

Excited State Photophysics of Squaraine Dyes for Photovoltaic Applications: an Alternative Deactivation Scenario

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Materials and method

Synthesis

General remarks

All the chemicals were purchased from Sigma Aldrich, except otherwise stated. The 2,3,3-trimethyl-3H-indole-5-carboxylic acid was supplied by Intatrade Chemicals GmbH, and was used without any further purification. All microwave reactions were performed in a single-mode Biotage Initiator 2.5. TLC was performed on silica gel 60 F254 plates using DCM and methanol (90:10) as eluents. ESI-MS spectra were recorded using a LCQ Deca XPThermo Advantage Max plus spectrometer (Thermo Finnigan), with electrospray interface and ion trap as mass analyzer. The flow injection effluent was delivered into the ion source using nitrogen as sheath and auxiliary gas.

Note that the name of the molecules (VG1-C8, VG2-C8 and VG4-C8) represent only internal reference codes. Since VG1-C8 and VG2-C8 have been already published under these codes, we decided to report them without altering their names, to avoid confusion with previous literature.

¹H NMR (600 MHz) and ¹³C-NMR (151 MHz) spectra were recorded on a Jeol ECZ-R 600 NMR in DMSO_{d6} using the DMSO signal as a reference.

Synthetic procedures

5-carboxy-2,3,3-trimethyl-1-octyl-3H-indol-1-ium iodide, VG1-C8 and VG2-C8 were synthesized as previously reported in the literature¹⁻³.

Triethylammonium 3-(1,3-dioxo-1H-inden-2(3H)-ylidene)-2-hydroxy-4-oxocyclobut-1-enolate (1)

3,4-diethoxycyclobut-3-ene-1,2-dione (0.44 ml, 3.0 mmol) and 1,3-indandione (658 mg, 4.5 mmol) were dissolved in ethanol (15 ml) at 55°C. Then, triethylamine (TEA, 0.63 ml, 4.5 mmol) was added dropwise to the mixture which assumed a dark red coloration. It was then heated at reflux for 4 hours, cooled down to room

temperature, ethanol was removed to obtain a black-brown viscous liquid which was then purified by flash chromatography (up to $\text{CHCl}_3/\text{CH}_3\text{OH} = 70/30$) (515 mg, yield = 50 %).

UV-Vis (λ_{max}): 382 nm in MeOH.

ESI-MS: 241.18 (M⁻) 505.01 (2M+Na)

¹H-NMR (600MHz, DMSO- d_6): $\delta = 7.53$ (m, 2H), 7.43 (m, 2H), 3.10 (q, 6H), 1.17 (t, $J_1 = 6$ Hz, $J_2 = 6$ Hz, 9H).

¹³C-NMR (151MHz, DMSO- d_6): $\delta = 192.1, 191.5, 173.6, 139.1, 132.7, 120.4, 103.9, 42.3, 9.2$.

VG4-C8

5-carboxy-2,3,3-trimethyl-1-octyl-3H-indol-1-ium iodide (474 mg, 1.07 mmol), triethylammonium 3-(1,3-dioxo-1H-inden-2(3H)-ylidene)-2-hydroxy-4-oxocyclobut-1-enolate (**1**) (183 mg, 0.53 mmol) and toluene/*n*-butanol (1:1, 10 mL) were introduced in a microwave vial and heated at 160 °C for 20 min when TLC and UV-Vis spectra showed reaction completion. After solvent evaporation, the crude product was washed in hot acetone under stirring for 1 hour and filtered to obtain VG4-C8 as a dark blue powder (184 mg, yield = 41 %).

UV-Vis (λ_{max}): 676 nm in MeOH

ESI-MS: 835.44 (M⁺)

¹H NMR (600MHz, DMSO- d_6 , ppm): $\delta = 8.07$ (d, $J = 3$ Hz, 2H), 8.00 (dd, $J_1 = 6$ Hz, $J_2 = 3$ Hz, 2H), 7.81 (s, 2H), 7.60 (m, 2H), 7.54 (m, 2H), 7.50 (d, $J = 6$ Hz, 2H), 4.23 (m, 4H), 1.78 (m, 4H), 1.75 (s, 9H), 1.46 (m, 4H), 1.32 (m, 4H), 1.21 (m, 4H), 1.14 (m, 8H), 0.73 (t, $J_1 = 8$ Hz, $J_2 = 8$ Hz, 6H).

