redox-controllable molecular switches.

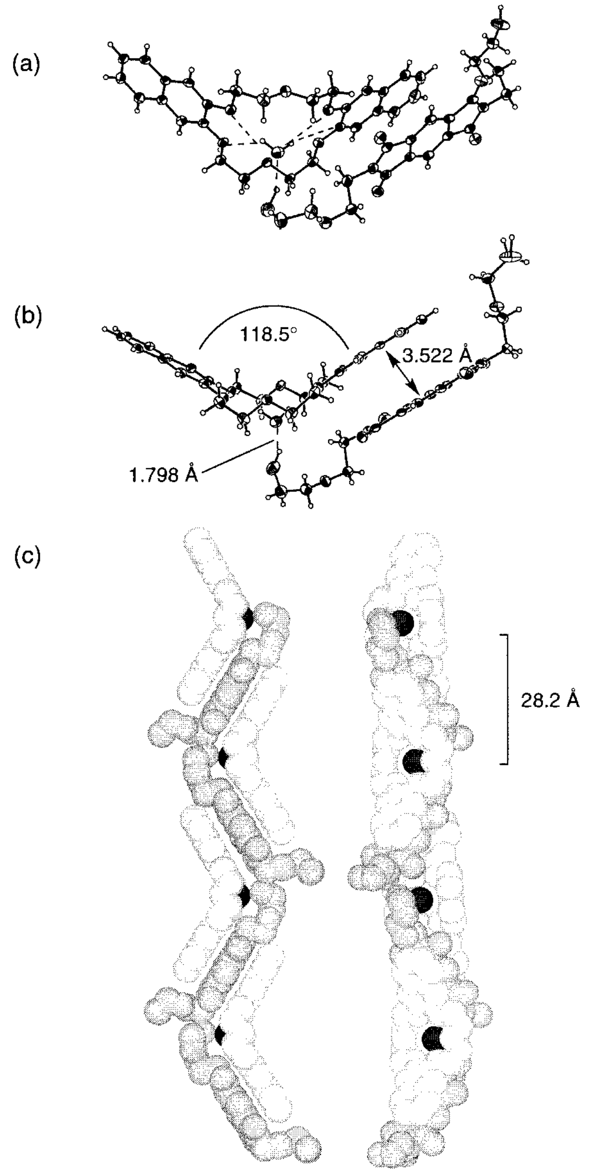


Figure 1. ORTEP plots of [**1**·**2**·H_2O] illustrating (a) the hydrogen bonding interactions between the included water molecule and **2** (shown as dotted lines), (b) the π–π interactions between the aromatic units of **1** and **2**, and (c) the supramolecular arrays formed (hydrogens ommitted) between **1** (grey), **2** (white) and H_2O (black).

Furthermore, the nature of the complex between **2** and a water molecule may also open up avenues to the self-assembling of carbohydrates with crown ethers.

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11 A Job plot using the charge transfer band at 400 nm, indicated that the 1:1 complex was the major supramolecular species in solution. While not always a reliable method for low K_a values, the predominance of a 1:1 complex is consistent with the low association constant and the results of the crystal structure data.

12 Crystal data for [**1**·**2**·H_2O]: $C_{46}H_{50}N_2O_{15}$, M_r = 870.91, monoclinic, a = 8.4171(1), b = 29.9974(4), c = 16.9232(2) Å, β = 103.9563(7)°, V = 4146.82(8) $Å^3$, space group $P2_1/n$, Z = 4, D_c = 1.395 g cm^{-3}, μ (Mo Kα) = 1.05 cm^{-1}. 41644 reflections ($2\theta \le 55.7°$) were measured on a Siemens P4 diffractometer; 9724 were unique. The structure was solved by direct methods and non-hydrogen atoms were refined anisotropically by full-matrix least-squares (F^2) to give R_1 = 0.048 and wR_2 = 0.057.

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