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Photodriven [2]Rotaxane-[2]Catenane Interconversion

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A [2]rotaxane, whose thread component comprises a central dibenzylammonium group and 9-alkoxyanthracene stoppers and is hosted by a 24-dibenzo-8-crown bead, undergoes an efficient photocatenation step resulting in a [2]rotaxane-to-[2]catenane topology interconversion via a fully reversible [4 π +4 π] photocyclomerization of terminal anthracene groups.

A wealth of multicomponent supermolecules exhibiting complex topologies, such as mechanically-interlocked molecules (MIMs) has been reported. Their synthesis relies on supramolecular interactions as well as reversible covalent chemistry.¹ Rotaxanes and catenanes are two major classes of MIMs and exhibit, depending on their structure, stimulus-driven processes including sub-component movement,^{1b} photoinduced electron transfer² and electronic energy transfer.³ However, examples of topology interconversion^{1d} from one class of MIM (e.g. from rotaxane to catenane) to another are rare and photodriven examples based on small molecules are unknown. Concerning non-photochemical versions, one example is based on conversion of a poly(ethylene glycol) 400 [2]rotaxane to the corresponding [2]catenane. This conversion was effected by a Zn/Cu coupling of the two triarylmethane stoppers of a [2]rotaxane precursor, leading to a macrocyclization of the thread in 14% yield.^{4a} A second interconversion was obtained by attaching a polymethylene bridge between a methylene group in the α -position of sulfonyl groups for the formation of a [2]catenane from a [2]rotaxane.^{4b} The formation of catenane architectures resulted from complexation of ditopic bridging ligands (DABCO or 4,4'-bipyridine) by a rotaxane incorporating bis-Zn-porphyrin molecular tweezers.^{4c} Finally, a radial hexapyridyl template was recently used to convert an alkyne-terminated [2]rotaxane into a cyclic [4]catenane porphyrin hexamer, via a Pd-catalysed Glaser coupling.^{4d}

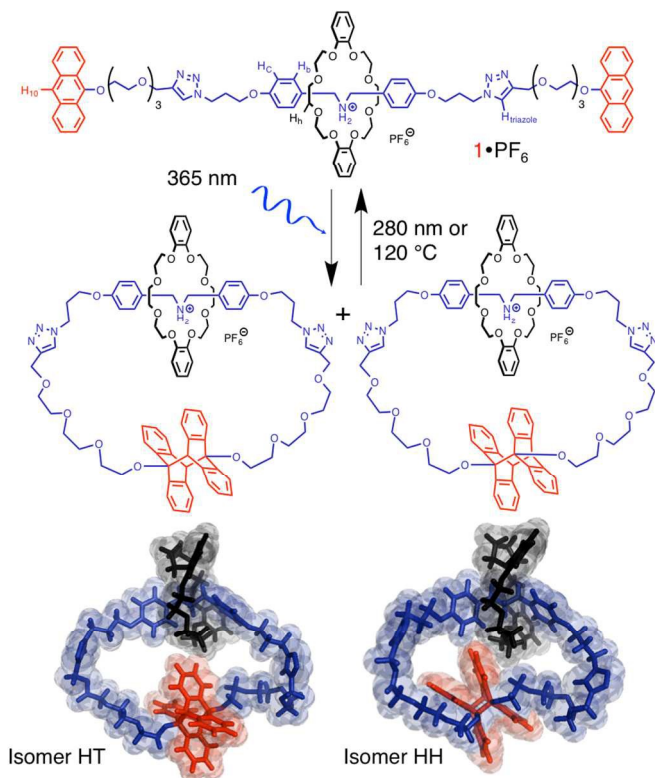
Light may be considered the least invasive switching stimulus, not requiring addition of any external chemical species or electrodes. In order to effect the photocatenation step leading to a topology interconversion, the [4 π +4 π] photodimerization of anthracene appeared to be suitable.⁵ Indeed, this reaction is high yielding, reversible and is compatible with different supramolecular recognition motifs.⁶ For example, upon irradiation of a 9-anthracene-capped polyrotaxane precursor for 1 day, a mixture of poly(polyrotaxane) species, with 2-10 repeat units, and a

