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Formation of dimers of inclusion cryptand/paraquat complexes driven by dipole–dipole and face-to-face π-stacking interactions†

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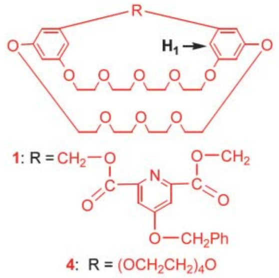
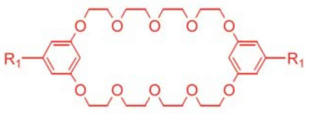
Dimers of inclusion complexes were formed from a new cryptand and viologens (paraquats) driven by dipole–dipole and face-to-face π-stacking interactions as shown by mass spectrometric characterization and X-ray analysis.

Supramolecular chemistry, chemistry beyond the covalent bond, aims at developing sophisticated chemical systems by molecular recognition, self-replication, and self-organization of components based on non-covalent interactions.[1] The study of dimers of supramolecular complexes is important and active due to their potential applications, including molecular muscles,[2] daisy chains,[3] nanoscale magnets,[4] capsules,[5] and host–guest complexation.[6] The main driving force for formation of almost all of these dimers is hydrogen bonding, though other driving forces such as metal coordination[5a,b] and multiple ionic interactions[5c] were also reported. However, to the best of our knowledge, dimers of complexes based on dipole–dipole or face-to-face π-stacking interactions have been rarely reported. This is surprising considering the wide study of these interactions in supramolecular chemistry.[7] Here we report the formation of two new dimers of inclusion complexes driven by dipole–dipole and face-to-face π-stacking interactions.

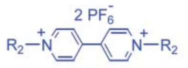


1: R =

4: R = $(OCH_2CH_2)_4O$



2: $R_1 = CH_2OH$; **5**: $R_1 = H$



3: $R_2 = CH_3$
6: $R_2 = CH_2CH_2OH$

Complexation of cryptand and pseudocryptand hosts with viologen (paraquat) derivatives has been studied in our group in order to prepare large supramolecular systems.[8] Recently, in order to add another binding site, we made new functionalized cryptand **1** by cyclization of bis(*m*-phenylene)-32-crown-10 derivative **2**[9] and 4-benzyloxypyridine-2,6-dicarbonyl dichloride.[10] A 1.00 mM equimolar acetone solution of **1** and **3** is yellow due to charge transfer between electron-rich aromatic rings of **1** and electron-poor pyridinium rings of **3**. The stoichiometry of the complex between **1** and **3** was determined to be 1 : 1 in solution by a Job plot[11] (Fig. 1) using proton NMR data. The association constant (K_a) for the complexation between **1** and **3** was determined by a competitive method[12] to be $9.0(\pm1.8) \times 10^5$ M^{-1}, an increase of 1600 times from $5.5(\pm0.5) \times 10^2$ M^{-1} for the complex based on the simple crown ether **5** and **3**.[8d]

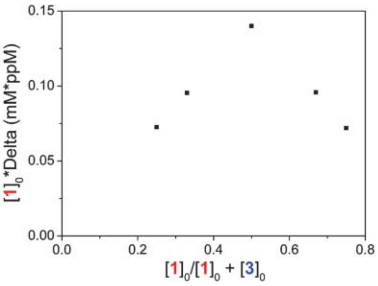


Fig. 1 Job plot showing the 1 : 1 stoichiometry of the complex between **1** and **3** in CD_3COCD_3 solution. $[\mathbf{1}]_0 + [\mathbf{3}]_0 = 1.00$ mM. Delta = the chemical shift change of H$_1$.

