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Aust. J. Chem. **2015**, *68*, 1359–1364
http://dx.doi.org/10.1071/CH15196

Full Paper

Enhanced Squaraine Rotaxane Endoperoxide Chemiluminescence in Acidic Alcohols

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Squaraine rotaxane endoperoxides (SREPs) are storable chemiluminescent compounds that undergo a clean cycloreversion reaction that releases singlet oxygen and emits near-infrared light when warmed to body temperature. This study examined the effect of solvent on SREP chemiluminescence intensity and found that acidic alcohols, such as 2,2,2-trifluoroethanol, α-(trifluoromethyl)benzyl alcohol, and 1,1,1,3,3,3-hexafluoroisopropanol, greatly increased chemiluminescence. In contrast, aprotic solvents, such as trifluoroethylmethyl ether, had no effect. The interlocked rotaxane structure was necessary as no chemiluminescence was observed when the experiments were conducted with samples containing a mixture of the two non-interlocked components (squaraine thread and macrocycle endoperoxide). Spectroscopic analyses of the enhanced SREP chemiluminescent reactions showed a mixture of products. In addition to the expected squaraine rotaxane product caused by cycloreversion of the endoperoxide, a diol derivative was isolated. The results are consistent with an endoperoxide O–O bond cleavage process that is promoted by the hydrogen bonding solvent and produces light emission from a squaraine excited state.

Manuscript received: 17 April 2015.
Manuscript accepted: 30 April 2015.
Published online: 27 May 2015.

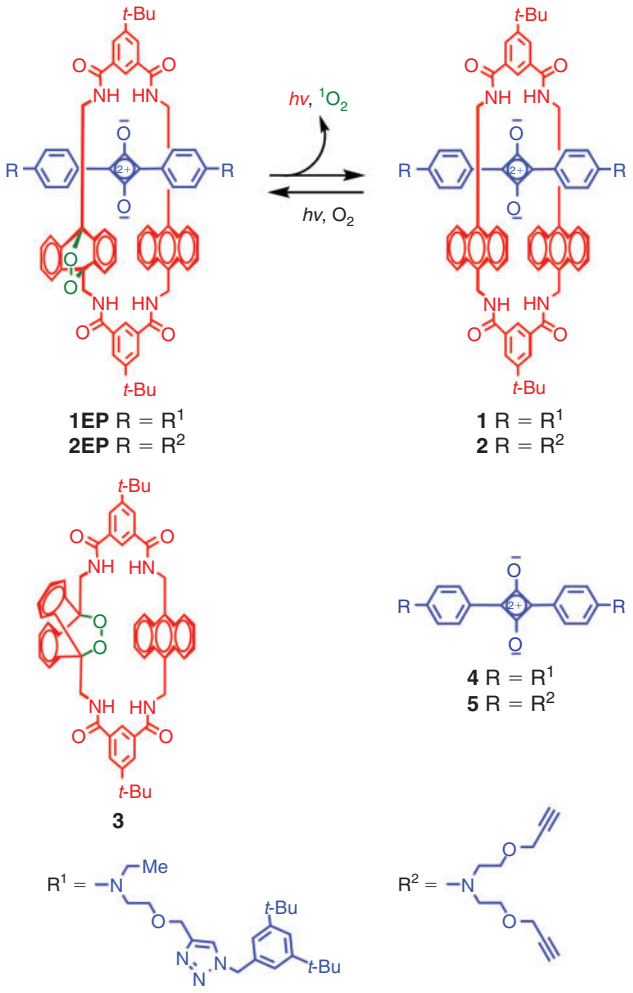
Introduction

An emerging theme in the field of interlocked molecules is modulation of chemical reactivity.[1–6] Typically with rotaxanes, the encapsulated thread component exhibits decreased reactivity due to steric protection by the surrounding macrocycle.[7–12] Examples of enhanced rotaxane reactivity are very rare.[13–16] A few years ago, we reported that squaraine rotaxane endoperoxides (SREPs) undergo an accelerated cycloreversion process that releases excited state singlet oxygen and emits near-infrared light (Scheme 1).[17] Detailed mechanistic studies indicated that the chemiluminescence is due to energy transfer from the released singlet oxygen to the encapsulated squaraine thread. The increased rate of cycloreversion is driven by cross component strain on the surrounding macrocycle caused by the rotaxane mechanical bond.[18]