polycatenane were obtained.^{7a} Recently, the photogeneration of a poly[3]rotaxane from an anthracene-capped [3]rotaxane was observed.^{7b} Here, we report the synthesis and characterisation of a discrete rotaxane assembled through hydrogen bonding, which bears photodimerizable 9-alkoxyanthracene stoppers and studies of its photochromic behaviour in solution leading to well-defined catenane photoproducts, concomitant fluorescence switching, and thermal and photochemical return to the initial state. Catenane synthesis generally requires macrocyclisation in the mechanical bond forming step, so is often thought more challenging than rotaxane formation.

The target [2]rotaxane (**1**•PF₆), along with its two anticipated photocatenated products (Fig. S1-S3) resulting from efficient topology interconversion, and as determined by molecular modelling (PM6), are shown in Scheme 1. An anthracene moiety functionalized at the 9-position was employed as the photoactive unit in order to limit the number of photoproduct regioisomers to: i) a stable antiparallel Head-to-Tail isomer (HT) and ii) an unstable Head-to-Head isomer (HH), see Scheme 1.⁵ The ammonium-crown ether recognition motif has the advantage of being electro-inactive. Indeed, the photochromic properties of anthracene derivatives are quenched when incorporated into donor-acceptor type rotaxanes^{2a} due to, for example, photoinduced electron transfer processes.⁸

A convergent synthetic approach was employed in order to synthesize [2]rotaxane **1**•PF₆ (Scheme S1).⁹ Condensation of 3-azidopropyl tosylate with 4-hydroxybenzaldehyde afforded **2** in 54% yield.¹⁰ Similarly, **3** was synthesized from *tert*-butyl(4-hydroxybenzyl) carbamate in 81% yield.¹¹ Quantitative deprotection of **3** with TFA afforded **4**, which reacted with **2** in boiling toluene. The freshly obtained Schiff base was then reduced with NaBH₄. The resulting amine was protonated and converted into the corresponding hexafluorophosphate salt (**5**•PF₆) by anion metathesis. The dumbbell precursor **5**•PF₆, which bears two terminal azide functional groups was obtained in 40% yield. The 9-alkoxyanthracene stoppers were then introduced, employing a copper-assisted azide-alkyne cycloaddition.¹² In the absence of the macrocycle, the free thread **8**•PF₆ was formed in 19% isolated yield, while **1**•PF₆ was formed as follows. Firstly, the supramolecular complex of **5**•PF₆ with the dibenzo-24-crown-8 (DB24C8) was formed in CHCl₃.¹³ After 1 h, two equivalents of alkyne-terminated stopper precursor (**7**) and a catalytic amount of Cu(CH₃CN)₄PF₆ and tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (TBTA) were added to the reaction

mixture. The desired [2]rotaxane ($\mathbf{1}\cdot\text{PF}_6$) was isolated after column chromatography in 23% yield, whose interlocked nature was confirmed by ^1H NMR spectroscopy (Fig. S4). Due to H-bonding interactions between DB24C8 and the ammonium station, the chemical shift values (δ) of the [2]rotaxane H_b and H_c protons show an upfield shift (ca. 0.1 ppm and 0.2 ppm, respectively) compared to the free dumbbell. The δ values of the aromatic protons of DB24C8 exhibit an upfield shift ($\Delta\delta$ = ca. 0.3 ppm) in $\mathbf{1}\cdot\text{PF}_6$ compared to the free macrocycle, as do the aliphatic H_h resonances ($\Delta\delta$ = 0.18 ppm).



Scheme 1. Structure of the target [2]rotaxane ($\mathbf{1}\cdot\text{PF}_6$) and two possible photoproduct regioisomers (HT and HH) formed by a $[4\pi+4\pi]$ photocycloaddition of 9-alkoxyanthracene stoppers (PM6 molecular modelling).

