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Halide anion directed assembly of luminescent pseudorotaxanes

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A series of new photo-active rhenium(I) bipyridyl based pseudorotaxane complexes is assembled *via* halide anion templation.

The template synthesis of interlocked supramolecular architectures is currently an area of intense research activity.[1] The control over the relative disposition of the interlocked molecular constituents in the final structure is usually derivative of the residual non-covalent interactions initially employed to construct them. Examples include hydrogen-bonding, π-stacking, metal–ligand dative bonding and hydrophobic interactions between species which are neutral or cationic in nature.[2] With few exceptions,[3] the participation of anions in the formation of the interlocked molecular entities has largely been unexplored. We have recently shown that pseudorotaxane[4] and rotaxane[5] formation can be templated selectively by a chloride anion which facilitates the interpenetration of a pyridinium bis-amide thread through the annulus of an isophthalamide macrocycle. Here we describe halide anion templated synthesis of a range of new photo-active pseudorotaxanes where the threading process can be detected by luminescence spectroscopy (Fig. 1).

The new rhenium(I) bipyridyl macrocycle **6** was prepared in four steps according to Scheme 1. As in related compounds[6] the ability of this macrocycle to bind halide anions was demonstrated by ^{1}H-NMR titration experiments. The addition of tetrabutylammonium halide salts to acetone-d_6 solutions of **6** resulted in significant perturbations of most notably the amide and 3,3′-bipyridyl receptor protons. WinEQNMR[7] analysis of the respective titration curves gave 1:1 receptor:anion stability constant values (Table 1) which suggest the macrocycle strongly binds halide anions, especially chloride and bromide.

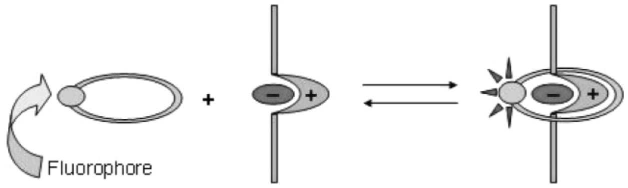
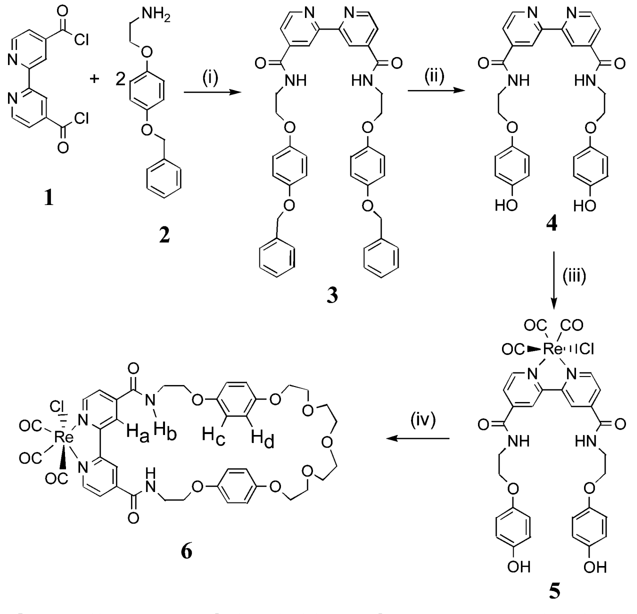


Fig. 1 Anion directed pseudorotaxane formation.



Scheme 1 (i) Et_3N, CH_2Cl_2 (97%); (ii) H_2, Pd–C, DMF, MeOH (85%); (iii) $Re(CO)_5Cl$, THF (85%); (iv) tetraethyleneglycol di-*p*-tosylate, K_2CO_3, CH_3CN, THF (15%).

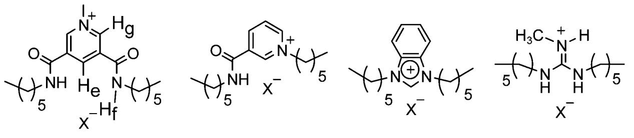
Analogous ^{1}H-NMR titration experiments with pyridinium bis-amide halide salts **7a–c** (Fig. 2) revealed evidence for pseudorotaxane formation. In addition to significant respective downfield and upfield amide proton perturbations of **6** and **7**, notable shifts were observed in the receptor's hydroquinone proton resonances, which can be attributed to π–π interactions between the pyridinium cation and hydroquinone rings (Fig. 3).

In acetone solution, ion-pairing between the pyridinium cation and halide anion is very strong,[4] and consequently halide complexation at the rhenium(I) bipyridyl amide recognition site of

Table 1 Stability constants of **6** with halide anions in acetone-d_6

	Anion			
	Cl^-	Br^-	I^-	PF_6^-
K [M^{-1}][a]:	> 10^5	8 × 10^4	1.7 × 10^3	–[b]

Anions were used as tetrabutylammonium salts;[a] Error < 10%. [b] No evidence of complexation.



7a: X=Cl
7b: X=Br
7c: X=I
7d: X=PF_6^-
8: X=Cl
9: X=Cl
10: X=Cl

Fig. 2 Structures of ion-paired threads.

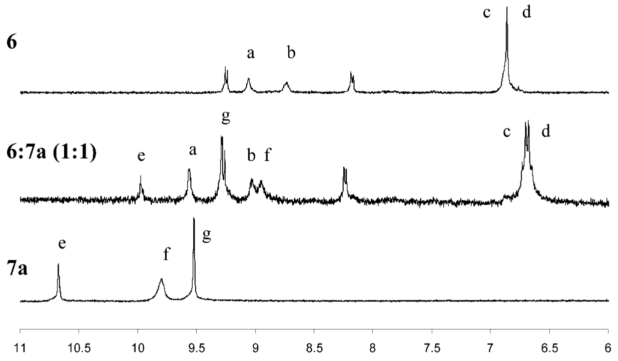


Fig. 3 Comparison of expanded ^{1}H-NMR spectra in acetone-d_6 for **6**, **7a** and a 1:1 mixture of both **6** and **7a**.

