Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information:

Different NIR Dye Scaffolds for Polymerization Reactions under NIR Light

Aude Bonardi[1,2], *Fabrice Bonardi*[3], *Guillaume Noirbent*[4], *Frédéric Dumur*[4], *Céline Dietlin*[1,2], *Didier Gigmes*[4], *Jean-Pierre Fouassier, and Jacques Lalevée**[1,2]

[1]Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

[2]Université de Strasbourg, France

[3]IBISC, Univ Evry, Université Paris-Saclay, 91025, Evry, France

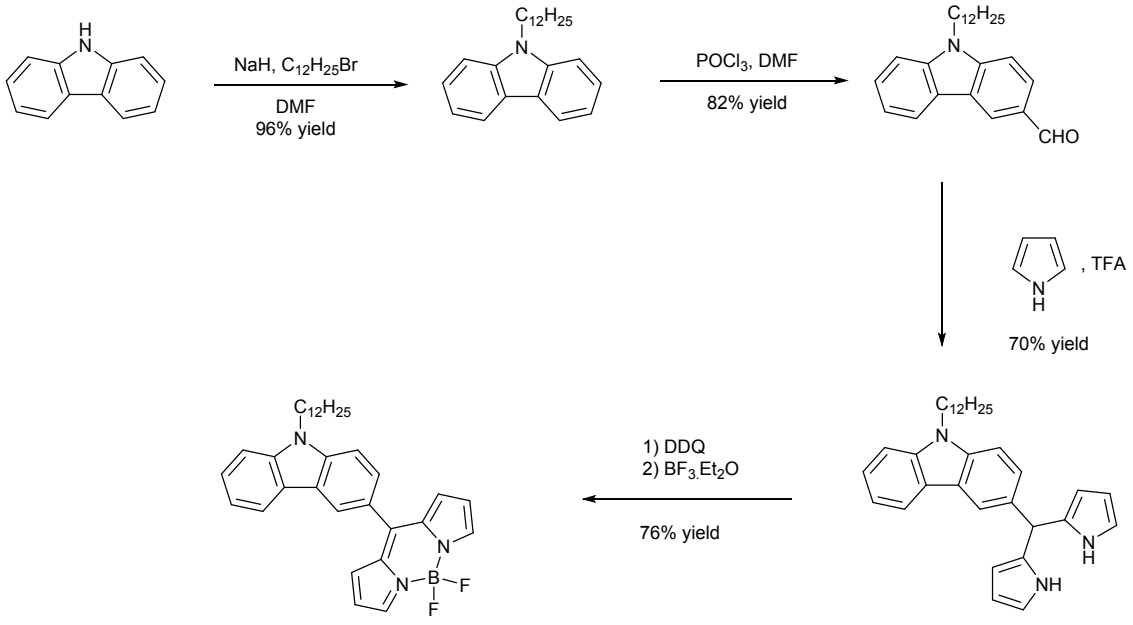
[4]Aix Marseille Univ, CNRS, ICR, UMR7273, F-13397 Marseille, France

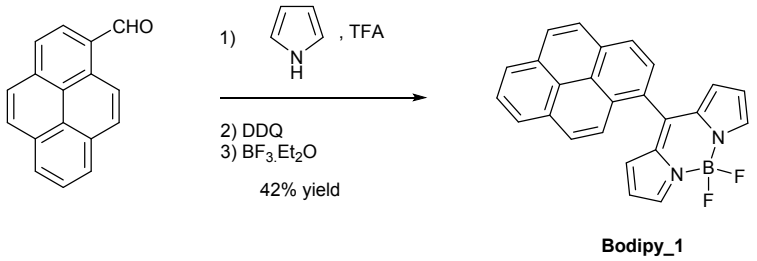
e-mail: ***jacques.lalevee@uha.fr***

Preparation of the different NIR dyes:

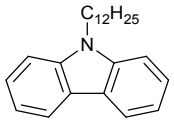
All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. Elemental analyses were recorded with a Thermo Finnigan EA 1112 elemental analysis apparatus driven by the Eager 300 software. 1H and 13C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole: ^{1}H (400 MHz) and ^{13}C (100 MHz). The ^{1}H chemical shifts were referenced to the solvent peak DMSO (2.49 ppm) and the ^{13}C chemical shifts were referenced to the solvent peak DMSO (49.5 ppm). All these carbazoles were prepared with analytical purity up to accepted standards for new organic compounds (>98%) which was checked by high field NMR analysis. **Porph_1** and **Porph_2** (Bioorg. Med. Chem., 2016, 24, 6040–6047), **Porph_3** (Dalton Trans., 2016, 45, 13284–13288), **SQ_1** (Organic Letters, 2011, 13, 3166–3169) were synthesized as previously reported, without modifications and in similar yields.

1) Preparation of the different Bodipys





Synthesis of 9-dodecyl-9H-carbazole

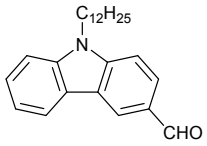


Chemical Formula: $C_{24}H_{33}N$
Exact Mass: 335.2613
Molecular Weight: 335.5350

Sodium hydride (0.468 g, 60% in mineral oil, 10.8 mmol, 1.80 eq.) was added carefully to a solution of carbazole (1.00 g, 5.98 mmol, 1.00 eq.) in anhydrous DMF (10 mL). After 20 min. of stirring, 1- bromododecane (1.51 g, 6.04 mmol, 1.01 eq.) was added and stirring was maintained overnight. After quenching with water, the solvent was removed under reduced pressure. The residue was suspended in water and the resulting solution was extracted several

times with diethyl ether. The organic layers were combined, dried over magnesium sulfate and the solvent removed under reduced pressure. The resulting oil was used without any further purification (1.93 g, 5.75 mmol, 96% yield). ^{1}H NMR $CDCl_3$ δ: 0.89 (t, 3H, J = 6.7 Hz), 1.25-1.42 (m, 18H), 1.88 (qt, 2H, J = 7.5 Hz), 4.30 (t, 2H, J = 7.2 Hz), 7.23 (td, 2H, J = 7.9 Hz, J = 1.0 Hz), 7.41 (d, 2H, J = 8.1 Hz), 7.47 (td, 2H, J = 7.0 Hz, J = 1.1 Hz), 8.11 (d, 2H, J = 7.7 Hz); ^{13}C NMR $CDCl_3$ δ: 14.1, 22.7, 27.3, 29.0, 29.3, 29.4, 29.5, 29.58, 29.60, 29.61, 31.9, 43.1, 108.6, 108.7, 120.3, 122.8, 125.5, 140.5; HRMS (ESI MS) m/z: theor: 335.2613 found: 335.2615 ($[M]^{+\cdot}$ detected).