¹³C-NMR (151 MHz, DMSO- d_6 , ppm): $\delta = 190.7, 177.8, 172.3, 169.8, 169.2, 167.5, 145.8, 142.7, 140.5, 132.8, 130.8, 126.9, 123.7, 120.4, 111.2, 105.2, 96.2, 49.1, 44.6, 31.6, 29.2, 29.0, 26.5, 26.4, 22.6, 14.4$.

Pump and probe spectroscopy

For the non-degenerate pump and probe measurements, we employed an amplified Ti:sapphire laser with 4 mJ output energy, 1kHz repetition rate and a central energy of 1.59 eV (800 nm). Two pump energies were used namely, 400 nm (3.18 eV) and 650 nm (1.92 eV) excitation, with the latter excitation energy in resonance with the $\pi \rightarrow \pi^*$ transition. Excitation pulses at 400 nm, with pulse duration of 150 fs were obtained via second-harmonic generation in a Barium Borate (BBO) crystal. The 650 probe pulse was generated by using a visible

optical parameter amplifier (OPA).⁴ Pump pulses were focused on a 200 μm spot, keeping pump fluences at $\approx 1 \text{ mJ cm}^{-2}$. As a probe pulse, we used a broadband white light super-continuum generated in a CaF_2 window in the probe region from 340 nm to 800 nm.

The three dyes were dissolved in ethanol ($d = 0.789 \text{ mg/mL}$, viscosity = 1.2 mPa·s at 25 °C) with a concentration optimised to give an absorbance of ≈ 1 in a 1 mm thick cuvette (0.2 mg/mL). Given the lower solubility of the three molecules in triacetin ($d = 1.16 \text{ g/mL}$, viscosity = 17 mPa·s at 25 °C), we used a lower concentration in this solvent (0.02 mM) to give an absorbance of ≈ 0.8 , 0.4, and 0.5 O.D. for VG1, VG2, and VG4, respectively.

Computational details

In the VG1, VG2 and VG4 model systems the alkyl chains on the indolenine groups have been replaced by methyl groups. The SQ7 model system represents the smallest squaraine system with a polymethine chain of seven carbon atoms.

The ground state geometry of the VG1 model has been optimized using Møller-Plesset perturbation method (MP2) with the split-valence def2-SVP basis set,⁵ and the geometries of VG2 and VG4 have been obtained by density functional theory (DFT) calculations with the meta M05-2X hybrid functional and the Pople 6-31G(d,p) basis set.⁶ The M05-2X functional has been adopted because, having a large fraction of Hartree–Fock exchange, it yields more accurate results than standard hybrid functionals for donor–acceptor conjugate dyes.⁷⁻⁹ Energies of the excited states, as well as all the potential energy profiles, have been computed using the second order algebraic diagrammatic construction (ADC(2)) method with the triple- ζ def2-TZVP basis set.¹⁰ Minimum Energy Conical Intersections (MECI) have been located using a methodology developed by Martinez in which the conical intersection (CI) geometry is obtained without the expensive calculation of the non-adiabatic derivative couplings.¹²⁻¹⁵ ADC(2) calculation for energy and energy gradients employing a def2-SVP basis set have been used to obtain CI geometries. In order to use the ADC(2) level of electronic structure theory a locally modified version of the CIOpt software by Martinez has been interfaced with the Turbomole software package.¹⁶ It is worth clarifying that we are mainly interested in exploring new decay routes rather than assessing the detailed topography of the potential energy surfaces, and ADC(2) has proven to be a reliable tool in this respect.⁷⁻⁹

In order to corroborate the results obtained with the ADC(2) methodology we have performed Coupled Cluster calculations with single and double excitations (CCSD) within the equation-of-motion approach (EOM-CCSD) for the determination of the excitation energies of the model system SQ7, see figure 3. The geometry of the electronic ground state of SQ7 has been optimized at MP2 level with triple- ζ def2-TZVP basis, imposing C_{2h} symmetry.¹⁷ EOM-CCSD calculations have been performed using the Dunning correlation consistent double zeta basis set (cc-pVDZ)¹⁸. All calculations have been performed with the Gaussian 09 software.¹⁹ The results of EOM-CCSD calculations on the SQ7 system are reported in table S1.

