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Photoswitchable interlocked thiodiglycolamide as a cocatalyst of a chalcogeno-Baylis–Hillman reaction†

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En route to a photoswitchable interlocked catalyst we have proved the ability of thiodiglycolamide to act as a template in the formation of hydrogen-bonded [2]rotaxanes. X-ray diffraction studies reveal the shielding of the sulfide atom by the macrocycle. A series of molecular shuttles are described as having an isomerizable fumaramide and thiodiglycolamide binding sites for controlling the relative ring position at will. By employing these systems as photoregulated catalysts, the TiCl_4 -mediated chalcogeno-Morita–Baylis–Hillman reaction is tested. In the presence of the maleamide shuttle, in which the sulfide function is encapsulated by the macrocycle, a complete loss in control of the geometry of the produced aldol is observed. The *E*-aldol adduct is predominantly obtained when the photoisomerized fumaramide shuttle, in which the sulfide function is exposed, is used.

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Introduction

Taking as model the majority of the enzymatically driven processes that are ubiquitous in nature,¹ chemists are devoting much effort to the designing of catalysts with switchable activity.² These compounds are able to control programmed multistep procedures or selectively afford synthetic targets. Among the external triggering stimuli, both light³ and chemical reactions,⁴ including coordination events,^{4c–e} redox reactions,^{4f} and changes in pH,^{4a,b} solvent^{4g} or temperature,^{4h} have been employed to control the catalytic activity and the regio- and stereoselectivity of the reactions in which they are involved.²

Although the first examples of the incorporation of catalytic centers in rotaxanes⁵ were reported in the last decade,⁶ the use of interlocked molecular architectures⁷ as switchable catalysts is a growing topic nowadays.^{2,8} In this area, pH-driven molecular shuttles have been used for controlling the catalytic activity or the result of a particular reaction. Some recent examples of these systems include the control of the rate⁹ and the stereochemistry¹⁰ of Michael addition reactions or participation in selected chemical transformations through different activation modes.¹¹ To the best of our knowledge, light-driven threaded

systems¹² programmed to modify their catalytic activity at will remain unexplored. In order to tackle this issue, herein we have designed a photo-responsive molecular shuttle that could communicate the reactivity of a nucleophilic center in one of its states, whereas the same feature remained silenced in the other state.

In this regard we have envisioned a photoswitchable interlocked catalyst by the incorporation of a sulfide functionality¹³ in one of the two binding sites of a hydrogen-bonded molecular shuttle^{5,7,8a,14} that also contains a photoisomerizable fumaramide station (Fig. 1).¹⁵ We expected that in the active mode of this catalyst, in which the sulfide is exposed to the surrounding reaction medium, the system catalyzes an organic transformation in a selective fashion (catalysis ON). This chemical

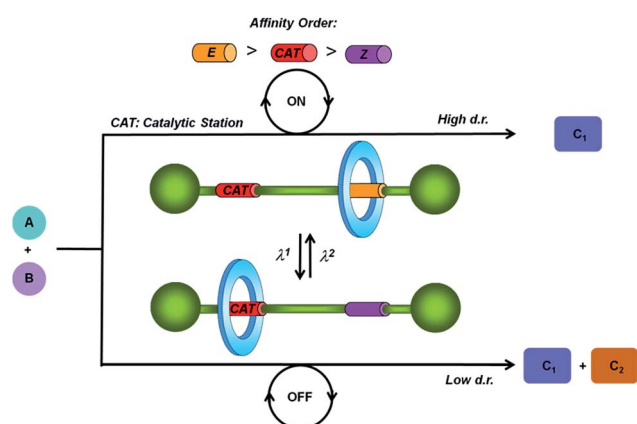


Fig. 1 Representation of a photoswitchable *E/Z* interlocked catalyst.

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behavior would drastically change by the light-promoted *E* to *Z* interconversion of the olefinic station promoting the coverage of the sulfur-based station by the macrocycle, and thus precluding its participation in the considered process (catalysis OFF).

