Supporting Information

Novel Semisquaraine Regioisomers: Isolation, Divergent Chemical Reactivity and Photophysical Properties

Rekha R. Avirah,[1] Kuthanapillil Jyothish,[1] Cherumuttathu H. Suresh,[2]
Eringathodi Suresh[3] and Danaboyina Ramaiah[1]*

[1]Chemical Sciences and Technology Division, [2]Computational Modelling and Simulation, National Institute for Interdisciplinary Science and Technology (NIIST), CSIR, Trivandrum
and
[3]Analytical Science Division, Central Salt and Marine Chemicals Research Institute, Bhavnagar

*To whom correspondence should be addressed at:

Tel: +91 471 2515362. Fax: +91 471 2490186, 2491712

E-mail : rama@niist.res.in or d_ramaiah@rediffmail.com

1. Experimental Section

1.1. General Techniques

The equipment and procedure for spectral recordings are described elsewhere.[1] All melting points are determined on a Mel-Temp II melting point apparatus. The IR spectra were recorded on a Perkin Elmer Model 882 infrared spectrometer. Elemental analyses were done using a Perkin-Elmer series-II 2400 CHN analyzer. The electronic absorption spectra were recorded on a Shimadzu UV-3101 or 2401 PC UV-VIS-NIR scanning spectrophotometer. ^{1}H and ^{13}C NMR were recorded on a 300 MHz and 500 MHz Bruker advanced DPX spectrometer. All the solvents used were purified and distilled before use.

1.2. Materials

6-Ethoxy-*N*-methyl-2-quinaldinium iodide (**1a**), m.p. 182-183 °C (lit. m.p. 182-183 °C),[1] 6-hydroxy-*N*-methyl-2-quinaldinium iodide (**1b**), m.p. 238-239 °C (lit. m.p. 238-240 °C),[1] 6-(dimethylamino)-*N*-methyl-2-quinaldinium iodide (**1c**), m.p. 210-212 °C, *N*-ethylalcohol-2-quinaldinium iodide (**1d**), m.p. 128-130 °C, 6-hydroxy-4-methyl-*N*-methyl-2-quinaldinium iodide (**1e**), m.p. 224-226 °C and 6-iodo-*N*-methyl-2-quinaldinium iodide (**1f**), m.p. 222-223 °C, 6-ethoxy substituted semisquaraine dye **2a**, m.p. 184-186 °C (lit. m.p. 184-186 °C)[1] and 6-hydroxy substituted semisquaraine dye **2b**, m.p. 150-152 °C (lit. m.p. 150-152 °C)[1] were prepared by the reported procedures.[1] 4-Aminophenol was purchased from SD Fine Chemicals, India and used as such while squaric acid was a gift from Professor Waldemar Adam, University of Würzburg, Germany.

1.3. General Procedure for Synthesis of Semisquaraine Dyes 2a-e

A mixture of the corresponding quinaldinium salt (0.06 mmol), squaric acid (0.06 mmol) and quinoline (0.5 mL) was refluxed in a mixture of *n*-butanol and benzene (6 mL each, 1:1) with azeotropic distillation of water for 12 h. The solvent was distilled off under reduced pressure to obtain a residue which was chromatographed over silica gel. Elution of the column with a mixture (1:9) of methanol and chloroform gave the semisquaraine derivatives **2a-e**. These derivatives were recrystallised by vapour diffusion of petroleum ether from a mixture (1:4) of methanol and chloroform.

2a: (90%) m.p. 184-186 °C (lit. 184-186 °C);[1] IR (KBr): ν_{max} 1760, 1602 cm^{-1}; UV/Vis (CH_3OH): λ_{max} 478 nm; $\varepsilon_{max} = 1.90 \times 10^4\ M^{-1}cm^{-1}$; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.45 (d, *J* = 9.3 Hz, 1H), 7.84 (d, *J* = 9.3 Hz, IH), 7.63 (d, *J* = 9.4 Hz, 1H), 7.33 (d, *J* = 9.5 Hz, 1H), 7.09 (s, 1H), 6.15 (s, 1H), 4.71 (t, *J* = 6.6 Hz, 2H), 4.14 (t, *J* = 6.9 Hz, 2H), 4.05 (s, 3H), 1.78 (m, 5H), 1.49 (m, 2H), 0.96 ppm (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 188.2, 178.9, 176.9, 176.8, 156.9, 153.9, 136.8, 133.8, 126.8, 126.3, 122.9, 117.4, 109.8, 94.9, 72.5, 64.3, 37.3, 32.1, 18.6, 14.6, 13.7 ppm; FAB-MS (*m/z*): $[M]^+$ Calcd for $C_{21}H_{23}NO_4$, 353.16; Found, 353.16; Elemental analysis: Calcd for $C_{21}H_{23}NO_4$: C 71.37; H 6.56; N 3.96. Found: C 71.09; H 6.82; N 4.04.