Table S1. Excitations energies and oscillator strengths of SQ7 computed at EOM-CCSD level with a cc-pVDZ basis set. The transition to the D state having B_g symmetry is forbidden by symmetry in the C_{2h} point group.

Electronic state	Excitation energy (eV)	Oscillator strength
$S_1 (B_u)$	2.9565	0.9676
$D (B_g)$	2.9870	0.0
$S_2 (B_g)$	4.9815	0.0

¹H NMR

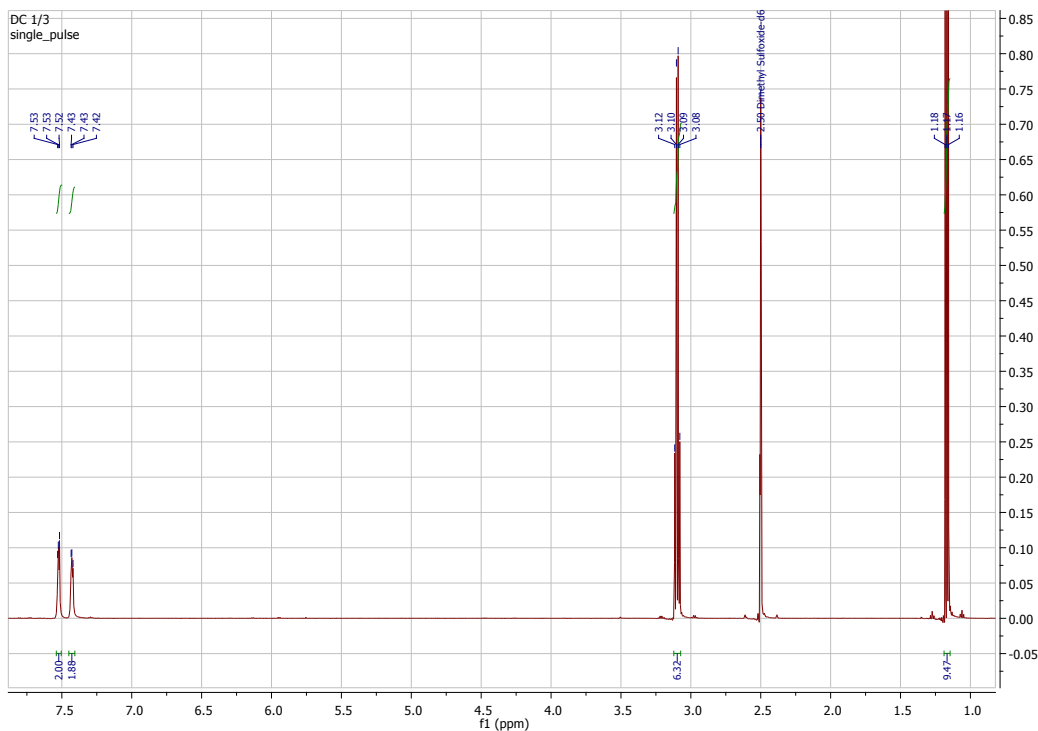


Figure S1. ¹H NMR of intermediate 1.