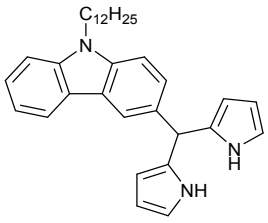
Synthesis of 9-dodecyl-9H-carbazole-3-carbaldehyde



Chemical Formula: $C_{25}H_{33}NO$
Exact Mass: 363.2562
Molecular Weight: 363.5450

DMF (10 mL) was added into a drying round-bottom flask and the system was cooled to 0 °C. A solution of $CHCl_3$ (100 mL) containing 9-dodecyl-9*H*-carbazole (7.7 g, 25 mmol) was then added following the addition of $POC1_3$ (10 mL). Then, the solution mixture was refluxed for 48 h. After most of $CHC1_3$ was removed, the residue was poured into ice water and pH was then adjusted to 7–8 by $NaHCO_3$. The water layer was extracted by CH_2C1_2 and the organic layer was washed by water for several times before dried with $MgSO_4$. The residue was purified by dissolution in a minimum of DCM followed by addition of an excess of pentane. Upon cooling in the fridge, a light beige solid formed. It was filtered off, washed several times with pentane and dried under vacuum (82% yield). ^{1}H NMR $CDCl_3$ δ: 0.88 (t, 3H, J = 6.7 Hz), 1.24-1.42 (m, 18H), 1.89 (qt, 2H, J = 7.4 Hz), 4.33 (t, 2H, J = 7.3 Hz), 7.32 (td, 1H, J = 7.8 Hz, J = 0.9 Hz), 7.44-7.48 (m, 2H), 7.52 (td, 1H, J = 8.2 Hz, J = 0.9 Hz), 8.01 (dd, 1H, J = 8.5 Hz, J = 1.5 Hz), 8.16 (d, 1H, J = 7.7 Hz), 8.61 (d, 1H, J = 1.2 Hz), 10.1 (s, 1H); ^{13}C NMR $CDCl_3$ δ: 14.1, 22.7, 27.2, 28.9, 29.31, 29.34, 29.46, 29.53, 29.58, 31.9, 43.4, 108.9, 109.4, 120.3, 120.7, 123.0, 123.1, 124.0, 126.7, 127.1, 128.5, 141.2, 144.1, 191.7; HRMS (ESI MS) m/z: theor: 363.2562 found: 363.5450 ($[M]^{+\cdot}$ detected).

Synthesis of 3-(di(1H-pyrrol-2-yl)methyl)-9-dodecyl-9H-carbazole

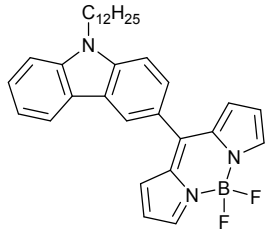


Chemical Formula: $C_{33}H_{41}N_3$
Exact Mass: 479.3300
Molecular Weight: 479.7120

9-Dodecyl-9*H*-carbazole-3-carbaldehyde (1.45 g, 4.0 mmol) and pyrrole (2.75 mL, 40 mmol) were added to a round-bottom flask and degassed with bubbling of argon for 10 min. Catalytic amount of TFA (30.6 µL, 0.4 mmol) was injected, and the solution was stirred at

room temperature for two hours. The solution was diluted with 50 mL of chloroform, washed with 0.1 M NaOH. The organic layer was dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was purified by column chromatography (SiO_2) using DCM as the eluent (70% yield). ^{1}H NMR $CDCl_3$ δ: 0.90 (t, 3H, J = 6.4 Hz), 1.24-1.46 (m, 18H), 1.88 (qt, 2H, J = 7.3 Hz), 4.29 (t, 2H, J = 7.2 Hz), 5.68 (brs, 1H), 6.01 (brs, 2H), 6.19-6.22 (m, 2H), 6.69-6.71 (m, 2H), 7.19 (t, 1H, J = 7.8 Hz), 7.35 (brs, 2H), 7.38-7.49 (m, 2H), 7.91-7.98 (m, 3H), 8.03 (d, 1H, J = 7.8 Hz); ^{13}C NMR $CDCl_3$ δ: 14.1, 22.7, 27.3, 29.0, 29.3, 29.4, 29.5, 29.6, 31.9, 43.2, 44.0, 107.1, 108.2, 108.4, 108.7, 108.9, 117.0, 118.8, 120.0, 120.4, 122.6, 126.3, 132.5, 133.4, 139.6, 140.8; HRMS (ESI MS) m/z: theor: 479.7120 found: 479.7122 ($[M]^{+\cdot}$ detected).

