Singlet oxygen generation using iodinated squaraine and squaraine-rotaxane dyes†

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The goal of this study was to assess the ability of squaraine-rotaxanes to generate singlet oxygen for potential application in photodynamic therapy (PDT). Specifically, we compare the aggregation and photophysical properties of an iodinated squaraine dye and an iodinated squaraine-rotaxane. Even under strongly aggregating conditions, the absorption spectra of both remain relatively sharp. An X-ray crystal structure of the iodinated squaraine dye shows that it adopts perpendicular, end-to-face orientations in the solid state. Singlet oxygen generation efficiency was measured by trapping with 1,3-diphenylisobenzofuran. The triplet state of the rotaxane was characterized using laser flash photolysis. The results of this study suggest that heavily halogenated squaraine-rotaxanes have potential as singlet oxygen photosensitizers for PDT.

Introduction

Photodynamic therapy (PDT) has been pursued for several decades, primarily for treatment of cancer.[1] In short, the excited state of a photosensitizer undergoes efficient intersystem crossing to produce an excited triplet state that either reacts directly with the surrounding molecules, producing reactive radicals (type I photoprocess); or alternatively, there is energy transfer with ground state oxygen to produce highly reactive singlet oxygen (type II photoprocess). In both cases, the eventual result is cell death. Two obvious constraints are the requirement for irradiation to reach the target cells and the presence of molecular oxygen. At present, porphyrin derivatives are approved for clinical use (*e.g.*, Photofrin), however, there is a need to develop next generation photosensitizers with improved photophysical and pharmacokinetic properties, and a variety of organic photosensitizers have been investigated including cyanines,[2] phthalocyanines,[3] perylene diimide based dyes,[4] aryl azonaphtholates,[5] texaphyrins,[6] and chalcogenopyrylium dyes.[7]

The focus of this report is on the squaraines, a promising class of highly fluorescent near-IR dyes that have been investigated extensively for various possible photonic applications.[8,9] Squaraines have a polarized donor–acceptor–donor structure with the anilino units acting as donors and the electron deficient central C_4O_2 ring as an acceptor. Non-halogentated squaraines exhibit poor intersystem crossing efficiency,[10] but about ten years ago, Ramaiah and co-workers

reported that halogentated versions can act as singlet oxygen photosensitizers.[8a–c] Since then several groups have investigated structural derivatives of the squaraines.[8d–g] Squaraine properties that limit their potential as photosensitizers include their propensity to aggregate which shortens the triplet-state lifetimes and reduces the singlet oxygen quantum yield, and their susceptibility to chemical bleaching by biological nucleophiles.[11] Recently, we reported a simple synthetic method of encapsulating squaraine dyes, such as **1**, inside macrocycles to form interlocked molecules called squaraine-rotaxanes.[12] These sterically protected dyes retain the favourable photophysical properties of the parent squaraines, but they are much more stable, especially in biological fluids.[13] The goal of this study was to assess the potential of squaraine-rotaxanes to generate singlet oxygen. Specifically, we describe the aggregation and photophysical properties of iodinated squaraine **2**, and we compare them to the properties of squaraine-rotaxane **3**. We find that the squaraine-rotaxane system is more resistant to photooxidation and thus is a more effective triplet photosensitizer. The study suggests that halogenated squaraine-rotaxanes may be useful as research tools that generate singlet oxygen without complications due to photosensitizer decomposition.

Results and discussion

Synthesis and dye aggregation

The squaraine derivatives **1–3** (Scheme 1) were prepared in straightforward fashion. The iodinated squaraine dye **2** was obtained in 42% yield by reacting the *N,N′*-dibenzyl derivative **5** with squaric acid. A templated macrocyclization reaction using **2**, *p*-xylylene diamine, and 2,6-pyridinedicarbonyl dichloride produced the squaraine-rotaxane **3** in 29% isolated yield (Scheme 2). All of the dyes were characterized by ¹H, ¹³C NMR and mass spectrometry.

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† This paper is dedicated to Professor George Gokel, an international leader in macrocyclic and supramolecular chemistry, on the occasion of his 60th birthday.
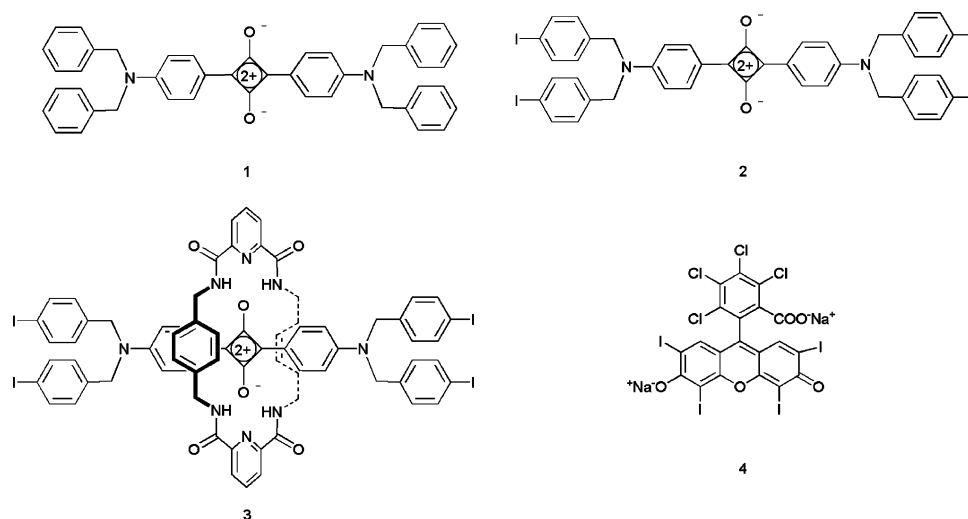
Scheme 1