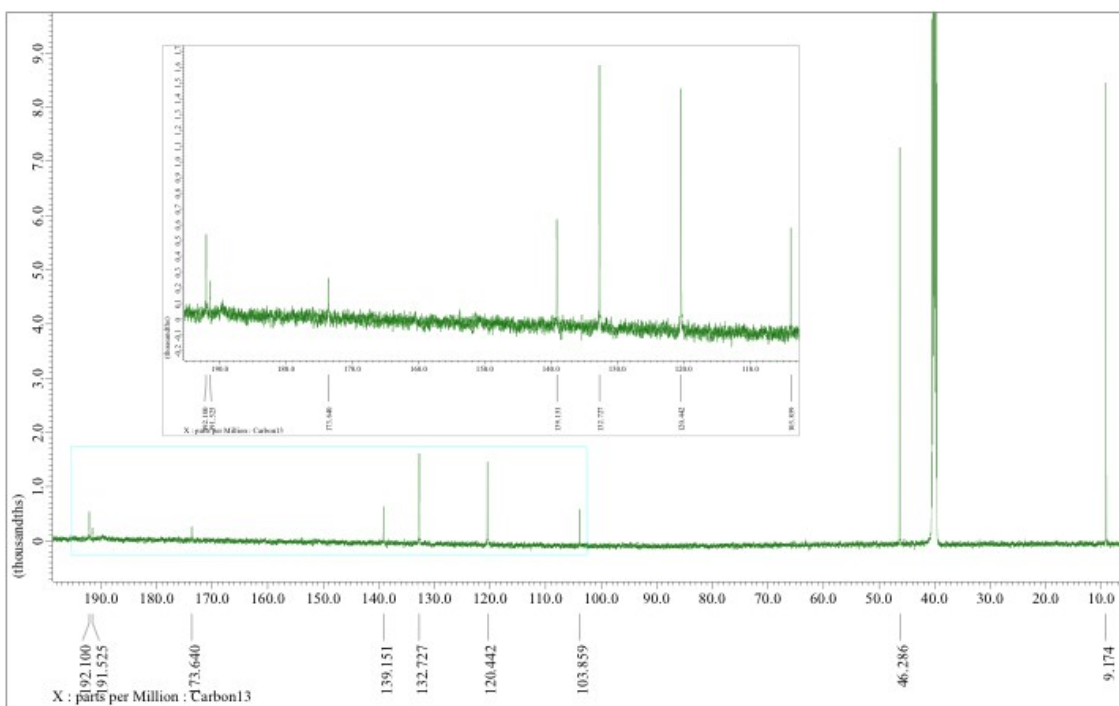


Figure S2. ¹³C NMR of intermediate 1.

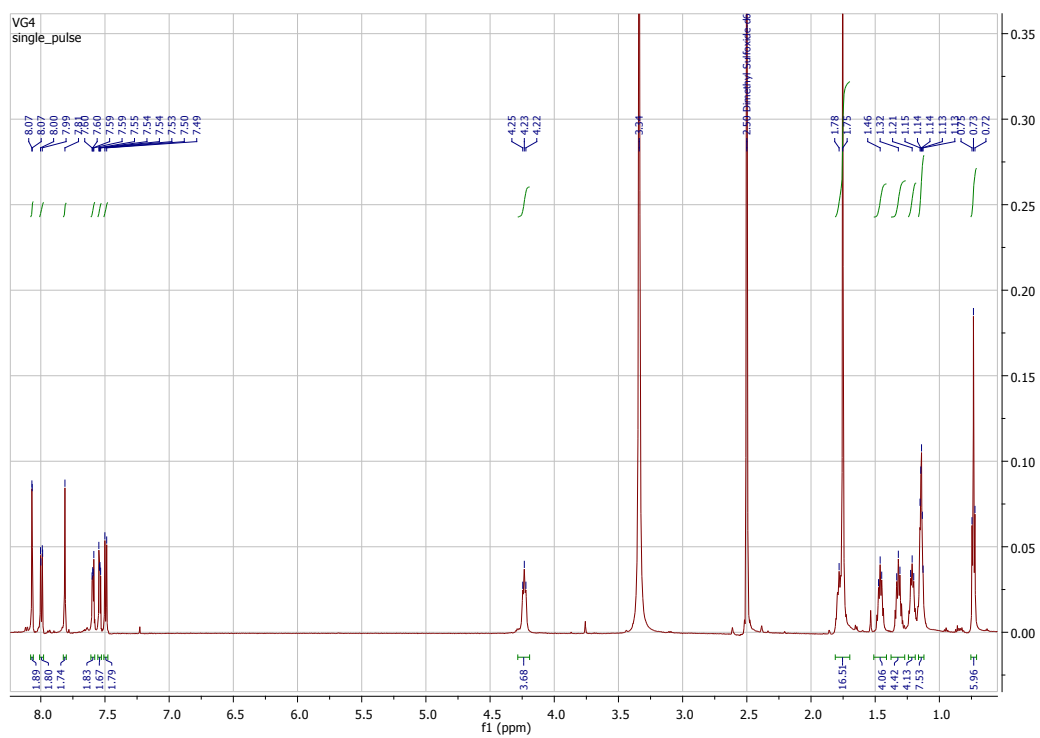


Figure S3. ¹H NMR of squaraine dye VG4-C8.