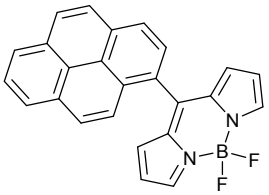
Synthesis of 3-(5,5-difluoro-5H-4l4,5l4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-10-yl)-9-dodecyl-9H-carbazole ***Bodipy_2***



Chemical Formula: $C_{33}H_{38}BF_2N_3$
Exact Mass: 525.3127
Molecular Weight: 525.4948

DDQ (280 mg, 1.23 mmol) was added to a solution of 3-(di(1*H*-pyrrol-2-yl)methyl)-9-dodecyl-9*H*-carbazole (590 mg, 1.23 mmol, 1 eq.) in toluene (25 mL). The reaction mixture was kept in the dark and stirred at room temperature. Following 5 minutes of stirring, triethylamine (1.2 mL, 8.61 mmol) was added followed immediately by boron trifluoride etherate (1.1 mL of BF_3-etherate, 8.61 mmol). The reaction mixture was stirred at room temperature for 1 hour, decanted from the dark green sludge which was washed with toluene (10 mL) and the combined toluene extracts washed with water, dried (Na_2SO_4) and evaporated to give a dark-green viscous oil. This was purified by column chromatography (silica gel, DCM) to give the compound as a red-orange crystalline solid (76% yield). ^{1}H NMR $CDCl_3$ δ: 0.88 (t, 3H, J = 6.5 Hz), 1.24-1.50 (m, 18H), 1.94 (qt, 2H, J = 7.1 Hz), 4.37 (t, 2H, J = 7.2 Hz), 6.57-6.58 (m, 2H), 7.04-7.05 (m, 2H), 7.31 (t, 1H, J = 7.5 Hz), 7.50-7.55 (m, 3H), 7.72 (dd, 1H, J = 8.5 Hz, J = 1.5 Hz), 7.95 (s, 2H), 8.14 (d, 1H, J = 7.7 Hz), 8.35 (d, 1H, J = 1.1 Hz); ^{13}C NMR $CDCl_3$ δ: 14.1, 22.6, 27.3, 29.0, 29.3, 29.4, 29.51, 29.57, 29.60, 29.61, 31.9, 43.5, 108.7, 109.3, 118.2, 119.9, 120.7, 122.5, 123.0, 123.6, 126.7, 128.7, 131.8, 135.2, 141.1, 142.1, 142.8, 149.0; ^{19}F NMR $CDCl_3$ δ: -145.15; HRMS (ESI MS) m/z: theor: 525.3127 found: 525.3129 ($[M]^{+\cdot}$ detected).

Synthesis of 5,5-difluoro-10-(pyren-1-yl)-5H-4l4,5l4-dipyrrolo[1,2-c:2',1'-f][1,3,2] diazaborinine ***Bodipy_1***

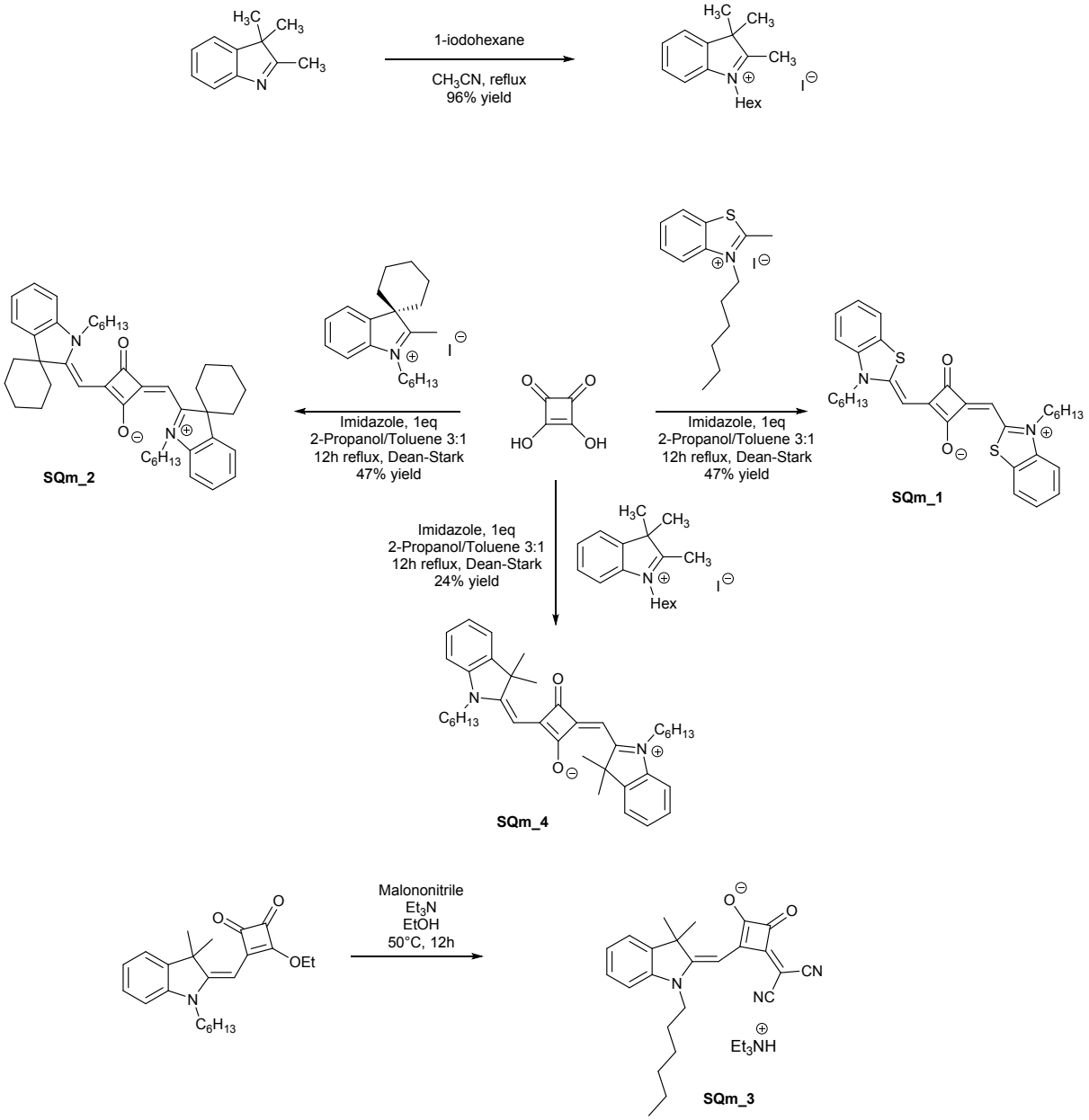


Chemical Formula: $C_{25}H_{15}BF_2N_2$
Exact Mass: 392.1296
Molecular Weight: 392.2158

