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A New Class of Hydroxy-Substituted Squaraine Rotaxane

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A templated macrocyclization reaction was used to permanently encapsulate a highly fluorescent hydroxy-substituted squaraine dye inside a tetralactam macrocycle. The free squaraine dye is quite rigid due to internal hydrogen bonding and its photophysical properties hardly change upon encapsulation. A combination of X-ray and NMR data show that the surrounding tetralactam macrocycle adopts an unusually rigid chair conformation and does not undergo rapid pirouetting. Because of its large size and conformational rigidity, the macrocycle creates anisotropic NMR shielding zones that extend over the *N*,*N*-dibutylamino groups at each end of the squaraine thread. This shielding anisotropy allows hindered aryl-N rotation to be observed by NMR spectroscopy and provides direct experimental evidence that quinoid-like resonance structures are major contributors to the bis(*N*,*N*-dialkylaminophenyl)squaraine resonance hybrid.

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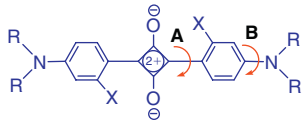
Introduction

An emerging topic in supramolecular chemistry is the encapsulation of fluorescent dyes inside container molecules as a method of improving dye performance.[1] We have contributed to this field by inventing squaraine rotaxanes, which are interlocked molecules comprised of a highly fluorescent squaraine dye permanently threaded through a tetralactam macrocycle.[2] The surrounding macrocycle greatly enhances the chemical stability of the squaraine dye and inhibits the formation of non-fluorescent self-aggregates. Because of these improvements, squaraine rotaxanes have promise as a new family of bright and highly stable red and near-infrared fluorescent dyes for various bio-imaging applications.[3] Furthermore, squaraine rotaxanes exhibit the inherent machine-like, dynamic properties of interlocked molecules, and they have long-term potential as functional devices such as shuttles, sensors, ratchets, and switches.[4] In order to improve our molecular designs and enhance functional performance, we are conducting a systematic study of the structural factors that control rotaxane co-conformational dynamics. A necessary prerequisite for these studies is the technical capability to synthesize squaraine rotaxanes with modified structures. To date, most of our work has focussed on bis(*N*,*N*-dialkylaminophenyl)squaraines (structure **1** in Fig. 1) and we have prepared various squaraine rotaxanes with different tetralactam macrocycles.[5] The key synthetic step is a templated macrocyclization reaction, and a typical example is the production of squaraine rotaxane **4** by simultaneous addition of pyridine-2,6-dicarbonyl dichloride and 1,4-xylylenediamine to a solution of **3** (Scheme 1). The interlocked rotaxane assembly is driven by hydrogen bonding of the squaraine oxygens with the NH residues in the penultimate linear triamide intermediate that undergoes the macrocyclization (Scheme 2).[6]

The initial goal of this present study was to determine whether hydroxy-substituted squaraines with the generic structure **2** (Fig. 1) can be converted into squaraine rotaxanes. The OH groups in **2** are known to form internal hydrogen bonds with the adjacent oxygen atoms on the central C_4O_2 squaraine core,[7] a process that inhibits rotation around the C-C bond labelled as **A** in Fig. 1. An unknown at the beginning of this work was how much the internal hydrogen bonding would inhibit the templated macrocyclization reaction. We find that the squaraine dye **5** can be converted into squaraine rotaxane **6** in low yield, but in sufficient amounts to allow structural and photophysical characterization. We report X-ray diffraction and NMR spectroscopy data showing that the structure of squaraine rotaxane **6** is endowed with unusual rigidity. In contrast to the original system **4**, the surrounding macrocycle does not undergo rapid conformational exchange and it does not pirouette around the encapsulated squaraine thread. Indeed, the only motion in **6** (Scheme 2) that can be observed by NMR is hindered rotation of the aryl-N single bonds at both the ends of the squaraine thread component (labelled as **B** in Fig. 1). The barrier to this bond rotation is a new experimental quantity that reflects the polyene character of the squaraine chromophore.



1 X = H
2 X = OH

Fig. 1. Generalized structures of bis(*N*,*N*-dialkylaminophenyl)squaraine **1** and bis(*N*,*N*-dialkylaminohydroxyphenyl)squaraine **2**, showing internal C-C bond rotation as (**A**), and aryl-N bond rotation as (**B**).

