

A Fluorescent Ditopic Rotaxane Ion Pair Host

Mathieu Denis,^{±[a]} Lei Qin,^{±[b]} Peter Turner,^[b] Katrina A. Jolliffe,^{*[b]} and Stephen M. Goldup^{*[a]}

Abstract: We report a rotaxane based on a simple urea motif that binds Cl[−] selectively as a separated ion pair with H⁺ and reports the anion binding event through a fluorescent switch-on response. The host selectively binds Cl[−] over more basic anions, which deprotonate the framework and less basic anions that bind more weakly. The mechanical bond also imparts size selectivity on the ditopic host.

Threading molecules through one another to form an interlocked architecture creates a well-defined three-dimensional space into which functional groups can be displayed. These functional groups often mediate attractive intercomponent interactions. Manipulation of these interactions in the design of molecular machines has led to significant advances in molecular shuttles, motors, ratchets and pumps.^[1] Less well studied is the use of interlocked molecules as scaffolds for the development of hosts and sensors. Indeed, the majority of reported interlocked molecules that do display a useful output in response to a small molecule binding event are relatively structurally complex molecular shuttles,^[2] with the attendant limitations on their synthetic accessibility. Furthermore, the response to confounding analytes is typically not reported.

The stand out exception to this is the use of interlocked molecules to bind and detect anions. Beer and co-workers^[3] have exploited anion binding extensively in the assembly of rotaxanes and catenanes by employing the anion to template mechanical bond formation. The interactions that assembled the host “live on” in the product, allowing these catenanes and rotaxanes to bind anions with a selectivity determined in part by size and shape complementarity of the host and guest. By tethering an electroactive or photoactive unit to the host, Beer and co-workers have developed a small number of interlocked anion sensors.^[4]

The anion responsive sensors reported by Beer and co-workers typically rely on the same interactions for anion binding that are used in the formation of the mechanical bond.^[5] Although effective, this can be limiting as only arrangements of anion-binding functionality that are productive in the formation of the interlocked molecule can be applied as hosts. Here we report an alternative approach to anion-responsive fluorescent rotaxanes in which the mechanical bond is used to alter the properties of simple anion-binding unit that plays no role in the rotaxane synthesis. As a consequence of the mechanical bond, significant differences were observed in the anion binding behavior of the rotaxane, resulting in a host that is selective for binding Cl[−] over more (F[−]) or less (Br[−]) basic anions. The crowded environment of

the mechanical bond presents other weak non-covalent interactions, in addition to a urea-based anion binding unit, and appears to impart restricted access to the binding pocket based on anion size.

Rotaxane **1** was synthesized in 92% yield using our small macrocycle modification^[6] of Leigh's active template^[7] Cu-mediated alkyne-azide cycloaddition (AT-CuAAC) reaction^[8,9] (see ESI). The design of rotaxane **1** is based on previous reports of the naphthalimide urea core for the binding and transport of anions.^[10] ¹H NMR analysis of rotaxane **1** provided evidence that the bipyridine unit H-bonds to the urea moiety; NH proton H₁ resonates at a higher chemical shift in rotaxane **1** (Figure 1bii) than axle **2** (Figure 1bi).^[11] This is consistent with the solid-state structure of **1** found by single crystal X-ray diffraction (SCXRD) (Figure 2a) in which the macrocycle encircles the urea moiety with N-H...N distances of 2.32, 2.58, 2.44 and 2.88 Å. The UV-vis spectra of **1** and **2** display absorbances at 402 nm and 386 nm in CHCl₃/CH₃CN (1:1), respectively, suggesting that the naphthalimide fluorophore suggesting H-bonding of the urea contributes to a red-shift of the absorbance. In contrast, **1** and **2** exhibit emissions at 470 and 474 nm respectively, suggesting that the mechanical bond does not significantly affect the fluorescence of the urea-naphthalimide unit.

