Supplementary Materials: Dicyanovinyl and Cyano-Ester Benzoindolenine Squaraine Dyes: The Effect of the Central Functionalization on the DSCs Performances

Simone Galliano, Vittoria Novelli, Nadia Barbero, Alessandra Smarra, Guido Viscardi, Raffaele Borrelli, Frédéric Sauvage and Claudia Barolo

1. Synthesis of Squaraine Dyes

1.1. Synthetic Procedures

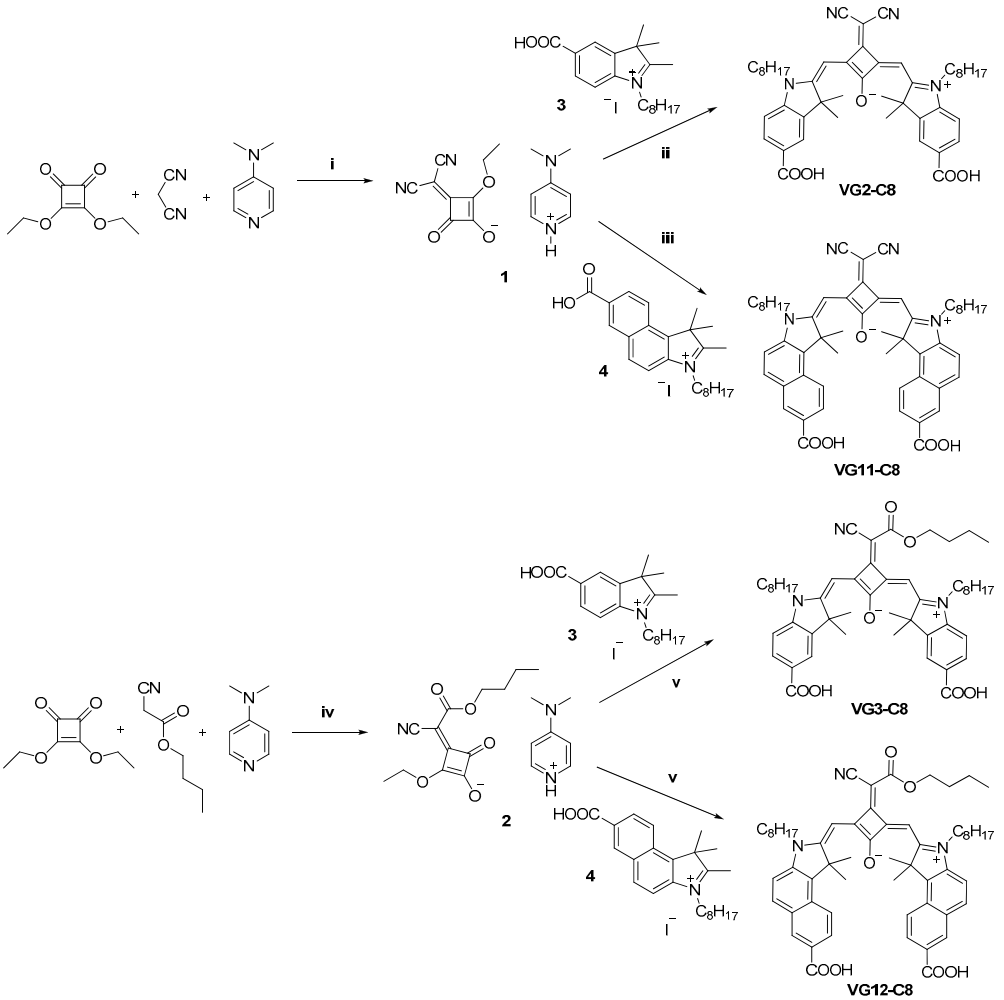

Figure S1. Synthetic procedures of VG2-C8, VG3-C8, VG11-C8, VG12-C8 and their intermediates. Experimental conditions: (i) toluene, 30 min, RT; (ii) toluene/BuOH, MW, 30 min, 155 °C; (iii) pyridine/BuOH, MW, 15 min, 155 °C; (iv) toluene, 90 min, RT; 3 h reflux; (v) toluene/BuOH, MW, 15 min, 155 °C.

1.2. ^{1}H-NMR

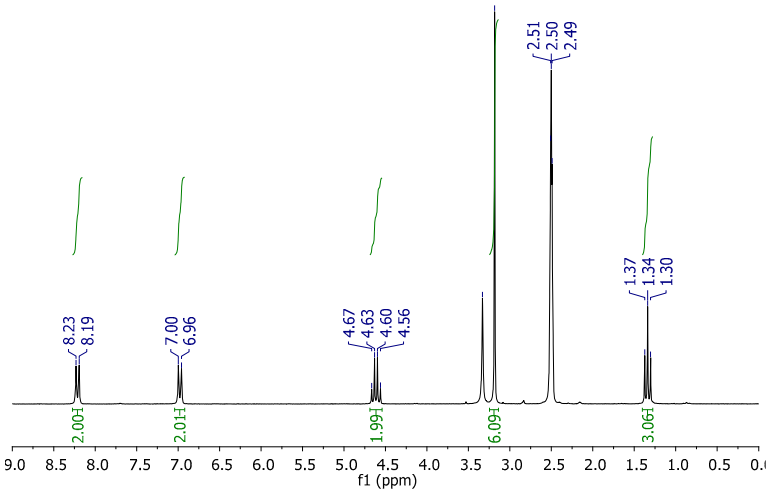

Figure S2. ^{1}H NMR of intermediate 1.