For the catalytic model reaction we selected one of the most appealing organic transformations that is catalyzed by sulfides,¹⁶ the Morita–Baylis–Hillman (MBH) reaction. This atom-economic carbon–carbon bond forming reaction is broadly used for the functionalization of activated alkenes or alkynes by reaction with different electrophiles under the influence of a catalytic system.¹⁷

Results and discussion

Hydrogen-bonding directed assembly of thiodiglycolamide [2]rotaxanes

The formation of amide-based rotaxanes requires the use of a suitable template to maximize the efficiency of the assembly.¹⁸ In the case of tetralactam-based rotaxanes having four benzylic amide functions in the ring, a variety of structural motifs have been employed, including 1,4-dicarboxamides,¹⁹ nitrones,²⁰ squaraines,²¹ organophosphorus species,²² di(acylamino)pyridines²³ and azodicarboxamides.^{6d,24}

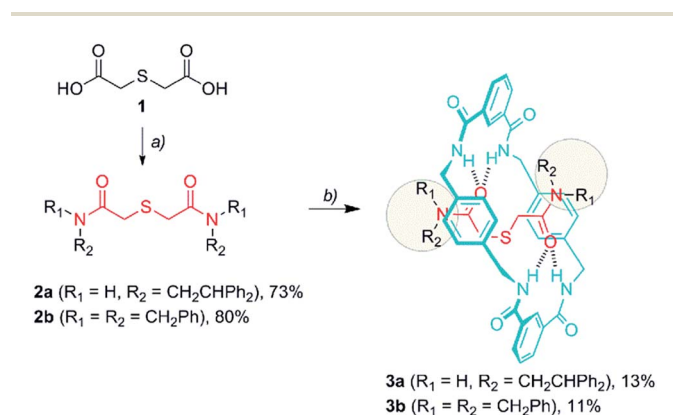
Thiodiglycolamides **2**, that are easily obtained from commercially available thiodiglycolic acid **1** (Scheme 1), were chosen as the sulfur-containing threads. These compounds contain two carbonyl groups as hydrogen bond acceptors, two bulky groups as stoppers and an embedded sulfur atom as the future catalytic active center. Firstly, the ability of these compounds to template the assembly of benzylic amide [2]rotaxanes was assayed. The five-component clipping reaction of **2a** using *p*-xylylenediamine and isophthaloyl chloride in the presence of triethylamine afforded the [2]rotaxane **3a**. The surrogate **3b** was also prepared, which bears two dibenzylamino groups as the stoppers of the interlocked species, enhancing its solubility in chlorinated solvents when compared to **3a**. As we expected, both of the rotaxanes were obtained in low yields (**3a**,

13%; **3b**, **11%**) indicating a moderate affinity of the thiodiglycolamide binding site for the macrocycle.

Molecular structure of the hydrogen-bonded [2]rotaxane **3a** in the solid state

In order to get a detailed view of the chemical environment of the active center once encapsulated by the macrocycle, we grew suitable monocrystals for X-ray diffraction analysis by slowly evaporating a solution of **3a** in acetonitrile. The resulting interlocked molecular structure of **3a** (Fig. 2) shows a bifurcated hydrogen bond (HB) between two of the NH groups of the macrocycle with one of the CO groups of the thiodiglycolamide thread, and a single HB between another NH group of the macrocycle with the second CO group of the thread. The CH₂SCH₂ skeleton between the HB acceptor of the thread adopts a folded conformation that is established by CH⋯π interactions between one of its methylenic hydrogen atoms and one of the *p*-xylylene groups of the tetralactam ring (3.4 Å, 86°) (Fig. S3, see ESI†). In contrast with other sulfur-containing functionalities used as templates in the building of amide based rotaxanes,^{13c} the sulfur atom incorporated in the thiodiglycolamide **2a** seems to be a mere spectator during the rotaxane formation.

An inspection of the structure of the interlocked thiodiglycolamide **3a** in the solid state reveals a reasonable shielding of the sulfur functionality which could reduce or even preclude its participation in a chemical reaction. The next step in our research was directed towards the incorporation of this binding site station into a photoswitchable molecular shuttle.



Scheme 1 Synthesis of thiodiglycolamides **2** and the [2]rotaxanes **3**. Reagents and conditions: (a) (i) (COCl)₂, DMF (cat) and CH₂Cl₂; (ii) 2,2-diphenylethylamine or dibenzylamine, Et₃N, CHCl₃, **2a** (73%) and **2b** (80%), and (b) isophthaloyl dichloride, *p*-xylylenediamine, Et₃N, CHCl₃, **3a** (13%), and **3b** (11%).