Results and Discussion

Synthesis and Solid State Structure

The known squaraine dye **5** was prepared in 80% yield by condensing 3-(*N*,*N*-dibutylamino)phenol with squaric acid.[7] In solution, the compound is a mixture of two slowly exchanging conformations with the hydroxyl substituents in *cis* or *trans*

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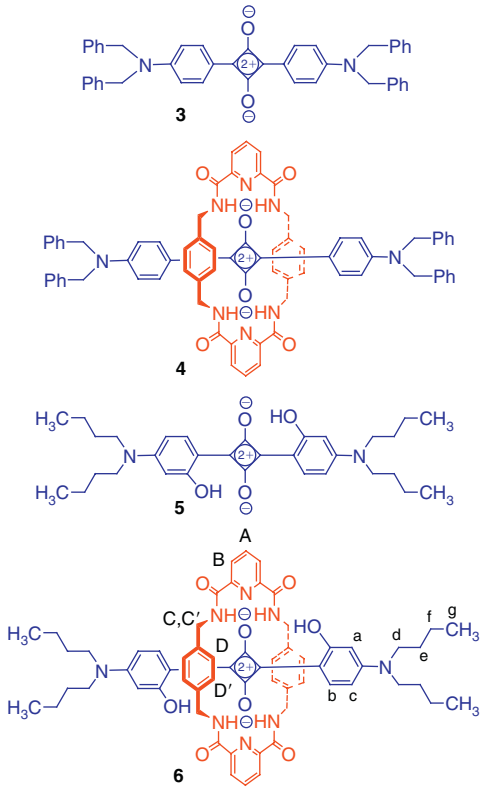
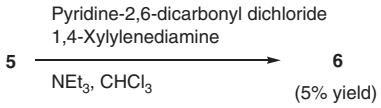


Scheme 1.



Scheme 2. Synthesis of squaraine rotaxane **6**.

orientations. As described in Scheme 2, a templated macrocyclization reaction gave the squaraine rotaxane **6** in 5% isolated yield. This is substantially lower than the 25–30% yields seen with the original squaraine rotaxanes, such as **4**, and the difference is attributed to a weakened template effect due to the internal hydrogen bonding within squaraine **5**.

A single crystal of **6** was obtained by diffusing hexane vapour into a solution of **6** in ethyl acetate/chloroform (1:3). Analysis by X-ray diffraction provided the solid-state structure that is shown in Fig. 2. The molecule exhibits C_{2h} symmetry with the squaraine's two hydroxyl groups in a *trans* orientation and the surrounding tetralactam in a macrocyclic chair conformation. The two squaraine oxygens are each engaged in three trifurcate hydrogen bonds, one with the nearby OH (OH···O 1.95 Å) and two with the NH residues of the surrounding macrocycle (NH···O 1.92, 2.09 Å). The macrocycle NH residues also form intramolecular hydrogen bonds with the adjacent pyridyl nitrogen atoms.[8] In addition, each pyridyl nitrogen is in close contact with the neighbouring squaraine aryl hydrogen, labelled as *b* on the chemical structure of **6** (N···H_b 2.40 Å). The distance between the centres of the two parallel phenylene units in the surrounding macrocycle in **6** is 6.65 Å, which matches the distance in other squaraine rotaxanes having macrocycles with two pyridine-2,6-dicarboxamide bridges (e.g. **4**).[5]

Fig. 2. Two views of the X-ray crystal structure of hydroxy-substituted squaraine rotaxane **6**.

Table 1. Photophysical properties

Solvent	Compound	λ_{abs} [nm]	λ_{em} [nm][A]	Φ_f[B]
THF	**3**[C]	631	647	0.70
THF	**4**[C]	640	658	0.70
$CHCl_3$	**5**	648	666	0.68
$CHCl_3$	**6**	651	672	0.67

[A] Excitation at 580 nm.
[B] Fluorescence quantum yields (error limit ± 5%) were determined using 4,4-[bis(*N*,*N*-dimethylamino)phenyl] squaraine dye as the standard (Φ_f = 0.70 in $CHCl_3$).
[C] Data taken from ref. [10].