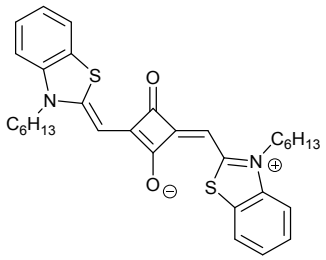
1-Pyrenecarboxaldehyde (921 mg, 4.0 mmol) and pyrrole (2.75 mL, 40 mmol) were added to a round-bottom flask and degassed with bubbling of argon for 10 min. Catalytic amount of TFA (30.6 μL, 0.4 mmol) was injected, and the solution was stirred at room temperature for two hours. The solution was diluted with 50 mL of chloroform, washed with 0.1 M NaOH. The organic layer was dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was dissolved in toluene (25 mL) and DDQ (910 mg, 4 mmol) was added. The reaction mixture was kept in the dark and stirred at room temperature. Following 5 minutes of stirring, triethylamine (3.9 mL, 28 mmol) was added followed immediately by boron trifluoride etherate (3.6 mL of BF_3-etherate, 28 mmol). The reaction mixture was stirred at room temperature for 1 hour, decanted from the dark green sludge which was washed with toluene (10 mL) and the combined toluene extracts washed with water, dried (Na_2SO_4) and evaporated to give a dark-green viscous oil. This was purified by column chromatography (silica gel, DCM) to give the compound as a crystalline solid (42% yield). ^{1}H NMR $CDCl_3$ δ: 6.47 (d, 2H, J = 4.1 Hz), 6.63 (d, 2H, J = 4.1 Hz), 8.03-8.14 (m, 6H), 8.14-8.29 (m, 5H); ^{13}C NMR $CDCl_3$ δ: 118.70, 118.72, 124.0, 124.2, 124.6, 124.9, 125.9, 126.2, 126.6, 127.1, 127.8, 127.9, 128.5, 129.0, 130.4, 130.7, 131.3, 131.7, 132.5, 136.5, 144.4, 146.5; HRMS (ESI MS) m/z: theor: 392.1296 found: 392.1299 ($[M]^{+\cdot}$ detected).

2) Preparation of the different Squarylium dyes

3-Hexyl-2-methylbenzo[*d*]thiazol-3-ium iodide [Org. Lett., 2011, 13, 3166–3169], 1'-hexyl-2'-methylspiro[cyclohexane-1,3'-indol]-1'-ium iodide [Dyes Pigm. 2011, 90, 146-162], were synthesized as previously reported, without modifications and in similar yields. 1,2,3,3-tetramethyl-3*H*-indol-1-ium iodide was purchased from Sigma Aldrich.



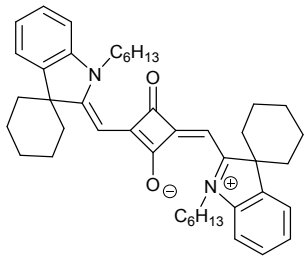
Synthesis of 2-((3-hexylbenzo[d]thiazol-2(3H)-ylidene)methyl)-4-((3-hexylbenzo[d]thiazol-3-ium-2-yl)methylene)-3-oxocyclobut-1-en-1-olate ***SQm_1***



Chemical Formula: $C_{32}H_{36}N_2O_2S_2$
Exact Mass: 544.2218
Molecular Weight: 544.7720

A mixture of 2-methyl-3-hexylbenzo[*d*]thiazol-3-ium iodide (2.78 g, 7.7 mmol), imidazole (0.52 mg, 7.7 mmol) and squaric acid (0.44 g, 3.8 mmol) in a solution composed of 480 mL of 2-propanol and 120 mL of toluene was refluxed for 12 h under a Dean-Stark trap to azeotropically remove the water formed during the reaction. After removing the solvent under reduced pressure, the dark residue was purified by column chromatography (silica gel, dichloromethane) to afford a green metallic solid (1.08 g, 1.8 mmol) in 47% yield. ^{1}H NMR ($CDCl_3$) δ: 0.90 (t, 6H, J = 6.9 Hz, 6H), 1.34 (m, 4H), 1.39-1.51 (m, 4H), 1.78-1.81 (m, 4H), 3.99-4.09 (m, 4H), 5.87 (s, 2H), 7.10 (d, 2H, J = 8.2 Hz), 7.18 (t, 2H, J = 7.6 Hz), 7.35 (t, 2H, J = 7.4 Hz, 2H), 7.52 (d, 2H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ: 13.9, 22.5, 26.6, 27.3, 31.4, 46.2, 85.3, 111.2, 122.1, 123.8, 126.9 128.8, 141.2, 159.4, 175.0; HRMS (ESI MS) m/z: theor: 544.2218 found: 544.2221 ($[M]^{+\cdot}$ detected). Analyses were consistent with those previously reported [Dyes Pigm., 2009, 81, 197-202].

