

Anion directed synthesis of a hydrogensulfate selective luminescent rotaxane†

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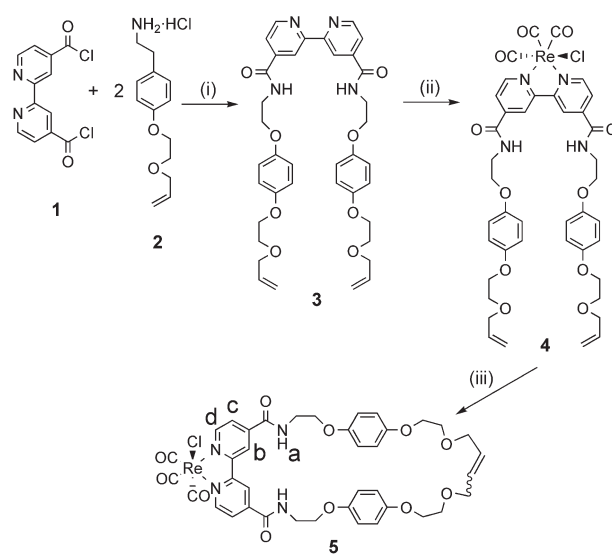
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A new photo-active rhenium(i) bipyridyl based rotaxane has been synthesised which by virtue of the unique interlocked structural cavity selectively senses hydrogensulfate using luminescence spectroscopy.

In an effort to fabricate innovative molecular switches, sensors and machines, imaginative template methodologies are increasingly being used in the construction of interlocked supramolecular assemblies such as rotaxanes, catenanes and knots.¹ Cationic and neutral species have dominated the templated synthetic strategies reported to date by employing metal–ligand coordination,² electron donor–acceptor interactions,³ hydrogen bonding⁴ and solvophobic effects⁵ to bring about assembly between two or more components. The challenge of using anions to direct supramolecular assembly remains largely underexploited, which may be attributed to their diffuse nature, pH-dependence and relatively high solvation energy as compared to cations.⁶ Although various serendipitous discoveries of cases where anions have templated the formation of, in particular, inorganic-based polymetallic cage complexes⁷ and circular double helicates⁸ have now appeared, strategic anion-templated syntheses and assemblies are rare.⁹ This is especially the case when employing anions in the construction of interpenetrated compounds.¹⁰ We have recently reported a general method of using anions to template the formation of a range of [2]pseudorotaxanes,¹¹ a [2]rotaxane¹² and [2]catenane.¹³ The assembly process is based on a coordinatively unsaturated chloride anion of a tight ion-pair threading component,^{11b} facilitating the interpenetration of a pyridinium, imidazolium or guanidinium thread through the annulus of an isophthalamide macrocycle. As a rare example of using a rotaxane topological cavity as a potential binding site domain, we describe here the anion directed synthesis of a novel photo-active rhenium(i) bipyridyl based [2]rotaxane which selectively senses hydrogensulfate using luminescence spectroscopy.

The bis-vinyl appended rhenium(i) bipyridyl derivative **4** was prepared in two high yielding synthetic steps *via* a condensation of 4,4'-bis(chlorocarbonyl)-2,2'-bipyridine **1** and two equivalents of amine **2**¹² to afford **3** followed by complexation with Re(CO)₅Cl (Scheme 1). Ring closing metathesis reaction of **4** with Grubbs' catalyst produced macrocycle **5** in 40% yield (Scheme 1).¹⁴ The new calix[4]arene stoppered pyridinium chloride axle component **9** was synthesised in five steps *via* mononitration of tetrapropoxy-calix[4]arene **6**,¹⁵ to give **7** which on reduction and reaction with

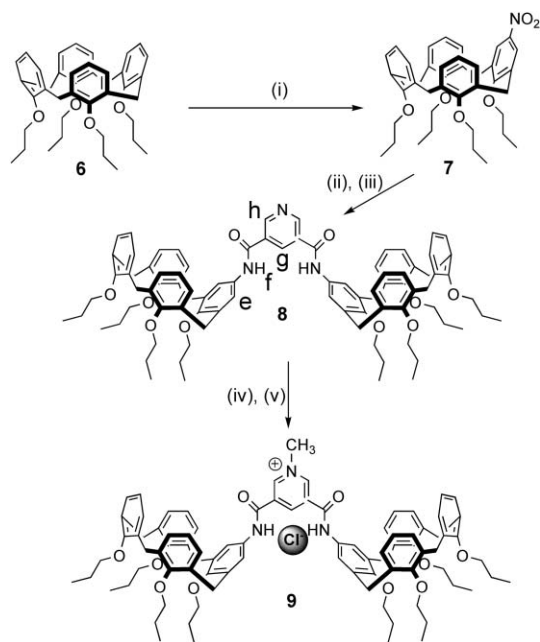


Scheme 1 (i) Et₃N, CH₂Cl₂ (98%); (ii) Re(CO)₅Cl, THF, reflux (90%); (iii) Grubbs' catalyst Ru[PCy₃]₂Cl₂CHPh, CH₂Cl₂ (40%).