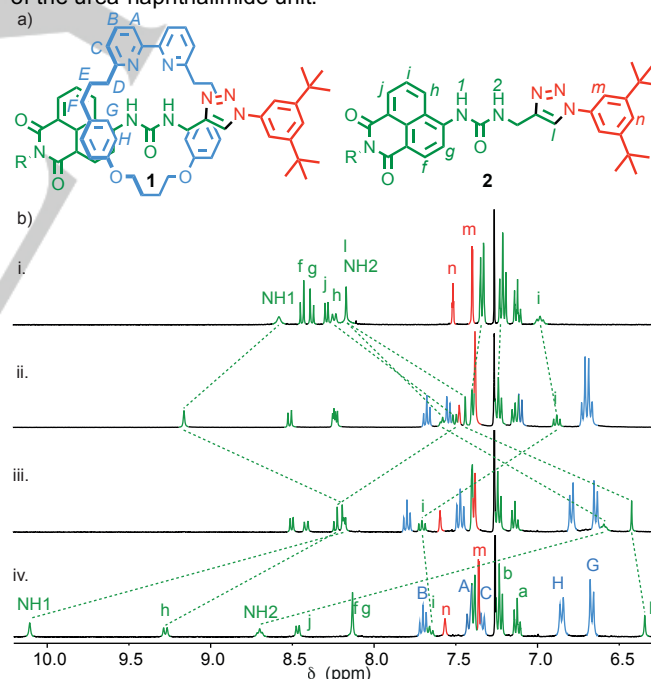


Figure 1. a) Structure of rotaxane **1** and non-interlocked axle **2** (R = CH₂C(H)Ph₂). b) Partial ¹H NMR (400 MHz, 1:1 v/v CDCl₃/CD₃CN, 298 K; peak assignment as in (a)) of i) **2**, ii) **1**, iii) 1-HBF₄, iv) 1-HBF₄ + TBACl (2 eq.).

Titration of axle **2** with the tetrabutylammonium (TBA) salt of AcO[−] led to increasing downfield shifts of the signals for the NH protons H₁ and H₂, a red shift of the absorbance at 386 nm to 400 nm and quenching of the emission associated with the

[a] Mr M. Denis, Professor S. M. Goldup
Chemistry, University of Southampton, Highfield, Southampton,
SO17 1BJ, UK.
E-mail: s.goldup@soton.ac.uk

[b] Mr L. Qin, Dr P. Turner, Professor K. A. Jolliffe
School of Chemistry, The University of Sydney, NSW 2006,
Australia.
Email: kate.jolliffe@sydney.edu.au

[±] These authors contributed equally.

Supporting information (synthetic details, NMR, MS, UV-vis, fluorescence data) can be found under <http://dx.doi.org/10.1002/anie...>

