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quenched with a solution of citric acid. The mixture was diluted with DCM (100 mL) and washed with sodium bicarbonate (sat.), water, and brine (25 mL each). The organic layer was dried (Na$_2$SO$_4$), evaporated, and the residue dissolved in DCM/MeOH (98:2) and filtered through a plug of silica gel. Evaporation gave the crude precursor of 2 (773 mg). To this crude product (357 mg) in DCM (40 mL) was added methanesulfonyl acid (300 mL). After stirring the mixture at RT for 72 h under nitrogen, pyridine (400 mL), DIPEA (1.5 mL), and acetic anhydride were added at 0 °C. After 2 h the solution was diluted with DCM (100 mL), washed with sodium bicarbonate (1 M), water, sodium bicarbonate (sat.), water, and brine (25 mL each). The organic layer was dried (Na$_2$SO$_4$), filtered, evapora
ted, and chromatographed (silica gel, DCM/MeOH (98:2)) to afford 2 (260 mg, 40% based on 1).

3: To 2 (60 mg, 0.051 mmol) in DCM (1 mL), TFA (0.5 mL) was added dropwise and stirred for 1 h at 0 °C. The reaction mixture was diluted with DCM (50 mL) and washed three times with sodium bicarbonate (sat.), water, and brine (10 mL each). The organic layer was dried (Na$_2$SO$_4$), evaporated, and redisolved in DCM (0.5 mL). Boc-(2S,3R,4S,5S,6R)-3-hydroxy-4-methyl-2-(methylamino)-6-octenoic acid (Boc-MethNHBoc) [11.8 mg, 0.062 mmol], triphenylphosphine, and DIPEA (37 mL) were added at 0 °C under nitrogen. After 2 h at 0 °C, the mixture was diluted with DCM (50 mL), washed with sodium bicarbonate (1 M), water, sodium bicarbonate (sat.), water, and brine (20 mL each). The organic layer was dried (Na$_2$SO$_4$), filtered, evaporated, and chromatographed (silica gel, EtOAc/EtOH (50:1)) to afford 3 (27 mg, 0.022 mmol).

5: To 3 (27 mg, 0.022 mmol) in DCM (1 mL), TFA (0.5 mL) was added dropwise and stirred for 1 h at 0 °C. The reaction mixture was diluted with DCM (50 mL) and washed three times with sodium bicarbonate (sat.), water, and brine (10 mL each). The organic layer was dried (Na$_2$SO$_4$), filtered, evaporated, and redisolved in DCM (30 mL). Fmoc-N-Melle (12 mg, 0.032 mmol), PyBroP (14 mg, 0.032 mmol) and DIPEA (15 mL) were added and the mixture was stirred for 6 h at 0 °C and then allowed to warm to RT overnight. The reaction mixture was diluted with DCM (50 mL), washed with sodium bicarbonate (1 M), water, sodium bicarbonate (sat.), water, and brine (20 mL each). The organic layer was dried (Na$_2$SO$_4$), filtered, evaporated, and chromatographed (silica gel, EtOAc/EtOH (10:1)) to afford 4 (19 mg, 60%).

6: To 4 (19 mg, 0.065 mmol) in THF/water (10:1, 200 mL), DBU (3 mL) and lithium bromide (2 mg) were added. After stirring overnight at RT, DBU (4 mL) and lithium bromide (3 mg) were added again. After 5 h, the reaction mixture was quenched with acetic acid (20 mL) and purified by reverse-phase HPLC (Beckman ODS ultrasphere 5 p 10 mm x 25 cm, acid (30 pL), the DCM evaporated, and the residue dissolved in acetonitrile and acetic acid (20 pL) and purified by reverse-phase HPLC (Beckman ODS ultrasphere 5 n 10 mm x 25 cm, 0.1 % TFA/MeCN 70/30 ->10/90 in 30 min, 70°C, 3 runs) to afford 6 (15 mg, 0.051 mmol) in 55% yield. A solution of this peptide precursor purified by reverse-phase HPLC (Beckman ODS ultrasphere 5 p 10 mm x 25 cm, acid (30 pL), the DCM evaporated, and the residue dissolved in acetonitrile and acetic acid (20 pL) and purified by reverse-phase HPLC (Beckman ODS ultrasphere 5 n 10 mm x 25 cm, 0.1 % TFA/MeCN 70/30 ->10/90 in 30 min, 70°C, 3 runs) to afford 7 (2 mg, 0.013 mmol).

4: To 3 (27 mg, 0.022 mmol) in DCM (1 mL), TFA (0.5 mL) was added dropwise and stirred for 1 h at 0 °C, diluted with DCM (50 mL), and washed with sodium bicarbonate (sat.), water, sodium bicarbonate (sat.), water, and brine (10 mL each). The organic layer was dried (Na$_2$SO$_4$), evaporated, and redisolved in DCM (30 mL). Fmoc-N-Melle (12 mg, 0.032 mmol), PyBroP (14 mg, 0.032 mmol) and DIPEA (15 mL) were added and the mixture was stirred for 6 h at 0 °C and 30 min at RT. Fmoc-N-Melle (3 mg, 0.013 mmol), PyBroP (3 mg, 0.011 mmol) were added again at 0 °C and allowed to warm to RT overnight. The reaction mixture was diluted with DCM (50 mL), washed with sodium bicarbonate (1 M), water, sodium bicarbonate (sat.), water, and brine (20 mL each). The organic layer was dried (Na$_2$SO$_4$), filtered, evaporated, and chromatographed (silica gel, EtOAc/EtOH (9:1)) to afford 4 (19 mg, 60%).