2b: (95%) m.p. 150-152 °C (lit. 150-152 °C)[1]; IR (KBr): ν_{max} 1761, 1606 cm^{-1}; UV/Vis (CH_3OH): λ_{max} 475 nm; $\varepsilon_{max} = 1.91 \times 10^4\ M^{-1}cm^{-1}$; ^{1}H-NMR (500 MHz, CD_3OD): δ = 9.13 (d, *J* = 9 Hz, 1H), 8.16 (d, *J* = 9.5 Hz, 1H), 8.02 (d, *J* = 9.5 Hz, 1H), 7.88 (s, 1H), 7.43 (d, *J* = 9.5 Hz, 1H), 7.23 (s, IH), 6.26 (s, 1H), 4.58 (t, *J* = 6.5 Hz, 2H), 4.21 (s, 3H), 1.79 (m, 2H), 1.50 (m, 2H), 1.00 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6,):

δ = 185.1, 177.1, 175.3, 171.5, 155.7, 152.4, 137.4, 132.7, 127.0, 124.4, 123.0, 119.4, 111.5, 95.5, 70.6, 37.8, 31.6, 18.7, 13.5 ppm; FAB-MS (*m/z*): $[M]^+$ Calcd for $C_{19}H_{19}NO_4$, 325.139; Found, 325.140.

2c: (91%) m.p. 222-224 °C; IR (KBr): ν_{max} 1759, 1597 cm^{-1}; UV/Vis (CH_3OH): λ_{max} 472 nm; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.32 (d, *J* = 9.5 Hz, 1H), 7.83 (d, *J* = 9 Hz, 1H), 7.61 (d, *J* = 9.5 Hz, 1H), 7.23 (m, 1H), 6.79 (s, 1H), 6.12 (s, 1H), 4.69 (t, *J* = 6.5 Hz, 2H), 4.03 (m, 3H), 3.09 (s, 6H), 1.81 (t, *J* = 7 Hz, 2H), 1.50 (t, *J* = 7.5 Hz, 2H), 0.97 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 185.8, 179.1, 177.0, 174.2, 152.4, 148.2, 136.9, 131.0, 127.3, 125.8, 119.1, 116.9, 107.9, 94.7, 72.1, 40.3, 37.1, 32.2, 18.7, 13.7 ppm; FAB-MS (*m/z*): $[M]^+$ Calcd for $C_{21}H_{24}N_2O_3$, 352.43; Found, 352.54.

2d: (90%) m.p. 182-184 °C; IR (KBr): ν_{max} 1761, 1593 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} 509 nm; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.36 (d, *J* = 9 Hz, 1H), 7.95 (d, *J* = 9 Hz, 2H), 7.78 (d, *J* = 10 Hz, 2H), 7.53 (m, 1H), 6.34 (s, 1H), 4.75 (t, *J* = 6.5 Hz, 2H), 4.58 (t, *J* = 7 Hz, 2H), 4.24 (t, *J* = 5.5 Hz, 2H), 1.78 (t, *J* = 6.5 Hz, 2H), 1.46 (m, 2H), 0.96 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, CD_3OD): δ = 184.7, 181.2,

178.7, 172.8, 156.8, 140.7, 134.3, 130.9, 130.3, 128.1, 126.0, 123.8, 116.4, 97.4, 73.4, 60.3, 52.6, 33.3, 19.7, 14.1 ppm; FAB-MS (*m/z*): $[M+1]^+$ Calcd for $C_{20}H_{21}NO_4$, 340.39; Found, 340.45.

2e: (95%) m.p. 231-233 °C; IR (KBr): ν_{max} 1759, 1618, cm^{-1}; UV/Vis (CH_3OH): λ_{max} 472 nm; ^1H NMR (500 MHz, CD_3OD): δ = 9.01 (s, 1H), 8.02 (d, *J* = 9.5 Hz, 1H), 7.42 (d, *J* = 9.5 Hz, 1H), 7.33 (s, 1H), 6.19 (s, 1H), 4.54 (t, *J* = 6.5 Hz, 2H), 4.18 (s, 3H), 2.68 (s, 3H), 1.78 (m, 2H), 1.50 (m, 2H), 1.00 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 184.3, 177.2, 175.4, 170.5, 155.8, 151.6, 145.9, 132.4, 127.0, 124.4, 122.5, 119.8, 108.3, 95.2, 79.1, 70.6, 31.6, 19.2, 18.1, 13.5 ppm; FAB-MS (*m/z*): $[M+1]^+$ Calcd for $C_{20}H_{21}NO_4$, 340.01; Found, 340.50.

1.4. General Procedure for Synthesis of Semisquaraine Dyes 3a-e

A mixture of the corresponding quinaldinium salt (0.06 mmol), dibutylsquarate (0.06 mmol) and triethylamine (0.5 mL) in butanol (10 mL) was stirred at 25 °C for 12 h. The solvent was distilled off under reduced pressure to obtain a residue which was chromatographed over silica gel. Elution of the column with a mixture (1:10) of methanol and chloroform gave the semisquaraine derivatives **3a-e**. These derivatives were recrystallised from a mixture (1:4) of diethyl ether and dichloromethane.

3a: (98%) m.p. 202-204 °C; IR (KBr): ν_{max} 1766, 1696 cm^{-1}; UV/Vis (CH_3OH): λ_{max} 476 nm; ε_{max} = 4.12 × 10^4 $M^{-1}cm^{-1}$; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.55 (bs, 1H), 7.34-7.26 (m, 2H), 7.12 (d, *J* = 9 Hz, 1H), 6.91 (s, 1H), 5.2 (s, 1H), 4.81 (t, *J* = 6.5 Hz, 2H), 4.1 (t, *J* = 7 Hz, 2H), 3.66 (s, 3H), 1.86 (m, 2H), 1.51 (m, 5H), 1.006 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 193.2, 185.9, 184.4, 173.1, 155.0, 151.1, 134.4, 132.6, 124.7, 119.9, 115.6, 111.0, 85.9, 73.4, 64.0, 35.8, 32.1, 18.6, 14.7, 13.7 ppm; FAB-MS (*m/z*): $[M]^+$ Calcd for $C_{21}H_{23}NO_4$, 353.16; Found, 353.18; Elemental analysis: Calcd for $C_{21}H_{23}NO_4$: C 71.37; H 6.56; N 3.96. Found: C 71.30; H 6.74; N 4.02.