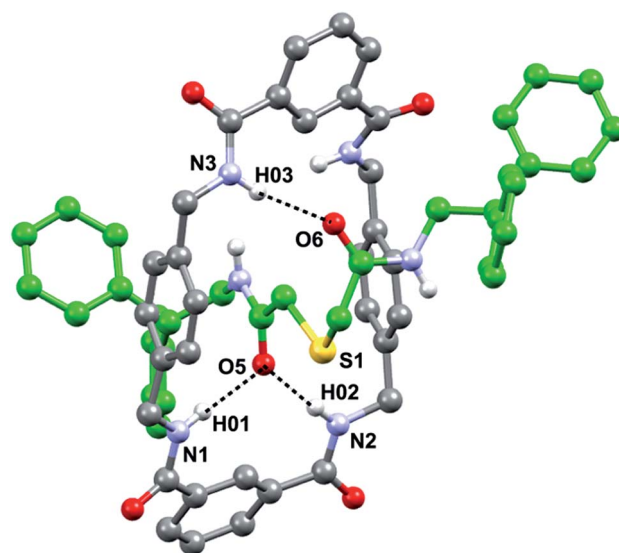


Fig. 2 X-ray structure of the thiodiglycolamide [2]rotaxane **3a** crystallized from CH₃CN. For clarity, the carbon atoms of the macrocycle are shown in grey, the carbon atoms of the thread are shown in green, the oxygen atoms are depicted in red, the nitrogen atoms are depicted in blue, and selected hydrogen atoms are shown in white. Also for clarity, the solvent molecules have been omitted. Intramolecular hydrogen-bond lengths [Å] (and angles [deg]): O5HN1 2.204 (176.8), O5HN2 2.096 (177.5) and O6HN3 2.096 (152.6).



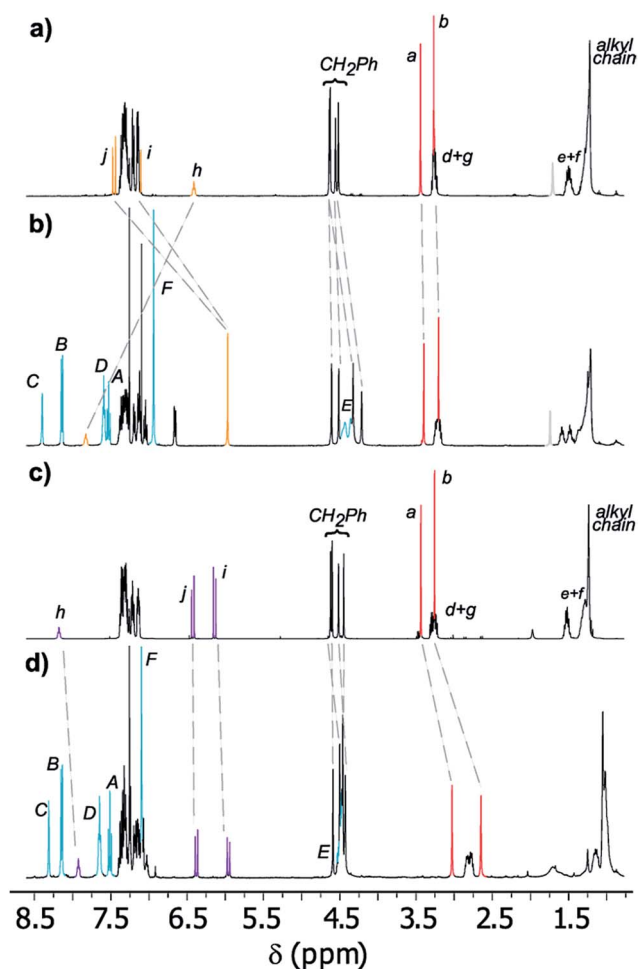


Fig. 3 Partial ^1H NMR spectra (400 MHz, CDCl_3 , 298 K) of (a) thread *E*-7b, (b) [2]rotaxane *E*-8b, (c) thread *Z*-7b, and (d) [2]rotaxane *Z*-8b. The assignments correspond to the lettering shown in Schemes 2 and 3.