Self-illuminating molecules are unusual, and the near-infrared emission of SREPs has many potential applications in molecular imaging and diagnostics.[19–21] However, to realize these applications, several performance features must be improved, and one of the most important features is the chemiluminescence intensity. A well-known literature strategy for increasing molecular chemiluminescence is to add a chemical promoter. For example, it is known that the chemiluminescence of dioxetanes is enhanced by the presence of hydrogen bond donors such as silica gel and relatively acidic alcohols.[22,23] It appears that hydrogen bonding with one of the dioxetane oxygens promotes an intramolecular electron transfer pathway with enhanced chemiluminescence.[23,24] This precedence has prompted us to test if hydrogen bond donors can increase SREP chemiluminescence. Here, we report that the chemiluminescence intensity in acidic fluorinated alcohols is >100-fold greater than that in weakly polar solvents. Analysis of the reaction products indicates that the enhancement is not simply due to an increase in the rate of SREP cycloreversion, but to a new endoperoxide cleavage pathway.

Results and Discussion

The study first examined SREP **1EP**, which was prepared in quantitative yield by direct photooxidation of the precursor squaraine rotaxane **1** (Scheme 1). In addition, the unthreaded components of **1EP**, namely the macrocycle endoperoxide **3**[25] and squaraine dye **4**,[26] were prepared by previously reported methods. SREP **1EP** can be permanently stored at −25°C, and undergoes clean cycloreversion in $CDCl_3$ when warmed to room temperature or above. This process emits near-infrared light and is easily monitored by placing the reaction vial inside a light-tight box that is equipped with a sensitive charge-coupled device (CCD) camera. Standard conditions were established that measured the time-integrated chemiluminescence emitted by a reaction vial containing **1EP** in various solvents at 38°C. The major results are shown in Fig. 1. Changing the solvent from aprotic $CDCl_3$ to acidic alcohol solvents led to a large increase in the integrated chemiluminescence intensity. Specifically, the order of the chemiluminescence intensity was $CDCl_3$ (1) < trifluoroethanol (11) < trifluoromethylbenzyl alcohol (29) < hexafluoroisopropanol (>100 which is the maximum dynamic range of the camera), a trend that correlates with the



Scheme 1. SREP cycloreversion and the compounds studied.