3b: (95%) m.p. 205-207 °C; IR (KBr): ν_{max} 1753, 1649 cm^{-1}; UV/Vis (CH_3OH): λ_{max} 475 nm; ε_{max} = 2.93 × 10^4 $M^{-1}cm^{-1}$; ^1H NMR (500 MHz, DMSO-d_6) δ 8.39 (bs, 1H), 7.65-7.59 (m, 2H), 7.12 (d, *J* = 9 Hz, 1H), 6.91 (s, 1H), 5.2 (s, 1H), 4.74 (t, *J* = 6.5 Hz, 2H), 3.7 (s, 3H), 1.79 (t, *J* = 7 Hz, 2H), 1.55 (m, 2H), 0.96 ppm (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 192.8, 184.7, 182.0, 171.2, 153.2, 150.1,

132.9, 124.2, 120.0, 116.7, 111.9, 84.6, 78.8, 72.3, 54.4, 35.6, 31.2, 17.8, 13.1 ppm; FAB-MS (*m/z*): $[M]^+$ Calcd for $C_{19}H_{19}NO_4$, 325.14; Found, 325.37.

3c: (94%) m.p. 212-214 °C; IR (KBr): ν_{max} 1757, 1681 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} 494 nm; ^1H NMR (300 MHz, $CDCl_3$) δ 8.46 (bs, 1H), 7.30 (m, 2H), 6.95 (d, *J* = 8.7 Hz, 1H), 6.61 (s, 1H), 5.23 (s, 1H), 4.75 (t, *J* = 6.3 Hz, 2H), 3.59 (s, 3H), 2.93 (s, 6H), 1.79 (m, 2H), 1.46 (m, 2H), 0.95 ppm (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 192.4, 184.3, 182.6, 171.4, 149.6, 145.9, 132.2, 130.7, 124.0, 123.1, 116.2, 114.3, 108.5, 84.4, 39.6, 34.6, 31.1, 28.6, 17.7, 12.7 ppm; FAB-MS (*m/z*): $[M]^+$ Calcd for $C_{21}H_{24}N_2O_3$, 352.43; Found, 352.48.

3d: (95%) m.p. 170-172 °C; IR (KBr): ν_{max} 1761, 1678 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} 471 nm; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.48 (bs, 1H), 7.52 (m, 2H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 9.5 Hz, 1H), 7.25 (m, 1H), 5.36 (s, 1H), 4.81 (t, *J* = 6.5 Hz, 2H), 4.37 (bs, 2H), 4.13 (t, *J* = 6.5 Hz, 2H), 1.86 (m, 2H), 1.51 (m, 2H), 1.01 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 193.3, 186.4, 185.0, 173.5, 151.0, 139.9, 133.2, 131.1, 128.7, 124.0, 123.6, 114.7, 99.9, 86.1, 73.6, 58.7, 49.1, 32.1, 18.7, 13.7; FAB-MS (*m/z*): $[M+1]^+$ Calcd for $C_{20}H_{21}NO_4$, 340.39; Found, 340.45.

3e: 95%, m.p. 230-232 °C; IR (KBr): ν_{max} 1757, 1676 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} 477 nm; ^1H NMR (300 MHz, DMSO-d_6): δ = 8.26 (bs, 1H), 7.63 (d, *J* = 9.3 Hz, 2H), 7.12 (d, *J* = 9.3 Hz, 1H), 7.05 (s, 1H), 5.16 (s, 1H), 4.74 (t, *J* = 6 Hz, 2H), 3.69 (s, 3H), 2.38 (s, 3H), 1.78 (t, *J* = 6.9 Hz, 2H), 1.45 (m, 2H), 1.28 ppm (t, *J* = 5.4 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 196.5, 190.0, 183.3, 167.2, 153.7, 140.6, 132.8, 124.9, 120.1, 117.5, 109.0, 99.4, 78.8, 72.5, 60.3, 35.9, 31.5, 18.9, 18.1, 13.8 ppm; FAB-MS (*m/z*): $[M+1]^+$ Calcd for $C_{20}H_{21}NO_4$, 340.39; Found, 340.50.

1.5. Synthesis of Semisquaric Acid 5

A solution of **3a** (1 mmol) in 5 mL acetic acid:water:2N HCl (50:50:4) is stirred for 4 h at room temperature. The resulting solution was extracted with $CHCl_3$ to give 30% of **5**. m.p. > 300 °C; IR (KBr): ν_{max} 3095, 1753, 1602, 1562, 1492, 1363 cm^{-1}; ^1H-NMR (300 MHz, DMSO-d_6): δ = 8.71 (d, *J* = 9.8 Hz, 1H), 7.14 (d, *J* = 8.5 Hz, 1H), 6.91 (m, 3H), 5.10 (s, 1H), 4.04 (m, 2H), 3.17 (s, 3H), 1.33 ppm (t, *J* = 6.9 Hz, 3H); FAB-MS (*m/z*): $[M+1]^+$ Calcd for $C_{17}H_{15}NO_4$, 298.31; Found, 298.10.