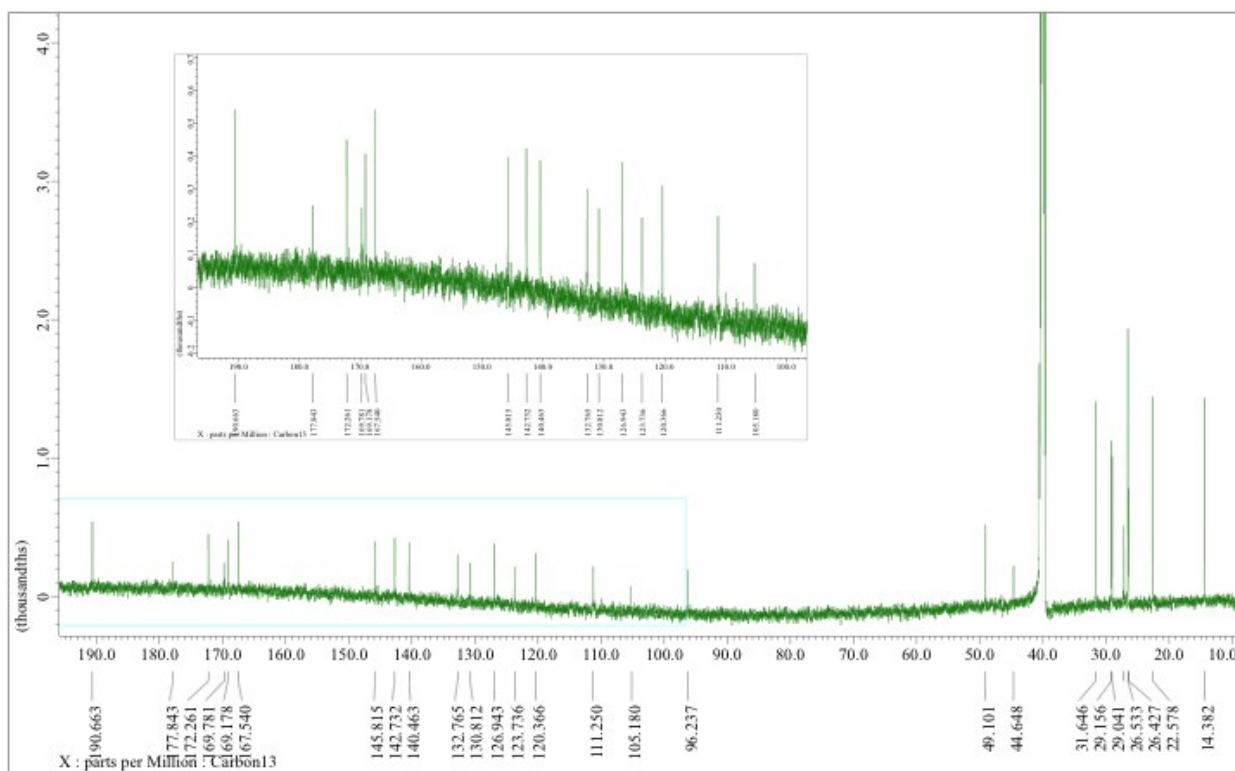


Figure S4. ¹³C NMR of squaraine dye VG4-C8.