Synthesis of 4-((1'-hexylspiro[cyclohexane-1,3'-indol]-2'-yl-1'-ium)methylene)-2-((1'-hexyl-spiro[cyclohexane-1,3'-indolin]-2'-ylidene)methyl)-3-oxocyclobut-1-en-1-olate ***SQm_2***

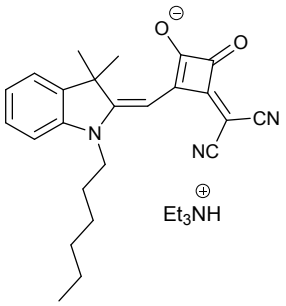


Chemical Formula: $C_{44}H_{56}N_2O_2$
Exact Mass: 644.4342
Molecular Weight: 644.9440

A mixture of 1'-hexyl-2'-methylspiro[cyclohexane-1,3'-indol]-1'-ium iodide (3.38 g, 7.7 mmol), imidazole (0.52 mg, 7.7 mmol) and squaric acid (0.44 g, 3.8 mmol) in a solution of 480 ml of 2-propanol and 120 mL of toluene was refluxed for 12 h under a Dean-Stark trap to azeotropically remove the water formed. The dark residue obtained after removing the solvent at reduced pressure was purified by column chromatography (silica gel, dichloromethane) to afford a green metallic solid (1.17 g, 1.8 mmol) in 47% yield. ^{1}H NMR ($CDCl_3$) δ: 0.86 (t, 6H, J = 7.5 Hz), 1.21-1.38 (m, 20H), 1.76-2.05 (m, 10H), 2.17-2.40 (m, 2H), 2.45-2.80 (m,

4H), 4.20 (t, 4H, J = 6.8 Hz), 6.04 (s, 2H), 7.01 (d, 2H, J = 7.8 Hz), 7.10 (t, 2H, J = 7.3 Hz), 7.32 (t, 2H, J = 7.6 Hz), 7.82 (d, 2H, J = 2.8 Hz); ^{13}C NMR ($CDCl_3$) δ: 14.0, 21.2, 22.5, 26.6, 27.2, 30.7, 31.5, 34.1, 44.5, 53.8, 110.3, 122.8, 125.8, 127.7, 134.6, 139.9, 143.2, 171.2, 179.4, 181.8; HRMS (ESI MS) m/z: theor: 644.4342 found: 644.4340 ($[M]^{+\cdot}$ detected).

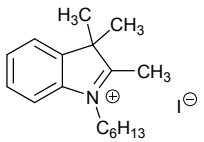
Synthesis of triethylammonium-3-dicyanomethylene-4-oxo-2-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidenmethyl)-1-cyclobuten-1-olate ***SQm_3***



Chemical Formula: $C_{30}H_{40}N_4O_2$
Exact Mass: 488,3151
Molecular Weight: 488,6760

This compound was synthesized by adapting a procedure reported in the literature [Dyes Pigm. 2005, 64, 125-134]. Triethylamine (0.94 mL, 6.7 mmol) was added dropwise to a mixture of 3-ethoxy-4-((1'-hexyl-3,3-dimethylindolin-2-ylidene)methyl)cyclo-but-3-ene-1,2-dione (2.5 g, 6.8 mmol), malononitrile (0.45 g, 6.8 mmol) dissolved in ethanol (20 mL) and the solution was stirred for 12 h at 50°C. Upon cooling, the targeted product was isolated as an orange solid (2.88 g, 86 % yield). ^{1}H NMR (Acetone-d_6) δ: 0.87 (t, 3H, J = 6.9 Hz). 1.12-1.54 (m, 6H), 1.64 (s, 6H), 1.65-1.78 (m, 2H), 3.79 (t, 2H, J = 7.3 Hz), 6.12 (s, 1H), 6.85-6.97 (m, 2H), 7.20 (t, 1H, J = 7.7 Hz), 7.28 (d, 1H, J = 7.2 Hz); ^{13}C NMR (Acetone-d_6) δ: 9.3, 14.4, 23.3, 27.2, 27.3, 28.0, 29.4, 29.5, 29.7, 29.9, 31.1, 30.3, 30.5, 32.5, 43.4, 47.5, 47.7, 108.4, 121.7, 122.6, 128.4; HRMS (ESI MS) m/z: theor: 488.3151 found: 488.3155 ($[M]^{+\cdot}$ detected)

Synthesis of 1-hexyl-2,3,3-trimethyl-3H-indolium iodide

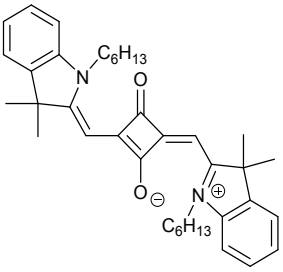


Chemical Formula: $C_{17}H_{26}IN$
Exact Mass: 371,1110
Molecular Weight: 371,3065

2,3,3-Trimethyl-3*H*-indole (15.91 g, 16 mL, 100 mmol) and 1-iodohexane (25.45 g, 17.7 mL, 120 mmol) were dissolved in acetonitrile (100 mL) and refluxed under nitrogen for 12 h. The solvent was evaporated under reduced pressure and the crude product was washed with diethyl ether three times, providing a violet sticky solid. It was used without any further

purification (96% yield). ^{1}H NMR DMSO-d_6 δ: 0.87 (t, 3H, J = 6.7 Hz), 1.25-1.45 (m, 6H), 1.54 (s, 6H), 1.83 (qt, 2H, J = 7.9 Hz), 2.85 (s, 3H), 4.46 (t, 2H, J = 7.7 Hz), 7.62 (m, 2H), 7.84-7.86 (m, 1H), 7.97-7.99 (m, 1H); ^{13}C NMR DMSO-d_6 δ: 13.8, 14.2, 21.8, 22.0, 25.5, 27.2, 30.7, 47.6, 54.1, 115.5, 123.5, 128.9, 129.3, 141.0, 141.8, 196.4; HRMS (ESI MS) m/z: theor: 385.0903 found: 385.0908 ($[M]^{+\cdot}$ detected).

