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COMMUNICATION

Colour coding the co-conformations of a [2]rotaxane flip-switch[†][‡]

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Fine-tuning the charge transfer chromophores in a series of [2]rotaxane flip-switches yields a unique optical signal (purple colour) for one of the interactions allowing for facile determination of the position of the flip-switch equilibrium.

A mechanically interlocked molecule (MIM) such as a [2]rotaxane can operate as a molecular switch if two different recognition sites are available on the axle for recognition and binding of the macrocyclic wheel.¹ In this type of [2]rotaxane molecular shuttle, the two states are translational co-conformers related by the relative positioning of the macrocycle along the length of the axle.² Similarly, we reported the concept of a molecular flip-switch that operates at a single recognition site on a simple [2]rotaxane.³ These flip-switches utilize the templating motif between 24-crown-8 wheels and 1,2-bis(pyridinium)-ethane axles that has been successful in creating a variety of unique rotaxanes⁴ and catenanes⁵ and has been incorporated into metal–organic frameworks (MORFs).⁶

An example of a [2]rotaxane flip-switch is shown in Fig. 1. Since both the axle and the wheel are unsymmetrical, the axle contains two different pyridinium groups and the crown contains two different aromatic rings, there are two possible co-conformers. At low temperature (slow exchange), ¹H NMR spectra could be attained, two sets of pyridyl protons ($\Delta \delta \approx 0.5$ ppm) were clearly visible due to differences in shielding and integration could be used to determine the co-conformer distribution. Alternatively, at room temperature (fast exchange) the weighted average positions of these peaks can sometimes be used to estimate the distribution.^{3a}

It was of interest to expand the scope of this switchable MIM system but the requirement of using NMR spectroscopy and studying systems with large differences in shielding was limiting and impractical. It was reasoned that optical spectroscopy would be a much more convenient method for studying these rapidly equilibrating systems. This communication describes the design, synthesis and characterization by visible



Fig. 1 A [2]rotaxane flip-switch with two possible co-conformations that operate at a single recognition site.

absorption spectroscopy of new rotaxane flip-switches with chromophores appropriate for easily identifying co-conformer distributions at room temperature. ¹H NMR spectroscopy was not capable of distinguishing co-conformers in this system as chemical shift differences for axle protons were negligible.

Fig. 2 shows a series of [2]rotaxanes in which we have attempted to manipulate the nature of the π - π interactions between electron-rich aromatic rings of the crown ether wheel



Fig. 2 Different coloured [2]rotaxanes with different charge transfer interactions due to π -stacking between the axle and wheel.

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and the electron-poor pyridinium rings of the axle. The intent was to produce a unique charge transfer chromophore and therefore a unique visible colour that could be used to identify and quantify one particular co-conformer.⁷

[2]Rotaxanes 1 and 2, containing dibenzo-24-crown-8, **DB24C8**, were previously shown to exhibit charge transfer absorptions giving rise to pale yellow and yellow-orange solutions, respectively; 2 showed a clear maximum at 433 nm in MeNO₂ solution. It was rationalized that since these absorption bands arise from charge transfer between the HOMO on the crown ether wheel and the LUMO on the pyridinium axle, the energy of the band could be manipulated by increasing or decreasing this HOMO–LUMO gap.⁸

For this purpose, the new crown ether 4,5,4',5'-tetramethoxydibenzo-24-crown-8, (MeO)₄DB24C8, was prepared in 43% yield from the known tetraiodo species I₄DB24C8 via a Cu(1) catalyzed reaction in MeOH solution under μ W assisted conditions (ESI‡). [2]Rotaxane, 3, containing (MeO)₄DB24C8 and ester stoppers was prepared from the [2]pseudorotaxane formed between (MeO)₄DB24C8 and 1,2-bis((4-phenylmethanol)4-pyridinium))ethane by reaction with 3,5-dimethylbenzoic anhydride using published conditions.⁹ [2]Rotaxane 4 was prepared by stoppering the [2]pseudorotaxane formed between (MeO)₄DB24C8 and 1,2-bis(4,4'-bipyridinium) ethane with 4-*tert*-butylbenzyl bromide employing μ W assisted conditions.⁹

Gratifyingly, solutions of the four [2]rotaxanes containing the four different pairs of charge transfer components yielded four different colours with the colour of **4** being distinctly different (purple, $\lambda_{max} = 551$ nm in MeNO₂) from the other three; Fig. 3. The visible absorption spectra of these solutions are shown in Fig. 4.

Crystals of 3 (yellow) and 4 (purple) containing the crown ether (MeO)₄DB24C8 were grown by diffusion of iPr_2O into MeCN solutions of the compounds and their structures are shown in Fig. 5. (The structures of both 1 and 2 containing DB24C8 were determined previously.)⁹ It is clear in both X-ray structures§ that the methoxy-substituted aromatic rings are involved in significant π -stacking interactions with the aromatic groups of the pyridinium axle as designed.

