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# Design and synthesis of sulfobetainic diketopyrrolopyrrole (DPP) laser dyes

Soumyaditya Mula,\*<sup>a</sup> Delphine Hablot,<sup>b</sup> Krishna K. Jagtap,<sup>cd</sup> Elodie Heyer<sup>b</sup> and Raymond Ziessel\*<sup>b</sup>

We have devised new diketopyrrolopyrrole dyes soluble in polar solvents. The colors of the dyes have been changed by substituting the 3,6-phenyl residues for thiophene groups. The solubility in polar solvents has been improved by alkylation of a dimethylaminopropyne fragment with a 1,3-sultone giving rise to sulfobetaine moieties. These dyes exhibit strong and broad absorption in the visible range (488 nm for the phenyl-DPP and 578 nm for the thiophene-DPP) and intense fluorescence at, respectively, 554 nm ( $\Phi_F$  0.36) and 609 nm ( $\Phi_F$  0.19). The phenyl-DPP dye exhibits a maximum broad band lasing efficiency of 14.6% and a maximum narrow band lasing efficiency of 9.5% with a wide tunable range (554 nm to 616 nm) on excitation with a second harmonic of a Q-switched Nd:YAG (532 nm) laser in MeOH/H<sub>2</sub>O. The lasing efficiency remains unaffected for hours. The thiophene-DPP dye does not show any lasing action.

### Introduction

The 3,6-diaryl-2,5-dihydro-1,4-diketopyrrolo[3,4-c]pyrrole (DPP) class of compounds are widely known as high-performance pigments used in inks, paints, and plastics,<sup>1</sup> owing to their brilliant shades and outstanding photostability. The strong fluorescence and moderate Stokes shifts of the DPP dyes<sup>2</sup> make them ideal candidates for designing chemosensors,<sup>3a</sup> light-emitting diodes,<sup>3b</sup> dye-sensitized solar cells,<sup>3c,d</sup> organic thinfilm transistors,<sup>4</sup> bulk heterojunction organic solar cells<sup>5</sup> and solid state lasers.<sup>6</sup> But their insolubility in common organic solvents because of strong intermolecular hydrogen bonding and  $\pi$ - $\pi$  interactions restricts their use in many applications. Thus the development of new synthetic routes to improve the solubility of these dyes is very important.

Replacement of the lactam N–H protons improves the solubility,<sup>7</sup> yet making them soluble in highly polar medium still remains a challenge. In the present study, we designed and developed a novel strategy to make DPP dyes soluble in polar organic solvents and in aqueous mixtures. Two new DPP dyes, **3** 

and **6**, were synthesised and their photo-physical properties were examined. The dyes were designed to contain phenyl or thiophene moieties as the 3,6-diaryl groups in order to provide different coloured DPP dyes (red and purple respectively). The sulfobetaine moiety is known to retain its zwitterionic character over a broad pH range and hence it was attached to the DPP core to improve the water solubility of the dyes. This strategy was based upon that developed during a research program aimed at solubilizing difluoroboron-dipyrromethane dyes (Bodipys) in water.<sup>8</sup>

Dye lasers are the most versatile and one of the most successful laser sources known today, contributing significantly to basic physics, chemistry, biology and other fields. Known since 1966, liquid dye lasers are expected to have high-efficiency, low laser threshold, wide wavelength-tunable range and long-lifetime coherent light sources.<sup>9a,b</sup> Although various dyes are known today for use in different wavelength regions,<sup>10</sup> the development of new organic materials having comparable or superior laser performances in terms of efficiency, tuning range, photochemical stability and photo-thermal characteristics is an important goal in dye laser chemistry. In the present study, we also examined the lasing properties as well as photo-chemical stability of new DPP dyes. To the best of our knowledge, the DPP dyes have not been used in liquid dye lasers so far.