3,5-bis(chlorocarbonyl)pyridine produced bis-calix[4]arene **8**. Reaction of **8** with methyl iodide followed by anion exchange with ammonium chloride gave the pyridinium chloride bis-calixarene stoppered thread **9** (Scheme 2). The target rotaxane was prepared *via* mixing **4** and **9** in dichloromethane solution followed by ring closing metathesis reaction with Grubbs' catalyst to produce [2]rotaxane **10** in 21% yield which was characterised by ¹H-NMR, ¹³C-NMR and electrospray mass spectrometry (Scheme 3).

In particular a comparison of the ¹H-NMR spectra of starting materials **4**, **9**, intermediate adduct **4·9** and **10** clearly shows a correlation of respective chemical shift values (Fig. 1). Also of note is the observation from ¹H and ¹³C-NMR spectra of **10** that the calix[4]arene stoppers are magnetically inequivalent. Presumably this is a consequence of the Re(CO)₃Cl-bipyridine moiety and the possible lack of planarity of the macrocycle which creates different calixarene environments on both sides of the macrocycle plane of the rotaxane. Interestingly this magnetic inequivalence is not observed in the **4·9** assembly which provides further evidence for rotaxane formation. Exchanging the chloride anion template for the non-coordinating hexafluorophosphate anion to afford rotaxane **11** was achieved by addition of AgPF₆ to a dichloromethane solution of **10** (Scheme 3). ¹H-NMR titrations of **11** with tetrabutylammonium (TBA) chloride in acetone-*d*₆ confirmed that anion recognition takes place in the rotaxane binding pocket,

† Electronic supplementary information (ESI) available: synthetic and characterisation details for **11** and additional fluorescence anion titration isotherms. See <http://www.rsc.org/suppdata/cc/b4/b418878k/>
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Scheme 2 (i) HNO_3 (conc.), H_2SO_4 (fuming) (58%); (ii) NH_2NH_2 ; (iii) 3,5-(COCl) $_2$ -Py, Et_3N , CH_2Cl_2 (38%); (iv) MeI, acetone, reflux (98%); (v) NH_4Cl , CHCl_3 , H_2O (96%).

where in particular significant downfield shifts of the respective amide protons were observed. As a consequence of overlapping peaks, however, difficulties were encountered in obtaining anion titration binding isotherms which thwarted quantitative association constant data being obtained.

Preliminary absorption and emission investigations reveal **4**, **5** and rotaxane **11** behave like the parent $\text{Re}(\text{bipy})(\text{CO})_3\text{Cl}$ complex.

Fluorescence spectroscopy anion binding studies were undertaken in order to evaluate the ability of rotaxane **11** to operate as a luminescent anion sensor. The addition of chloride, nitrate and especially hydrogensulfate tetrabutylammonium salts to acetone solutions of **11** led to significant enhancement in emission intensity

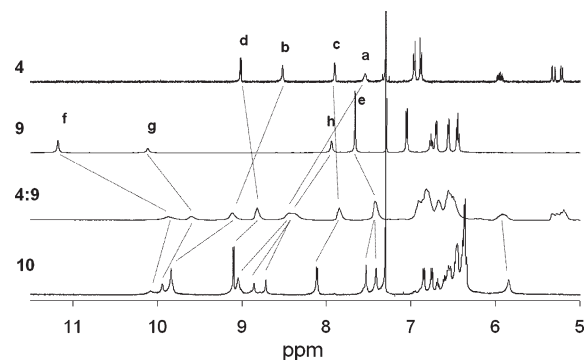


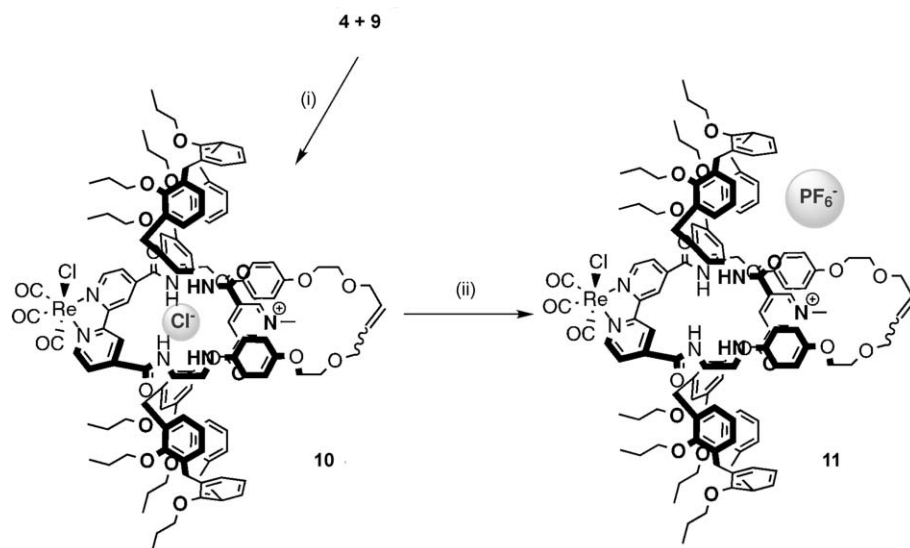
Fig. 1 Comparison of the $^1\text{H-NMR}$ spectra of **4**, **9**, intermediate ensemble **4:9** (1 : 1 ratio) and **10** in CDCl_3 .