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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 n–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


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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 pre-
sented.

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

Addition of 3-Cl2 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.1, 6 7, 8 Fast atom bombardment mass spectrom­
try (FAB MS) showed a peak at m/z 1094 (matrix: 1-nitrobenzyl
alcohol), which corresponds to the mass of the host-guest com­
plex. 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 layerd with 3-Cl2 in methanol. The X-ray structure
of complex is shown in Figure 1 (top).17 It reveals a

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:

$$E_{1/2}(2+/1+) = -0.423 \text{ V, } E_{1/2}(1+/0) = -0.840 \text{ V (vs. SCE,}
$$

for both transitions $\Delta E_p = 60 \text{ mV.}$ Upon the addition of one
equivalent of 2a the first redox transfer shifted 100 mV to more
negative potential, whereas the second electron transfer poten­
tial 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 ex­
plains the unaltered second redox potential.9

Polymeric paraquat derivatives have previously been investi-
gated as redox-active films and more recently as optical data
storage materials and show a wide variety of electrochromic
and thermochromic behavior.4, 9, 10 The polymeric paraquat
derivative with tosylate counterions has been shown to possess
liquid crystalline properties.11 12 We felt that host-guest com­
plexation 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 baks
complexed to adjacent paraquat units. The overall lower
binding constants reflect this steric hindrance, which is less for

**Table 1. Binding constants $K_r$ of the complexes between hosts 1 and 2 and guests 3, 4, and 5.**

<table>
<thead>
<tr>
<th>Host</th>
<th>Guest</th>
<th>$K_r$ [M$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3-Cl2</td>
<td>60 [b]</td>
</tr>
<tr>
<td>2a</td>
<td>3-(PF6)2</td>
<td>57000 [c]</td>
</tr>
<tr>
<td>2a</td>
<td>2-(PF6)2</td>
<td>20600 [d]</td>
</tr>
<tr>
<td>2b</td>
<td>3-Cl2</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-Hildebrand equation
[b] Good correlations ($R > 0.995$) were obtained for all titration curves assuming a 1:1 host-guest complexation. Estimated error in $K_r$ is 10%. For the $K_r$ measured in acetone, the error is 20% due to the poor solubility of the guest molecule in this solvent.

perfect complementarity between host and guest. The paraquat

Fig. 1 Top: Crystal structure of the complex between 2b and 3-(PF6)$_2$. Left top

right side view [14]. Bottom: Computer-generated model of the complex

between 2b and 5.
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: \( \eta = 0.006 \); 4a + 2a \( \eta = 0.008; \) 4b + 2a \( \eta = 0.070 \). 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 reactions in acetonitrile: 

\[ E_{1/2}(2a+/0) = -0.387 \text{ V}, \]

\[ E_{1/2}(4a+/0) = -0.840 \text{ V (vs. SCE, for both transitions, } \Delta E = 60 \text{ mV). } \]

Results indicate that the electrochemical behavior of polymeric paraquat derivatives can easily be tuned by the addition of bases to these polymers as optical data storage systems or as molecular switches, etc.

In conclusion, we have shown that host molecules of the type 2 strongly bind paraquat 3 and that it is possible to clip these switches, etc. paraquat derivatives can easily be tuned by the addition of bases to these polymers as optical data storage systems or as molecular switches, etc.

The coordination chemistry of linear oligomeric nitrogendonor 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-11,41 and triple-helicate15 and double-stranded non-helical metal complexes, which do not possess units with helical chirality.16 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.17-18 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.19-20 Initially we chose the (CH$_2$)$_2$ group as a spacer.

Formation of a "meso-Helicate" by Self-Assembly of Three Bis(catecholate) Ligands and Two Titanium(IV) Ions

Markus Albrecht* and Sirpa Kotila

Double- or triple-helical oligomeric coordination compounds that are formed spontaneously by self-assembly of two or three oligoferolate ligands and several metal ions are called helicates. Due to their helicity, such molecules are chiral.12 On the other hand, meso-helicates are analogous metal complexes with two differently configured helical units and are thus achiral. In a topological sense, the meso-helicates are helices that reverse their helical twist.13

An octahedral complex formed by one metal center and three bidentate ligands is the most simple helical unit. It can have two configurations \( (A,A) \) or \( (A,L) \).21 Triple bridging between the ligands of two such octahedrons results in the formation of three different coordination compounds: the enantiomeric \( A,A- \) and \( A,L- \) helicates, and the diastereomeric \( A,A- \) form—the most simple triple-stranded meso-helicate (Fig. 1). The coordination chemistry of linear oligomeric nitrogen 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-

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