**Strong Binding of Paraquat and Polymeric Paraquat Derivatives by Basket-Shaped Hosts**

Albertus P. H. J. Schenning, Bas de Bruin, Alan E. Rowan,* Huub Kooijman, Anthony L. Spek, and Roeland J. M. Nolte

Clip-shaped host molecules of type 1 can bind uncharged aromatic guest molecules, for example resorcinol, by π-stacking and hydrogen bonding interactions.[1] Basket-shaped derivatives of 1 containing crown ether moieties (compounds of type 2) are, in addition, able to bind alkali metal ions and protonated amines.[2] We report here on the binding affinities of these host molecules towards charged aromatic compounds, such as paraquat 3 and the polymeric paraquat derivatives 4 and 5.

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compound 2 is an exceptionally good host for paraquat. This opens the possibility of clipping host molecules of type 2 to polymeric chains containing paraquat units. The X-ray structure and properties of the complex between 2 and paraquat are also presented.

Compounds 1 and 2 were synthesized as described previously.[1, 2] For the synthesis of 2b, 4,4'-dimethylbenzil was used as the starting material. Compounds 3 and 4 were prepared by using literature procedures.[3-5] Compound 5 was prepared by the condensation of N,N'-bis(2-hydroxyethyl)-4,4'-bipyrindini-um hexafluorophosphate in acetonitrile with one equivalent of adipoyl chloride with triethylamine as the base,[6] and purified by precipitation from ethyl acetate.

Addition of 3-C12 to a solution of host 2b in for example methanol/chloroform led to an immediate color change from colorless to yellow-orange, indicative of the formation of a charge-transfer complex.[7] NMR spectroscopic studies revealed that in this complex the paraquat guest is located in the cleft of the cavity.[8] Fast atom bombardment mass spectrometry (FAB MS) showed a peak at m/z 1094 (matrix: nitrobenzyl alcohol), which corresponds to the mass of the host–guest complex. Crystals of the complex between 2b and 3-(PF6)2 suitable for X-ray analysis were grown from a mixture of 2b and tetra-butylammonium hexafluorophosphate dissolved in chloroform, which was layered with 3-C12 dissolved in methanol. The X-ray crystal structure of complex is shown in Figure 1 (top).[9] It reveals a perfect complementarity between host and guest. The paraquat guest sits symmetrically within the walls of the basket; the methyl substituents are partially encapsulated by the crown ether rings. The crystal structure is different from that of the complex of paraquat with “bis(paraphenylenylene)-[34]crown-10” (the same macrocycle as compound 2a, but without the diphenyglycoluril unit), as published by Stoddart et al.[10] In the case of the latter the bipyrindinium guest is flat, whereas in the crystal structure described herein the two bipyrindinium units are twisted by an angle of 22.5(3)°. This is a consequence of being less sterically constrained by the aromatic side walls of the basket. In Stoddart’s compound the bipyrindinium is tilted at an angle of about 28° with respect to the O–O axis of the paraphenylenylene unit; in our case the bipyrindinium guest is not tilted. The binding constant of the bis(paraphenylenylene)-[34]crown-10 macrocycle with 3-(PF6)2 in acetone is 730 M⁻¹. The binding properties of 1 and 2 were evaluated by recording the intensity of the charge-transfer absorption band at approximately 425 nm at different host–guest ratios. The results for different solvents are presented in Table 1. The basket-shaped host molecules 2 bind paraquat approximately 25–75 times stronger than the bis(paraphenylenylene)-[34]crown-10 macrocycle.[10] This result can be explained from the fact that compounds 2 are more preorganized for binding than Stoddart’s compound.[11] Only a very small Ks of 80 M⁻¹ was found for the binding of 3 in the cavity of clip molecule 1. This clearly demonstrates the importance of the crown ether moieties in 2 for the complexation of paraquat.

Table 1. Binding constants [a] of the complexes between hosts 1, 2, and guests 3, 4, and 5.

<table>
<thead>
<tr>
<th>Host</th>
<th>Guest</th>
<th>Ks [M⁻¹]</th>
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<tbody>
<tr>
<td>1</td>
<td>3-C12</td>
<td>60 [b]</td>
</tr>
<tr>
<td>2a</td>
<td>3-(PF6)2</td>
<td>57000 [c]</td>
</tr>
<tr>
<td>2b</td>
<td>2-PF6</td>
<td>20000 [d]</td>
</tr>
<tr>
<td>3-C12</td>
<td>3-(PF6)2</td>
<td>22000 [f]</td>
</tr>
<tr>
<td>2a</td>
<td>4a [f]</td>
<td>1800 [e, e]</td>
</tr>
<tr>
<td>2a</td>
<td>4b [g]</td>
<td>4500 [e, e]</td>
</tr>
<tr>
<td>2a</td>
<td>5 [h]</td>
<td>19000 [e, e]</td>
</tr>
</tbody>
</table>

[a] Association constants were calculated using the Benesi–Hilderbrand equation [13]. Good correlations (R > 0.995) were obtained for all titration curves assuming a 1:1 host–guest complexation. Estimated error in Ks is 10%. [b] Estimated error in Ks is 50% due to the poor solubility of the host molecule in this solvent. [c] Methanol-chloroform (1:1, v/v). [e] Acetonitrile. [d] Acetone. [e] Per polymer repeat unit. [f] Intrinsic viscosity of polymer [η] = 0.066 dl·g⁻¹ (acetonitrile, 25°C), [g] viscometric viscosity of polymer [η] = 0.20 dl·g⁻¹ (acetonitrile, 25°C). [h] Average degree of polymerization 4 (NMR, endgroup analysis).