If the single-binding site rotaxanes **3** are used as the sulfide sources, the stereochemical control is null and a practically equimolar mixture of *E* and *Z* aldols is obtained (Table 1, entries 3 and 4) as a consequence of the shielding of the sulfide fragment by the macrocycle, which precludes its participation in the reaction. The use of the interlocked catalyst *E*-8a affords aldol **9** in a 56 : 44 ratio in favor of the *E* isomer (Table 1, entry 5). When the most soluble derivative *E*-8b is employed, better control is obtained (80 : 20) as a result of an increase in the interlocked sulfide concentration in the reaction (Table 1, entry 6) (see Fig. S1†). Finally, a 1 : 1 mixture of both isomers of **9** are obtained in the presence of the interlocked catalyst *Z*-8b in which the ring is positioned over the thiodiglycolamide station (Table 1, entry 7). As expected, the diastereomeric ratios achieved in the presence of **3a**, **3b** and *Z*-8b are similar to the one obtained in the absence of the chalcogenide derivative (Table 1, entry 8). Notably, the respective sulfide-based catalyst remains unaltered at the end of these experiments, and it could be recovered for further use.

Although the reaction conversion using the two station [2] rotaxane decreased with respect to those obtained using non-

Table 1 Thiodiglycolamide-catalyzed Baylis–Hillman reaction mediated by TiCl_4 ^a

Entry	Sulfide "S"	% conversion ^b	d.r. (<i>E</i> : <i>Z</i>) ^c
1	2a	94	85 : 15
2	2b	92	91 : 9
3	3a	90	55 : 45
4	3b	85	50 : 50
5	<i>E</i> -8a	70	56 : 44
6	<i>E</i> -8b	71	80 : 20
7	<i>Z</i> -8b	54	50 : 50
8	—	92	50 : 50

^a Reaction conditions: a mixture of *p*-nitrobenzaldehyde (0.10 mmol), 3-butyn-2-one (0.30 mmol) and the corresponding sulfide "S" (0.01 mmol) in dry CH_2Cl_2 under an N_2 atmosphere was stirred at 5 °C. TiCl_4 (0.10 mmol) was added and the mixture was stirred for 3 h at the indicated temperature. ^b The conversions were determined using ^1H NMR analysis. ^c The diastereomeric ratio was determined using ^1H NMR analysis.

interlocked catalysts, the employment of the optimized *trans* co-conformer *E*-8b allowed a maximum 80 : 20 ratio to be achieved in favor of the chloromethylene aldol **9**. The photoisomerized *cis* co-conformer *Z*-8 keeps the sulfide function in a latent state and is kinetically protected by the surrounding ring against other external reagents.^{8d}

This example shows for the first time that the employment of photoswitchable interlocked catalysts can be useful to control the stereochemical course of a reaction. In contrast to pH-driven catalysts, this unprecedented light-responsive interlocked catalyst is enabled to work in neutral media, expanding its potential applicability to a broad variety of transformations in which these molecular shuttles can play an important role in regulating the outcome of the reactions at will.

Conclusions

In summary, we have shown that thiodiglycolamides are able to act as a template in the formation of benzylic amide rotaxanes. The molecular structure of one of these interlocked compounds in the solid state reveals that its sulfide functional group is well covered by the macrocyclic tetralactam and so is isolated from its surroundings. These findings were used to design a switchable interlocked sulfide which includes a fumaramide binding site as a photoisomerizable unit for controlling the relative ring position. Two versions of this prototype varying the number of secondary amides in the thread (and then differing in solubility in halogenated solvents) were straightforwardly synthesized from thiodiglycolic anhydride. The behavior of the sulfide function of both translational co-conformers of these molecular shuttles was assayed in a MBH type reaction promoted by TiCl_4



using *p*-nitrobenzaldehyde and 3-butyn-2-one. With the fumaramide shuttle, in which the sulfide function is exposed, the *E*-aldol adduct is predominantly obtained. Using the photoisomerized shuttle, in which the sulfide function is encapsulated by the macrocycle, a complete loss of diastereoselectivity is observed.