Electrospray ionization mass spectrometry (ESIMS) of solutions of **1** with **3** or **6** confirmed the 1 : 1 stoichiometry of the complexation and the existence of dimers of cryptand–paraquat complexes. Two relevant peaks were found for **1·3** (Fig. 2): *m*/*z* 1164.5 (51%) [**1·3** − PF$_6$]$^+$ and 509.9 (100%) [**1·3** − 2PF$_6$]$^{2+}$. Five weaker peaks were consistent with (**1·3**)$_2$ (Fig. 2): *m*/*z* 1196.5 (4%) [(**1·3**)$_2$ − HPF$_6$ − C$_6$H$_6$ − H]$^{2+}$, 1120.6 (3%) [(**1·3**)$_2$ − 2PF$_6$ − C$_7$H$_7$ − CH$_3$ + H$_2$O]$^{2+}$, 1057.5 (2%) [(**1·3**)$_2$ − 3PF$_6$ − C$_7$H$_7$ + Na]$^{2+}$, 969.5 (3%) [(**1·3**)$_2$ − 2PF$_6$ − 2HPF$_6$ − C$_7$H$_7$ − 2CH$_3$ + Na]$^{2+}$, and 526.2 (7%) [(**1·3**)$_2$ − PF$_6$ − 2HPF$_6$ − C$_6$H$_5$]$^{4+}$. Three relevant peaks were found for **1·6**: *m*/*z* 1224 (87%) [**1·6** − PF$_6$]$^+$, 927 (100%) [**1·6** − PF$_6$ − HPF$_6$ − CH$_2$CH$_2$OH − OCH$_2$C$_6$H$_5$]$^+$ and 661 (41%) [**1·6** − OH − CH$_2$OH]$^{+2}$. Two weaker peaks were consistent with (**1·6**)$_2$: *m*/*z* 714 (7.6%) [(**1·6**)$_2$ − 4PF$_6$ − H$_2$O]$^{3+}$ and 708 (17%) [(**1·6**)$_2$ − 4PF$_6$ − 2H$_2$O]$^{3+}$. Interestingly the strong peak at *m*/*z* 888 (76%) appears to be due to the [3] complex **1**$_2$·**6** [**1**$_2$·**6** − 2PF$_6$ − CH$_2$OH − OCH$_2$C$_6$H$_5$]$^{2+}$; this is noteworthy because in several cases analogous (cryptand)$_2$·paraquat complexes have been isolated and characterized.[8d] Another possible contribution to this peak is from the dimer (**1·6**)$_2$: [(**1·6**)$_2$ − **1** − 2PF$_6$ − CH$_2$OH − OCH$_2$C$_6$H$_5$]$^{2+}$. ESIMS of a solution of **1** provided no evidence of the dimer **1**$_2$. Thus, we inferred that involvement of the pyridyl nitrogen in hydrogen bonding to polarize the benzyloxypyridine moiety is a prerequisite for dimerization of **1·3** and **1·6**.

The formation of the dimer (**1·3**)$_2$ was confirmed by X-ray analysis of a single crystal prepared by the vapor diffusion of pentane into an acetone solution of **3** and excess **1**.¶ **1·3** is stabilized

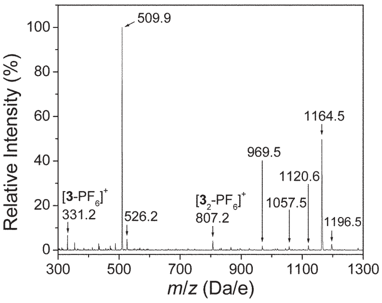


Fig. 2 ESIMS of a solution of **1** and **3** in acetonitrile–chloroform (4 : 1).

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† Electronic supplementary information (ESI) available: synthesis of **1**, the electrospray mass spectrum of a solution of **1** and **6**. See http://www.rsc.org/suppdata/cc/b4/b411234b/

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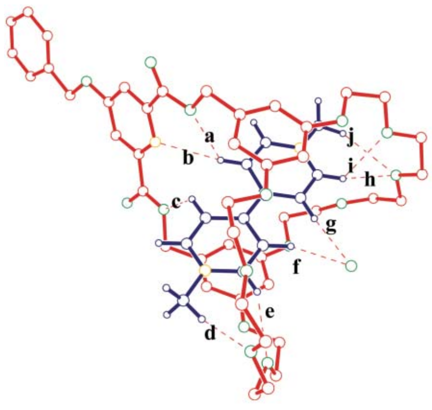