The absorption and emission properties of squaraines **1–3** are listed in Table 1. In dry THF, they all absorb strongly at 630–640 nm with high fluorescence quantum yields. As the solvent polarity is increased by the addition of water, the absorption maximum of squaraine **1** becomes very broad (Fig. 1), and the fluorescence quantum yield is greatly decreased due to formation of dye aggregates with strong interchromophoric interactions.[14] Surprisingly, the absorption maximum of the iodo squaraine **2** remained relatively sharp under the identical aggregation conditions—the fluorescence quantum yield, however, was greatly decreased.

To gain insight into the aggregation behaviour of iodo squaraine **2**, a single crystal was obtained and analyzed by X-ray diffraction. Squaraine dyes with sterically small substituents are known to adopt face-to-face orientations in the solid state.[15] In contrast, iodo squaraine **2** with bulky iodobenzyl groups at each end of the molecule prefers perpendicular end-to-face packing of the chromophores in the solid state (Fig. 2). Squaraines have a single isolated transition dipole along the long axis of the molecule, and if this intermolecular T-shaped orientation is maintained when the dye is aggregated in aqueous solution, it would explain why there is negligible exciton coupling and little absorption broadening.

At the same time, the intermolecular T-shaped packing of **2** closely surrounds each chromophore with four iodobenzyl groups which provides an energy transfer pathway that quenches the fluorescence emission.[16]

Flash-photolysis

Dye molecules **1–3** possess an absorption tail at 355 nm which allows direct excitation of the chromophores by nanosecond flash photolysis (third harmonic of Nd:YAG laser). Laser pulse irradiation of squaraines **1** and **2** resulted in rapid destruction of the chromophores which prevented characterization of the transient intermediates. Therefore, we employed the more stable squaraine-rotaxane **3** for detailed laser studies in acetonitrile (a replacement solvent for the less photostable THF). As shown in Fig. 3, the transient spectrum of **3**, recorded immediately after 355 nm laser pulse excitation, exhibits an absorption maximum at 570 nm. The transient is formed completely by the end of the 10 ns laser pulse and it has a lifetime of 9 µs. Evidence that the transient is the excited triplet state includes: (a) the transient absorption profile is very

Table 1 Photophysical properties of squaraine derivatives **1–3**

Compound	Solvent	λ_{abs}/nm	$\lambda_{em}{}^{a}$/nm	$\Phi_f{}^{b}$
1	THF	631	650	0.61
	THF–water (1 : 4)	737, 540	—[c]	[c]
2	THF	630	647	0.72
	THF–water (1 : 4)	637	651	0.001
3	THF	638	657	0.74
	THF–water (1 : 4)	642	673	0.005

[a] Solutions were excited at 580 nm and emission monitored in the region 600–750 nm for estimating Φ_f. [b] Fluorescence quantum yields were determined using 4,4-[bis(N,N-dimethylamino)phenyl]squaraine as the standard ($\Phi_f = 0.70$ in CHCl₃), error limit ±5%. [c] Emission was too low to measure the maxima and fluorescence quantum yield.
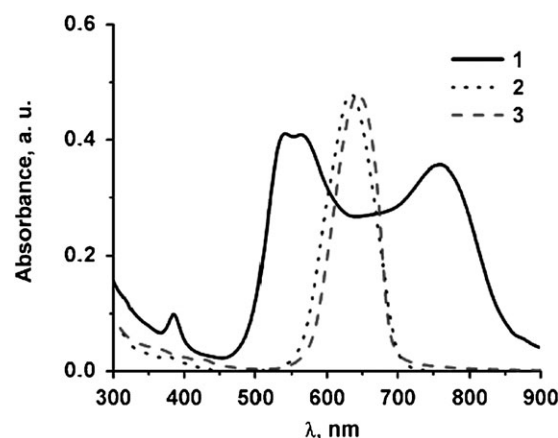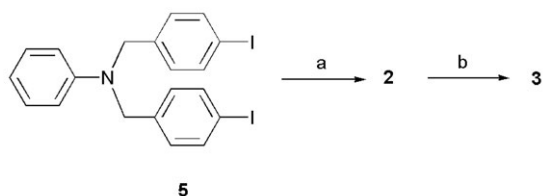

Fig. 1 UV/Vis spectra of dyes **1–3** in THF–water (1 : 4).