Solution-State Studies

The photophysical properties of compounds **3**–**6** are listed in Table 1. The conversion of squaraine **5** into rotaxane **6** produces a comparatively smaller red shift in absorption and emission maxima than the conversion of regular squaraine **3** into rotaxane **4**. Since the red shift effect is primarily due to decreased deformation of the encapsulated squaraine chromophore,[9] it appears that the encapsulation of **5** does not greatly change its structural rigidity, which is inherently high due to the intramolecular hydrogen bonding.

Previous NMR studies of the original squaraine rotaxanes, such as **4**, have shown that the surrounding macrocycle undergoes rapid flipping between chair and boat conformations.[10] In contrast, the solution-state ^{1}H NMR spectrum of new squaraine rotaxane **6** indicates that its solid-state structure is maintained in solution and that there is a high degree of structural rigidity. This conclusion is based on the following spectral evidence. As shown in Fig. 3a, the macrocycle methylene protons H_C and $H_{C'}$ are diastereotopic with large differences in chemical shift. The two peaks exhibit strong geminal coupling (14.4 Hz) and unequal vicinal couplings with the adjacent NH (8.9 and 1.2 Hz at +50°C). These coupling constants are consistent with the different HC-NH dihedral angles seen in the X-ray structure. The diastereoptopic signals and splitting patterns are maintained over the temperature range of +50°C to −50°C, indicating that the macrocycle does not flip to other conformations, such as the alternate chair or a boat, that exchange psuedoaxial and psuedoequatorial CH positions. Shown in Fig. 3b are the inequivalent aryl signals, H_D and $H_{D'}$, for the phenylene units in the macrocycle, and this pair of doublets remains essentially unchanged over the +50°C to −50°C temperature range. The inequivalence of H_D and $H_{D'}$ unambiguously demonstrates that (a) the phenylene units in the macrocycle do not spin rapidly about the connected C-C single bonds, and (b) the macrocycle does not undergo rapid pirouetting about the encapsulated squaraine. This appears to be the first example of complete macrocycle

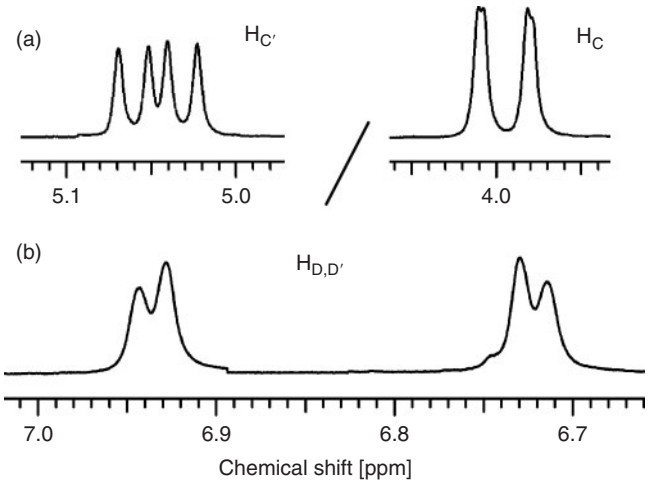


Fig. 3. Partial ^{1}H NMR spectra (500 MHz, +50°C) of the macrocycle component in **6** showing: (a) diastereotopic methylene protons $H_{C'}$ with $J_1 = 8.9$ Hz, $J_2 = 14.4$ Hz and H_C with $J_1 = 1.2$ Hz, $J_2 = 14.4$ Hz; (b) phenylene protons H_D and $H_{D'}$ each with $J = 7.8$ Hz.

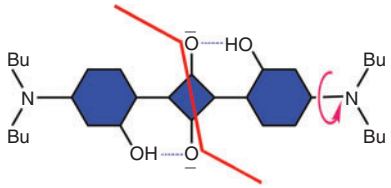


Fig. 4. Schematic side view of rotaxane **6** showing internal hydrogen bonding, aryl-N bond rotation, and extended NMR shielding by rigid chair-conformation macrocycle.

immobility in a Leigh-type rotaxane.[6] The reason for the structural rigidity can be understood by inspecting the X-ray structure in Fig. 2 and the schematic picture in Fig. 4. Internal hydrogen bonding with the adjacent OH sterically blocks one side of each squaraine oxygen and thus the macrocycle NH residues prefer the vacant lone pair on the other side. Conformational exchanges, such as macrocycle chair-boat or chair-chair flips, and macrocycle pirouetting motions such as 180° circumrotation, are all disfavoured because they require the NH residues to disengage from the vacant lone pair side of the squaraine oxygen and associate with the other side that is sterically blocked.