^1H NMR spectroscopy also allowed the investigation of the photoswitching properties of $\mathbf{1}\cdot\text{PF}_6$ (Fig. 1). A 1 mM solution of [2]rotaxane in degassed CD_3CN was irradiated at 365 nm.¹⁴ After 1 h, >95% conversion denoted by disappearance of specific anthracene proton resonances (from 8.60 to 8.00 ppm) was observed, while new signals appeared at 6.80 ppm. This is consistent with the photodimerization of the anthracene stoppers, resulting in xylene-like units, concomitant with the loss of aromaticity of the central anthracene ring. Another indication of the photodimerization process was the appearance of a singlet at 4.53 ppm (8.29 ppm in the monomer) corresponding to the bridgehead H_{10} proton in the HT photodimer, accompanying the sp^2 -to- sp^3 hybridization of the adjacent carbon. The evolution of the UV absorption spectrum of $\mathbf{1}\cdot\text{PF}_6$ upon irradiation (Fig. S5a) fully supports the formation of plano-symmetric photodimers involving only the meso vertices of the central anthracene ring and not the lateral aromatic rings, as there is no absorption beyond 300 nm. The intramolecular character of the photoreaction is corroborated by its high efficiency at high dilution and its non dependence on the concentration (*vide infra*). Closer scrutiny of the ^1H NMR spectrum after irradiation also revealed only one signal for the triazole ring proton (7.72 ppm) and one signal for the H_h proton (3.47 ppm) of the DB24C8 macrocycle, further suggesting that only one stable photoproduct was formed.

The thermal cycloreversion of the anthracene photodimer was investigated and no change in the ^1H NMR was observed, even after heating the solution to 50 °C for a week. However, decatenation occurred when the sample was heated to higher temperatures. After 3 h at 120 °C in a sealed tube, the ^1H NMR spectrum of the [2]rotaxane $\mathbf{1}\cdot\text{PF}_6$ was restored. The relative thermal stability of the photoproduct suggests the formation of the HT photoproduct since HH isomers have been shown to be less stable under these conditions.^{5,14} After complete restoration of the ^1H NMR spectrum, subsequent irradiation of the higher energy anthracene absorption band using shorter wavelength light (254 nm) also led to the same photoproduct, as judged by ^1H NMR analysis.

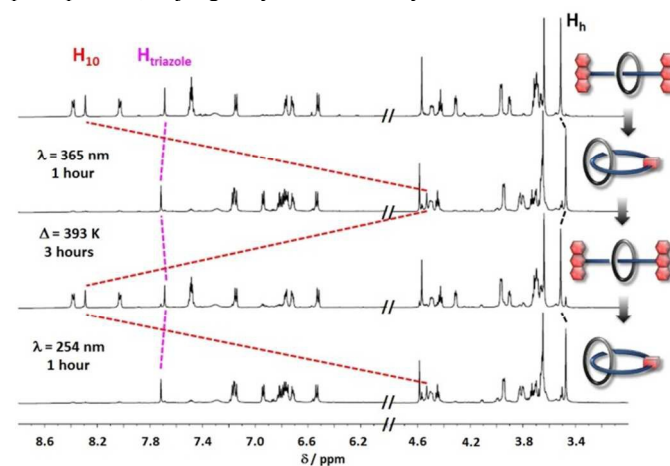


Fig. 1 ^1H NMR (CD_3CN , 600 MHz, 25 °C) spectra of a 1 mM solution of the [2]rotaxane $\mathbf{1}\cdot\text{PF}_6$, after irradiation at 365 nm (1 h), heating at 120 °C (3 h) and irradiation at 254 nm (1 h).

High-resolution mass spectrometry characterization (ESI) of the mixture after irradiation gave some insights into the identity of the key photoproduct. Only one peak was detected, which presented the same characteristics as $\mathbf{1}\cdot\text{PF}_6$: i) monocharged species, ii) m/z value of 1572.7536 Th (1572.7865 Th for unirradiated $\mathbf{1}\cdot\text{PF}_6$) and iii) same isotopic profile, implying that no polyrotaxanes were formed. This is consistent with intramolecular dimerization of the 9-alkoxyanthracene stoppers where no mass change occurs. In other words, the photoproduct corresponds to a [2]catenane (Fig. S7) resulting from a topology interconversion of the [2]rotaxane $\mathbf{1}\cdot\text{PF}_6$.