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Scheme 2 *Conditions*, a: squaric acid, 1-butanol/benzene (1 : 2), reflux 24 h, 42%; b: 2,6-pyridinedicarbonyl dichloride, *p*-xylylene diamine, TEA, rt, 29%.

similar to previously reported triplet squaraines,[10] (b) the transient lifetime is reduced by the presence of molecular oxygen,[17] (c) the same transient is formed when pyreneformaldehyde is employed as a triplet sensitizer.[18] This latter experiment used a mixture of pyreneformaldehyde (10 μM) and squaraine rotaxane **3** (6 μM) in acetonitrile. The pyreneformaldehyde absorbs most of the laser excitation pulse at 355 nm producing an excited triplet state with an absorption band at 440 nm (Fig. 3). The spectrum recorded 5 μs after
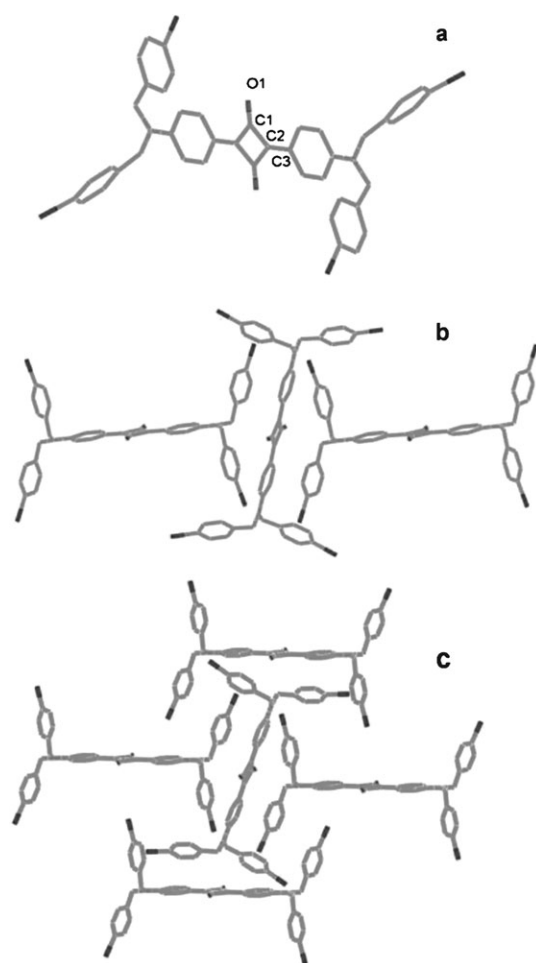

Fig. 3 (Top) Transient absorption spectrum of **3** (6 μM) in acetonitrile recorded immediately after the laser pulse (355 nm) excitation. Inset shows the decay of the transient absorption at 570 nm in the absence of oxygen. (Bottom) Transient absorption spectrum of a mixture of **3** (6 μM) and pyreneformaldehyde (10 μM) recorded immediately (filled circles) and 5 μs (open circles) after the laser pulse (355 nm). Inset shows the decay of the pyreneformaldehyde triplet absorption at 440 nm and the growth of the squaraine triplet absorption at 570 nm.

Fig. 2 X-ray structure of dye **2**: (a) stick model; (b) packing with two neighbouring molecules; (c) extended view of packing. Not shown are chloroform molecules in the lattice voids. Selected distances for atoms O1–C1 = 1.236 Å; C1–C2 = 1.466 Å; C2–C3 = 1.401 Å.
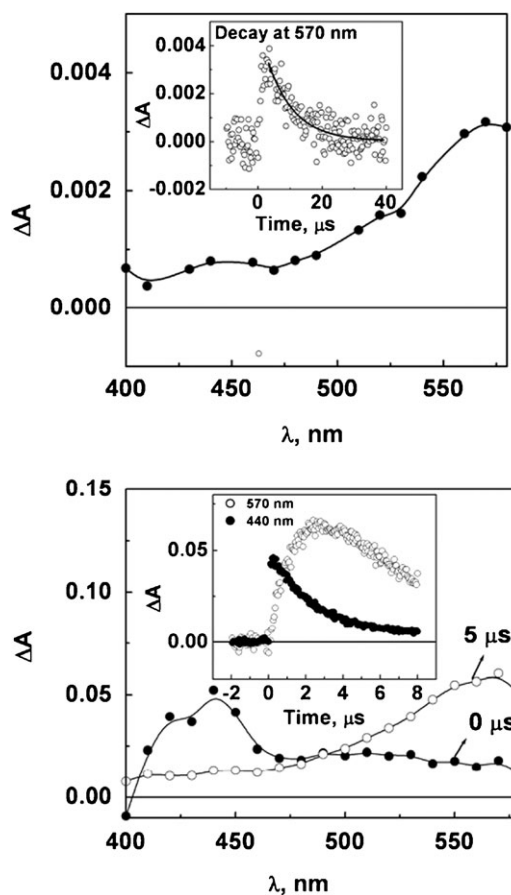
the pulse excitation is consistent with strong energy transfer from the pyreneformaldehyde to the squaraine-rotaxane producing the triplet squaraine-rotaxane absorption band at 570 nm.