As shown in Fig. 5, the only ^{1}H NMR peaks that exhibit dynamic behaviour are the signals for the two equivalent *N*,*N*-dibutylamino groups. At low temperature, the four *N*-butyl proton signals each split into an inequivalent pair, a phenomena that is only consistent with hindered rotation of the corresponding aryl-N single bond (labelled as **B** in Fig. 1). Usually, it is not possible to detect hindered rotation in *N*,*N*-dialkylaniline compounds that lack *ortho* substituents because there is not enough shielding difference to differentiate the two *N*-alkyl groups.[11] This is the case with free squaraine dye **5** where the hindered aryl-N rotation is unobservable by NMR. However, the structure of rotaxane **6** is remarkable because the surrounding macrocycle acts as a non-covalent appendage that provides long-range shielding of NMR chemical shifts. As illustrated in Fig. 4, the macrocycle (shown in red) is fixed rigidly in a chair conformation and creates anisotropic shielding zones that extend over the ends of the encapsulated squaraine thread. Because of this shielding anisotropy, the hindered aryl-N rotation in **6** is an NMR observable phenomenon. Listed in Table 2 are the

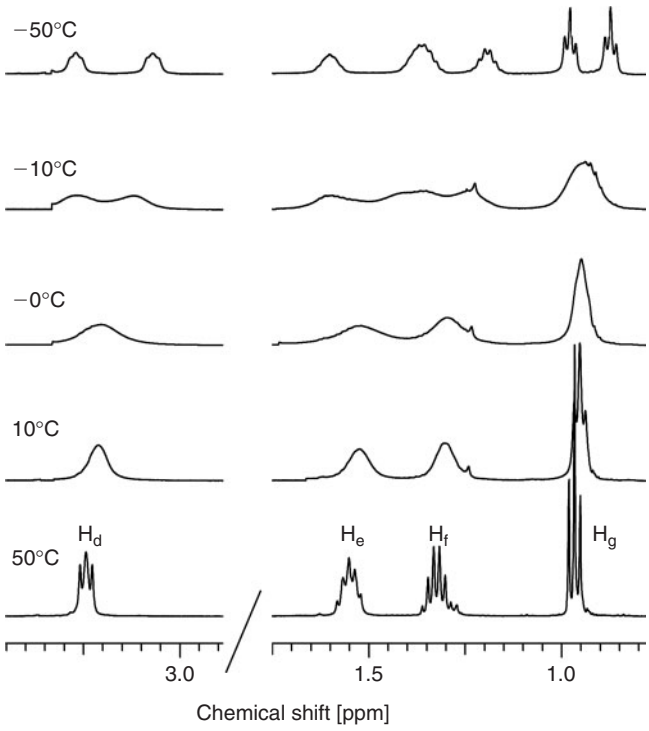


Fig. 5. Partial variable temperature ^{1}H NMR (500 MHz) spectra of the four *N*-butyl signals for rotaxane **6** in $CDCl_3$.

Table 2. NMR data for hindered aryl-N bond rotation in 6

Proton	$\Delta\nu$ [Hz][A]	T_c [K][B]	k [s^{-1}][C]	$\Delta G^{\neq}$ [kJ mol^{-1}][D]
H_d	100	274	222	54.6
H_g	55	264	122	53.8

[A]Frequency difference of limiting chemical shifts at −50°C.
[B]Coalescence temperature, error ± 1 K.
[C]Exchange rate constant at coalescence.
[D]Calculated free energy of activation.

coalescence temperatures and limiting chemical shifts for the exchanging *N*-butyl protons H_d and H_g. This dynamic NMR data was treated as a classic two-site exchange phenomenon,[12] and the free energy of activation for the aryl-N rotational was calculated to be 54.2 ± 0.4 kJ mol^{-1}. This value is close to the rotational barriers for extended polymethine dyes.[13]

To the best of our knowledge this is the first experimental observation of hindered aryl-N bond rotation in a bis(aminophenyl)squaraine. These fascinating compounds have been studied experimentally and theoretically for 40 years.[14] One structural question that has generated considerable attention is whether the best resonance representations for the bis(aminophenyl)squaraine chromophore are the degenerate quinoid-type structures (**I**) and (**II**) in Fig. 6 or the structure (**III**) with an aromatic cyclobutenium dication core. Our observation here of a large barrier to aryl-N bond rotation is new experimental evidence that structures (**I**) and (**II**) are major contributors, a view that agrees with the modern literature.[15]