1.6. Synthesis of Unsymmetrical Squaraine Dye 4

A solution of **5** in *n*-butanol is refluxed for 12 h to yield the 1,3-isomer (**2a**), which was then refluxed with 1 mmol of 6-iodo-*N*-methyl-2-quinaldinium iodide (**1f**) in 1:1 butanol:benzene (5 mL) at 100 °C for 12 h. The solvent was distilled off under reduced pressure to obtain a residue, which was chromatographed over silica gel. Elution of the column with a mixture (1:9) of methanol and chloroform gave the unsymmetrical squaraine dye **4**. (90%) m.p. >300 °C; IR (KBr): ν_{max} 1614, 1564 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} 720 nm; ^1H NMR (500 MHz, $CDCl_3$): δ = 9.40 (d, *J* = 9.5 Hz, 1H), 9.15 (d, *J* = 9.5 Hz, 1H), 7.68 (s, 1H), 7.67 (d, *J* = 9 Hz, 1H), 7.55 (d, *J* = 9.5 Hz, 1H), 7.43 (d, *J* = 9.5 Hz, 1H), 7.20 (d, *J* = 9 Hz, 1H), 7.15 (d, *J* = 9.5 Hz, 1H), 6.99 (s, 1H), 6.97 (s, 1H), 5.87 (s, 1H), 5.66 (s, 1H), 4.12 (m, 2H), 3.85 (s, 3H), 3.60 (s, 3H), 1.46 ppm (t, *J* = 7 Hz, 3H); FAB-MS (*m/z*): $[M+1]^+$ Calcd for $C_{28}H_{23}IN_2O_3$, 563.40; Found, 563.21.

1.7. X-Ray Structure Analysis Data of Semisquaraine Dyes 2e and 3a

Crystal data for both the compounds **2e** and **3a** were collected at 110 K with a SMART APEX diffractometer equipped with a CCD area detector with monochromatized MoK_α radiation source (λ=0.7107Å). Crystal of suitable size was selected, mounted on the tip of a glass fibre and cemented using epoxy resin. Data collection, data reduction, and structure solution/refinement were carried out using the software package SMART APEX.[2] Empirical absorption corrections were performed using equivalent reflections with the program SADABS.[3] While solving the structure of **3a**, it was observed that two carbon atoms (C16, C17) of the terminal O-butyl group moiety was disordered at two positions and the occupancy factor for these disordered atoms were fixed using the FVAR command of the SHELXTL program.[4] All non-hydrogen atoms were refined anisotropically till convergence is reached for both the compounds. All hydrogen atoms for compound **2a** was stereochemically fixed, while only hydrogen atoms attached to the non-disordered atoms is geometrically fixed in the case of compound **3a**.

Crystal data for 2e: Crystal size : 0.18 x 0.11 x 0.04 mm^3; T=110(2) K; Monoclinic, space group $P2_1/c$; a=7.7932(8) Å b= 8.7008(9) Å, c= 24.571(3) Å, β= 96.845(2) °, V= 1654.2(3) $Å^3$, Z= 4, ρ_{calcd}=1.363gcm^{-3}, μ= 0.095 mm^{-1} ; F(000)= 720; 8006 reflections collected of which 2903 were unique with R_{int} = 0.0486; 230 parameters were refined; R1= 0.0958, wR2= 0.1988; Goodness-of-fit on F^2=1.263; max./min. residual electron density 0.412 / -0.350 e $Å^{-3}$; CCDC number-809673.

Crystal data for 3a: Crystal size : 0.24 x 0.14 x 0.08 mm^3; T=110(2) K; Triclinic, space group P-1 ; a= 8.6579(12)Å, b=9.1217(12)Å, c=13.0877(18)Å , α=85.292(2)° , β=75.940(2)°, γ= 62.358(2)°, V=887.6(2)$Å^3$, Z=2, ρ_{calcd}=1.288 gcm^{-3}, μ= 0.090 mm^{-1}, F(000)= 358; 6776 reflections collected of which 3416 were unique with R_{int} = 0.0308, 243 parameters were refined; R1= 0.1044, wR2= 0.2244; Goodness-of-fit on F^2=1.183; max./min. residual electron density 0.563 / -0.354e $Å^{-3}$. CCDC number -809674.