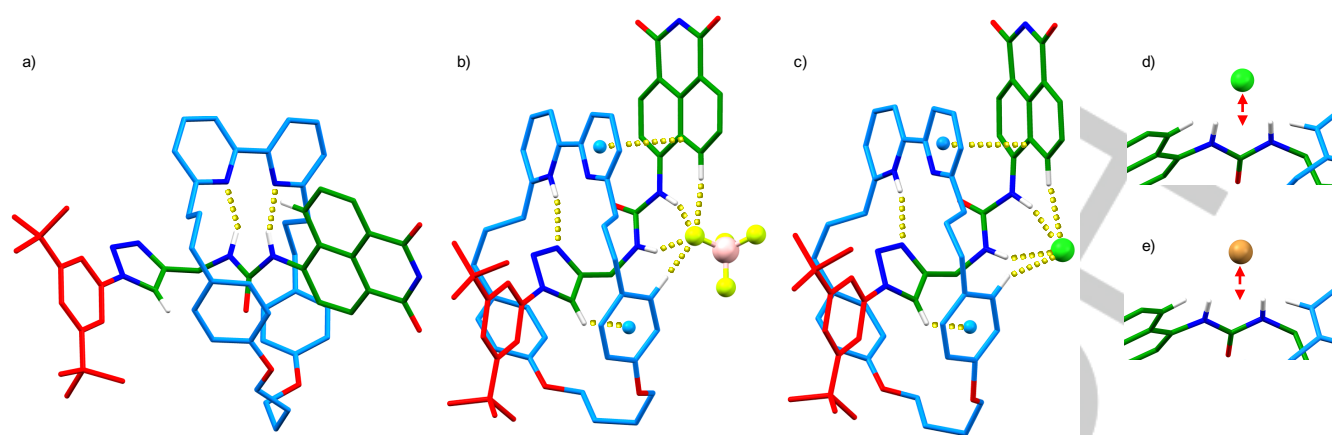


Figure 2. SCXRD structures with selected angles ($^{\circ}$) and distances (\AA) of a) **1** ($\text{NH}_1\cdots\text{N} = 2.45$, $\text{NH}_2\cdots\text{N} = 2.32$, $\text{C-N}_1\text{-C-C}_{\text{ipso}} = 16.1$), b) **1**·**HBF₄** ($\text{NH}_1\cdots\text{F} = 1.99$, $\text{NH}_2\cdots\text{F} = 2.16$, $\text{CH}_6\cdots\text{F} = 2.56$, $\text{CH}_7\cdots\text{F} = 2.16$, $\text{H(py)}\cdots\text{N} = 2.05$, $\text{H}_1\cdots\text{centroid} = 2.91$, $\text{centroid}\cdots\text{naphthalimide} = 3.39$, $\text{C-N}_1\text{-C-C}_{\text{ipso}} = 11.83$), c) **1**·**HCl** ($\text{NH}_1\cdots\text{Cl} = 2.24$, $\text{NH}_2\cdots\text{Cl} = 2.42$, $\text{CH}_6\cdots\text{Cl} = 2.92$, $\text{CH}_7\cdots\text{Cl} = 2.59$, $\text{H(py)}\cdots\text{N} = 2.64$, $\text{H}_1\cdots\text{centroid} = 2.80$, $\text{centroid}\cdots\text{naphthalimide} = 3.42$, $\text{C-N}_1\text{-C-C}_{\text{ipso}} = 32.43$). Anion binding unit showing the displacement of the anion from the $\text{H}_1\text{-H}_2\text{-H}_3\text{-H}_4$ plane for d) **1**·**HCl** (1.61 \AA) and e) **1**·**HBr** (1.84 \AA). 1,1'-Diphenylethyl substituents omitted for clarity.

Table 1. Binding Constants for Non-Interlocked Axle **2** and Rotaxane **1**·**HBF₄**

Anion	Binding constants (K_a) / M^{-1}	
	2	1 · HBF₄
F^-	4930 ^[a]	.. ^[b]
Cl^-	1780 ^[a]	$>10^4$ (28,000 ^[c])
Br^-	390 ^[a]	4660 ^[a]
I^-	70 ^[a]	580 ^[a]
AcO^-	7770 ^[a]	.. ^[b]
HSO_4^-	610 ^[a]	2270 ^[a]
TsO^-	690 ^[a]	1514 ^[a]
MsO^-	950 ^[a]	2600 ^[a]

Titration experiments were carried out in $\text{CDCl}_3\text{-CD}_3\text{CN}$ (1:1). K_a determined by non-linear regression analysis (RMS error < 15%, see ESI). Anions were added as TBA salts. [a] Determined by ^1H NMR ($c = 2.5$ mM). [b] Host deprotonation observed. [c] Determined by UV-vis ($c = 0.13$ mM).

naphthalimide. Non-linear regression analysis of the ^1H NMR, UV-vis and fluorescence titration data (see ESI) fit well to 1:1 binding models, allowing binding constants to be determined (Table 1). Similar effects were observed for a range of anions with the observed order of anion affinity found to be $\text{I}^- < \text{Br}^- < \text{HSO}_4^- < \text{TsO}^- < \text{MsO}^- < \text{Cl}^- < \text{F}^- < \text{AcO}^-$; a trend in keeping with their H-bond acceptor strengths.^[12]

We anticipated that addition of H-bond accepting anions to rotaxane **1** would lead to displacement of the bipyridine-urea interaction and that this competition between inter- and intra-molecular H-bonding might impart selectivity to **1** that is different from axle **2**. However, titration of **1** with a panel of anions led to no observable change by ^1H NMR, UV-vis or fluorescence spectroscopy, suggesting that the $\text{NH}\cdots\text{anion}$ interaction is unable to compete with the inter-component H-bonds.