Conclusions

A low-yielding templated macrocyclization reaction was used to encapsulate the hydroxy-substituted squaraine dye **5** inside a

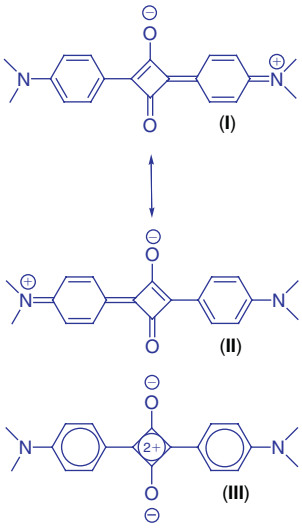


Fig. 6. Resonance structures for bis(aminophenyl)squaraines

Leigh-type tetralactam macrocycle and produce squaraine rotaxane **6**. A combination of X-ray and NMR studies show that the surrounding macrocycle adopts a rigid chair conformation and does not undergo rapid pirouetting around the encapsulated squaraine. The free squaraine dye **5** is quite rigid due to internal hydrogen bonding and its photophysical properties hardly change upon encapsulation as rotaxane **6**. Because of its large size and conformational rigidity, the surrounding macrocycle provides anisotropic NMR shielding zones that extend over the *N*,*N*-dibutylamino groups at each end of the squaraine thread. This shielding anisotropy allows hindered aryl-N rotation to be observed for the first time with a bis(aminophenyl)squaraine dye, and provides direct experimental evidence that quinoid-like resonance structures are major contributors to the resonance hybrid. Compound **6** represents the first example of a new class of squaraine rotaxane, and future studies will evaluate its performance as a bio-imaging probe. It also has potential as a new building block for incorporation into bistable squaraine rotaxane shuttles and related molecular machines.[16] From a broader perspective, this work shows how molecular encapsulation can be used as a novel non-covalent NMR shielding strategy to investigate previously inaccessible questions concerning molecular structure.

Experimental

Synthesis of rotaxane **6**: Clear solutions of the pyridine-2,6-dicarbonyl dichloride (392 mg, 1.92 mmol) and 1,4-xylylenediamine (261 mg, 1.92 mmol) in anhydrous chloroform (30 mL) were added dropwise over 5 h, using a mechanical syringe pump, to a stirred solution containing squaraine **5** (200 mg, 0.38 mmol),[13] and triethylamine (446 mg, 4.42 mmol) in anhydrous chloroform (150 mL). After stirring overnight, the reaction was filtered through a pad of Celite to remove any polymeric material. The solvent was removed by rotary evaporation, and the crude product purified by column chromatography using a column of silica gel with MeOH/$CHCl_3$ (1:19). Yield 5%. δ_H (500 MHz, 20°C, $CDCl_3$) 11.24 (2H, s, OH), 9.88 (4H, d, *J* 8.8, NH), 8.50 (4H, d, *J* 7.8, H_B), 8.12 (2H, t, *J* 7.8, H_A), 7.73 (2H, d, *J* 8.0, H_b), 6.93 (4H, d, *J* 9.0, H_D), 6.73 (4H, d, *J* 9.0, $H_{D'}$), 6.03 (2H, d, *J* 2.0, H_a), 5.12 (2H, dd, *J* 2.0, 8.0, H_c), 5.10 (4H, dd, *J* 14.0, 8.0, $H_{C'}$), 4.02 (4H, d, *J* 14.0, H_C), 3.22 (8H, br t, *J* 6.6, H_d), 1.52 (8H, br s, H_e), 1.30 (8H, br m, H_f), 0.96 (12H, t, *J* 7.4, H_g). δ_H (75 MHz, 20°C, $CDCl_3$) 184.2, 169.7, 163.7, 163.1, 156.2, 149.7, 138.5, 136.4, 133.5, 129.9, 125.1, 108.2, 105.8, 98.2, 51.2, 43.7, 29.5, 20.1, 13.8. *m/z* (FAB-MS) 1054 $[M+H]^+$.