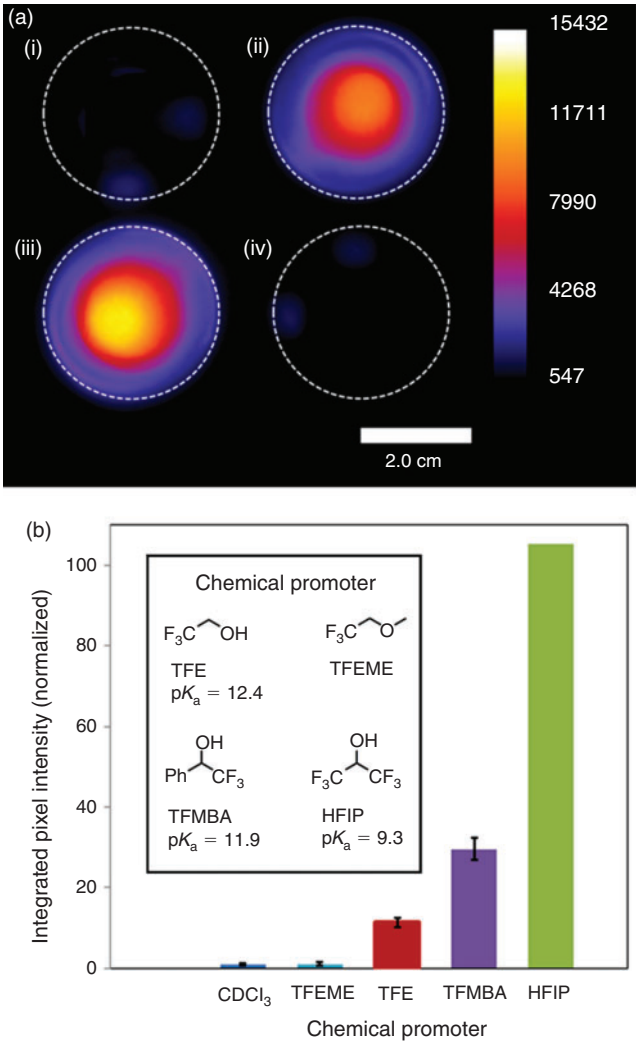


Fig. 1. (a) Chemiluminescence pixel intensity maps (arbitrary units) of vials containing **1EP** (50 μM) in various solvents (1 mL): (i) $CDCl_3$, (ii) trifluoroethanol, (iii) hexafluoroisopropanol, and (iv) trifluoroacetic acid. Chemiluminescence was acquired over 30 s. (b) Mean chemiluminescence pixel intensity of a region of interest, acquired over 30 s, of **1EP** (500 μM) in various solvents at 38°C. All values are normalized to the chemiluminescence of **1EP** in $CDCl_3$. TFE = trifluoroethanol, TFEME = trifluoroethylmethyl ether, TFMBA = trifluoromethylbenzyl alcohol, HFIP = hexafluoroisopropanol. The value obtained for HFIP represents a minimum value, imposed by the dynamic range of the instrument, and could be much higher.

increasing acidity of the alcohol functionality (Fig. 1). No chemiluminescence enhancement was observed when the solvent was trifluoroethylmethyl ether, demonstrating the crucial role of the alcohol functional group. Moreover, no chemiluminescence was observed when the solvent was trifluoroacetic acid. In this latter case, the solvent was sufficiently acidic to protonate the terminal nitrogen atoms on the encapsulated squaraine dye in **1EP**.

Control experiments examined solutions containing a 1 : 1 mixture of the unthreaded rotaxane components, that is, the macrocycle **3** and squaraine dye **4** in the solvents listed above, and no chemiluminescence was observed (Fig. 2). NMR analyses of the samples confirmed that there was no chemical reaction. Only the permanently interlocked SREP is capable of producing the enhanced chemiluminescence, confirming the necessity of the interlocked structure.

A more practical demonstration of the chemiluminescence enhancement was gained by examining samples of SREP on heated solid supports. Fig. 3 shows a comparison analysis of two equal spots of **1EP** on either an untreated silica gel plate or a plate that had been pre-treated with hexafluoroisopropanol. The plates were warmed to 38°C and the pixel intensity images show a 3-fold increase in chemiluminescence for the plate that had been activated with hexafluoroisopropanol.

In order to gain mechanistic insight regarding the enhanced chemiluminescence, SREP **2EP** was investigated. The primary

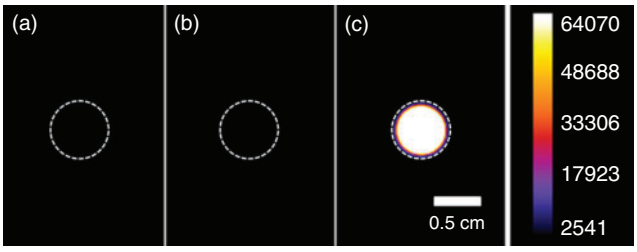


Fig. 2. Chemiluminescence pixel intensity maps (arbitrary units), acquired over 30 s, of vials (viewed from above) containing solutions of (a) **3**, (b) **3** + **4**, and (c) **1EP**, each at 500 μM in hexafluoroisopropanol (38°C).

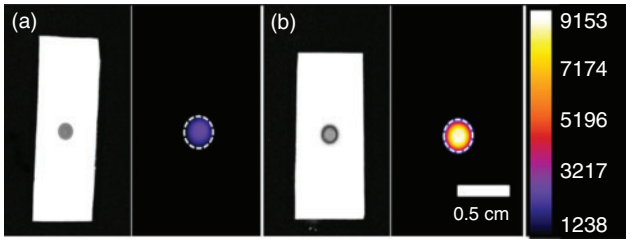


Fig. 3. Photographs and chemiluminescence pixel intensity maps, acquired over 10 s at 38°C (arbitrary units), showing a spot of **1EP** (3.0 nmol) adsorbed onto (a) silica gel plate and (b) silica gel plate pre-treated with hexafluoroisopropanol.