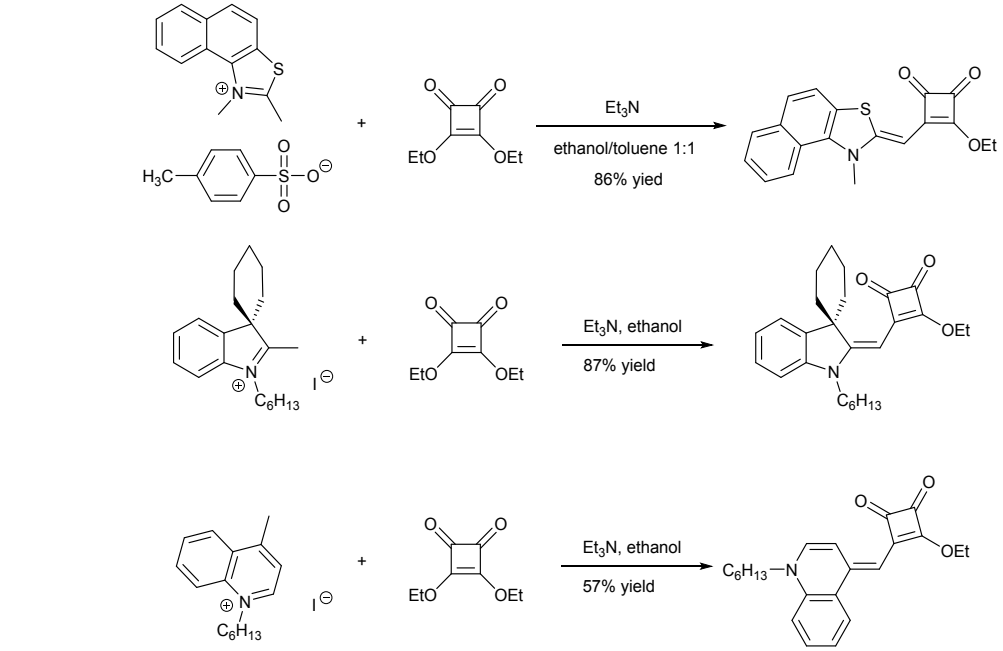
Synthesis of 4-((1-hexyl-3,3-dimethyl-indol]-2'-yl-1'-ium)methylene)-2-((1-hexyl-3,3-dimethylindolin-2-ylidene)methyl)-3-oxocyclobut-1-en-1-olate ***SQm_4***



Chemical Formula: $C_{38}H_{48}N_2O_2$
Exact Mass: 564.3716
Molecular Weight: 564.8140

A mixture of 1-hexyl-2,3,3-trimethyl-3*H*-indolium iodide (4.0 g, 11.0 mmol), imidazole (0.73 g, 11.0 mmol) and squaric acid (0.61 g, 5.4 mmol) in a solution composed of 480 mL of 2-propanol and 120 mL of toluene was refluxed for 12 h under a Dean-Stark trap to azeotropically remove the water formed during the reaction. After removal of the volatiles, the dark residue was purified by column chromatography (silica gel, dichloromethane) to afford a green solid (0.75 g, 1.3 mmol) in 24% yield. ^{1}H NMR ($CDCl_3$) δ: 0.89 (t, 6H, J = 8.2 Hz, 6H), 1.28-1.38 (m, 8H), 1.42-1.46 (m, 4H), 1.73-1.87 (m, 16H), 3.98-3.99 (m, 4H), 5.96 (s, 2H), 6.97 (d, 2H, J = 7.9 Hz), 7.14 (t, 2H, J = 7.4 Hz), 7.30 (t, 2H, J = 7.3 Hz), 7.35 (d, 2H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ: 13.9, 22.5, 26.7, 26.9, 27.0, 31.5, 43.7, 49.2, 86.5, 109.3, 122.2, 123.6, 127.7, 142.2, 142.5, 170.0, 179.6, 182.3; HRMS (ESI MS) m/z: theor: 564.3716 found: 564.3714 ($[M]^{+\cdot}$ detected).

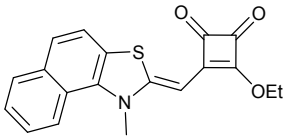
3) Preparation of the different Squaraine dyes



1,2-Dimethylnaphtho[1,2-*d*]thiazol-1-ium 4-methylbenzenesulfonate [J. Am. Chem. Soc. 2016, 138, 10112-10115] and 3-hexanoyl-2-methylbenzo[*d*]thiazol-3-ium iodide [Biosensors

and Bioelectronics 2015, 70,145–152] were synthesized as previously reported in the literature, without modifications and in similar yields.

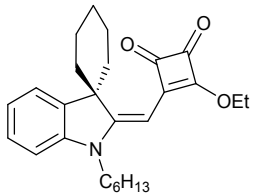
Synthesis of 3-ethoxy-4-((1-methylnaphtho[1,2-d]thiazol-2(1H)-ylidene)methyl)cyclobut-3-ene-1,2-dione



Chemical Formula: $C_{19}H_{15}NO_3S$
Exact Mass: 337.0773
Molecular Weight: 337.3930

A solution of 1,2-dimethylnaphtho[1,2-d]thiazol-1-ium 4-methylbenzenesulfonate (2.27 g, 5.9 mmol), triethylamine (0.6 g, 5.9 mmol, 0.82 mL) and ethyl squarate (0.5 g, 2.9 mmol, 0.43 mL) in ethanol:toluene (1:1, 60 mL) was refluxed overnight. The solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2) using DCM + 5% acetone as the eluent and isolated as a solid in 86% yield. ^{1}H NMR ($CDCl_3$) δ: 1.53 (t, 3H, J = 7.1 Hz), 4.08 (s, 3H), 4.85 (q, 2H, J = 7.1 Hz), 5.53 (s, 1H), 7.50-7.60 (m, 3H), 7.65 (d, 1H, J = 8.6 Hz), 7.92 (d, 1H, J = 7.5 Hz), 8.34 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ: 15.9, 39.7, 69.7, 80.1, 118.9, 120.9, 121.9, 123.7, 125.1, 125.9, 126.8, 129.8, 133.6, 136.5, 162.0, 172.6, 185.3, 185.6, 192.9; HRMS (ESI MS) m/z: theor: 337.0773 found: 337.0771 ($[M]^{+\cdot}$ detected).