Crystallographic summary of **6**: Single crystals were obtained as blue plates by slow diffusion of hexane into an ethyl acetate/$CHCl_3$ (1:3) solution. Triclinic, $C_{62}H_{70}N_8O_8$, $M_r = 1055.26$, $P-1$, $Z = 2$ in a cell of dimensions $a = 9.6985(12)$ Å, $b = 11.5667(14)$ Å, $c = 25.0947(15)$ Å, $\alpha = 100.086(4)°$, $\beta = 90.925(10)°$, $\gamma = 102.845(11)°$, $V = 2697.8(5)$ Å^3, $\rho_{calcd} = 1.299$ g cm^{-3}, $F(000) = 1124$. The structure was refined on F^2 to $wR_2 = 0.2436$, conventional $R_1 = 0.0855$ [11505 reflections with $I > 2\sigma(I)$], and a goodness of fit = 1.060 for 719 refined parameters. Two chemical moieties were found in the asymmetric unit, one thread molecule $C_{32}H_{44}N_2O_4$, one macrocycle $C_{30}H_{26}N_6O_4$. Atomic coordinates, bond lengths and angles, and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC number 759095). These data can be obtained free-of-charge by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

NMR studies were conducted using a 500 MHz spectrometer and the temperature was measured using a calibrated thermocouple. The ^{1}H NMR coalescence temperatures (T_c) for the exchanging *N*,*N*-dibutylamino signals are listed in Table 2 and the corresponding rate constants were calculated from the relationship $k = \pi\Delta\nu/2^{0.5}$ s^{-1}, where $\Delta\nu$ is the frequency difference at limiting slow exchange. $\Delta G^{\neq}$ was calculated according to the Eyring equation.[12]

Accessory Publication

Variable temperature ^{1}H NMR spectra of **6** are available on the Journal's website.

Acknowledgements

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References

[1] E. Arunkumar, C. C. Forbes, B. D. Smith, *Eur. J. Org. Chem.* **2005**, 4051. doi:10.1002/EJOC.200500372

[2] (a) E. Arunkumar, C. C. Forbes, B. C. Noll, B. D. Smith, *J. Am. Chem. Soc.* **2005**, *127*, 3288. doi:10.1021/JA042404N
(b) E. Arunkumar, N. Fu, B. D. Smith, *Chem. Eur. J.* **2006**, *12*, 4684. doi:10.1002/CHEM.200501541
(c) E. Arunkumar, P. K. Sudeep, P. V. Kamat, B. C. Noll, B. D. Smith, *New J. Chem.* **2007**, *31*, 677. doi:10.1039/B616224J
(d) J. J. Gassensmith, E. Arunkumar, L. Barr, J. M. Baumes, K. M. DiVittorio, J. R. Johnson, B. C. Noll, B. D. Smith, *J. Am. Chem. Soc.* **2007**, *129*, 15054. doi:10.1021/JA075567V
(e) N. Fu, J. J. Gassensmith, B. D. Smith, *Supramol. Chem.* **2009**, *21*, 118. doi:10.1080/10610270802468454

[3] J. R. Johnson, N. Fu, E. Arunkumar, W. M. Leevy, S. T. Gammon, D. Piwnica-Worms, B. D. Smith, *Angew. Chem. Int. Ed.* **2007**, *46*, 5528. doi:10.1002/ANIE.200701491

[4] (a) J. J. Gassensmith, L. Barr, J. M. Baumes, A. Paek, A. Nguyen, B. D. Smith, *Org. Lett.* **2008**, *10*, 3343. doi:10.1021/OL801189A
(b) J. J. Gassensmith, S. Matthys, A. Wojcik, P. V. Kamat, B. D. Smith, *Chem. Eur. J.* **2010**, *16*, 2916.