The electrochemical behavior of the complex between 3-(PF6)2 and compound 2a was studied in acetonitrile. In this solvent the guest showed two reversible one-electron transfers: $E_{1/2}(2/1) = -0.423$ V, $E_{1/2}(1/0) = -0.840$ V (vs. SCE, for both transitions $\Delta E_p = 60$ mV). Upon the addition of one equivalent of 2a the first redox transfer shifted 100 mV to more negative potential, whereas the second electron transfer potential remained unaffected. These data indicate that 2a binds and stabilizes the doubly charged paraquat species, which results in a more negative redox potential for the first redox transfer. It is well known that in this type of host–guest system the guest reduced by one electron dissociates form the host, and this explains the unaltered second redox potential.[12]

PolymERIC PARAquat DeRIVatives have previously been investigated as redox-active films and more recently as optical data storage materials and show a wide variety of electrochromic and thermochromic behavior.[14, 9, 10] The polymeric paraquat derivative with losylate counterions has been shown to possess liquid crystalline properties.[11, 12] We felt that host–guest complexation might be an interesting way to modify and control the physical properties of this interesting class of polymers. The results of binding studies carried out in acetonitrile, showed that 2a can be clipped to polymeric paraquat derivatives 4a, 4b, and 5 with association constants of 1800 M⁻¹, 4500 M⁻¹, and 19000 M⁻¹, respectively (per polymer repeat unit, see Table 1, Fig. 1). The binding constants of 4a and 4b are lower than those observed for paraquat itself. Molecular modeling studies have revealed that in the case of 4a and 4b, complexation of a basket to a paraquat unit in the polymer is sterically hindered by baskets complexed to adjacent paraquat units. The overall lower binding constants reflect this steric hindrance, which is less for

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the polymer with a longer spacer (4b) than for the one with the smaller spacer (4a). Viscosity measurements showed that the specific viscosity of the polymers solubilized in acetonitrile increases upon the addition of 0.03 equivalents of the host molecule 2a per repeat unit: for example, 4a: \eta_2 = 0.006, 4a + 2a \eta_2 = 0.0068; 4b: \eta_2 = 0.068, 4b + 2a \eta_2 = 0.070. These results indicate that the average molecular mass of the polymers increases on complexation with 2a. The redox potentials of the polymers were also influenced by the hosts. Polymer 4a displayed the following redox transitions in acetonitrile: \( E_{U2}(2+/1+) = -0.387 \text{ V} \) (vs. SCE), for both transitions \( \Delta E = 60 \text{ mV} \). Upon the addition of one equivalent of 2a per repeat unit the first redox transfer shifted 20 mV to more negative potential, whereas the second redox transfer remained unchanged. Addition of three equivalents of 2a resulted in a 35 mV shift in the negative direction. These shift values are smaller than the 100 mV shift measured for paraquat (3) which may be the result of the lower binding affinity of 2a.

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The coordination chemistry of linear oligonitrogen metal donor ligands with soft metal ions has recently become the focus of a great deal of attention. To our knowledge, investigations towards the metal-directed self-assembly of helicates have resulted only in the characterization of double- and triple-helicates [10] and double-stranded non-helical metal complexes, which do not possess units with helical chirality [11]. In this context, the triple-stranded meso-helicate is a missing structural motif. This stimulated our interest in self-assembly processes based on oxygen donor ligands in combination with hard metal ions [12]. The use of early transition metals should provide access to new supramolecular aggregates, whose properties should differ from those of the "traditional" compounds. Catechol ligands seem to be ideal bidentate chelating units for this purpose. [10] Initially we chose the (CH\(_2\))\(_3\) group as a spacer for the polymer with a longer spacer (4b) than for the one with the smaller spacer (4a). Viscosity measurements showed that the specific viscosity of the polymers solubilized in acetonitrile increases upon the addition of 0.03 equivalents of the host molecule 2a per repeat unit: for example, 4a: \eta_2 = 0.006, 4a + 2a \eta_2 = 0.0068; 4b: \eta_2 = 0.068, 4b + 2a \eta_2 = 0.070. These results indicate that the average molecular mass of the polymers increases on complexation with 2a. The redox potentials of the polymers were also influenced by the hosts. Polymer 4a displayed the following redox transitions in acetonitrile: \( E_{U2}(2+/1+) = -0.387 \text{ V} \) (vs. SCE), for both transitions \( \Delta E = 60 \text{ mV} \). Upon the addition of one equivalent of 2a per repeat unit the first redox transfer shifted 20 mV to more negative potential, whereas the second redox transfer remained unchanged. Addition of three equivalents of 2a resulted in a 35 mV shift in the negative direction. These shift values are smaller than the 100 mV shift measured for paraquat (3) which may be the result of the lower binding affinity of 2a.

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