CCDC-809673 and CCDC-809674 contains the supplementary crystallographic data for compounds **2e** and **3a** associated with this manuscript. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1.8. Table S1. Selected bond distances(Å) and angles (º) for compounds **2e** and **3a.**

Atoms	**Bond distance in Å**	
	Compound 2e	**Compound 3a**
C(1)-C(6)	1.408(5)	1.391(5)
C(6)-N(1)	1.404(5)	1.408(5)
N(1)-C(7)	1.357(5)	1.374(4)
C(7)-C(8)	1.419(6)	1.439(5)
C(8)-C(9)	1.355(5)	1.342(5)
C(9)-C(1)	1.431(5)	1.433(5)
C(7)-C(10)	1.430(5)	1.395(5)
C(10)-C(11)	1.363(5)	1.401(5)
C(11)-C(12)	1.466(5)	1.501(5)
C(12)-C(13)	1.429(5)	1.515(5)
C(13)-C(14)	1.460(5)	1.457(5)
C(14)-C(11)	1.512(5)	1.408(5)
C(12)-O(2)	1.245(5)	----
C(14)-O(4)	1.224(5)	----
C(12)-O(1)	--	1.209(4)
C(13)-O(2)	--	1.226(4)
Atoms	**Bond angles in º**	
	Compound 2e	**Compound 3a**
C(3)-C(2)-C(1)	121.3(4)	119.7(3)
C(2)-C(3)-C(4)	119.3(3)	119.4(3)
C(5)-C(4)-C(3)	120.7(4)	121.7(3)
C(4)-C(5)-C(6)	120.5(4)	119.7(3)
N(1)-C(6)-C(5)	120.5(3)	120.9(3)
C(7)-N(1)-C(6)	121.7(3)	122.0(3)
N(1)-C(7)-C(8)	117.5(3)	116.5(3)
C(9)-C(8)-C(7)	123.2(3)	122.8(3)
C(8)-C(9)-C(1)	118.7(4)	120.1(3)
N(1)-C(7)-C(10)	120.4(4)	122.3(3)
C(11)-C(10)-C(7)	127.8(4)	126.6(3)
C(10)-C(11)-C(12)	128.6(4)	142.1(3)
C(13)-C(12)-C(11)	90.7(3)	89.0(3)
C(12)-C(13)-C(14)	92.5(3)	86.8(3)
C(13)-C(14)-C(11)	87.7(3)	95.1(3)
C(12)-C(11)-C(14)	89.0(3)	89.1(3)
O(2)-C(12)-C(11)	132.2(4)	----
O(2)-C(12)-C(13)	137.1(4)	----
O(4)-C(14)-C(13)	136.8(4)	----
O(4)-C(14)-C(11)	135.5(3)	
O(1)-C(12)-C(11)		137.0(3)

O(1)-C(12)-C(13)		134.0(3)
O(2)-C(13)-C(14)		138.4(4)
O(2)-C(13)-C(12)		134.8(3)

2. Supplementary Figures S1-S6

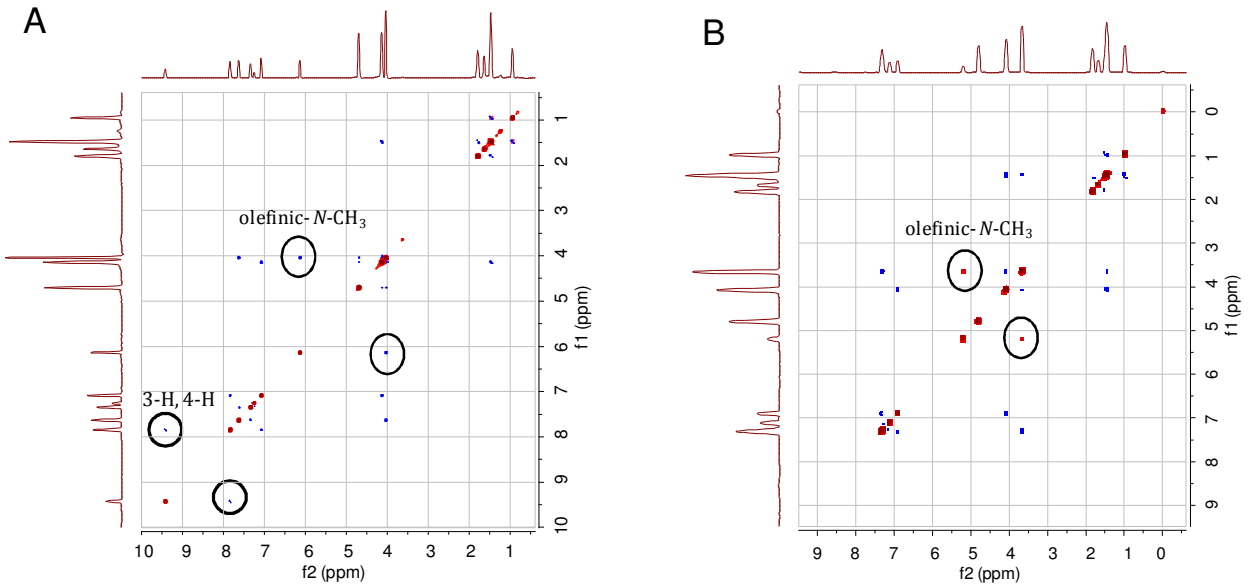


Fig. S1 ROESY spectrum for A) **2a** and B) **3a** in $CDCl_3$.