Generation of singlet oxygen

The abilities of dyes **1–3** to generate singlet oxygen were determined in two different solvents (acetonitrile and THF–water 1 : 4). The appearance of singlet oxygen was detected by trapping with 1,3-diphenylisobenzofuran (DPBF).[8] The DPBF has an absorption maximum at 415 nm and forms a colorless endoperoxide product when it reacts with singlet oxygen. In each case, air saturated samples of the dye (6 μM) and DPBF (75 μM) were irradiated with light from a 150 W lamp (filtered to remove wavelengths below 520 nm), and consumption of the DPBF was monitored over time. Shown in Fig. 4 are the results in acetonitrile where the dyes are monodispersed. In the case of squaraine **1**, the DPBF band
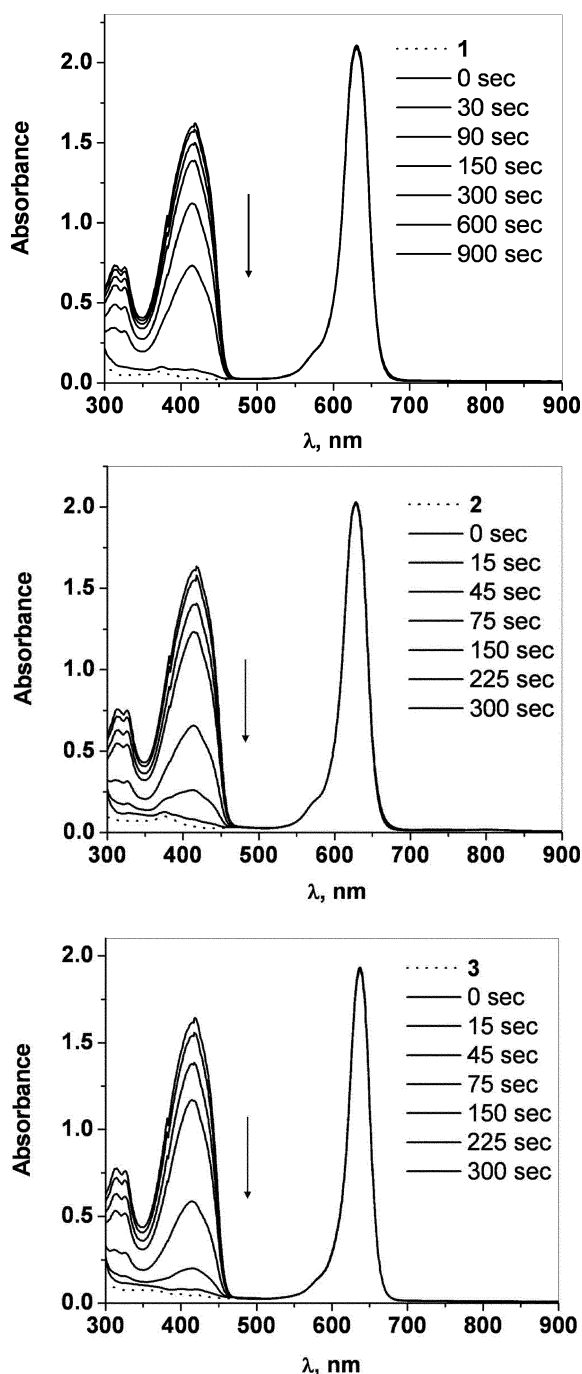
Fig. 4 Time evolution of the UV-spectrum of DPBF (75 µM) and dye (6 µM) in acetonitrile solution. Top **1**, Middle **2**, Bottom **3**.

was consumed with a half-life of around 600 s, whereas the half-lives with iodo squaraine **2** and iodo squaraine-rotaxane **3** were both around 100 s. Thus the iodinated dyes are better singlet oxygen photosensitizers, presumably because the heavy iodine substituents promote excited-state intersystem crossing.