### **Results and discussion**

### Syntheses

For the synthesis of the target dyes (Scheme 1), dimethylaminopropyne was coupled with the bromo dyes  $1^{11}$  and  $4^{12}$  respectively,

<sup>&</sup>lt;sup>a</sup> Bio-Organic Division, Bhabha Atomic Research Centre, Mumbai-400085, India. E-mail: smula46@yahoo.com

<sup>&</sup>lt;sup>b</sup> Laboratoire de Chimie Moléculaire et Spectroscopies Avancées (LCOSA), UMR 7515 au CNRS, Ecole Européenne de Chimie, Polymères et Matériaux, 25 rue Becquerel, 67087 Strasbourg Cedex 02, France. E-mail: ziessel@unistra.fr; http://www-lmspc.u-strasbg.fr/lcosa

<sup>&</sup>lt;sup>c</sup> Laser and Plasma Technology Division, Bhabha Atomic Research Centre, Mumbai-400085. India

<sup>&</sup>lt;sup>d</sup> Department of Chemistry, University of Pune, Pune-411007, India



via Sonogashira coupling to furnish compounds 2 and 5. In order to have reasonable solubility in organic solvents for the post-functionalization, dyes 1 and 4 carry lipophilic benzyl and ethylhexyl side chains respectively. The reaction was catalyzed by a Pd(0) species, generated in situ from a Pd(II) precursor and CuI. Compounds 2 and 5 were individually reacted with 1,3-propanesultone<sup>8</sup> in dimethylformamide or 1,2-dichloroethane to furnish the zwitterions 3 and 6 in 72% and 76% yields respectively. This is the first application of this strategy to solubilize DPP dyes. The new dyes 3 and 6 were soluble in polar solvents including aqueous mixtures and could be purified by reverse phase (C<sub>18</sub>-silica) column chromatography. These dyes were unambiguously characterized by NMR spectroscopy giving well-defined spectra excluding any formation of aggregates in DMSO, MeOH or MeOH-water solvents. A typical example is depicted in Fig. 1 giving a first order spectrum in which the bridging phenyl rings exhibit two doublets of an AA'BB' system. Diagnostic signals are provided by the methylene groups at 5.01 and 4.63 ppm, respectively, assigned to the DPP benzyl and dimethylaminopropyne residues. This assignment has safely been made by comparing the chemical shifts of the methylene group in compound 1 and analogues ( $\delta_{CH_2Ph}$  about 5.0 ppm in each case), and the methylene group in compound 5 and analogues ( $\delta_{CH_2C} \equiv c$  about 4.70 ppm in each case). The methylene group of the ethylhexyl lateral chain resonates as a doublet at about 3.90 ppm. The ammonium signal resonate at 3.15 ppm and the sultone signals were found as multiplets centered at 3.60, 2.50 and 2.10 ppm with the expected four



**Fig. 1** (a) <sup>1</sup>H NMR spectra of dye **3** in  $d_6$ -DMSO (S<sub>1</sub>) at rt and peak attribution. The insets represent the signal of protons **k** found in  $d_4$ -methanol (right hand side) and expansion of the benzyl protons windows (left-hand side). S<sub>2</sub> correspond to residual water. (b) <sup>13</sup>C NMR of dye **3** in  $d_6$ -DMSO.

protons integration for each signal. The methylene residue nearby the sulfonate resonates as a triplet at 2.50 ppm (Fig. 1a). The carbon spectra presented the expected six signals for the alkyl atoms, the ethynyl signals at 80.3 and 89.4 ppm and the expected aromatic CH (five signals) and CC (six signals). The lactam signal was found at 161.4 ppm (Fig. 1b).

### **Optical properties**

The absorption spectral profile of dye **2** in  $CH_2Cl_2$  was broad and centred at 488 nm with a moderately high absorption coefficient of log  $\varepsilon$  = 4.15 (Fig. 2 and Table 1). When excited in the absorption band at 450 nm dye **2** exhibits an intense fluorescence centered at 544 nm. This emission band is characterized by a vibrational-like structure which is weakly solvent dependent. The Stokes shift



Fig. 2 Absorption (black line), emission (dashed line) and excitation (dotted line) spectra of dye 2 in CH<sub>2</sub>Cl<sub>2</sub> at room temperature.