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Notes and references

- (a) E. Kuah, S. Toh, J. Yee, Q. Ma and Z. Gao, *Chem.–Eur. J.*, 2016, **22**, 8404–8430; (b) R. Wolfenden and M. J. Snider, *Acc. Chem. Res.*, 2001, **34**, 938–945; (c) M. Garcia-Viloca, J. Gao, M. Karplus and D. G. Truhlar, *Science*, 2004, **303**, 186–195.
- V. Blanco, D. A. Leigh and V. Marcos, *Chem. Soc. Rev.*, 2015, **44**, 5341–5370.
- (a) R. S. Stoll and S. Hecht, *Angew. Chem., Int. Ed.*, 2010, **49**, 5054–5075; (b) J. Wang and B. L. Feringa, *Science*, 2011, **331**, 1429–1432; (c) D. Wilson and N. R. Branda, *Angew. Chem., Int. Ed.*, 2012, **51**, 5431–5434; (d) A. Nojiri, N. Kumagai and M. Shibasaki, *Chem. Commun.*, 2013, **49**, 4628–4630; (e) L. Osorio-Planes, C. Rodriguez-Esrich and M. A. Pericas, *Org. Lett.*, 2014, **16**, 1704–1707; (f) D. Zhao, T. M. Neubauer and B. L. Feringa, *Nat. Commun.*, 2015, **6**, 6652; (g) Q. Zhang, W.-Z. Wang, J.-J. Yu, D.-H. Qu and H. Tian, *Adv. Mater.*, 2017, **29**, 1604948.
- pH: (a) X. Tian, C. Cassani, Y. Liu, A. Moran, A. Urakawa, P. Galzerano, E. Arceo and P. Melchiorre, *J. Am. Chem. Soc.*, 2011, **133**, 17934–17941; (b) S. A. Moteki, J. Han, S. Arimitsu, M. Akakura, K. Nakayama and K. Maruoka, *Angew. Chem., Int. Ed.*, 2012, **51**, 1187–1190, Coordination; (c) S. De, S. Pramanik and M. Schmittel, *Angew. Chem., Int. Ed.*, 2014, **53**, 14255–14259; (d) C. M. McGuirk, J. Mendez-Arroyo, A. M. Lifschitz and C. A. Mirkin, *J. Am. Chem. Soc.*, 2014, **136**, 16594–16601; (e) J. T. Foy, D. Ray and I. Aprahamian, *Chem. Sci.*, 2015, **6**, 209–213, Redox; (f) P. Neumann, H. Dib, A.-M. Caminade and E. Hey-Hawkins, *Angew. Chem., Int. Ed.*, 2015, **54**, 311–314, Solvent; (g) Y. Sohtome, S. Tanaka, K. Takada, T. Yamaguchi and K. Nagasawa, *Angew. Chem., Int. Ed.*, 2010, **49**, 9254–9257, Temperature; (h) G. Storch and O. Trapp, *Angew. Chem., Int. Ed.*, 2015, **54**, 3580–3586.
- M. Xue, Y. Yang, X. Chi, X. Yan and F. Huang, *Chem. Rev.*, 2015, **115**, 7398–7501.
- For some examples see: (a) P. Thordarson, E. J. A. Bijsterveld, A. E. Rowan and R. J. M. Nolte, *Nature*, 2003, **424**, 915–918; (b) Y. Tachibana, N. Kihara and T. Takata, *J. Am. Chem. Soc.*, 2004, **126**, 3438–3439; (c) G. Hattori, T. Hori, Y. Miyake and Y. Nishibayashi, *J. Am. Chem. Soc.*, 2007, **129**, 12930–12931; (d) J. Berna, M. Alajarin and R.-A. Orenes, *J. Am. Chem. Soc.*, 2010, **132**, 10741–10747; (e) B. Lewandowski, G. De Bo, J. W. Ward, M. Papmeyer, S. Kuschel, M. J. Aldegunde, P. M. E. Gramlich, D. Heckmann, S. M. Goldup, D. M. D'Souza, A. E. Fernandes and D. A. Leigh, *Science*, 2013, **339**, 189–193; (f) M. Galli, J. E. M. Lewis and S. M. Goldup, *Angew. Chem., Int. Ed.*, 2015, **54**, 13545–13549; (g) S. Hoekman, M. O. Kitching, D. A. Leigh, M. Papmeyer and D. Roke, *J. Am. Chem. Soc.*, 2015, **137**, 7656–7659; (h) Y. Cakmak, S. Erbas-Cakmak and D. A. Leigh, *J. Am. Chem. Soc.*, 2016, **138**, 1749–1751.