The inhibition of anion binding in **1** corresponds to Lewis basic inhibition of the receptor. We have previously observed inhibition

of an interlocked Au^{I} -catalyst due to a similar Lewis basic interaction of the bipyridine moiety with the metal ion.^[13] In that case, catalytic activity was restored by binding of cations into the cavity of the rotaxane, and we speculated that a similar interaction between a cation and the bipyridine ring might be used to turn-on anion binding by **1**. To demonstrate proof of concept, we investigated if protonation of the bipyridine moiety could lead to the binding of exogenous anions by the urea moiety. Furthermore, binding of anions by $[\text{1H}]^+$ would correspond to ditopic binding of HX , which is relatively unusual;^[14] although anion binding motifs are known in which the host requires protonation, the donated proton is typically part of the anion coordination sphere.^[15] In contrast, we anticipated that the proton would be sequestered in the rotaxane cavity leading to separated ion-pair binding.^[16,17]

When **1** was treated with an aqueous solution of HBF_4 a new species, with a significantly different ^1H NMR spectrum (Figure 1biii), was obtained which was assigned to be **1**·**HBF₄**. Key changes include an upfield shift of the signals attributable to NH protons H_1 and H_2 suggesting that they are no longer involved in H-bonding to the bipyridine unit and an upfield shift of the signal attributable to H_i , consistent with the presence of a $\text{CH}\cdots\pi$ contact in the protonated rotaxane. The UV-vis spectrum of rotaxane **1** also changes upon protonation; a new absorbance appeared at 310 nm that was assigned to the protonated bipyridine moiety^[18] and the absorbance band attributable to the naphthalimide blue-shifted to 381 nm, consistent with the urea moiety no longer being involved in H-bonding interactions.

SCXRD analysis confirmed the formation of the HBF_4 salt and revealed interactions consistent with the solution phase data; protonation causes large scale structural rearrangement to a (co)conformation in which one bipyridine N is protonated and engaged in a hydrogen bond with N3 of the triazole and, as a result, H_i is held in close proximity to the face of one of the macrocycle aromatic rings. The naphthalimide residue of **1**·**HBF₄** was found to be disordered about two orientations, one of which exhibits a short face-face contact between one of the bipyridine rings and the naphthalimide unit (Figure 2b). Thus, at least in the solid state, protonation also seems to induce π -stacking of the bipyridine moiety and the naphthalimide ring.^[19] Furthermore, in

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the solid state the BF_4^- anion interacts with the urea protons, H_h of the naphthalimide and one of H_G (Figure 2b).

The solid-state structure of $\mathbf{1} \cdot \text{HBF}_4$ suggests the urea NHs are no longer encumbered by the bipyridine donors and are thus available to bind exogenous anions.^[20] Titration of $\mathbf{1} \cdot \text{HBF}_4$ with basic anions such as AcO^- or F^- led to deprotonation of the host to regenerate $\mathbf{1}$, as determined by ^1H NMR and UV-vis analysis, and thus no anion binding.^[21] Conversely, when $\mathbf{1} \cdot \text{HBF}_4$ was treated with TBACl, the signals attributable to NH protons H_I and H_2 shift downfield upon addition of the anion (Figure 1biv), consistent with H-bonding of Cl^- to the urea moiety. Simultaneously, *peri* proton H_h also shifts downfield, consistent with a $\text{CH} \cdots \text{Cl}^-$ hydrogen bond and triazole proton H_l shifts upfield, suggesting that the $\text{CH} \cdots \pi$ contact becomes stronger. SCXRD analysis of crystals grown from a solution of $\mathbf{1} \cdot \text{HBF}_4$ in $\text{CH}_2\text{Cl}_2/\text{MeCN}$ (1:1 v/v) in the presence of TBACl (10 eq.) revealed that Cl^- is bound as expected by the urea moiety in the protonated host with an additional $\text{C-H} \cdots \text{Cl}^-$ contact with H_h (Figure 2c) and a longer contact with H_G . The $\text{CH} \cdots \pi$ contact between H_l and the flanking aromatic is also shorter than in $\mathbf{1}$ ($\Delta d = 0.15 \text{ \AA}$), consistent with the solution state data.