To further investigate the intramolecular process, the photoreaction was monitored by UV-vis spectroscopy using a dilute solution ($c = 2 \times 10^{-5}$ M) of $\mathbf{1}\cdot\text{PF}_6$ in degassed CH_3CN . Before irradiation, $\mathbf{1}\cdot\text{PF}_6$ exhibited the characteristic low energy structured anthracene absorption band attributed to the $\text{S}_1 \leftarrow \text{S}_0$ transition of anthracene ($^1\text{L}_a$; $\epsilon = 8100 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ at 370 nm). Only small changes in the UV-vis spectrum (Fig. S6a) compared to the free thread are consistent with minimal bead-stopper interaction in the ground state (Table S1). After 1 h of irradiation at 365 nm, the total disappearance of the $\text{S}_1 \leftarrow \text{S}_0$ anthracene absorption band was observed (Fig. S5a), as anticipated for an intramolecular photodimerization (*vide supra*), in this case affording the photocatenation product. A similar conclusion can be drawn from fluorescence studies (Fig. S5b). Characteristic anthracene stopper emission of $\mathbf{1}\cdot\text{PF}_6$ in the 400 - 530 nm region is switched "off" upon UV irradiation, mirroring non-fluorescence photodimer formation.

Cycloreversion was performed by irradiating the solution at 280 nm, corresponding to the absorption of the photodimer. After 1 h, the UV-vis and fluorescence spectra were globally restored to those observed prior to irradiation. A fatigue study showed that more than 90% of the anthracene monomer emission signal was recovered after each cycle (Fig. 2). On repeating this cycle, slow

decomposition was observed, estimated at 32% after 9 cycles. An alternative irradiation/thermal-return cycle (*vide supra*) to effect the topology interconversion exhibited 21% fatigue after 4 cycles (Fig. S8).

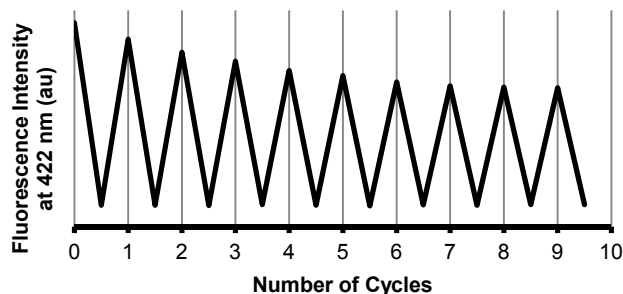


Fig. 2 Fatigue study of a 2×10^{-5} M solution of 1-PF_6 in CH_3CN monitored by spectrofluorometry. Each cycle corresponds to irradiation at 365 nm (1 h) leading to the photocyclomerization followed by irradiation at 280 nm (1 h) leading to the cycloreversion.

Finally, chemical actinometry afforded the quantum yield of photodimerization reaction ($\lambda_{\text{ex}} = 365$ nm).¹⁵ For solutions of 1-PF_6 at concentrations: i) 2×10^{-5} M, ii) 1×10^{-4} M and iii) 1×10^{-3} M, the measured quantum yields were found to be the same (0.14). This concentration-independent value (similar to free thread 8-PF_6 value of 0.15, suggesting that the ring does not influence the photoreaction) demonstrates that the 9-alkoxyanthracene stoppers of the [2]rotaxane photodimerized via an intramolecular process at concentrations below 10^{-3} M, as anticipated due to the nanosecond lifetime of the excited anthracene singlet state. This short lifetime would preclude a diffusion-limited encounter of a second ground-state molecule, which could participate in an intermolecular process. The relatively elevated value for photodimerization and fluorescence emission quantum yield (0.18) also indicate that there is minimal steric encumbrance or additional deexcitation pathways to hinder the efficiency of the topology interconversion.¹⁶