Changing the solvent to THF–water 1 : 4 enhanced the rate of DPBF trapping. As shown in Fig. 5, the half-life for DPBF consumption with squaraine **1** was around 20 s. It is important

to note that in this organic–aqueous solvent, the absorption maximum for **1** is broadened due to aggregation, which should promote self-quenching and diminished effectiveness as a photosensitizer.[19] With iodo squaraine **2**, the half-life for DPBF consumption was around 40 seconds. This is surprisingly inefficient because the dye does not exhibit a broadened absorption, and the heavy iodine substituents should improve the efficiency of singlet oxygen generation compared to **1**. But as shown in Fig. 5b, nearly half of the iodo squaraine **2** is photobleached during the experiment which likely explains why the rate of DPBF trapping is so slow.[20] When the more stable squaraine-rotaxane **3** is employed, the half-life for DPBF consumption is around 12 s and there is no significant photobleaching of the dye. Compared to well-known sensitizer Rose Bengal, the iodo rotaxane **3** is approximately three time less efficient at generating singlet oxygen (Fig. 5d); which can be attributed to the greater number of halogen atoms present in Rose Bengal. In addition, it must be remembered that these two photosensitizers have different excitation wavelengths. It should be possible to improve the singlet oxygen generation efficiency of these chromophores by placing the heavy halogen atoms directly on the squaraine chromophore rather than on the terminal benzyl groups.[8]

Conclusions

The iodinated squaraine **2** does not exhibit the expected broadened absorptions when the dye is aggregated in aqueous solution. An X-ray crystal structure suggests that **2** adopts perpendicular, end-to-face orientations when aggregated, which inhibits exciton coupling but still allows fluorescence self-quenching. Irradiation of the iodo squaraine-rotaxane **3** produces an excited triplet state which can generate singlet oxygen by energy transfer. Compared to iodo squaraine **2**, the squaraine-rotaxane system is much more resistant to photobleaching and thus is a more effective singlet oxygen photosensitizer. The results of this study suggest that heavily halogenated squaraine-rotaxanes have potential as singlet oxygen photosensitizers for PDT. Furthermore, as highly stable photosensitizers, halogenated squaraine-rotaxanes may have utility as research tools that create reactive oxygen species in a clean and controlled manner.

Experimental section

Measurements

^{1}H and ^{13}C NMR spectra were acquired with Varian Unity Plus spectrometers. Fast atom bombardment (FAB) mass spectra (MS) were recorded on a JEOL AX 505 HA instrument. Fluorescence quantum yields were determined in spectroscopic grade CH$_3$CN using optically matching solutions of bis[4-(dimethylamino)phenyl]squaraine (ϕ_f = 0.70) as standard at an excitation wavelength of 580 nm. Nanosecond laser flash photolysis experiments employed 355 nm laser pulses (5 mJ, pulse width 6 ns) from a quanta Ray Nd:YAG laser system.
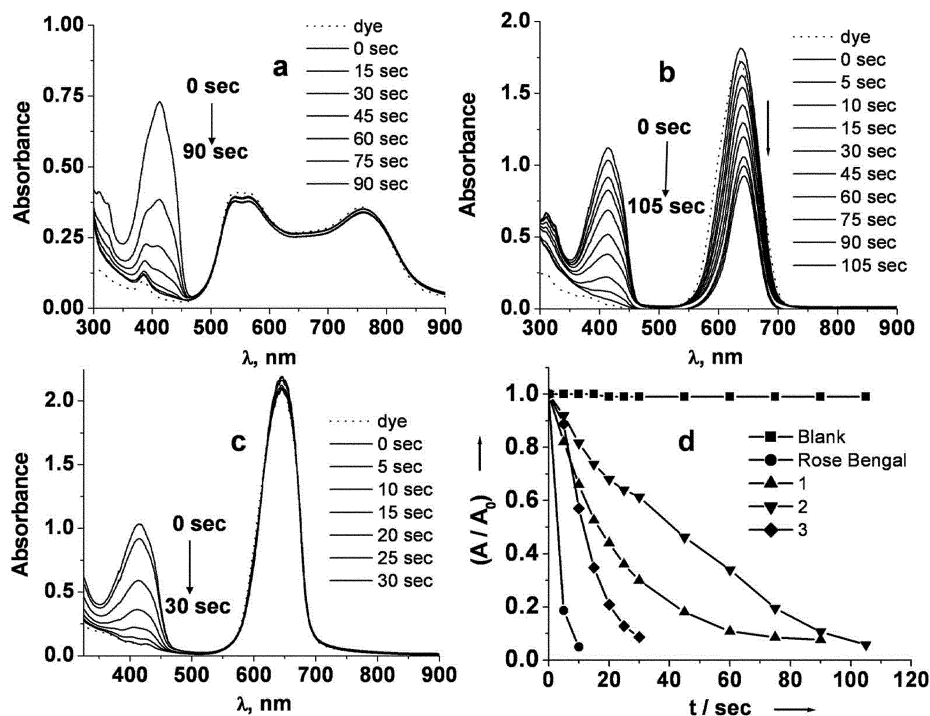
Fig. 5 Time evolution of the UV-spectrum of DPBF (75 μM) and dye (6 μM) in THF–water (1 : 4) solution. (a) **1**; (b) **2**; (c) **3**; (d) Variation of absorbance at 415 nm of DPBF band in the presence and absence (blank) of dye solutions upon irradiation.