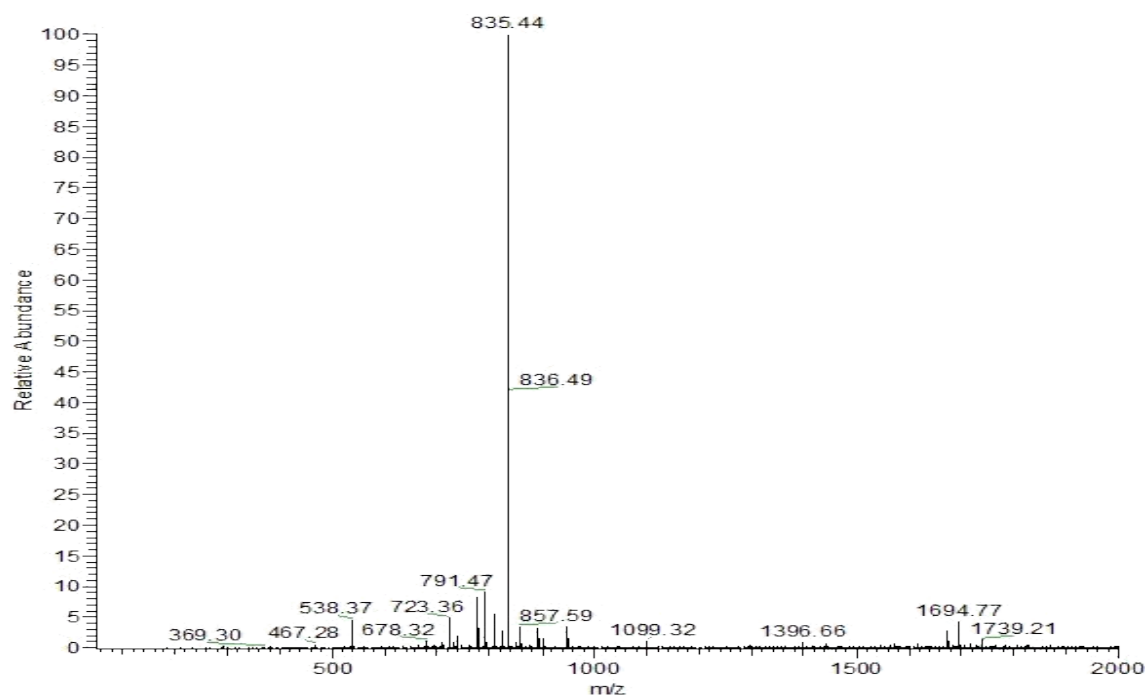


Figure S5. ESI-MS of squaraine dye VG4-C8.

PL quantum yield and Cyclic Voltammetry

The PL quantum yield (PLQY) of VG4-C8 was determined combining Quanta- ϕ with Fluorolog 3. The reported quantum yields are the average of the values obtained after three measurements using three different dye solutions. The PLQY values of the three dyes are 36%, 37% and 24% for VG1-C8, VG2-C8 and VG4-C8, respectively. Cyclic voltammetry was performed using a Bio-Logic SP150 (Bio-Logic, Claix, France) in DMF with 0.1 M TBAPF₆ as supporting electrolyte. A conventional three-electrode system was used with a glassy carbon electrode (1 mm diameter) as working electrode; a platinum wire was used as counter electrode and a Ag/Ag⁺, TBAPF₆ 0.1 M in ACN as reference electrode. CVs were obtained at a scan rate of 100 mV/s. Ferrocene was used as internal reference and added in the last potential scans.

Note that the PLQY values for VG1-C8 and VG2-C8, as well as complete the electrochemistry characterisations, were reported previously in refs. [15] and [16] of the main text.