Table 1 Selected optical properties of the DPP dyes

Dyes	$\lambda_{abs} \ (nm)$	$\epsilon (M^{-1} cm^{-1})$	$\begin{array}{c} \lambda_{em} \ (nm) \end{array}$	$\begin{array}{c} \tau_{\mathrm{F}} \ (\mathrm{ns}) \end{array}$	${\Phi_{ m F}}^b$	Rad. rate, $k_{\rm r}^{\ c} (10^8 \ {\rm s}^{-1})$	Non-rad. rate, $k_{\rm nr}^{\ c} (10^8 \ {\rm s}^{-1})$
2	488	23 300	554	5.0	0.80	1.6	0.4
3	480	17500	554	5.4	0.36	0.7	1.2
6	576	23 000	609	2.8	0.19	0.7	2.9

<sup>*a*</sup> Measured at room temperature in CH<sub>2</sub>Cl<sub>2</sub> for dye 2, in MeOH/H<sub>2</sub>O (8/2, v/v) for dye 3 and 6. <sup>*b*</sup> Determined using  $\Phi = 0.88$  for Rhodamine 6G in ethanol as the reference,<sup>17</sup>  $\lambda_{exc} = 488$  nm for dyes 2 and 3, or determined using  $\Phi = 0.51$  for Cresyl Violet in ethanol as the reference,<sup>17</sup>  $\lambda_{exc} = 578$  nm for dye 6. <sup>*c*</sup> Radiative (Rad.) and non-radiative (Non-rad.) rates were calculated using the following equations:  $k_r = \Phi_F/\tau_F$ ,  $k_{nr} = (1 - \Phi_F)/\tau_F$ , assuming that the emitting state is produced with unit quantum efficiency.

(2440 cm<sup>-1</sup>) revealed significant change in the molecular structure in the excited state (Fig. 2).<sup>13</sup> This is likely due to the presence of the flexible aromatic side chains which can freely rotate along the C–C linking bond. This is in stark contrast to Bodipy dyes, which display emission profiles which mirror the absorption spectra due to the rigidity of the emitting dipyrromethene core.<sup>14</sup> The fluorescence spectral profile was broad and can be assigned as a single electronic transition. The fluorescence quantum yield of dye **2** was high (0.80) and the emission lifetime (5.0 ns) was comparable to those recorded for related organic dyes including Bodipys.<sup>15</sup> The excitation spectrum perfectly matches the absorption spectrum (Fig. 2) excluding the presence of aggregates or fluorescent impurities.

The substitution of the bromo-phenyl or bromo-thiophene in compounds **1** and **4** by alkyne substituents has little influence on the absorption and emissive properties of dyes **2** and **5**. Such weak effects have also been previously observed in similar derivatives.<sup>11</sup>

The absorption and emission profiles of dye **3**, recorded in pure MeOH or MeOH/H<sub>2</sub>O (8/2, v/v, Fig. 3), were essentially the same as those of dye **2**. Dye **3** had a yellow fluorescence, although its emission quantum yield (0.36) was about two times weaker than that of **2**. Importantly, the excited state lifetime (5.4 ns) of dye **3** in a polar medium was higher than that of **2** recorded in an aprotic (CH<sub>2</sub>Cl<sub>2</sub>) medium (Table 1). It was noticed that dye **3** was not completely soluble in pure



Fig. 3 Absorption (black line), emission (dashed line) and excitation (dotted line) spectra of dye 3 in MeOH/H<sub>2</sub>O (8/2, v/v) at room temperature.

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Fig. 4 Absorption (black line), emission (dashed line) and excitation (dotted line) spectra of dye 6 in MeOH/H<sub>2</sub>O (8/2, v/v) at room temperature.

water, forming aggregates with large absorption bands with maxima at 500 and 535 nm. An unresolved emission band spanning over 250 nm and peaking about 575 nm was observed in water with relatively low fluorescence quantum yields (about 7%). Under these aqueous conditions the excitation spectrum does not match the absorption spectrum. In strong contrast the excitation spectra of dye **3** in MeOH/H<sub>2</sub>O overlap with the absorption spectra proving that all transitions participate to the emission detected at 554 nm (Fig. 3).