[5] J. J. Gassensmith, J. M. Baumes, B. D. Smith, *Chem. Commun.* **2009**, 6329. doi:10.1039/B911064J

[6] (a) D. A. Leigh, A. Murphy, J. P. Smart, A. M. Z. Slawin, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 728. doi:10.1002/ANIE.199707281

(b) F. G. Gatti, D. A. Leigh, S. A. Nepogodiev, A. M. Z. Slawin, S. J. Teat, J. K. Y. Wong, *J. Am. Chem. Soc.* **2001**, *123*, 5983. doi:10.1021/JA001697R
(c) A. S. Lane, D. A. Leigh, A. Murphy, *J. Am. Chem. Soc.* **1997**, *119*, 11092. doi:10.1021/JA971224T
(d) W. Clegg, C. Gimenez-Saiz, D. A. Leigh, A. Murphy, A. M. Z. Slawin, S. J. Teat, *J. Am. Chem. Soc.* **1999**, *121*, 4124. doi:10.1021/JA9841310
(e) G. Brancato, F. Coutrot, D. A. Leigh, A. Murphy, J. K. Y. Wong, F. Zerbetto, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4967. doi:10.1073/PNAS.072695799
(f) E. R. Kay, D. A. Leigh, F. Zerbetto, *Angew. Chem. Int. Ed.* **2007**, *46*, 72. doi:10.1002/ANIE.200504313

[7] (a) P. M. Kazmaier, G. K. Hamer, R. A. Burt, *Can. J. Chem.* **1990**, *68*, 530.
(b) K.-Y. Law, *J. Phys. Chem.* **1989**, *93*, 5925. doi:10.1021/J100352A054

[8] (a) C. A. Schalley, *J. Phys. Org. Chem.* **2004**, *17*, 967. doi:10.1002/POC.826
(b) G. M. Affeld, C. Hübner, C. Seel, C. A. Schalley, *Eur. J. Org. Chem.* **2001**, 2877. doi:10.1002/1099-0690(200108)2001:15<2877::AID-EJOC2877>3.0.CO;2-R

[9] D. Jacquemin, E. A. Perpete, A. D. Laurent, X. Assfeld, C. Adamo, *Phys. Chem. Chem. Phys.* **2009**, *11*, 1258. doi:10.1039/B817720A

[10] N. Fu, J. M. Baumes, E. Arunkumar, B. C. Noll, B. D. Smith, *J. Org. Chem.* **2009**, *74*, 6462. doi:10.1021/JO901298N

[11] L. Lunazzi, C. Magagnoli, D. Macciantelli, *J. Chem. Soc., Perkin Trans. 2* **1980**, *11*, 1704. doi:10.1039/P29800001704

[12] M. L. Martin, G. J. Martin, J.-J. Delpuech, *Practical NMR Spectroscopy* **1980** (Heydon: London).

[13] J. Dale, R. G. Lichtenhaler, G. Teien, *Acta Chem. Scand. A* **1979**, *B33*, 141. doi:10.3891/ACTA.CHEM.SCAND.33B-0141

[14] (a) A. H. Schmidt, in *Oxocarbons* (Ed. R. West) **1980**, Ch. 10, p. 185 (Academic Press: New York, NY).
(b) K.-Y. Law, in *Organic Photochemistry* (Eds V. Ramamurthy, K. S. Schanze) **1997**, Ch. 12, pp. 519–584 (Marcel Dekker: New York, NY).
(c) S. Das, K. G. Thomas, M. V. George, in *Organic Photochemistry* (Eds V. Ramamurthy, K. S. Schanze) **1997**, Ch. 11, pp. 467–517 (Marcel Dekker: New York, NY).
(d) J. J. McEwan, K. J. Wallace, *Chem. Commun.* **2009**, 6339. doi:10.1039/B909572A

[15] (a) G. Maahs, P. Hegenberg, *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 888. doi:10.1002/ANIE.196608881
(b) R. W. Bigelow, H. J. Freund, *Chem. Phys.* **1986**, *107*, 159.
(c) J. V. Ros-Lis, R. Martínez-Máñez, F. Sancenón, J. Soto, M. Spieles, K. Rurack, *Chem. Eur. J.* **2008**, *14*, 10101. doi:10.1016/0301-0104(86)85001-7

[16] (a) A. Rescifina, C. Zagni, D. Iannazzo, P. Merino, *Curr. Org. Chem.* **2009**, *13*, 448. doi:10.2174/138527209787582222
(b) R. E. Kay, D. A. Leigh, *Pure Appl. Chem.* **2008**, *80*, 17. doi:10.1351/PAC200880010017
(c) K. E. Griffiths, J. F. Stoddart, *Pure Appl. Chem.* **2008**, *80*, 485. doi:10.1351/PAC200880030485
(d) S. J. Loeb, *Chem. Soc. Rev.* **2007**, *36*, 226. doi:10.1039/B605172N