In the ^{1}H NMR spectrum of **2a**, the olefinic peak at δ 6.2 ppm showed 1 ppm downfield shift as compared to the isomer **3a** (δ 5.2 ppm) (Fig. S1). A notable difference in the spectra of the two isomers is the chemical shift value of the 3–H aromatic proton, which appears as a doublet at δ 9.5 ppm in **2a**. Interestingly, this proton is observed as a broad signal at δ 8.5 ppm in the case of **3a**, which splits into a well-resolved doublet (δ 8.7 ppm) with J = 9.5 Hz at 233 K (Fig. S1c). The splitting of the 3–H proton peak at lower temperatures can be attributed to the hydrogen bonding interaction with one of the squaryl oxygen atoms. DFT level electron density (ρ(r)) analysis confirmed the hydrogen bonding *via* the identification of a bond critical point (bcp). At the bcp, ρ(r) was 0.022 and 0.107 a.u. for **2a** and **3a**, respectively. Analysis of the calculated molecular electrostatic potential (MEP) at the DFT level augment the NMR-based assessment of the charge separation in **2a** and **3a**. The MEP shows larger positive region in the aromatic heterocycle and larger negative region in the squaryl portion in **2a** than **3a** (Fig. S3). Further, the theoretical calculations indicated that the 1,2–isomer is *ca*. 1.8 kcal/mol more stable than the 1,3–isomer.

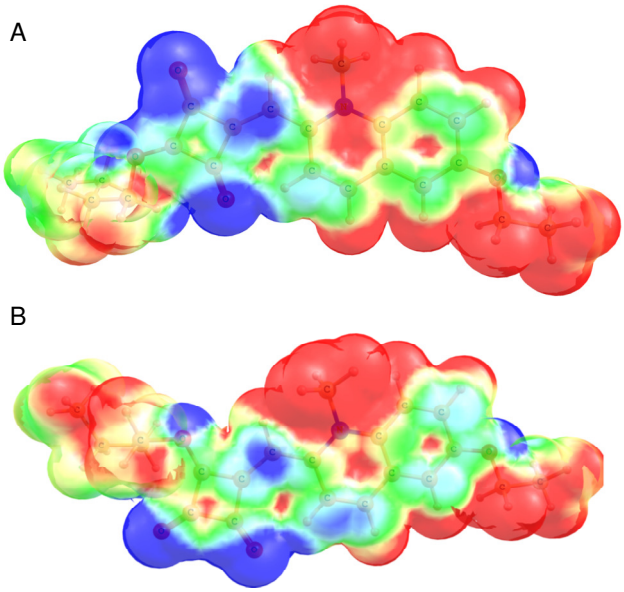


Fig. S2 Molecular electrostatic potential pasted on the Van der Waals' surface of A) **2a** and B) **3a** (colour coding from blue to red corresponds to -6 kcal/mol to +19 kcal/mol).

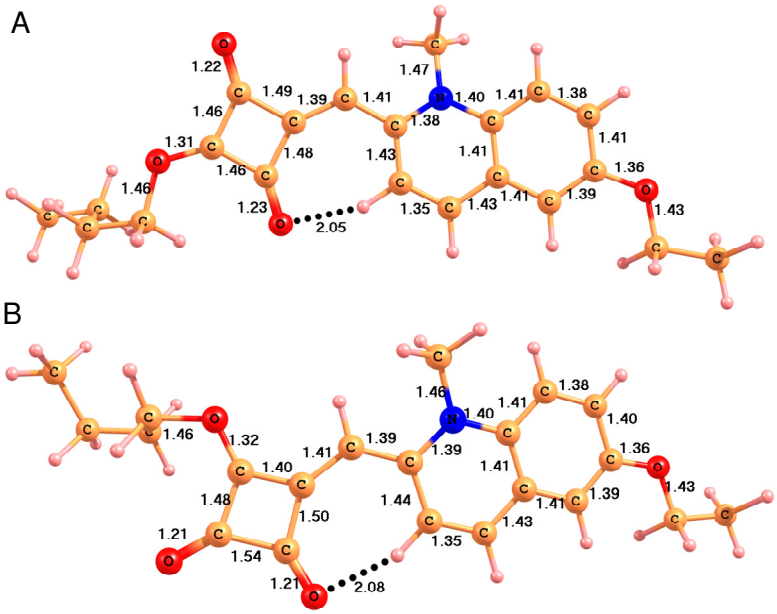
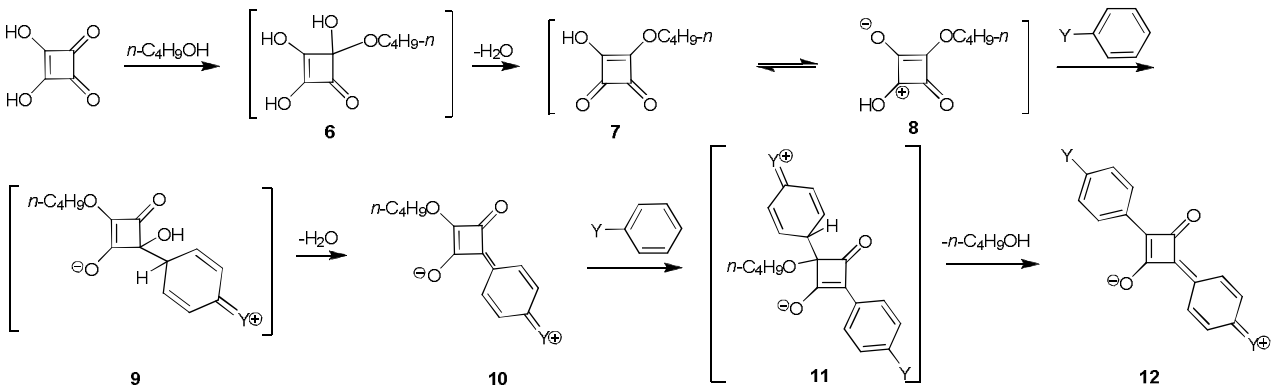


Fig. S3 Optimized geometries of A) **2a** and B) **3a** at B3LYP/6-311+G (d,p) level.