The absorption and emission profiles of dye 6 in MeOH/H<sub>2</sub>O (8/2, v/v) are presented in Fig. 4. Similar spectra were obtained in pure MeOH but dye 6 is insoluble in pure water. The absorption band was quite broad, spanning over 180 nm. The 3,6-thiophene moieties of 6 extend the delocalization along the thiophene-lactam main axis as previously observed for related derivatives.<sup>16</sup> Consistent with this, the low energy absorption band of 6 was shifted bathochromically by about 96 nm compared to that of dye 3 (Table 1). The shape of the emission band was consistent with that expected for a singlet emitter. The emission band was also bathochromically shifted but only by 55 nm, which effectively reduced the Stokes shift (941  $\text{cm}^{-1}$ ) as compared to 3. Dye 6 showed reddish fluorescence but fluorescence lifetime (2.8 ns) and quantum yield (0.19) were also much lower than those of dye 3. The excitation spectrum is in good agreement with the absorption spectra (Fig. 4).

### Lasing characteristics

The lasing characteristics of dye **3** were evaluated in MeOH/H<sub>2</sub>O (8/2, v/v) solution. The concentration-dependent broadband lasing efficiency of dye **3** followed an expected pattern (Fig. 5), with a maximum lasing efficiency ( $\eta$ ) of 14.6% at a concentration of 2 mM. However, the narrow-band lasing efficiency ( $\eta_{max} = 9.5\%$ ) of the dye solution (1.8 mM) in MeOH/H<sub>2</sub>O (8/2, v/v), measured at 580 nm ( $\lambda_L$ ) using the second harmonic of a Q-switched (PRF-10 Hz, pulse width ~6 ns) Nd:YAG (532 nm) laser, was slightly less (Fig. 6). More significantly, dye **3** had a much wider wavelength tunability (554 nm to 616 nm), although less efficiency than commercially available Rh6G. The increased tuning range of dye **3** should be very useful



Fig. 5 Broadband lasing efficiency of dye 3 in MeOH/H<sub>2</sub>O (8/2,  $\nu/\nu$ ) determined by pumping with 532 nm radiation of a Q-switched pulsed Nd-YAG laser.



Fig. 6 Narrow band lasing efficiency of dye 3 in MeOH/H<sub>2</sub>O (8/2, v/v) determined by pumping with 532 nm radiation of a Q-switched pulsed Nd-YAG laser.

for its applications. The slope efficiency of the dye at  $\lambda_L$  with a threshold pump energy of 3 mW was 8.5% (Fig. 7).

It is important to mention that the aqueous mixture is always preferred over pure organic solvents as large amounts of solvent are required in a dye laser. This is for making safer dye lasers in terms of fire hazard, environmental pollution, and easy treatment and disposal of wastes. Also, due to the weaker dependence of its refractive index on temperature (dn/dT), water has higher photothermal figure of merit (*F*).<sup>18</sup> The high *F* value of water is particularly beneficial with high repetitionrate dye lasers to reduce the divergence of the dye laser beam.



Fig. 7 Dye laser slope efficiency of dye 3 at  $\lambda_{\rm L}$  in MeOH/H<sub>2</sub>O (8/2, v/v).



Fig. 8 Time-dependent broadband lasing efficiency of dye 3 in MeOH/H<sub>2</sub>O (8/2, v/v).

Unfortunately, dye 6 did not produce any lasing action light on excitation with the second harmonic of a Q-switched (PRF-10 Hz, pulse width ~ 6 ns) Nd:YAG (532 nm) laser. This may be attributed to the low fluorescence quantum yield, shorter excited state lifetime and smaller Stokes shift with respect to dye 3. The small Stokes shift would increase the ground state absorption (GSA) of the dye molecules at the high concentration used for the lasing experiments. Based on the above results, dye 3 was chosen for studying the photo-chemical stability.

### Photostability of dye 3

The time dependent broadband lasing efficiencies of dye **3** is shown in Fig. 8. The lasing efficiency remained unchanged over 2 h of exposure but started decreasing gradually thereafter. Even then, the lasing efficiency dropped by only 9% of its initial value after 4 h of exposure. These results clearly demonstrated that dye **3** is very stable under lasing conditions, promising for its long term use as a laser dye.