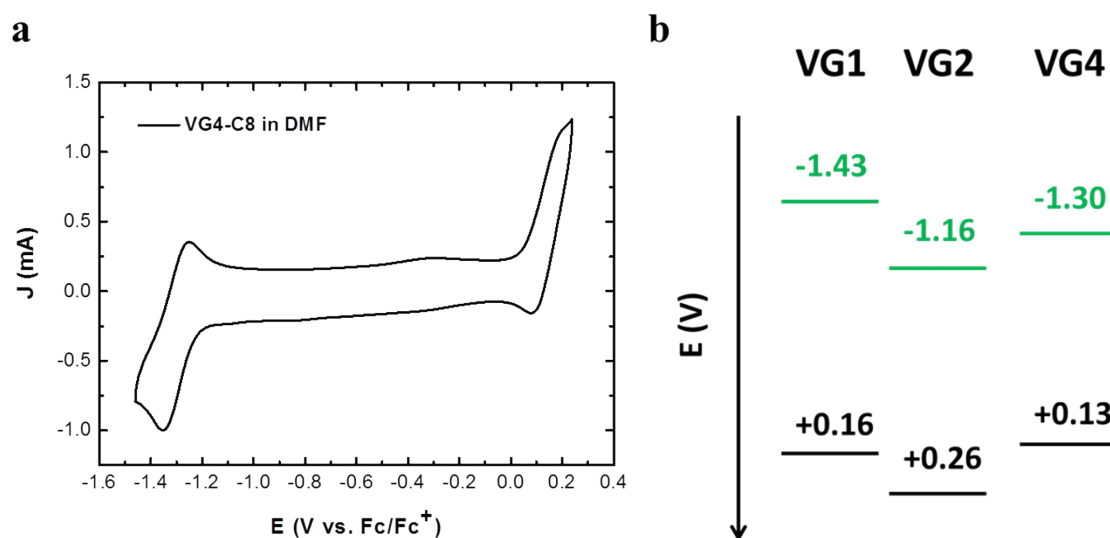


Figure S6. (a) Cyclic Voltammetry of VG4-C8 and (b) energy diagram for the three dyes, with the E_{red} (black) and E_{ox} (green) potentials of the molecules vs. Fc/Fc⁺ (in V). Note that the complete electrochemical characterisation of VG1-C8 and VG2-C8 are reported in refs. [15] and [16] in the main text, respectively.

Supplementary TA and time-resolved PL

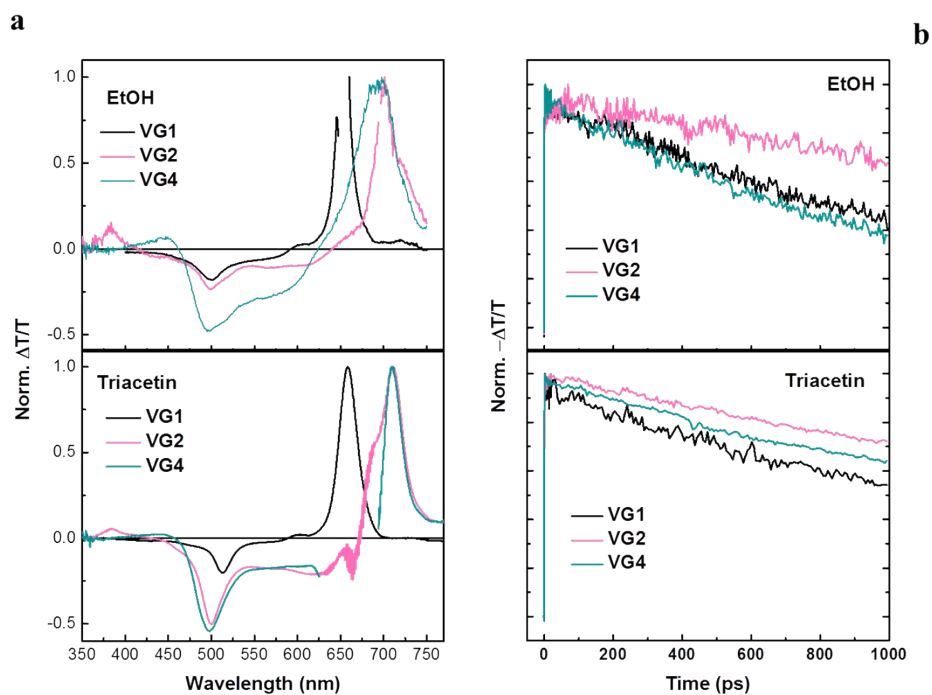


Figure S7. Transient absorption spectra (a) and Time-decay profiles at a probe wavelength of 500 nm (b) of the dyes in ethanol and triacetin obtained by pumping at 650 nm (solid lines).

Table S2. Decay lifetimes of the transient ground state bleaching of three SQs at pump wavelength of 650 nm in ethanol and triacetin.