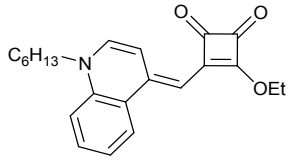
Synthesis of 3-ethoxy-4-((1'-hexylspiro[cyclohexane-1,3'-indolin]-2'-ylidene)methyl)cyclobut-3-ene-1,2-dione



Chemical Formula: $C_{26}H_{33}NO_3$
Exact Mass: 407.2460
Molecular Weight: 407.5540

A solution of 1'-hexyl-2'-methylspiro[cyclohexane-1,3'-indol]-1'-ium iodide (3.70 g, 9.0 mmol) in ethanol (25 mL) was added dropwise to a solution of triethylamine (1.3 g, 12.6 mmol) and ethyl squarate (1.5 g, 8.8 mmol) in ethanol (2 mL). The reaction mixture was stirred at room temperature for 20 h, and then refluxed for 3 h, while it turned green. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (elution: toluene:ethyl acetate from 9:1 to 1:1) to afford the product as a yellow solid in 87% yield. ^{1}H NMR $CDCl_3$ δ: 0.89 (t, 3H, J = 6.6 Hz), 1.22-1.43 (m, 8H), 1.52 (t, 3H, J = 7.1 Hz), 1.71-1.88 (m, 6H), 1.92-2.02 (m, 2H), 2.37-2.41 (m, 2H), 3.81 (t, 2H, J = 7.4 Hz), 4.89 (q, 2H, J = 7.0 Hz), 5.38 (s, 1H), 6.91 (d, 1H, J = 7.9 Hz), 7.03 (t, 1H, J = 7.5 Hz), 7.31 (t, 1H, J = 7.6 Hz), 7.80 (d, 1H, J = 7.4 Hz); ^{13}C NMR $CDCl_3$ δ: 13.9, 16.0, 21.0, 22.0, 22.5, 26.1, 26.6, 31.4, 33.8, 43.1, 52.2, 69.7, 81.4, 108.6, 121.6, 125.8, 127.7, 138.6, 143.3, 168.4, 173.6, 187.3, 187.4, 192.5; HRMS (ESI MS) m/z: theor: 407.5540 found: 407.5538 ($[M]^{+\cdot}$ detected)

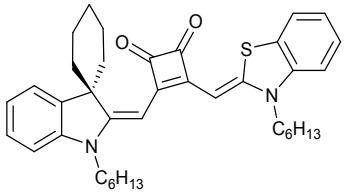
Synthesis of 3-ethoxy-4-((1-hexylquinolin-4(1H)-ylidene)methyl)cyclo-but-3-ene-1,2-dione



Chemical Formula: $C_{22}H_{25}NO_3$
Exact Mass: 351.1834
Molecular Weight: 351.4460

A solution of 1-hexyl-4-methylquinolin-1-ium iodide (3.2 g, 9.0 mmol) in ethanol (20 mL) was added dropwise to a solution of triethylamine (1.33g, 13.2 mmol) and ethyl squarate (1.5 g, 8.8 mmol) in ethanol (10 mL). The reaction mixture was stirred at room temperature for 20 h, and then refluxed for 3 h. The product was isolated as a purple solid in 57% yield. ^{1}H NMR ($CDCl_3$) δ: 0.85 (t, 3H, J = 6.5 Hz), 1.05-1.35 (m, 6H), 1.47 (t, 3H, J = 7.1 Hz), 1.70-1.81 (m, 2H), 3.95 (t, 2H, J = 7.2 Hz), 4.80 (q, 2H, J = 7.1 Hz), 5.99 (s, 1H), 7.06 (d, 1H, J = 7.6 Hz), 7.21-7.28 (m, 2H), 7.51 (t, 1H, J = 7.7 Hz), 7.89 (d, 1H, J = 7.6 Hz), 8.06 (d, 1H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ: 13.9, 15.9, 22.5, 26.4, 28.7, 31.3, 53.3, 69.6, 91.4, 110.7, 115.4, 123.7, 123.1, 125.8, 131.3, 137.4, 138.3, 146.8, 174.4, 185.8, 186.8, 193.7; HRMS (ESI MS) m/z: theor: 351.1834 found: 351.1835 ($[M]^{+\cdot}$ detected)

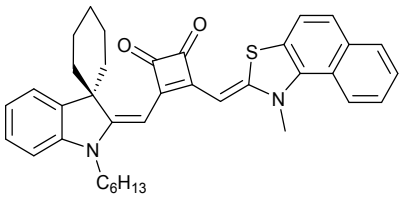
3-((1'-hexylspiro[cyclohexane-1,3'-indolin]-2'-ylidene)methyl)-4-((1-hexylbenzo[d]thiazol-2(1H)-ylidene)methyl)cyclobut-3-ene-1,2-dione ***SQ_2***



Chemical Formula: $C_{38}H_{46}N_2O_2S$
Exact Mass: 594.3280
Molecular Weight: 594.8580