(Fig. 2) which may be a consequence of anion complexation in the rotaxane recognition site increasing the rigidity of the rotaxane superstructure, disfavoring non-radiative decay processes.¹⁶

Specfit/32¹⁷ analysis of the resulting titration curves (Fig. 3) gave anion association constant values for the 1 : 1 complexes shown in Table 1 along with determined values with acyclic **4** and macrocyclic **5** rhenium(i) bipyridyl derivatives. It is noteworthy that Table 1 reveals rotaxane **11** exhibits selectivity for hydrogensulfate¹⁸ in preference to chloride and nitrate. This contrasts with acyclic **4** and macrocycle **5** receptors preferentially binding chloride which suggests the rotaxane cavity of **11** is of complementary topology and dimensions for the tetrahedral hydrogensulfate anion.¹⁹

In summary a novel photo-active rhenium(i) bipyridyl [2]rotaxane has been constructed and shown to selectively sense hydrogensulfate using luminescence spectroscopy. This rotaxane receptor system serves to illustrate the potential such interlocked molecular receptors have in future chemical sensor design and fabrication.

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Scheme 3 (i) Grubbs' catalyst $\text{Ru}[\text{PCy}_3]_2\text{Cl}_2\text{CHPh}$, CH_2Cl_2 (21%); (ii) AgPF_6 , CH_2Cl_2 (91%).

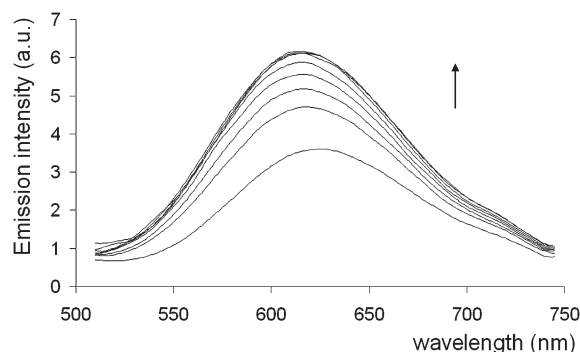


Fig. 2 Fluorescence enhancement upon titration of **11** (10^{-5} M in acetone) ($\lambda_{\text{exc}} = 390$ nm) with TBAHSO₄: 0, 0.2, 0.4, 0.6, 0.8, 1, 2, 4, 10 equivalents.

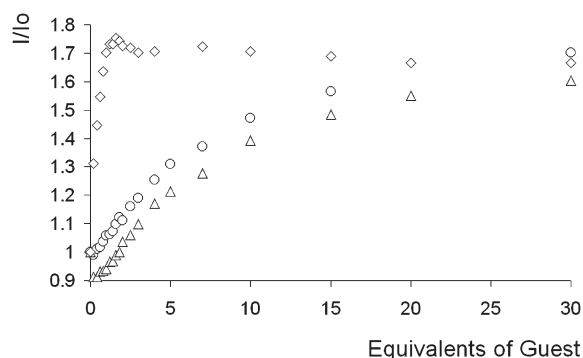


Fig. 3 Fluorescence titration curves in acetone at room temperature ($\lambda_{\text{exc}} = 390$ nm); [Host] = 10^{-5} M; $\circ = 4$, $\triangle = 5$, $\diamond = 11$ with TBAHSO₄.

Table 1 Association constants^a of **4**, **5** and **11** with a series of anions determined by fluorescence titration at room temperature ($\lambda_{\text{exc}} = 390$ nm)

	Cl ⁻	HSO ₄ ⁻	NO ₃ ⁻
4	3.10×10^5	3.52×10^3	1.82×10^3
5	8.67×10^4	4.65×10^3	3.87×10^3
11	1.81×10^5	$>10^6$	5.13×10^4

^a [Host] = 10^{-5} M in acetone; error <10%

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- Fluorescence titration experiments of **11** with TBA dihydrogenphosphate also caused significant enhancement of emission intensity suggesting strong complexation of this tetrahedral anion guest. Specfit analysis of the resulting titration curves however failed to give an association constant value.