- (a) A. Credi, S. Silvi and M. Venturi, *Molecular Machines and Motors: Recent Advances and Perspectives*, Springer, Switzerland, 2014; (b) C. J. Bruns and J. F. Stoddart, *The Nature of the Mechanical Bond: From Molecules to Machines*, Wiley, New York, 2016.
- (a) D. A. Leigh, V. Marcos and M. R. Wilson, *ACS Catal.*, 2014, **4**, 4490–4497; (b) S. Erbas-Cakmak, D. A. Leigh, C. T. McTernan and A. L. Nussbaumer, *Chem. Rev.*, 2015, **115**, 10081–10206; (c) T. Pan and J. Liu, *ChemPhysChem*, 2016, **17**, 1752–1758; (d) J. E. M. Lewis, M. Galli and S. M. Goldup, *Chem. Commun.*, 2017, **53**, 298–312.
- V. Blanco, A. Carlone, K. D. Hänni, D. A. Leigh and B. Lewandowski, *Angew. Chem., Int. Ed.*, 2012, **51**, 5166–5169.
- V. Blanco, D. A. Leigh, V. Marcos, J. A. Morales-Serna and A. L. Nussbaumer, *J. Am. Chem. Soc.*, 2014, **136**, 4905–4908.
- (a) V. Blanco, D. A. Leigh, U. Lewandowska, B. Lewandowski and V. Marcos, *J. Am. Chem. Soc.*, 2014, **136**, 15775–15780; (b) J. Beswick, V. Blanco, G. De Bo, D. A. Leigh, U. Lewandowska, B. Lewandowski and K. Mishiro, *Chem. Sci.*, 2015, **6**, 140–143.
- (a) D.-H. Qu, Q.-C. Wang and H. Tian, *Angew. Chem., Int. Ed.*, 2005, **44**, 5296–5299; (b) V. Balzani, A. Credi and M. Venturi, *Chem. Soc. Rev.*, 2009, **38**, 1542–1550; (c) D.-H. Qu, Q.-C. Wang, Q.-W. Zhang, X. Ma and H. Tian, *Chem. Rev.*, 2015, **115**, 7543–7588; (d) G. Ragazzon, M. Baroncini, S. Silvi, M. Venturi and A. Credi, *Nat. Nanotechnol.*, 2015, **10**, 70–75; (e) C. Cheng, P. R. McGonigal, J. F. Stoddart and R. D. Astumian, *ACS Nano*, 2015, **9**, 8672–8688; (f) A. Martinez-Cuevas, S. Valero-Moya, M. Alajarin and J. Berna, *Chem. Commun.*, 2015, **51**, 14501–14504; (g) K. Iwasa, Y. Takashima and A. Harada, *Nat. Chem.*, 2016, **8**, 625–632; (h) F. B. Schwarz, T. Heinrich, A. Lippitz, W. E. S. Unger and C. A. Schalley, *Chem. Commun.*, 2016, **52**, 14458–14461.
- (a) S. Saito, E. Takahashi and K. Nakazono, *Org. Lett.*, 2006, **8**, 5133–5136; (b) H. Zheng, Y. Li, C. Zhou, Y. Li, W. Yang, W. Zhou, Z. Zuo and H. Liu, *Chem.–Eur. J.*, 2011, **17**, 2160–2167; (c) A. Altieri, V. Aucagne, R. Carrillo, G. J. Clarkson, D. M. D'Souza, J. A. Dunnett, D. A. Leigh and K. M. Mullen, *Chem. Sci.*, 2011, **2**, 1922–1928; (d) E. M. Peck, C. G. Collins and B. D. Smith, *Org. Lett.*, 2013, **15**, 2762–2765.
- (a) L. Liu, Y. Liu, P. Liu, J. Wu, Y. Guan, X. Hu, C. Lin, Y. Yang, X. Sun, J. Ma and L. Wang, *Chem. Sci.*, 2013, **4**, 1701–1706; (b) C. G. Collins, E. M. Peck, P. J. Kramer and