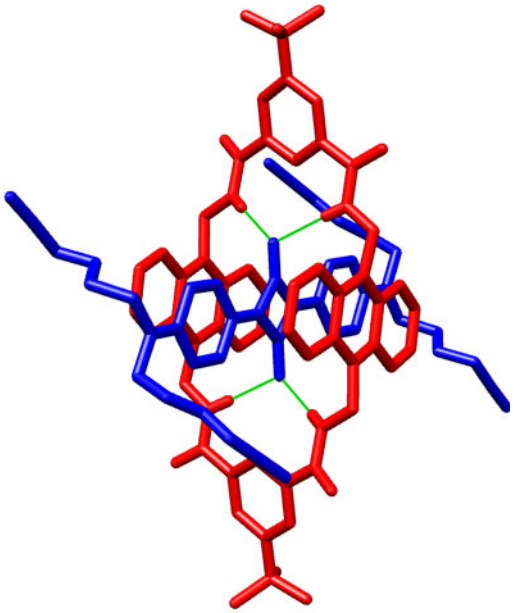


Fig. 4. X-Ray crystal structure of rotaxane **2**.

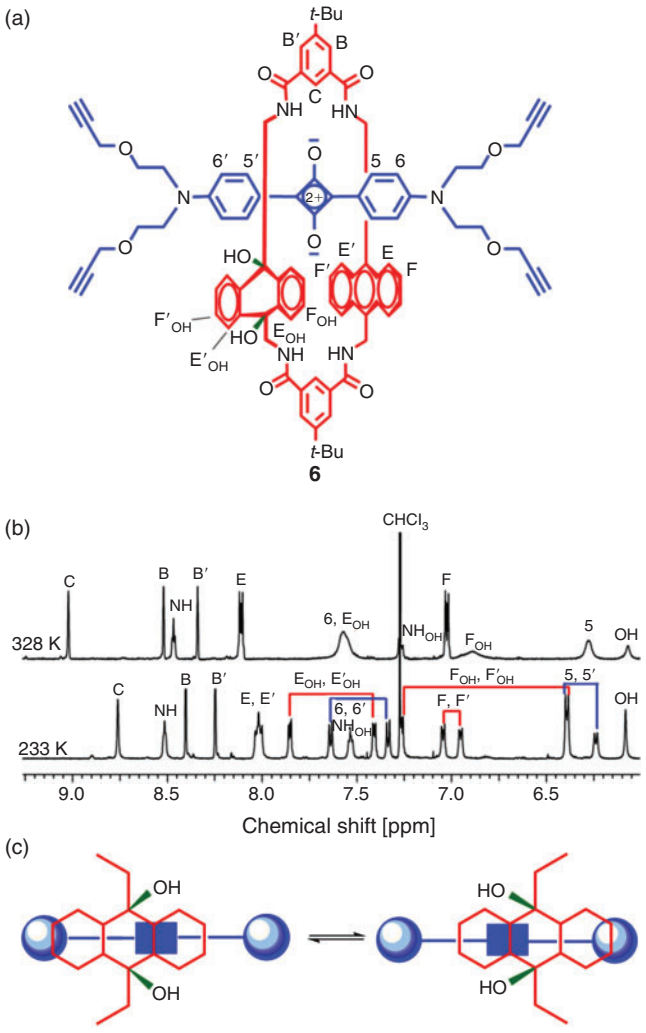


Fig. 5. (a) Structure of squaraine rotaxane **6**. (b) Partial NMR spectra of **6** ($CDCl_3$, 600 MHz) at two temperatures with the relevant peak assignments. (c) Cartoon depicting shuttling of **6** between two degenerate rotaxane co-conformations with the macrocycle component in a boat orientation.