A solution of 3-ethoxy-4-((1'-hexylspiro[cyclohexane-1,3'-indolin]-2'-ylidene)methyl)cyclo-but-3-ene-1,2-dione (1.16 g, 2.84mmol) in ethanol (25 mL) was added dropwise to a solution of triethylamine (0.3g, 2.9mmol) and 1-methyl-2-hexylbenzo[d]thiazol-1-ium iodide(1.13 g, 3.0mmol) in ethanol (10 mL). The reaction mixture was stirred under reflux during 3 days. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (elution: Dichloromethane: diethyl ether: pentane from 1:4:1) to afford the product (0.96g, 1.61mmol) in 57% yield. ^{1}H NMR ($CDCl_3$) δ: 0.86-0.94 (m, 6H), 1.20-1.54 (m, 12H), 1.67-2.03 (m, 12H), 2.69 (t, 2H, J = 11.0 Hz), 3.85 (t, 2H, J =7.1 Hz), 3.93-4.02 (t, 2H, J = 7.3 Hz), 5.30 (s, 1H), 5.54 (s, 1H), 6.87 (d, 1H, J = 7.9 Hz), 6.98 (t, 1H, J = 7.5 Hz), 7.04 (d, 1H, J = 8.4 Hz), 7.12 (t, 1H, J = 7.6 Hz), 7.30 (m, 3H), 7.46 (d, 1H, J = 7.7 Hz); HRMS (ESI MS) m/z: theor: 594.3280 found: 594.3283 ($[M]^{+\cdot}$ detected); Anal. Calc. for $C_{38}H_{46}N_2O_2S$: C, 76.7; H, 7.8; O, 5.4; Found: C, 76.6; H, 7.4; O, 5.3 %

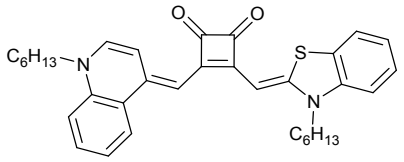
Synthesis of 3-((1'-hexylspiro[cyclohexane-1,3'-indolin]-2'-ylidene)methyl)-4-((1-methyl-naphtho[1,2-d]thiazol-2(1H)-ylidene)methyl)cyclobut-3-ene-1,2-dione ***SQ_3***



Chemical Formula: $C_{37}H_{38}N_2O_2S$
Exact Mass: 574.2654
Molecular Weight: 574.7830

A solution of 3-ethoxy-4-((1'-hexylspiro[cyclohexane-1,3'-indolin]-2'-ylidene)methyl)cyclo-but-3-ene-1,2-dione (0.944 g, 2.3 mmol) in DMF (30 mL) was added dropwise to a solution of triethylamine (0.24 g, 2.37 mmol) and 1,2-dimethylnaphtho[1,2-d]thiazol-1-ium 4-methylbenzenesulfonate (0.89 g, 2.3 mmol) in DMF (20 mL). The reaction mixture was stirred at 150°C for 12h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (elution: dichloromethane) to afford the product (0.42g, 0.73mmol) in 31% yield. ^{1}H NMR ($CDCl_3$) δ: 0.92 (t, 3H, J = 7.1 Hz), 1.20-1.54 (m, 8H), 1.67-2.03 (m, 8H), 2.69 (t, 2H, J = 7.0 Hz), 3.85 (t, 2H, J =7.1 Hz), 4.12 (s, 3H), 5.30 (s, 1H), 5.54 (s, 1H), 6.87 (d, 1H, J = 7.9 Hz), 7.01 (d, 1H, J = 7.5 Hz), 7.30 (d, 1H, J = 7.8 Hz), 7.46-7.57 (m, 3H), 7.64 (d, 1H, J = 8.2 Hz), 7.83 (d, 1H, J = 7.0 Hz), 7.93 (d, 1H, J = 8.0 Hz), 8.34 (d, 1H, J = 8.4 Hz); HRMS (ESI MS) m/z: theor: 574.2654 found: 574.2659 ($[M]^{+\cdot}$ detected); Anal. Calc. for $C_{37}H_{38}N_2O_2S$: C, 77.3; H, 6.7; O, 5.6; Found: C, 77.0; H, 6.4; O, 5.3 %

Synthesis of 3-((1-hexylquinolin-4(1H)-ylidene)methyl)-4-((1-hexylbenzo[d]thiazol-2(1H)-ylidene)methyl)cyclobut-3-ene-1,2-dione ***SQ_4***



Chemical Formula: $C_{34}H_{38}N_2O_2S$
Exact Mass: 538,2654
Molecular Weight: 538,7500

A solution of 3-ethoxy-4-((1-hexylquinolin-4(1*H*)-ylidene)methyl)cyclo-but-3-ene-1,2-dione (1.0 g, 2.84 mmol) in ethanol (25 mL) was added dropwise to a solution of triethylamine (0.3 g, 2.9 mmol) and 1-methyl-2-hexylbenzo[*d*]thiazol-1-ium iodide (1.13 g, 3.0 mmol) in ethanol (10 mL). The reaction mixture was stirred under reflux for 3 days. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (elution: dichloromethane: diethyl ether: pentane from 1:4:1) to afford the product (0.82 g, 1.52 mmol) in 53% yield. ^{1}H NMR ($CDCl_3$) δ: 0.86-0.94 (m, 6H), 1.27-1.50 (m, 12H), 1.74-1.81 (m, 4H), 3.87 (t, 2H, J = 7.3 Hz), 3.93-4.02 (t, 2H, J = 7.3 Hz), 5.51 (s, 1 H), 5.98 (s, 1H), 6.92 (d, 1H, J = 7.8 Hz), 6.97 (d, 1H, J = 8.2 Hz), 7.04 (t, 1H, J = 7.4 Hz), 7.17-7.28 (m, 3H), 7.38 (d, 1H, J = 7.3 Hz), 7.42-7.51 (m, 1H), 7.95-8.04 (m, 2H); ^{13}C NMR ($CDCl_3$) δ: 13.9, 14.0, 22.49, 22.51, 26.4, 26.5, 26.6, 28.6, 30.9, 31.4, 45.5, 52.8, 81.5, 93.7, 110.3, 110.6, 115.1, 121.7, 122.7, 123.5, 124.0, 125.2, 126.4, 127.3, 130.6, 136.3, 138.5,

141.3, 143.8, 157.4, 174.5, 175.2, 191.5, 192.2; HRMS (ESI MS) m/z: theor: 538.2654 found: 538.26.52 ([M]$^{+\cdot}$ detected)