### Conclusions

Using a new strategy for the synthesis of DPP dyes soluble in polar solvents (alcohol or alcohol/water), two differently coloured-dyes were synthesized and their optical properties were evaluated. It provides the evidence that approach via sultone-chemistry gives rise to modified DPPs possessing good water solubility combined with useful optical properties. It will certainly have impact on functional dyes community especially on research focused on fluorescence imaging. One of the dyes, compound 3, showed a maximum narrow-band lasing efficiency of 9.5% and its wide wavelength tunability coupled with a very high stability under lasing conditions makes it a promising fluorophore for further investigations. Although dye 6 did not exhibit lasing behaviour, the present studies have established the efficacy of the strategy for developing laser dyes soluble in alcohol or aqueous alcohols. Further work is dedicated to the replacement of the benzyl or ethylhexyl lateral chains with water compatible solubilising chains such as polyethyleneglycol.

### **Experimental**

### **General details**

The <sup>1</sup>H and <sup>13</sup>C spectra were recorded at room temperature with a 200 MHz, 300 MHz, or 400 MHz spectrometer, using perdeuterated solvents as the internal standards. The <sup>1</sup>H and <sup>13</sup>C chemical shifts are given in ppm relative to the residual protiated solvent or the solvent, respectively. The FT-IR spectra were recorded as thin solid layers using an apparatus equipped with an ATR "diamond" apparatus. The steady-state emission and excitation spectra were recorded with a spectrofluorimeter (Fluoromax-4 Horiba Jobin Yvon). All fluorescence spectra were corrected. The following equation was used to determine the relative fluorescence quantum yield:

$$\phi(\mathbf{X}) = (A_{\mathrm{S}}/A_{\mathrm{X}})(F_{\mathrm{X}}/F_{\mathrm{S}})(n_{\mathrm{X}}/n_{\mathrm{S}})^{2}\phi(\mathbf{S})$$

where *A* is the absorbance at the excitation wavelength (in the range 0.01–0.1 a.u.), *F* is the area under the corrected emission curve, *n* is the refractive index of the solvents (at 25 °C) used in measurements, and the subscripts S and X represent standard and unknown, respectively. The following standards were used: Rhodamine 6G ( $\Phi_{\rm em} = 0.88$  in ethanol) and Cresyl Violet ( $\Phi_{\rm em} = 0.51$  in ethanol) as the references.<sup>17</sup> The luminescence lifetimes were measured with a spectrofluorimeter equipped with a R928 photomultiplier and a pulsed diode, connected to a delay generator, without using any filter for excitation. The emission wavelengths were selected by a monochromator. The lifetimes were deconvoluted with the adequate software, using a light-scattering solution (LUDOX) for the instrument response.

### Syntheses

Compound 2. To a degassed solution of 2,5-dibenzyl-3,6-bis-(4-bromophenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione 1 (220.0 mg, 0.35 mmol) and [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (25.0 mg, 0.04 mmol, 0.1 equiv.) in benzene/Et<sub>3</sub>N (22 mL/10 mL) were added CuI (10.0 mg, 0.05 mmol) and 1-dimethylamino-2-propyne (114 µL, 1.06 mmol, 3.0 equiv.). After heating the reaction mixture at 60 °C overnight, it was brought to room temperature, filtered through a pad of Celite, and concentrated under reduced pressure. The resultant solid taken in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was washed with aqueous saturated NaCl (20 mL) and then extracted with  $CH_2Cl_2$  (3  $\times$  50 mL) and dried over MgSO<sub>4</sub>. After concentration in vacuo, the residue was purified by column chromatography (silica gel, eluting with CH<sub>2</sub>Cl<sub>2</sub> followed by 5-15% EtOH/CH<sub>2</sub>Cl<sub>2</sub>) to furnish dye 2 (174.0 mg, 78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 2.37 (s, 12H), 3.49 (s, 4H), 4.99 (s, 4H), 7.15–7.35 (8 line-m, 12H), 7.61 (AB sys,  $J_{AB}$  = 7.6 Hz,  $\nu_O \delta$  = 97.3 Hz, 10H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 14.2, 22.7, 24.9, 29.1, 29.4, 29.7, 31.9, 44.1, 44.3, 45.8, 48.4, 48.7, 53.5, 63.4, 65.3, 69.7, 73.7, 84.9, 88.1, 110.1, 126.5, 126.7, 127.2, 127.5, 128.9, 129.0, 132.1, 137.3, 148.3, 162.7. ESI-MS in  $CH_2Cl_2 + 1\%$  TFA, positive mode, m/z (%): 630.2 (100), 573.2 (35). Anal. calcd for C<sub>42</sub>H<sub>38</sub>N<sub>4</sub>O<sub>2</sub>: C, 79.97; H, 6.07; N, 8.88. Found: C, 79.82; H, 5.79; N, 8.64%.