Singlet oxygen formation

Dye solutions (6 μM) were prepared in THF–water (1 : 4) mixture and aerated for 5 minutes. An aliquot of DPBF (75 μM) was added and irradiated using a 150 W tungsten lamp with a yellow filter to remove light with $\lambda < 520$ nm. This avoids direct excitation of the DPBF molecule.

Synthesis

Squaraine 1. was prepared by the method reported in ref. 11.

Iodo squaraine 2. The dibenzylaniline derivative **5**, (410 mg, 0.78 mmol) was added to a solution of squaric acid (44 mg, 0.39 mmol) in a mixture of n-butanol (15 mL) and benzene (30 mL) in a 100 mL round bottom flask equipped with a Dean Stark apparatus. The reaction mixture was refluxed, while the water formed in the reaction mixture was trapped in the Dean Stark apparatus. After 24 h the deep green colored reaction mixture was concentrated to remove the solvent and the crude product was precipitated by adding 30–40 mL hexane. After filtering, the product was washed several times with hexane to give the dark green squaraine dye which was further purified using column chromatography over silica gel using MeOH–CHCl₃ (1 : 19). Yield 42%; ¹H NMR (600 MHz, CDCl₃, TMS): δ 4.7 (s, 8H), 6.83 (d, J = 9 Hz, 4H), 6.93 (d, J = 7.8 Hz, 8H), 7.68 (d, J = 8.4 Hz, 8H), 8.38 (d, J = 9.6 Hz, 4H); ¹³C NMR (150 MHz, CDCl₃, TMS); 53.8, 93.4, 113.2, 116.5, 121.4, 128.6, 134, 135.6, 138.4, 154.9, 182.9; FAB-MS (NBA matrix): m/z 1128.5 [M + H]⁺.

Iodo squaraine-rotaxane 3. Clear solutions of the 2,6-pyridinedicarbonyl dichloride (43 mg, 0.21 mmol) and p-xylylene-diamine (29 mg, 0.21 mmol) in 5 mL chloroform were simultaneously added dropwise using a mechanical syringe pump (kd Scientific) apparatus over five hours to a stirred solution of **2** (60 mg, 0.053 mmol) and triethylamine (74 μL, 0.53 mmol) in 40 mL of CHCl₃. After stirring overnight, the reaction mixture was filtered through a pad of celite to remove any polymeric material, and the resulting crude product chromatographed using a silica column and a mixture of methanol–chloroform (1 : 19) as eluent. Yield 29%; TLC rf = 0.4, methanol–chloroform (1 : 19); ¹H NMR (300 MHz, CDCl₃, TMS): δ 4.5 (d, J = 5.7 Hz, 8H, –Ph–CH₂ (wheel)), 4.57 (s, 8H, –Ph–CH₂ (thread)), 6.21 (d, J = 9 Hz, 4H, thread), 6.54 (s, 8H, wheel), 6.83 (d, J = 8.1 Hz, 4H, thread) 7.72 (d, J = 8.4 Hz, 8H, thread), 7.98 (t, J = 7.6 Hz, 2H, wheel), 8.1 (d, J = 9 Hz, 4H, thread), 8.39 (d, J = 11.4 Hz, 4H, wheel), 9.82 (t, J = 5.1 Hz, 4H, –NH); ¹³C NMR (150 MHz, CDCl₃, TMS): δ 43.4, 54, 93.7, 112.6, 120.4, 125.4, 128.5, 129.1, 134.1, 135.2, 137, 138.5, 138.8, 149.5, 155, 163.6, 184.8, 188; FAB-MS (NBA matrix): m/z 1662.6 [M + H]⁺.

X-Ray crystallographic structure determinations

Squaraine dye (2). Crystallization was carried out in chloroform–diisopropyl ether (1 : 1). Molecular formula = $C_{44}H_{32}I_4N_2O_2 \cdot 2CHCl_3$, Mw = 1367.05, Crystal size = 0.17 × 0.16 × 0.04 mm³ orthorhombic, Pbca, translucent intense blue/gold plate, a = 14.2033(3) Å, b = 16.4470(4) Å, c = 20.4164(5) Å, β = 90°, V = 4769.31(19) Å³, Z = 4, ρ (calcd) = 1.904 Mg m⁻³. Crystals were examined under a light hydrocarbon oil. The datum crystal was affixed to a thin glass fiber mounted atop a tapered copper mounting-pin and