In conclusion, the synthesis of a new hydrogen-bonding [2]rotaxane bearing 9-alkoxyanthracene stoppers is reported, and the photoswitching behavior was investigated by ^1H NMR, UV-vis and fluorescence spectroscopies. It was found that the intramolecular photodimerization of the anthracene stoppers occurred upon irradiation at 365 nm (or 254 nm). The photoreaction resulted in an intramolecular catenation process, leading to an unusual topology interconversion from a [2]rotaxane (rather than a pseudorotaxane) to a [2]catenane and concomitant fluorescence switching "off", and vice versa. The interconversion of the photoproduct (HT isomer) is thermally ($\Delta = 120$ °C) and photochemically reversible ($\lambda = 280$ nm) and was shown to be highly efficient.

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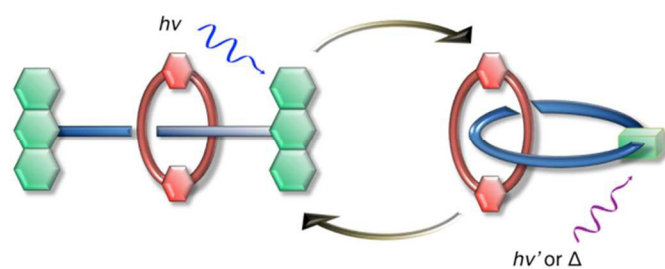
Notes and references

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† Electronic Supplementary Information (ESI) available: Synthetic procedures and full characterization of compounds **1** - **8**, photoproducts,

electronic absorption and fluorescence spectra, fatigue study and molecular modeling. See DOI: 10.1039/c000000x/