- B. D. Smith, *Chem. Sci.*, 2013, **4**, 2557–2563; (c) M. J. Langton and P. D. Beer, *Acc. Chem. Res.*, 2014, **47**, 1935–1949; (d) K. Zhu, C. A. O’Keefe, V. N. Vukotic, R. W. Schurko and S. J. Loeb, *Nat. Chem.*, 2015, **7**, 514–519; (e) P. Wei, X. Yan, T. R. Cook, X. Ji, P. J. Stang and F. Huang, *ACS Macro Lett.*, 2016, **5**, 671–675; (f) D. C. Jagesar, P. G. Wiering, E. R. Kay, D. A. Leigh and A. M. Brouwer, *ChemPhysChem*, 2016, **17**, 1902–1912; (g) T. Legigan, B. Riss-Yaw, C. Clavel and F. Coutrot, *Chem.–Eur. J.*, 2016, **22**, 8835–8847; (h) X. Ma, J. Zhang, J. Cao, X. Yao, T. Cao, Y. Gong, C. Zhao and H. Tian, *Chem. Sci.*, 2016, **7**, 4582–4588; (i) G. Ragazzon, A. Credi and B. Colasson, *Chem.–Eur. J.*, 2017, **23**, 2149–2156; (j) V. N. Vukotic, K. Zhu, G. Baggi and S. J. Loeb, *Angew. Chem., Int. Ed.*, 2017, DOI: 10.1002/anie.201612549.
- 15 (a) A. Altieri, G. Bottari, F. Dehez, D. A. Leigh, J. K. Y. Wong and F. Zerbetto, *Angew. Chem., Int. Ed.*, 2003, **42**, 2296–2300; (b) G. Bottari, D. A. Leigh and E. M. Perez, *J. Am. Chem. Soc.*, 2003, **125**, 13360–13361; (c) E. M. Perez, D. T. F. Dryden, D. A. Leigh, G. Teobaldi and F. Zerbetto, *J. Am. Chem. Soc.*, 2004, **126**, 12210–12211.
- 16 E. M. McGarrigle, E. L. Myers, O. Illa, M. A. Shaw, S. L. Riches and V. K. Aggarwal, *Chem. Rev.*, 2007, **107**, 5841–5883.
- 17 (a) E. Ciganek, in *Organic Reactions*, ed. L. A. Paquette, Wiley, New York, 1997, vol. 51, pp. 201–350; (b) V. Declerck, J. Martinez and F. Lamaty, *Chem. Rev.*, 2009, **109**, 1–48; (c) D. Basavaiah, B. S. Reddy and S. S. Badsara, *Chem. Rev.*, 2010, **110**, 5447–5674; (d) D. Basavaiah and G. Veeraraghavaiah, *Chem. Soc. Rev.*, 2012, **41**, 68–78; (e) T. Y. Liu, M. Xie and Y. C. Chen, *Chem. Soc. Rev.*, 2012, **41**, 4101–4112.
- 18 (a) C. A. Schalley, T. Weilandt, J. Brüggemann and F. Vögtle, *Top. Curr. Chem.*, 2004, **248**, 141–200; (b) C. A. Schalley, W. Reckien, S. Peyerimhoff, B. Baytekin and F. Vögtle, *Chem.–Eur. J.*, 2004, **10**, 4777–4789; (c) E. R. Kay, D. A. Leigh and F. Zerbetto, *Angew. Chem., Int. Ed.*, 2007, **46**, 72–191; (d) G. T. Spence and P. D. Beer, *Acc. Chem. Res.*, 2013, **46**, 571–586; (e) A. Tron, P. J. Thornton, B. Kauffmann, J. H. R. Tucker and N. D. McClenaghan, *Supramol. Chem.*, 2016, **28**, 733–741; (f) A. Vidonne, T. Kosikova and D. Philp, *Chem. Sci.*, 2016, **7**, 2592–2603.