Pump 650 nm	Ethanol (ns)	Triacetin (ns)
VG1-C8	1.3	1.7
VG2-C8	3.1	3
VG4-C8	1.1	2.3

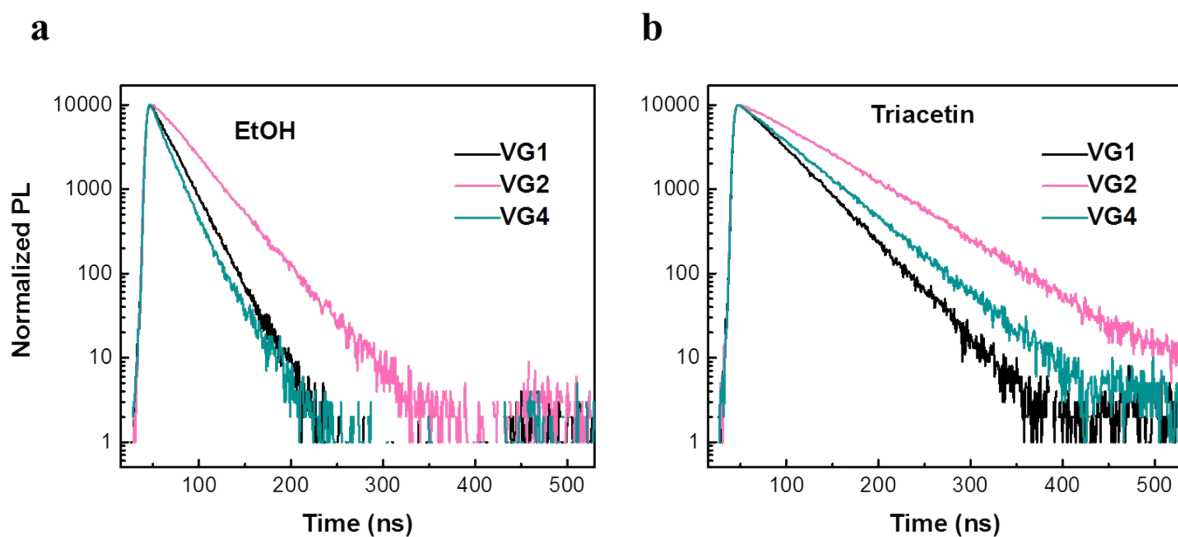


Figure S8. (a) Normalized time-resolved PL profiles for the three dyes in ethanol and (b) triacetin taken with an excitation wavelength of 650 nm. The y-axis is reported in logarithmic scale to highlight the monoexponential decay of the time-profiles.

Table S3. PL decay lifetimes of the three SQs at pump wavelength of 650 nm in ethanol and triacetin.

	Time-constant in ethanol (ns)	Time-constant in Triacetin (ns)
VG1-C8	21.1	42.3
VG2-C8	35.8	72.5
VG4-C8	16.5	50.4

Computation of the energy profile of Figure 3e

Following the work by Martinez,[R3] the MECI point has been located by minimization of the objective function

$$F_{IJ}(\mathbf{R}) = E_{IJ}(\mathbf{R}) + G_{IJ}(\Delta E_{IJ}; \mathbf{R})$$

where \mathbf{R} is the column vector with the 3N Cartesian coordinates of the N atoms of the system and

$$E_{IJ} = [E_I(\mathbf{R}) + E_J(\mathbf{R})]/2$$

$$\Delta E_{IJ} = E_I(\mathbf{R}) - E_J(\mathbf{R}).$$

$G_{IJ}(\Delta E_{IJ}; \mathbf{R})$ is a properly chosen penalty function that increases monotonically with the energy gap. Once the C.I. geometry (\mathbf{R}_{CI}) has been located we use a linear interpolation scheme to displace the atoms from the equilibrium geometry, \mathbf{R}_0 , of S_0 to the C.I. point, and define a reaction parameter ρ such that

$$\mathbf{R}(\rho) = \mathbf{R}_0 + \rho \Delta \mathbf{R}$$

With $\Delta \mathbf{R} = \mathbf{R}_{CI} - \mathbf{R}_0$. Clearly $\mathbf{R} = \mathbf{R}_0$ when $\rho=0$ and $\mathbf{R} = \mathbf{R}_{CI}$ when $\rho=1$. Intermediate geometries are obtained by letting ρ vary between 0 and 1.

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