Scheme S1 Revised mechanism for the squaraine dye reaction through the isolation of the 1,3–isomer of the semisquaraine dye intermediate.

Illustration of the mechanism presented in Scheme S1 using theoretically derived structures and energetics. Calculations are done at PM6 with PCM option to incorporate solvation (*n*–butanol) effect[5-11]. Total mechanism is given in three parts in Figures S6-S8.

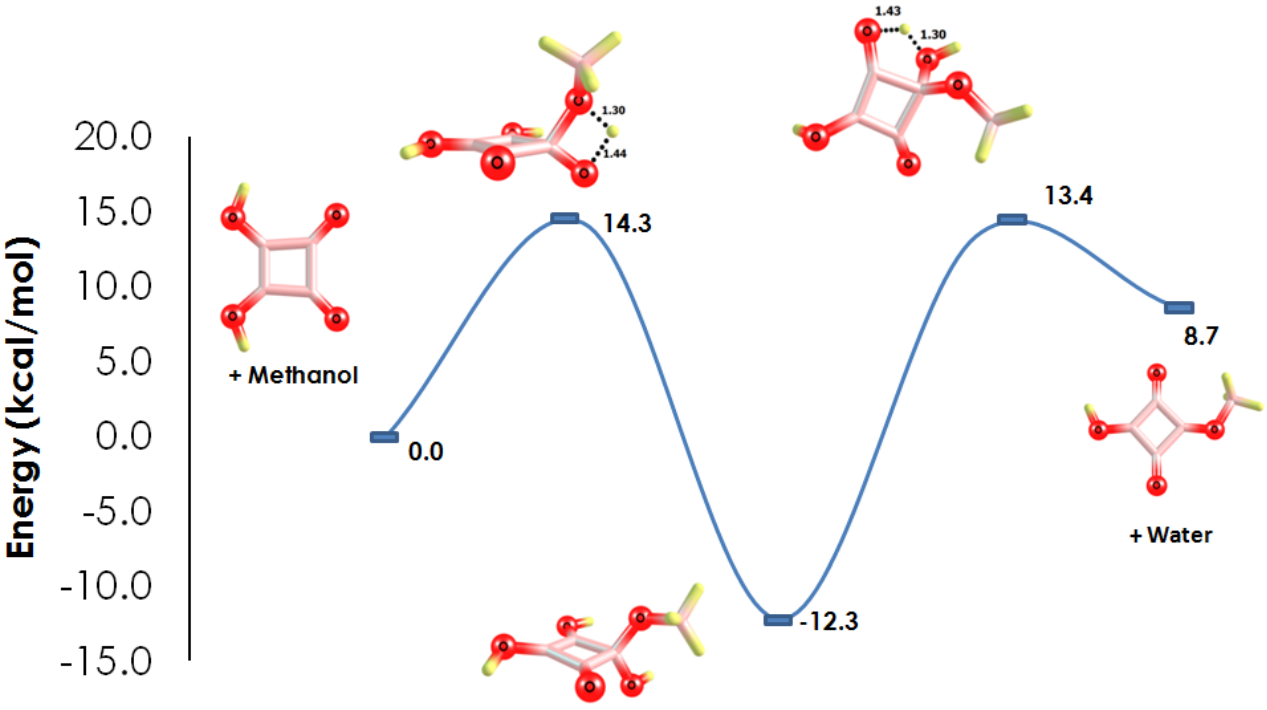


Fig. S4 Nucleophilic addition of alcohol to squaric acid to form alkoxy derivative.