- 19 (a) J. Berna, G. Bottari, D. A. Leigh and E. M. Perez, *Pure Appl. Chem.*, 2007, **79**, 39–54; (b) J. Berna, M. Alajarin, J. S. Martinez-Espin, L. Buriol, M. A. P. Martins and R.-A. Orenes, *Chem. Commun.*, 2012, **48**, 5677–5679; (c) M. R. Panman, B. H. Bakker, D. den Uyl, E. R. Kay, D. A. Leigh, W. J. Buma, A. M. Brouwer, J. A. J. Geenevasen and S. Woutersen, *Nat. Chem.*, 2013, **5**, 929–934; (d) A. Martinez-Cuezva, C. Lopez-Leonardo, D. Bautista, M. Alajarin and J. Berna, *J. Am. Chem. Soc.*, 2016, **138**, 8726–8729.
- 20 (a) V. Bermudez, N. Capron, T. Gase, F. G. Gatti, F. Kajzar, D. A. Leigh, F. Zerbetto and S. Zhang, *Nature*, 2000, **406**, 608–611; (b) D. M. D’Souza, D. A. Leigh, L. Mottier, K. M. Mullen, F. Paolucci, S. J. Teat and S. Zhang, *J. Am. Chem. Soc.*, 2010, **132**, 9465–9470.
- 21 (a) E. Arunkumar, C. C. Forbes, B. C. Noll and B. D. Smith, *J. Am. Chem. Soc.*, 2005, **127**, 3288–3289; (b) J. J. Gassensmith, J. M. Baumes and B. D. Smith, *Chem. Commun.*, 2009, 6329–6338; (c) C. G. Collins, J. M. Lee, A. G. Oliver, O. Wiest and B. D. Smith, *J. Org. Chem.*, 2014, **79**, 1120–1130.
- 22 R. Ahmed, A. Altieri, D. M. D’Souza, D. A. Leigh, K. M. Mullen, M. Papmeyer, A. M. Z. Slawin, J. K. Y. Wong and J. D. Woollins, *J. Am. Chem. Soc.*, 2011, **133**, 12304–12310.
- 23 (a) A. Martinez-Cuezva, J. Berna, R.-A. Orenes, A. Pastor and M. Alajarin, *Angew. Chem., Int. Ed.*, 2014, **53**, 6762–6767; (b) A. Martinez-Cuezva, A. Pastor, G. Cioncoloni, R.-A. Orenes, M. Alajarin, M. D. Symes and J. Berna, *Chem. Sci.*, 2015, **6**, 3087–3094; (c) A. Martinez-Cuezva, F. Carro-Guillen, A. Pastor, M. Marin-Luna, R.-A. Orenes, M. Alajarin and J. Berna, *ChemPhysChem*, 2016, **17**, 1920–1926; (d) A. Tron, I. Pianet, A. Martinez-Cuezva, J. H. R. Tucker, L. Pisciotanni, M. Alajarin, J. Berna and N. D. McClenaghan, *Org. Lett.*, 2017, **19**, 154–157.
- 24 J. Berna, M. Alajarin, C. Marin-Rodriguez and C. Franco-Pujante, *Chem. Sci.*, 2012, **3**, 2314–2320.
- 25 Y. Nagao, S. Miyamoto, K. Hayashi, A. Mihira and S. Sano, *Tetrahedron Lett.*, 2002, **43**, 1519–1522.
- 26 A. Carlone, S. M. Goldup, N. Lebrasseur, D. A. Leigh and A. Wilson, *J. Am. Chem. Soc.*, 2012, **134**, 8321–8323.
- 27 The corresponding *Z* isomers of threads 7 were obtained for an analytical purpose and their syntheses are described in the ESI.†
- 28 (a) T. Kataoka, H. Kinoshita, S. Kinoshita, T. Iwamura and S.-I. Watanabe, *Angew. Chem., Int. Ed.*, 2000, **39**, 2358–2360; (b) S. Kinoshita, H. Kinoshita, T. Iwamura, S.-I. Watanabe and T. Kataoka, *Chem.–Eur. J.*, 2003, **9**, 1496–1502; (c) H. Kinoshita, S. Kinoshita, Y. Munechika, T. Iwamura, S.-I. Watanabe and T. Kataoka, *Eur. J. Org. Chem.*, 2003, 4852–4861.