transferred to the 100 K nitrogen stream of a Bruker d_8-ApexII diffractometer equipped with an Oxford Cryosystems 700 series low-temperature apparatus. Cell parameters were determined using reflections harvested from three orthogonal sets of 12 0.5° φ scans. The orientation matrix derived from this was passed to COSMO to determine the optimum data collection strategy. Average 9.6-fold redundancy was achieved using 5ω scan series and 1φ scan series. Data were collected to 0.80 Å. Cell parameters were refined using 6322 reflections with $I \geq 10\sigma(I)$ and $2.4767° \leq \theta \leq 28.6811°$ harvested from the entire data collection. In total, 56 848 reflections were measured, 4884 unique, 4049 observed, $I > 2\sigma(I)$. The overall coverage was 99.8% to 0.80 Å. All data were corrected for Lorentz and polarization effects. An absorption correction was applied using SADABS (Sheldrick, 2004). The structure was solved using direct methods in the SHELXTL (Sheldrick, 2004) program package. This revealed the complete non-hydrogen structure. The asymmetric unit consists of 1/2 squaraine molecule located about a crystallographic inversion center and one molecule of chloroform. The chloroform of solvation is linked to the squaraine by well-defined C23–H23$\cdots$O^i hydrogen bonds (where the superscript i indicates equivalent position $(x-1, y, z)$ with H$\cdots$O 2.06 Å, C$\cdots$O 2.997(3) Å and C–H$\cdots$O 154°). After making proper atom assignments, the structure was refined by usual least-squares techniques. Hydrogens were placed at calculated geometries and allowed to ride on the position of the parent atom. Hydrogen thermal parameters were set to 1.2$\times$ the equivalent isotropic U of the parent atom. The largest peak in the final difference map, 0.489 e$^-$ Å^3, is located 0.76 Å from Cl1 of the chloroform. CCDC 626189 contains the supplementary crystallographic data for this paper.‡

Acknowledgements

References

1 (a) R. Bonnet, Chem. Soc. Rev., 1995, 19–33; (b) M. Wainwright, Chem. Soc. Rev., 1996, 351–359; (c) H. Kato, J. Photochem. Photobiol. B, Biol., 1998, **42**, 96–99.

2 (a) A. R. Oseroff, D. Ohuoha, G. Ara, D. McAuliffe, J. Foley and L. Cincotta, Proc. Natl. Acad. Sci. U. S. A., 1986, **83**, 9729–9733; (b) G. Ara, J. R. Aprille, C. D. Malis, S. B. Kane, L. Cincotta, J. Foley, J. V. Bonventre and A. R. Oseroff, Cancer Res., 1987, **47**, 6580–6585; (c) A. R. Oseroff, G. Ara, K. S. Wadwa and T. A. Dahl, in Photodynamic Therapy of Neoplastic Disease, ed. D. Kessel, CRC Press, Boca Raton, FL, 1990, pp. 291–306; (d) C. Lee, S. S. Wu and L. B. Chen, Cancer Res., 1995, **55**, 2063–2069; (e) E. Delaey, F. van Laar, D. De Vos, A. Kamuhabwa, P. Jaobs and P. De Witte, J. Photochem. Photobiol., B, 2000, **55**, 27–36.

3 (a) R. W. Boyle, C. C. Leznoff and J. E. van Lier, Br. J. Cancer, 1993, **67**, 1177–1181; (b) D. Wohrle, M. Shopova, S. Muller, A. D. Milev, V. N. Mantareva and K. K. Krastev, J. Photochem. Photobiol., B, 1999, **50**, 124–128.

4 F. Yukruk, A. Lale Dogan, H. Canpinar, D. Guc and E. U. Akkaya, Org. Lett., 2005, **7**, 2885–2887.

5 P. B. Merkel and W. F. Smith, Jr, J. Phys. Chem., 1979, **83**, 2834–2840.

6 T. D. Mody, L. Fu and J. L. Sessler, in Progress in Inorganic Chemistry, ed. K. D. Karlin, John Wiley and Sons Inc., New York, NY, 2001, pp. 551–598.

7 (a) M. R. Detty and P. B. Merkel, J. Am. Chem. Soc., 1990, **112**, 3845–3855; (b) K. A. Leonard, M. I. Nelen, L. T. Anderson, S. L. Gibson, R. Hilf and M. R. Detty, J. Med. Chem., 1999, **42**, 3942–3952.

8 (a) D. Ramaiah, A. Joy, N. Chandrasekhar, N. V. Eldho, S. Das and M. V. George, Photochem. Photobiol., 1997, **65**, 783–790; (b) D. Ramaiah, I. Eckert, K. T. Arun, L. Weidenfeller and B. Epe, Photochem. Photobiol., 2002, **76**, 672–677; (c) D. Ramaiah, I. Eckert, K. T. Arun, L. Weidenfeller and B. Epe, Photochem. Photobiol., 2004, **79**, 99–104; (d) P. F. Santos, L. V. Reis, P. Almeida, A. S. Oliveira and L. F. V. Ferreira, J. Photochem. Photobiol., A, 2003, **160**, 159–161; (e) P. F. Santos, L. V. Reis, P. Almeida, J. P. Serrano, A. S. Oliveira and L. F. V. Ferreira, J. Photochem. Photobiol., A, 2004, **163**, 267–269; (f) P. F. Santos, L. V. Reis, I. Duarte, J. P. Serrano, P. Almeida, A. S. Oliveira and L. F. V. Ferreira, Helv. Chim. Acta, 2005, **88**, 1135–1143; (g) L. Beverina, A. Abbotto, M. Landenna, M. Cerminara, R. Tubino, F. Meinardi, S. Bradamante and G. A. Pagani, Org. Lett., 2005, **7**, 4257–4260.