With the visible absorption properties of these four [2]rotaxanes established, it was important to incorporate these features into a [2]rotaxane flip-switch and test the validity of using optical spectroscopy to quantify the co-conformer distribution in such a system. To this end, two *test* [2]rotaxanes **5** and **6** and the [2]rotaxane flip-switch, **7** were prepared utilising the crown ether (**MeO**)₂**DB24C8** which contains both benzo and dimethoxy-benzo aromatic groups (ESI[‡]). By design, the [2]rotaxanes **5** and **6** must



Fig. 3 From left to right: MeNO₂ solution (10^{-3} M) of [2]rotaxanes 1, 2 containing DB24C8 and 3, 4 containing (MeO)₄DB24C8.



Fig. 4 Visible absorption spectra of [2]rotaxanes 1–4 in $MeNO_2$ solution (10⁻³ M).



Fig. 5 Ball-and-stick representations of the cationic portion of the X-ray crystal structures of [2]rotaxanes 3 (left) and 4 (right) (atoms: red = O, blue = N, black = C. Bonds: axle = gold, wheel = silver).

contain equal contributions of two chromophores since the ends of the axles are identical while rotaxane 7 could potentially display all four chromophores since the ends of the axle are different. The distribution of co-conformers for 7 is however unknown, since there may be a preference for a co-conformer with a particular set of π - π interactions (Fig. 6).

As designed, solutions of [2]rotaxanes 5 and 6 displayed colours indicative of equal mixing of the individual chromophores of 1 with 3 and 2 with 4, respectively; Fig. 7 (left). The visible absorption spectra of 5 and 6 were then successfully simulated¹⁰ based on equal contributions from their two constituent chromophores; 1 plus 3 for 5 and 2 plus 4 for 6 (ESI‡). These results served to verify the spectral modelling criteria and using the same methodology it was possible to simulate the spectrum of 7 (Fig. 8) and solve for the relative distribution of conformers A and B. It was determined that at room temperature, in the MeNO₂ solvent, the [2]rotaxane



Fig. 6 The co-conformers (A and B) of [2]rotaxane flip-switch 7.



Fig. 7 Left: MeNO₂ solutions (10^{-3} M) of [2]rotaxanes **5** and **6**. Right: MeNO₂ solution (10^{-3} M) of [2]rotaxane flip-switch **7**.



Fig. 8 Visible absorption spectrum of [2]rotaxane flip-switch 7 and simulated contributions from 1-4 (MeNO₂ solution at 10^{-3} M).

flip-switch 7 prefers co-conformer A over co-conformer B with a distribution ratio A : B of 60 : 40. In co-conformer A, the interaction of the most electron-rich crown aromatic ring containing the MeO groups with the most electron-poor pyridinium ring presumably stabilizes this arrangement of the axle and wheel components.

In summary, we have demonstrated that the rapid equilibration between co-conformers inherent in a [2]rotaxane flip-switch can be probed and ultimately the distribution of isomers determined by visible absorption spectroscopy. Finetuning of the molecular interactions in the system to produce a distinct colour that was easily observed by the naked eye and quantifiable by optical spectroscopy bodes well for the detection of such isomer ratios in solid state materials such as liquid crystals or metal–organic frameworks.

Notes and references

§ Crystal data¹¹ for [3][OTf]₂.(MeCN)₂: C₇₈H₈₈F₆N₄O₂₂S₂, M = 1611.64, T = 173(2) K, monoclinic, space group $P2_1/c$, a = 16.268(2), b = 12.443(1), c = 20.841(2) Å, $\beta = 110.648(1)^{\circ}$, V = 3947.7(7) Å³, $\rho_{calc} = 1.356$ g cm⁻³, $\mu = 0.158$ mm⁻¹, Z = 2, reflections collected = 36743 ($R_{int} = 0.0942$), final R indices [$I > 2\sigma I$]: $R_1 = 0.0827$, $wR_2 = 0.2020$, R indices (all data): $R_1 = 0.1275$, $wR_2 = 0.2400$, GoF = 1.015 with data/variables/restraints = 6942/506/0. Crystal data for [4][OTf]₄.(Pr_2O)₂(MeCN)₂(H₂O): C₉₂H₁₂₆F₁₂N₆O₂₇S₄, M = 2104.23, T = 173(2) K, monoclinic, space group $P2_1/c$, a = 13.845(2), b = 36.778(4), c = 20.786(2) Å, $\beta = 96.962(2)^{\circ}$, V = 10.506(2) Å³, $\rho_{calc} = 1.330$ g cm⁻³, $\mu = 0.186$ mm⁻¹, Z = 4, reflections collected = 100 488 ($R_{int} = 0.1698$). R indices [$I > 2\sigma I$]: $R_1 = 0.0990$, $wR_2 = 0.2029$, R indices (all data): $R_1 = 0.2350$, $wR_2 = 0.2715$, GoF = 0.999 with data/variables/restraints = 18466/1325/348.

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