reason for studying **2EP** was the symmetry of the two bisalkyne stopper groups (R^2 in Scheme 1), which made it easier to monitor the reaction products by ^{1}H NMR spectroscopy. The precursor to **2EP** is the squaraine rotaxane **2**, which was prepared by conducting a Leigh-type clipping reaction in the presence of squaraine dye **5**.[27] Fig. 4 shows the X-ray crystal structure of rotaxane **2**. Similarly to previously obtained squaraine rotaxane structures, the macrocycle adopts a flattened chair conformation, and there are four bifurcated hydrogen bonds between the macrocycle amide NH residues and the two oxygens on the squaraine thread.[28,29] SREP **2EP** was generated in quantitative yield by direct photoxidation of rotaxane **2** and found to exhibit the same chemiluminescence properties as **1EP**.

In contrast to the clean thermal cycloreversion reaction that occurs in $CDCl_3$,[17] a sample of **2EP** in hexafluoroisopropanol at 38°C undergoes a more complex set of reactions. Chromatographic purification of the crude residue revealed three major products, i.e. the cycloreverted squaraine rotaxane **2** (38 % recovered mass), free squaraine thread **5** (13 % recovered mass), and the diol-containing squaraine rotaxane **6** (13 % mass). The structure of **6** (Fig. 5a) was elucidated using ^{1}H NMR, variable temperature NMR, HPLC–MS (mass spectrometry), infrared (IR) spectroscopy, UV-visible absorption spectroscopy, and fluorescence spectroscopy (see Supplementary Material). The ^{1}H NMR spectrum of squaraine rotaxane **6** was broad at room temperature, but upon cooling, the peaks split and became sharp which greatly facilitated signal assignment. The important diagnostic spectral features were: (1) chemical shift inequivalence of aryl protons **B** and **B′** that indicates a loss of front/back symmetry for the macrocycle; (2) chemical shift equivalence of protons **C** that indicates a plane of vertical symmetry for the macrocycle; and (3) squaraine protons **5** and **6** and anthracene protons **E**, $\mathbf{E_{OH}}$, **F**, $\mathbf{F_{OH}}$ undergo two-site exchange, consistent with a rotaxane co-conformation that shuttles the boat-like macrocycle between two degenerate locations away from the centre of the squaraine thread (Fig. 5c). The barrier for this exchange ($\Delta G^{\neq}$) was determined to be 13.7 ± 0.4 kcal mol^{-1}, which is significantly higher than that observed for non-oxidized squaraine rotaxanes (see Supplementary Material).[30] The presence of the diol in rotaxane **6** was suggested by deuterium exchange studies. Upon addition of D_2O to a $CDCl_3$ solution of **6**, the ^{1}H NMR signal at 6.1 ppm disappeared, but re-appeared after subsequent addition of H_2O. The presence of a diol group in **6** is further supported by the broad and intense peak at 3290 cm^{-1} observed in the IR spectrum, which is absent in the spectrum of parent **2**.

The results suggest that the enhanced SREP chemiluminescence in the acidic alcohols is not due to an increase in the rate of cycloreversion. In the specific case of **2EP** in hexafluoroisopropanol, a reduced amount of cycloreversion product **2** and a diol-containing squaraine rotaxane **6** were obtained. It is tempting to associate the appearance of **6** with the enhanced chemiluminescence. Indeed, there is considerable literature precedence to propose logical mechanisms. For example, (1) previous studies of 9,10-endoperoxides have shown that upon cleavage of the O–O bond, numerous reaction pathways are possible[31] including diol formation,[32] which can be facilitated by strong hydrogen bond donors; (2) squaraines are known to have an inherently low oxidation potential;[33] and (3) hydrogen bonding of hexafluoroisopropanol to the endoperoxide could lower the energy necessary for internal electron transfer from the squaraine dye to the endoperoxide.[23] Thus, it is likely that O–O cleavage is promoted by hydrogen bonding with the solvent, and the process may be a variation of the intramolecular chemically initiated electron exchange luminescence (CIEEL) mechanism that is observed with dioxetane compounds substituted with a *p*-(dimethylamino)phenyl moiety.[34] Thus, electron transfer from the squaraine promotes cleavage of the hydrogen-bonded O–O bond and diol formation. A subsequent back electron transfer leads to an excited state squaraine, which emits near-infrared light. Further detailed studies are needed to confirm this mechanistic hypothesis.