Fig. 3 X-ray structure of **1·3**. Oxygens are green, **1** is red, **3** is blue, and nitrogens are yellow. Solvent molecules, two PF_6 counter ions, and hydrogens except the ones on **3** have been omitted for clarity. Selected hydrogen bond parameters: C–O(N) distances (Å) **a** = 3.22, **b** = 3.62, **c** = 3.38, **d** = 3.41, **e** = 3.32, **f** = 3.37, **g** = 3.28, **h** = 3.33, **i** = 3.14, **j** = 3.56; H···O(N) distances (Å) **a** = 2.52, **b** = 2.68, **c** = 2.70, **d** = 2.44, **e** = 2.58, **f** = 2.43, **g** = 2.29, **h** = 2.37, **i** = 2.60, **j** = 2.62; C–H···O(N) angles (°) **a** = 127, **b** = 157, **c** = 126, **d** = 164, **e** = 130, **f** = 158, **g** = 174, **h** = 161, **i** = 114, **j** = 157. Face-to-face π-stacking parameters: centroid–centroid distances (Å) 3.73, 3.91; ring plane–ring plane inclinations (°): 7.6, 5.0.

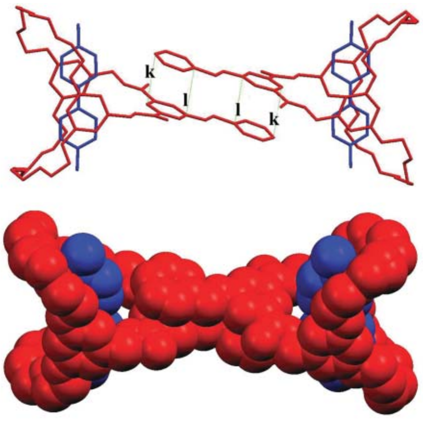

Fig. 4 Two views of the dimer structure $(\mathbf{1{\cdot}3})_2$. **1** molecules are red and **3** molecules are blue. Solvent molecules, four PF_6 counter ions, and hydrogens have been omitted for clarity. Face-to-face π-stacking parameters: centroid–centroid distances (Å) 3.60, 3.60; ring plane–ring plane inclinations (°): 3.8, 3.8; **k** = 3.61 Å; **l** = 3.62 Å.

by hydrogen bonding and face-to-face π-stacking interactions in the solid state (Fig. 3). As designed, H-bonding of the pyridyl N with the β-H of **3** (**b**) adds stability.

Dimer formation is driven by dipole–dipole and face-to-face π-stacking interactions (Fig. 4). The pyridine ring of **1** is electron-poor due to the electron-withdrawing effects of the two carbonyl substituents and hydrogen bonding of its nitrogen atom with a β-pyridinium hydrogen of the electron-poor guest **3**. Therefore, the relatively electron-rich phenyl ring of **1** forms a dipole with the pyridine ring. In the dimer two dipoles are arranged in opposite directions to allow π–π interactions between donor–acceptor pairs. The centroid–centroid distances and ring plane–ring plane dihedral angle for these face-to-face π-stacking interactions are smaller than the above discussed interactions between the electron-rich phenylene rings of **1** and the electron-poor pyridinium rings of **3**. This demonstrates that the face-to-face π-stacking interactions here are strong.

In summary, two new dimers of inclusion complexes were successfully prepared, as shown by electrospray ionization mass spectrometry and X-ray analysis. Future work will be to apply **1** to the construction of other supramolecular systems.

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Notes and references

¶ Crystal data for **1·3**: prism, yellow, 0.39 × 0.25 × 0.14 mm^3, $C_{59}H_{67}F_{12}N_3O_{18}P_2$, FW 1396.11, triclinic, space group $P\bar{1}$, a = 13.2363(15), b = 16.1803(16), c = 16.5673(15) Å; α = 102.397(8)°, β = 93.336(8)°, γ = 110.76(1)°; V = 3205.1(6) $Å^3$, Z = 2, D_c = 1.447 g cm^{-3}, T = 100 K, μ = 1.75 cm^{-1}, 35061 measured reflections, 16428 independent reflections [R(int) = 0.06], 865 parameters, F(000) = 1448, R_1 = 0.1335, wR_2 = 0.1243 (all data), R_1 = 0.0946, wR_2 = 0.1197 [$I > 1\sigma(I)$], and GooF (F^2) = 1.0343. Non-hydrogen atoms were treated anisotropically and hydrogen atoms were placed in calculated positions. 10613 reflections were used in refinements by full-matrix least-squares on F^2. The structure was solved by direct methods using SIR[13] and refined by full-matrix least squares, using the Crystals software.[14] CCDC 220318. See http://www.rsc.org/suppdata/cc/b4/b411234b/ for crystallographic data in .cif or other electronic format.

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