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Table 2 Stability constants of **6** with **7a–d**, **8–10** in acetone-d_6

	Thread						
	7a	**7b**	**7c**	**7d**	**8**	**9**	**10**
K [M^{-1}]^a:	1.5×10^3	1.2×10^3	1.4×10^2	–^{b}	6.1×10^3	$> 10^5$	1.3×10^3

^{a} Error $<$ 10%. ^{b} No evidence of complexation.

6 results in the cationic pyridinium moiety forming an interlocked assembly with the macrocycle. Interestingly no evidence of interpenetration was seen with the hexafluorophosphate pyridinium salt **7d** which suggests threading of the pyridinium cation is accomplished and driven by recognition of the halide anion by the receptor.[8] Stability constant determinations (Table 2) reveal pseudorotaxane complex thermodynamic stability mirrors the strength of halide binding by the receptor (Table 1) where chloride and bromide pyridinium salts form the strongest pseudorotaxane complexes.

Solid state evidence for pseudorotaxane formation comes from the X-ray structural determination† of the complex **6·7a**.

The structural analysis reveals the expected interlocked product in which the macrocycle encircles the ion-pair. The chloride anion fits into the cleft of the pyridinium ring, forming five short X–H···Cl(2) contacts indicative of hydrogen bonding (distances: N(3) 3.417 (0.006) Å, N(4) 3.351 (0.006) Å, N(6) 3.473 (0.013) Å, N(7) 3.281 (0.006) Å, C(42) 3.459 (0.006) Å). These may be regarded as the vertices of a highly distorted octahedron. The macrocycle surrounds the cation such that the two phenyl rings are approximately parallel and sandwich the central pyridinium ring. Least squares calculations show that the two phenyl rings are ~7 Å apart and are parallel to within 6.6°. These two rings therefore allow enough room for π-stacking with enclosed cation.

As evidenced by ^{1}H-NMR titration experiments it is noteworthy that other strongly ion-paired[4] nicotinamide **8**, benzoimidazolium **9**, and methylguanidinium **10** chloride anion salts also form strong pseudorotaxane complexes in acetone-d_6 solutions (Table 2). Because the respective cationic species is strongly ion-paired to the chloride counterion, halide recognition by **6** results in threading of the cationic component through the macrocyclic cavity.

Preliminary absorption and emission investigations reveal **6** behaves like the parent Rebipy(CO)$_3$Cl complex. As was hoped the addition of **7a**, **8**, **9** and **10** was found to affect the luminescence spectrum of **6** with a significant enhancement in emission intensity (Fig. 5) which may be a consequence of pseudorotaxane complex formation increasing the rigidity[6] of the receptor, disfavouring non-radiative decay processes.

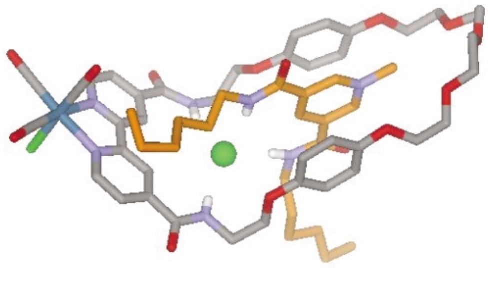

Fig. 4 Stick representation of the solid state structure of pseudorotaxane **6**+**7a**.

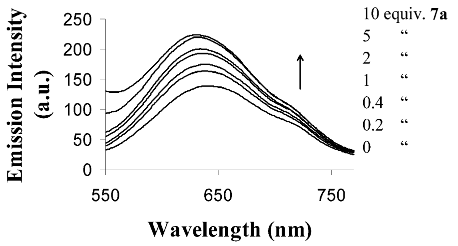

Fig. 5 Emission spectral variations upon titration of **6** (2×10^{-5} M in acetone) with **7a** in acetone; ($\lambda_{exc.}$ = 400 nm)

In summary a series of new photo-active rhenium(I) bipyridyl based pseudorotaxane complexes containing various pyridinium, benzoimidazolium and guanidinium threading components have been assembled *via* halide anion templation.

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Notes and references

† Single crystals were grown by slow diffusion of Et$_2$O into CHCl$_3$. Crystallographic data were collected in an Enras-Nonius KappaCCD diffractometer using graphite monocromatised Mo–K$_\alpha$ radiation (λ = 071073 Å). Intensity data were processed using the DENZO-SMN package.[9] The structure was solved by direct methods using the SIR92 program.[10] Full matrix least-squares refinement was carried out using the CRYSTALS program suite.[11] A Chebychev polynomial weighting scheme was applied.

Crystal data for **6+7a·**CH$_2$Cl$_2$: T = 150 K, crystal size $0.20 \times 0.20 \times 0.10$ mm, monoclinic, space group $P2_1/c$, a = 13.6751 (2), b = 22.3512 (2), c = 22.6383 (3) Å, β = 105.9996 (5) °, V = 6651.47 (14) Å^3, Z = 4, d_{calcd} = g cm^{-3}, μ = 1.990 mm^{-1}, $R1$ ($wR2$) = 0.0541 (0.0604) for the 8504 unique data with $I > 3\sigma(I)$ and 781 parameters.

CCDC 231488. See http://www.rsc.org/suppdata/cc/b4/b401900h/ for crystallographic data in .cif or other electronic format.

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