Conclusion

SREP chemiluminescence in fluorinated alcohols is more than 100-fold higher than that in $CDCl_3$. Enhanced SREP emission is also observed when the compound is immobilized on silica gel that has been pre-treated with hexafluoroisopropanol. Analysis of the SREP reaction in hexafluoroisopropanol shows a mixture of products including the expected squaraine rotaxane caused by cycloreversion of the endoperoxide and a diol derivative due to cleavage of the O–O bond. The results are consistent with a chemiluminescent endoperoxide cleavage reaction that is promoted by hydrogen bonding of the solvent leading to near-infrared light emission from a squaraine excited state. No similar chemical reaction is observed in a control mixture of unthreaded components (squaraine thread and endoperoxide-containing macrocycle), confirming that the cross component strain caused by the rotaxane mechanical bond is responsible for the observed reactivity.

Experimental

General Methods and Materials

All starting materials and solvents were of reagent grade, unless otherwise indicated, and were purchased from commercial sources and used without further purification. Squaraine rotaxane **1**,[26] SREP **1EP**,[17] monoendoperoxide macrocycle **3**,[25] and squaraine dyes **4**[26] and **5**[35] were synthesized as previously reported and characterized by NMR, UV-visible spectroscopy, and/or fluorescence spectroscopy. ^1H and ^{13}C NMR spectra were collected using a Varian 500 MHz and 600 MHz spectrometer. Photophysical measurements were determined using a PerkinElmer Lambda 25 UV-visible spectrometer and a Horiba Scientific Fluoromax-4 spectrofluorometer. Spectrophotometric grade solvents were purchased from commercial sources and used without further purification. All measurements were carried out at 25°C, unless otherwise noted. Dyes were excited at an absorbance of 0.10, and bis[4-(dimethylamino)phenyl] squaraine (fluorescence quantum yield $\Phi_f = 0.70$ in chloroform) was used as a standard for quantum yield measurements. For IR studies, solutions of **2** and **6** in chloroform were added dropwise onto a KBr pellet and the solvent was allowed to dry, creating a thin film. The samples were placed between two KBr pellets and run on a PerkinElmer Spectrum One Fourier transform (FT)-IR spectrometer.

*Squaraine Rotaxane **2***

Squaraine dye **5** (110 mg, 0.19 mmol) was dissolved in anhydrous $CHCl_3$ (100 mL) in a dry round-bottom flask. Anthracene dimethylenediamine (216 mg, 0.93 mmol) and triethylamine (260 μL, 1.9 mmol) were dissolved in anhydrous $CHCl_3$ (80 mL) and placed in a large syringe. 3,5-Di-*tert*-butyldicarbonyl chloride (242 mg, 0.94 mmol) was dissolved in anhydrous $CHCl_3$ (80 mL) and placed in a separate syringe. The solutions were added dropwise using a syringe pump over 8 h to a stirring solution of **5** under inert atmosphere. Upon complete consumption of **5** indicated by TLC analysis, the solvent was removed under reduced pressure. The reaction mixture was redissolved in a minimum amount of $CHCl_3$ and passed through a pad of Celite. The mixture was concentrated under reduced pressure and then purified via silica gel chromatography in 0–5 % acetone in $CHCl_3$ as eluent to yield **2** (227 mg, 0.16 mmol, 85 %) as a dark green, flaky solid. λ_{abs} (absorbance wavelength) = 657 nm. λ_{em} (emission wavelength) = 699 nm. $\log \varepsilon$ (molar absorptivity) = 5.3. $\Phi_f = 0.51$. δ_H ($CDCl_3$, 600 MHz, 25°C) 9.35 (2H, s), 8.52 (4H, m), 8.20 (4H, t, *J* 4.5), 7.68 (8H, dd, *J* 7.0, *J* 3.0), 6.96 (4H, d, *J* 9.0), 6.70 (8H, dd, *J* 7.5, *J* 3.0), 6.16 (4H, d, *J* 9.0), 5.12 (8H, d, *J* 4.0), 4.26 (8H, d, *J* 2.0), 3.80 (8H, t, *J* 5.5), 3.76 (8H, t, *J* 5.5), 2.58 (4H, t, *J* 2.0), 1.54 (18H, s). δ_C ($CDCl_3$, 150 MHz, 25°C) 183.7, 180.3, 167.0, 153.5, 152.9, 133.2, 133.0, 130.3, 129.0, 128.5, 125.9, 123.8, 122.6, 117.3, 111.8, 79.1, 75.5, 67.3, 58.7, 51.2, 37.9, 35.4, 31.4. HRMS (electrospray ionization time-of-flight; ESI TOF) *m*/*z* 1437.6633: calcd for $C_{92}H_{89}N_6O_{10}$ 1437.6635.