**Compound 3.** To a stirred solution of dye 2 (89.0 mg, 0.14 mmol) in anhydrous 1,2-dichloroethane (20 mL) under argon was added 1,3-propanesultone (124  $\mu$ L, 1.40 mmol). After heating the reaction mixture at 60 °C for 15 h, it was brought to room temperature, centrifuged, and the precipitate was washed

with EtOAc (3 × 10 mL) and finally with Et<sub>2</sub>O (3 × 10 mL). The residue was purified on a RP18 column, eluting first with H<sub>2</sub>O + 1% TFA, followed by H<sub>2</sub>O + 1% TFA/THF (H<sub>2</sub>O/THF = 9/1 to 7/3) to furnish dye 3 (89.0 mg, 72%). <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO),  $\delta$  (ppm): 2.03–2.15 (m, 4H), 2.53 (t, *J* = 6.9 Hz, 4H), 3.15 (s, 12H), 3.57–3.69 (m, 4H), 4.63 (s, 4H), 5.01 (s, 4H), 7.13 (d, *J* = 7.4 Hz, 4H), 7.19–7.37 (m, 6H), 7.80 (AB sys, *J*<sub>AB</sub> = 8.2 Hz,  $\nu_O \delta$  = 37.0 Hz, 8H); <sup>13</sup>C NMR (100.6 MHz, *d*<sub>6</sub>-DMSO),  $\delta$  (ppm): 19.0, 44.5, 47.6, 49.9, 54.1, 62.9, 80.3, 89.4, 109.5, 123.1, 126.2, 127.1, 128.1, 128.5, 128.7, 132.1, 137.1, 147.3, 161.4; ESI-MS in H<sub>2</sub>O/MeOH + 1% TFA, positive mode, *m*/*z* (%): 875.3 (100), 438.1 (45, doubly charged). Anal. calcd for C<sub>48</sub>H<sub>50</sub>N<sub>4</sub>O<sub>8</sub>S<sub>2</sub> + H<sub>2</sub>O: C, 64.55; H, 5.87; N, 6.27%. Found: C, 64.38; H, 5.65; N, 6.09%.

Compound 5. To a degassed solution of 3,6-bis(5-bromothien-2yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione 4 (138.8 mg, 0.203 mmol) and [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (7.1 mg, 0.010 mmol) in benzene/Et<sub>3</sub>N (15 mL/5 mL) were added CuI (3.1 mg, 0.016 mmol) and 1-dimethylamino-2-propyne (100 µL, 0.929 mmol, 4.5 equiv.). The reaction mixture was heated at 60 °C overnight. The concentrated residue was purified by column chromatography on silica gel by eluting with CH<sub>2</sub>Cl<sub>2</sub>/ EtOH (gradient from 100 to 90/10) to give dye 5 (115.9 mg, 83%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 0.85 (t, 6H, J = 7.4 Hz), 0.88 (t, 6H, J = 7.9 Hz), 1.18–1.40 (m, 16H), 1.81–1.90 (m, 2H), 2.39 (s, 12H), 3.55 (s, 4H), 3.97 (d, 2H, J = 7.4 Hz), 3.98 (d, 2H, J = 7.9 Hz), 7.28 (d, 2H, J = 4.1 Hz), 8.82 (d, 2H, J = 4.1 Hz); $^{13}\text{C}$  NMR (75 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 10.6, 14.1, 14.1, 23.2, 23.7, 28.5, 30.3, 39.3, 44.4, 46.2, 49.0, 78.4, 93.5, 108.9, 128.4, 130.2, 133.1, 135.5, 139.7, 161.7. ESI-MS in CH<sub>2</sub>Cl<sub>2</sub> + 1% TFA, positive mode, m/z (%): 687.3 (100). Anal. calcd C<sub>40</sub>H<sub>54</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C, 69.93; H, 7.92; N, 8.16%. Found: C, 69.74; H, 7.62; N, 7.85%.