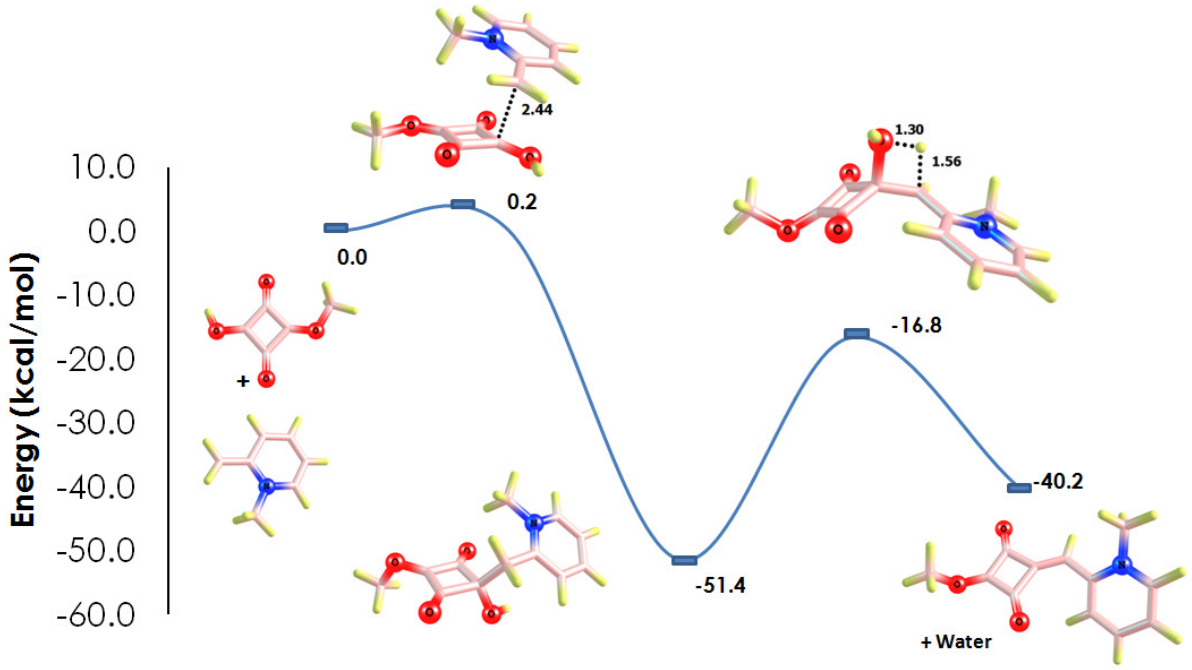


Fig. S5 Nucleophilic addition of enamine to alkoxy derivative of squaric acid to form semisquaraine dye.

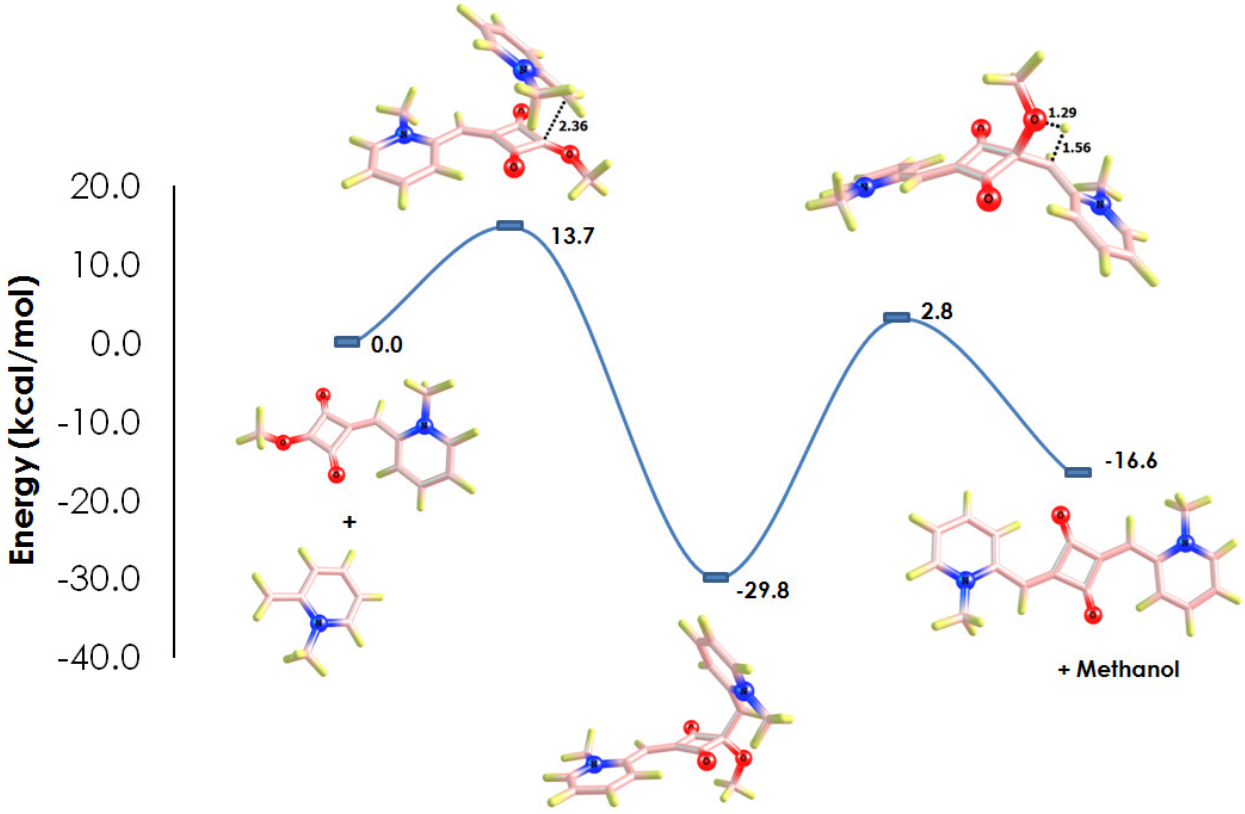


Fig. S6 Nucleophilic addition of enamine to semisquaraine dye to form squaraine dye.

3. References

1. K. Jyothish, K. T. Arun and D. Ramaiah, *Org. Lett.* 2004, **6**, 3965.
2. Bruker AXS: Madison, WI, 1999.
3. *SADABS, Empirical Absorption Correction Program*; University of Göttingen: Göttingen, Germany, 1997.
4. G. M. Sheldrick in *SHELXTL Reference Manual:* V*ersion 5.1*; Bruker AXS: Madison, WI, 1997.
5. A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648.
6. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* 1988, **37**, 785.
7. S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys*. 1980, **58**, 1200.
8. K. Wolinski, J. F. Hilton and P. Pulay, *J. Am. Chem. Soc.* 1990, **112**, 8251.
9. J. J. P. Stewart, *J. Mol. Model.* 2007, **13**, 1173.
10. J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev*. 2005, **105**, 2999.
11. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010.