The titration of $\mathbf{1} \cdot \text{HBF}_4$ with anions could also be followed by UV-vis and fluorescence spectroscopy. Addition of Cl^- resulted in a red shift ($\Delta\lambda = 15 \text{ nm}$) and increase in the absorbance at 380 nm, and a 2-fold increase in the naphthalimide emission. Titrations with Br^- , HSO_4^- , MsO^- or TsO^- revealed similar, although less pronounced changes. Although I^- showed similar changes by ^1H NMR and UV-vis spectroscopies the emission was quenched, presumably due to Stern-Volmer collisional effects.^[22]

Comparison of the binding constants determined for $\mathbf{1} \cdot \text{HBF}_4$ with those of $\mathbf{2}$ reveal a number of clear differences. Firstly, the potential for deprotonation of $\mathbf{1} \cdot \text{HBF}_4$, which renders it insensitive to anions, ensures that, whereas $\mathbf{2}$ binds more basic anions more strongly, this is not the case for $\mathbf{1} \cdot \text{HBF}_4$ which fails to bind the more basic F^- and AcO^- guests. Secondly, the binding of the less basic anions is much stronger to $\mathbf{1} \cdot \text{HBF}_4$ than to the neutral host $\mathbf{2}$. This is unsurprising as charge-charge interactions are expected to stabilize the interlocked complex significantly.^[23]

The relative order of binding strength is also different in $\mathbf{2}$ and $\mathbf{1} \cdot \text{HBF}_4$. Whereas binding runs in the order $\text{I}^- < \text{Br}^- < \text{HSO}_4^- < \text{TsO}^- < \text{MsO}^- < \text{Cl}^-$ for $\mathbf{2}$, the relative preference of the sulfonate anions is lower for $\mathbf{1} \cdot \text{HBF}_4$ resulting in the order $\text{I}^- < \text{HSO}_4^- < \text{TsO}^- < \text{MsO}^- < \text{Br}^- < \text{Cl}^-$. The relative preference of $\mathbf{1} \cdot \text{HBF}_4$ for MsO^- over TsO^- is also higher. These results suggest that the crowded environment resulting from the presence of the threaded macrocycle adjacent to the urea motif in $\mathbf{1} \cdot \text{HBF}_4$ provides some size and shape selection; the spherical Br^- anion (ionic radius = 168 pm)^[24] is preferred over the tetrahedral HSO_4^- and the larger MsO^- and TsO^- anions. Comparison of the solid-state structure of $\mathbf{1} \cdot \text{HCl}$ and $\mathbf{1} \cdot \text{HBr}$ (Figure 2d) suggests that as the anionic radius increases, the “fit” of the anion between the urea nitrogen protons, *peri* proton H_h and macrocycle proton H_G decreases, forcing the anion out of the plane of the four H-anion contacts.

Finally, it is noteworthy that $\mathbf{1} \cdot \text{HBF}_4$ exhibits a fluorescent switch-on response upon anion binding, whereas $\mathbf{2}$ exhibits a switch-off response. The origin of this photophysical difference is not obvious – in both cases binding of the anion is expected to increase the electron density in the naphthalimide fluorophore and, on simple charge transfer grounds, would be expected to enhance the stability of the excited state, whereas the proximity of anions has previously been reported to result in PET

quenching.^[25] The explanation probably lies in the naphthalimide-bipyridine $\pi-\pi$ interaction observed in the solid-state structure of $\mathbf{1} \cdot \text{HBF}_4$ that is necessarily absent in the case of $\mathbf{2}$. Anion binding may affect this interaction by rigidifying the framework in some way, thus reducing non-radiative decay linked to bond rotation.

In conclusion, we have demonstrated that the AT-CuAAC reaction can be used to synthesize interlocked hosts for anions in which functional groups used or generated during the method of synthesis are not involved in the binding of the guest, opening up new targets for study. In doing so, we serendipitously discovered a rotaxane framework in which anion binding is activated allosterically by protonation, leading to a system that acts as a ditopic host for an HX ion pair. The binding event is reported by a clear fluorescence response and anion selectivity is determined both by the strength of the H-bonding interaction between the host and anion, and the anion $\text{p}K_a$. Furthermore, the mechanical bond introduces size selectivity into this receptor.

Acknowledgements

MD thanks the University of Southampton and EPSRC for financial support. SMG acknowledges funding from the European Research Council (Consolidator Grant Agreement no. 724987). SMG thanks the Royal Society for a Research Fellowship. LQ acknowledges financial support from a John A. Lamberton scholarship. The authors gratefully acknowledge support from the Royal Society (International Exchange grant). The authors thank P. Horton and G. Tizzard of the UK National Crystallography Service for assistance with the analysis of $\mathbf{1}$, $\mathbf{1} \cdot \text{HBF}_4$ and $\mathbf{1} \cdot \text{HCl}$.

Keywords: rotaxane • sensor • fluorescent • mechanical bond • anions

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