9 (a) S. Das, K. G. Thomas and M. V. George, in Organic Photochemistry, ed. V. Ramamurthy, K. S. Schanze, Marcel Dekker, New York, 1997, pp. 467–517; (b) M. Emmelius, G. Pawlowski and H. W. Vollmann, Angew. Chem., Int. Ed. Engl., 1989, **28**, 1445–1471; (c) A. Ajayaghosh, E. Arunkumar and J. Daub, Angew. Chem., Int. Ed., 2002, **41**, 1766–1769; (d) E. Arunkumar, P. Chithra and A. Ajayaghosh, J. Am. Chem. Soc., 2004, **126**, 6590–6598; (e) E. Arunkumar, A. Ajayaghosh and J. Daub, J. Am. Chem. Soc., 2005, **127**, 3156–3164; (f) A. Ajayaghosh and E. Arunkumar, Org. Lett., 2005, **7**, 3135–3138; (g) E. Arunkumar and A. Ajayaghosh, Chem. Commun., 2005, 599–601; (h) A. Ajayaghosh, Acc. Chem. Res., 2005, **38**, 449–459.

10 (a) P. V. Kamat, S. Das, K. G. Thomas and M. V. George, J. Phys. Chem., 1992, **96**, 195–199; (b) K.-Y. Law, Chem. Rev., 1993, **93**, 449–486.

11 (a) J. V. Ros-Lis, B. García, D. Jiménez, R. Martínez-Máñez, F. Sancenón, J. Soto, F. Gonzalvo and M. C. Valldecabres, J. Am. Chem. Soc., 2004, **126**, 4064–4065; (b) J. V. Ros-Lis, R. Martínez-Máñez and J. Soto, Chem. Commun., 2002, 2248–2249.

12 (a) E. Arunkumar, C. C. Forbes, B. C. Noll and B. D. Smith, J. Am. Chem. Soc., 2005, **127**, 3288–3289; (b) for a recent review on this topic see E. Arunkumar, C. C. Forbes and B. D. Smith, Eur. J. Org. Chem., 2005, 4051–4059.

13 E. Arunkumar, N. Fu and B. D. Smith, Chem.–Eur. J., 2006, **12**, 4684–4690.

14 The two major aggregation bands for **1** are the J aggregate (red shifted) and H aggregate (blue shifted) bands. (a) G. J. Ashwell, P. C. Williamson, A. Green, G. S. Bahra and C. R. Brown, Aust. J. Chem., 1998, **51**, 599–606; (b) H. Chen, K.-Y . Law, J. Perlstein and D. G. Whitten, J. Am. Chem. Soc., 1995, **117**, 7257–7258; (c) K. Liang, K.-Y. Law and G. Whitten, J. Phys. Chem., 1994, **98**, 13379–13384; (d) S. Das, K. G. Thomas, K. J. Thomas, V. Madhavan, D. Liu, P. V. Kamat and M. V. George, J. Phys. Chem., 1996, **100**, 17310–17315; (e) K. T. Arun, B. Epe and D. Ramaiah, J. Phys. Chem. B, 2002, **106**, 11622–11627.

15 K. J. Wallace, M. Gray, Z. Zhong, V. M. Lynch and E. V. Anslyn, Dalton Trans., 2005, 2436–2441.

16 (a) S. P. McGlynn, T. Azumi and M. Kinoshita, Molecular Spectroscopy of the Triplet State, Prentice Hall, Eaglewood, Cliffs NJ, 1969, pp. 172–174; (b) N. J. Turro, Modern Molecular Photochemistry, Benjamin Cumings, Menlo Park, CA.

17 (a) J. B. Birks, in Photophysics of Aromatic Molecules, Wiley-Interscience, New York, 1970, p. 518; (b) J. Saltiel and B. W. Atwater, in Advances in Photochemistry, Wiley-Interscience, New York, 1987, vol. 14, p. 1.

18 (a) S. Das, P. V. Kamat, B. D. la Barre, K. G. Thomas, A. Ajayaghosh and M. V. George, *J. Phys. Chem.*, 1992, **96**, 10327–10330; (b) U. Santhosh and S. Das, *J. Phys. Chem. A*, 2000, **104**, 1842–1847.

19 M. Kostka, P. Zimcik, M. Miletin, P. Klemera, K. Kopecky and Z. Musil, *J. Photochem. Photobiol., A*, 2006, **178**, 16–25.

20 It appears that the face-to-face stacking of **1** protects the dye from photobleaching better than the end-to-face stacking of **2**.