*SREP **2EP***

A solution of **2** (95 mg, 66 μmol) was dissolved in CH_2Cl_2 (10 mL). The solution was irradiated with 540 nm light (long-pass) for 1.5 h in the presence of a stream of oxygen. The solvent was removed under reduced pressure in an ice bath to yield **2EP** (97 mg, 66 μmol, quantitative) as a green, flaky solid. δ_H (CD_2Cl_2, 600 MHz, 0°C) 9.19 (2H, s), 8.52 (2H, t, *J* 4.5), 8.50 (2H, s), 8.36 (2H, s), 7.77 (4H, dd, *J* 7.0, *J* 3.0), 7.21 (2H, t, *J* 5.0), 7.07–7.15 (8H, m), 6.80 (4H, dd, *J* 7.5, *J* 2.5), 6.48 (4H, dd, *J* 5.5, *J* 3.0), 6.24 (4H, d, *J* 9.0), 5.25 (4H, d, *J* 4.0), 4.21 (8H, d, *J* 1.0), 4.15 (4H, d, *J* 4.0), 3.77 (8H, t, *J* 5.0), 3.74 (8H, t, *J* 5.0), 2.59 (4H, t, *J* 3.0), 1.51 (18H, s). δ_C (CD_2Cl_2, 150 MHz, 0°C) 184.5, 178.9, 168.0, 167.5, 154.2, 152.8, 135.9, 134.5, 134.2, 133.7, 130.8, 130.5, 130.5, 129.6, 129.2, 125.9, 124.6, 123.3, 122.1, 118.2, 112.6, 81.4, 79.7, 75.5, 67.7, 58.9, 54.4, 51.5, 38.9, 37.4, 35.6, 31.5. HRMS (ESI TOF) *m*/*z* 1469.6510; calcd for $C_{92}H_{89}N_6O_{12}$ 1469.6533.

*Squaraine Rotaxane **6***

SREP **2EP** (40 mg, 27 μmol) was dissolved in hexafluoroisopropanol (10 mL). The reaction mixture was stirred at 38°C for 48 h. After this time, the solvent was removed under reduced pressure to yield a flaky blue–green solid. The crude mixture was purified twice via silica gel chromatography in 0–10 % acetone in $CHCl_3$ as eluent to yield parent squaraine

rotaxane **2** (15 mg, 15 μmol, 38 % recovered mass) as a dark green, flaky solid, squaraine dye **5** (5 mg, 8 μmol, 13 % recovered mass) as a light blue film, and rotaxane **6** (5 mg, 3.3 μmol, 13 % mass) as a dark green film. $\lambda_{abs} = 668$ nm. $\lambda_{em} = 698$ nm. log $\varepsilon = 5.32$. $\Phi_f = 0.46$. δ_H ($CDCl_3$, 600 MHz, −40°C) 8.76 (2H, s), 8.51 (2H, t, *J* 3.5), 8.40 (2H, s), 8.24 (2H, s), 7.97–8.06 (4H, m), 7.85 (2H, dd, *J* 6.0, *J* 3.0), 7.63 (2H, d, *J* 9.0), 7.53 (2H, t, *J* 6.0), 7.41 (2H, dd, *J* 6.0, *J* 3.0), 7.34 (2H, d, *J* 9.0), 7.25 (2H, m), 7.04 (2H, dd, *J* 7.0, *J* 2.5), 6.95 (2H, dd, *J* 7.0, *J* 2.5), 6.35–6.42 (4H, m), 6.24 (2H, d, *J* 9.0), 6.08 (2H, s), 5.35–5.45 (4H, m), 4.12–4.25 (8H, m), 3.97 (2H, dd, *J* 14.5, *J* 7.0), 3.65–3.85 (16H, m), 2.52 (2H, t, *J* 2.5), 2.46 (2H, t, *J* 2.5), 1.82–1.85 (2H, m), 1.50 (18H, s). HRMS (ESI TOF) m/z 1471.6695; calcd for $C_{92}H_{91}N_6O_{12}$ 1471.6689.