Compound 6. As described earlier, reaction of 1,3-propanesultone (300 µL, 3.419 mmol, 20.0 equiv.) with dye 5 (116.0 mg, 0.169 mmol, 1.0 equiv.) in 1,2-dichloroethane (12 mL) at 80 °C for 2 days, followed by the usual isolation and chromatography (RP18 column, eluting with  $H_2O/THF + 1\%$  TFA ( $H_2O/THF = 8/2$  to 7/3) afforded dye 6 (124.0 mg, 76%). <sup>1</sup>H NMR (400 MHz, MeOD),  $\delta$  (ppm): 0.82–0.90 (m, 12H), 1.19-1.34 (m, 16H), 1.71-1.77 (m, 2H), 2.28-2.34 (m, 4H), 2.94–2.97 (m, 4H), 3.29 (s, 12H), 3.73–3.78 (m, 4H), 3.90 (d, 4H, <sup>3</sup>J = 7.2 Hz), 4.72 (s, 4H), 7.61 (d, 2H,  ${}^{3}J = 4.1$  Hz), 8.64 (d, 2H,  ${}^{3}J = 4.1$  Hz). <sup>13</sup>C NMR (100 MHz, MeOD),  $\delta$  (ppm): 10.9, 14.3, 14.4, 20.2, 23.7, 24.0, 24.8, 26.7, 29.4, 29.5, 30.7, 31.2, 31.3, 33.0, 33.1, 35.4, 40.4, 43.1, 44.5, 46.9, 51.3, 56.3, 58.7, 61.9, 64.5, 70.4, 72.3, 72.4, 84.9, 85.7, 85.7, 110.4, 126.6, 133.3, 136.0, 136.1, 136.8, 140.7, 162.4. ESI-MS in H<sub>2</sub>O/ MeOH + 1% TFA, positive mode, m/z (%): 931.3 (100), 466.3 (15, doubly charged). Anal. calcd for  $C_{46}H_{66}N_4O_8S_4 + 2H_2O$ : C, 57.12; H, 7.29; N, 5.79%. Found: C, 56.89; H, 7.03; N, 5.56%.

### Lasing studies

The lasing study of dye 3 in MeOH/H<sub>2</sub>O (8/2) was carried out using a narrow-band dye laser set-up, transversely pumped by the second harmonic (at 532 nm) output of a Q-switched pulsed Nd:YAG laser at a repetition rate of 10 Hz with ~6 mJ pulse energy and 5–7 ns fwhm pulses. A schematic of the dye laser setup is shown in Fig. 9. The dye laser was set up in Littrow configuration (with a grating of 2400 lines per mm) a with  $25 \times 4$ -prism pre-expander. The pump and dye laser



powers were measured by the same power meter (OPHIR). The dye solution of 3 (O.D. = 0.66 at 532 nm, 1 mm cell) in MeOH/H<sub>2</sub>O (8/2, v/v) was used to determine the lasing efficiency. The tuning curve of the dye solution was obtained by scanning the wavelength of dye laser through the gain profile of dye, and measuring the average pump and dye laser powers with a power meter. For determining the pump laser threshold ( $L_T$ ) and slope efficiency ( $\eta_s$ ) of the dye solution, the power of the dye laser, while tuning the laser wavelength at the peak of the respective gain curves, was measured as a function of input pump power at 532 nm.

### Photostability studies

The photostability of dye 3 was measured from the change in its lasing efficiency. For this, a MeOH/H<sub>2</sub>O (8/2, v/v) solution of dye 3 was exposed to the second harmonic of a Nd:YAG (532 nm) laser for 4 h and the lasing efficiencies were measured at different times (0–240 min).

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