- (a) H. Deng, M. A. Olson, J. F. Stoddart and O. M. Yaghi, *Nature Chem.*, 2010, **2**, 439; (b) A. Coskun, M. Banaszak, R. D. Astumian, J. F. Stoddart and B. A. Grzybowski, *Chem. Soc. Rev.*, 2012, **41**, 19; (c) A. Tron, P. J. Thornton, M. Rocher, H.-P. Jacquot de Rouville, J.-P. Desvergne, B. Kauffmann, T. Buffeteau, D. Cavagnat, J. H. R. Tucker and N. D. McClenaghan, *Org. Lett.*, 2014, **16**, 1358; (d) B. M. Walba, *Tetrahedron*, 1985, **41**, 3161; (e) O. Lukin, A. Godt and F. Vögtle, *Chem. Eur. J.*, 2004, **10**, 1878; (f) P. Wei, X. Yan, J. Li, Y. Ma, Y. Yao and F. Huang, *Tetrahedron*, 2012, **68**, 9179.
- (a) A. Mateo-Alonso, *Chem. Commun.* 2010, **46**, 9089; (b) M. R. Panman, P. Bodis, D. J. Shaw, B. H. Bakker, A. C. Newton, E. R. Kay, A. M. Brouwer, W. J. Buma, D. A. Leigh and S. Woutersen, *Science*, 2010, **328**, 1255; (c) H. Zhang, B. Zhou, H. Li, D. Qu and H. Tian, *J. Org. Chem.*, 2013, **78**, 2091.
- (a) H. Zhang, X. Kou, Q. Zhang, D. Qu and H. Tian, *Org. Biomol. Chem.*, 2011, **9**, 4051; (b) L. Scarpantonio, A. Tron, C. Destribats, P. Godard and N. D. McClenaghan, *Chem. Commun.*, 2012, **48**, 3981; (c) T. Ogoshi, D. Yamafuji, T. Yamagishi and A. M. Brouwer, *Chem. Commun.*, 2013, **49**, 5468.
- (a) G. Agam, A. Zilkha, *J. Am. Chem. Soc.*, 1976, **98**, 5214; (b) G. Schill, N. Schweickert, H. Fritz, W. Vetter, *Chem. Ber.*, 1988, **121**, 961; (c) D. I. Schuster, K. Li, D. M. Guldi, J. Ramay, *Org. Lett.*, 2004, **6**, 1919; (d) M. J. Langton, J. D. Matichak, A. L. Thompson, H. L. Anderson, *Chem. Sci.*, 2011, **2**, 1897.
- (a) H. Bouas-Laurent, A. Castellán, J.-P. Desvergne and R. Lapouyade, *Chem. Soc. Rev.*, 2000, **29**, 43; (b) J.-P. Desvergne and H. Bouas-Laurent, *Isr. J. Chem.*, 1979, **18**, 220; (c) A. Tron, P. J. Thornton, C. Lincheneau, J.-P. Desvergne, N. Spencer, J. H. R. Tucker and N. D. McClenaghan, *J. Org. Chem.*, DOI: 10.1021/jo502452t.
- (a) Y. Molard, D. M. Bassani, J.-P. Desvergne, P. N. Horton, M. B. Hursthouse and J. H. R. Tucker, *Angew. Chem., Int. Ed.*, 2005, **117**, 1096; (b) K. Hirose, K. Ishibashi, Y. Shiba, Y. Doi and Y. Tobe, *Chem. Eur. J.*, 2008, **14**, 5803; (c) D. Marquis, J.-P. Desvergne, H. Bouas-Laurent, *J. Org. Chem.*, 1995, **60**, 7984; (d) G. McSkimming, J. H. R. Tucker, H. Bouas-Laurent, J.-P. Desvergne, S. J. Coles, M. B. Hursthouse and M. E. Light, *Chem. Eur. J.*, 2002, **8**, 3331; (e) J. H. R. Tucker, H. Bouas-Laurent, P. Marsau, S. W. Riley and J.-P. Desvergne, *Chem. Commun.* 1997, 1165.
- (a) M. Okada and A. Harada, *Macromolecules* 2003, **36**, 9701; (b) P. Wei, X. Yan and F. Huang, *Chem. Commun.*, 2014, **50**, 14105.
- R. Ballardini, V. Balzani, A. Credi, M. T. Gandolfi, D. Marquis, L. Perez-Garcia and J. F. Stoddart, *Eur. J. Org. Chem.*, 1998, 81.
- All new compounds were characterized by NMR spectroscopy and mass spectrometry (Fig. S7, S9, S10 and S11). Proton assignments were made by 2D NMR experiments (COSY, HSQC and HMBC).
- V. Aucagne, K. D. Hänni, D. A. Leigh, P. J. Lusby and D. B. Walker, *J. Am. Chem. Soc.*, 2006, **128**, 2186.
- K. S. Chichak, A. J. Peters, S. J. Cantrill and J. F. Stoddart, *J. Org. Chem.*, 2005, **70**, 7956.
- (a) R. Huisgen, *Pure & Appl. Chem.*, 1989, **61**, 613; (b) V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2002, **41**, 2596; (c) K. D. Hänni and D. A. Leigh, *Chem. Soc. Rev.*, 2010, **39**, 1240.
- Formation of $1\text{-PF}_6\text{-DB24C8}$ was followed by ^1H NMR (CDCl_3 , 300 MHz, 295 K). A binding constant (K_{ass}) of 130 M^{-1} in CH_3CN was determined for a related recognition motif. P. R. Ashton, M. C. T. Fyfe, S. K. Hickingbottom, J. F. Stoddart, A. J. P. White and D. J. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2117.
- (a) H. Wang, F. Liu, R. C. Helgeson and K. N. Houk, *Angew. Chem. Int. Ed.*, 2012, **51**, 1; (b) S. Grimme, S. D. Peyerimhoff, H. Bouas-Laurent, J.-P. Desvergne, H.-D. Becker, S. M. Sarge and H. Dreeskamp, *PhysChemChemPhys*, 1999, **1**, 2457.
- M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi, *Handbook of Photochemistry*, 3rd ed., CRC Press, New York, 2006, pp. 601 – 604.
- $\phi_{\text{F}} = 0.29$ for 9-methoxyanthracene in MCH in the absence of photodimerization. J.-P. Desvergne, N. Bitit, A. Castellán, M. Webb and H. Bouas-Laurent, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1885.

TABLE OF CONTENTS



The reversible photocyclomerization of terminal anthracene units enables the interconversion between [2]rotaxane and [2]catenane molecular topologies.