Chemiluminescence Studies

All chemiluminescence measurements were made on a Xenogen IVIS Lumina imaging system (Caliper Life Sciences) with a thermoelectrically cooled CCD camera. Solution samples in glass vials were placed on a heated stage set to 38°C and with a 5-cm field of view. Typically, the chemiluminescence was acquired over 30 s with 8 × 8 binning, Cy 5.5 filter set, and the lens aperture fully open ($F_{stop} = 1$). Pixel intensity maps were acquired using *Living Image* software version 3.0, and the data were analyzed using *ImageJ* software.

For the silica gel plate studies, silica gel plates were dipped in hexafluoroisopropanol for 10 s, then allowed to dry for 30 s. Subsequently, 3.0 μL of 1.0 mM stock solutions of **1EP** in $CDCl_3$ was dropped using a syringe onto individually treated and untreated plates, and the spots were allowed to dry. The plates were then imaged. The experiment was repeated a total of four times and the integrated chemiluminescence intensities (mean pixel intensity for a region of interest drawn around a spot when viewed from the top) for all four trials were recorded. In each case, the chemiluminescence was acquired over 10 s with 8 × 8 binning, Cy 5.5 filter set, and the lens aperture fully open ($F_{stop} = 1$).

*X-Ray Crystallography Data of Rotaxane **2***

Single crystals were obtained as follows: a solution of **2** in chloroform was prepared in a 2 mL vial and placed inside a 20 mL vial filled with a 1 : 1 ether/pentane mixture. The 20 mL vial was sealed to allow slow diffusion of hexanes into chloroform. Crystal data for $C_{94}H_{90}Cl_6N_6O_{10}$: *M* 1676.41, triclinic, space group *P*-1, *a* 11.045(3), *b* 13.672(3), *c* 15.910(4) Å, *α* 106.365(3)°, *β* 109.154(3)°, *γ* 102.317(3)°, *V* 2050.0(8) Å^3, *Z* 1, D_c 1.358 g cm^{-3}, *T* 150(2) K, *λ*(synchrotron) 0.77490 Å, *μ*(synchrotron) 0.348 mm^{-1}, 21701 reflections collected, 8343 unique (R_{int} 0.0376), R_1 0.0443, wR_2 0.1082 for 6162 data with $I > 2\sigma(I)$, R_1 0.0675, wR_2 0.1186 for all 8343 data. Residual electron density (e Å^{-3}) max/min: 0.318/–0.526. An arbitrary sphere of data were collected on a turquoise plate-like crystal, having approximate dimensions of 0.05 × 0.04 × 0.01 mm^3, on a Bruker APEX-II diffractometer using a combination of *ω*- and *φ*-scans of 0.3°. Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by dual-space methods and expanded routinely.[36] The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 × for methyl, 1.2 × for all others). Samples for synchrotron crystallographic analysis were submitted through the SCrALS (Service Crystallography at Advanced Light Source) program. Crystallographic data were collected at Beamline 11.3.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The ALS is supported by the USA Department of Energy, Office of Energy Sciences (Contract No. DE-AC02–05CH11231).

The crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1059800. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk.

Supplementary Material

Spectral data for **2**, **2EP**, and **6** are available on the Journal's website.

Acknowledgements

We are grateful for funding support from the NSF (USA).

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