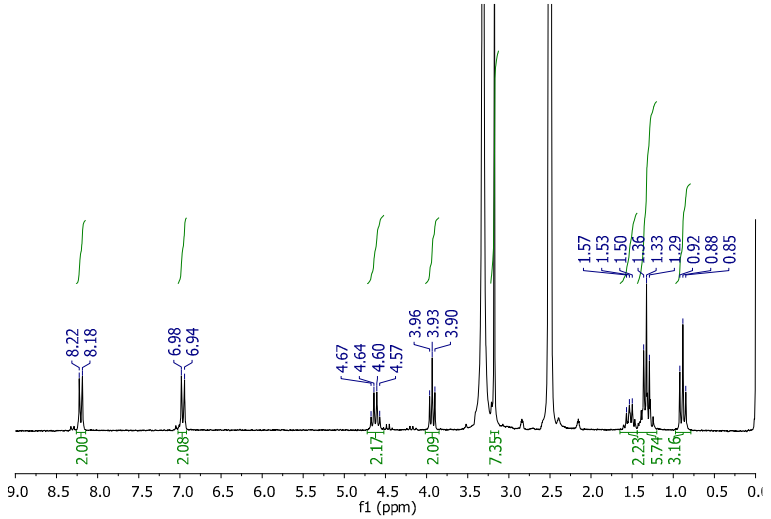

Figure S3. ^{1}H NMR of intermediate 2.

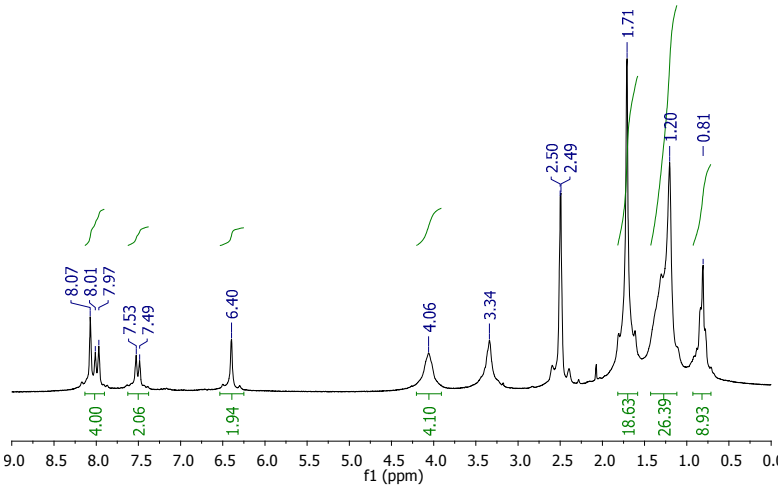

Figure S4. ^{1}H NMR of VG2-C8.

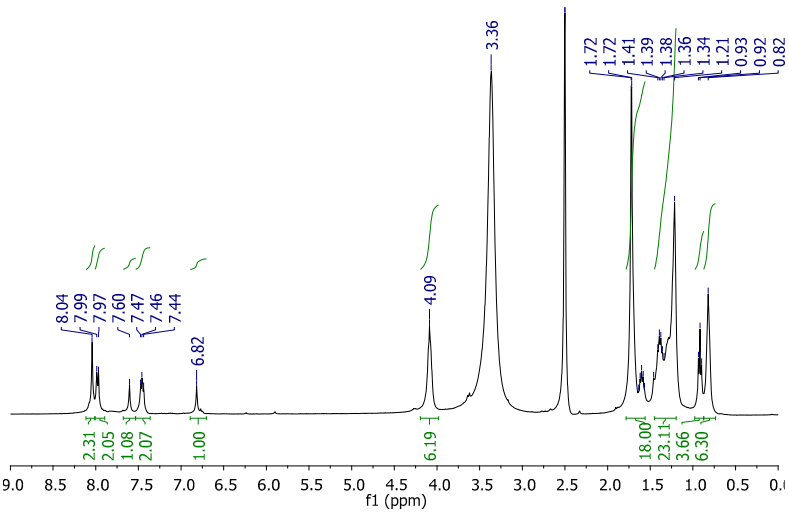

Figure S5. [1]H NMR of VG3-C8.

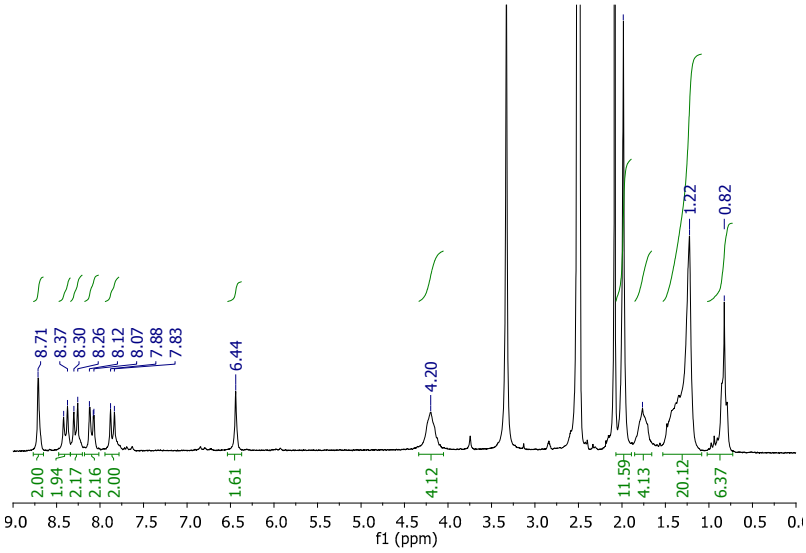

Figure S6. [1]H NMR of VG11-C8.

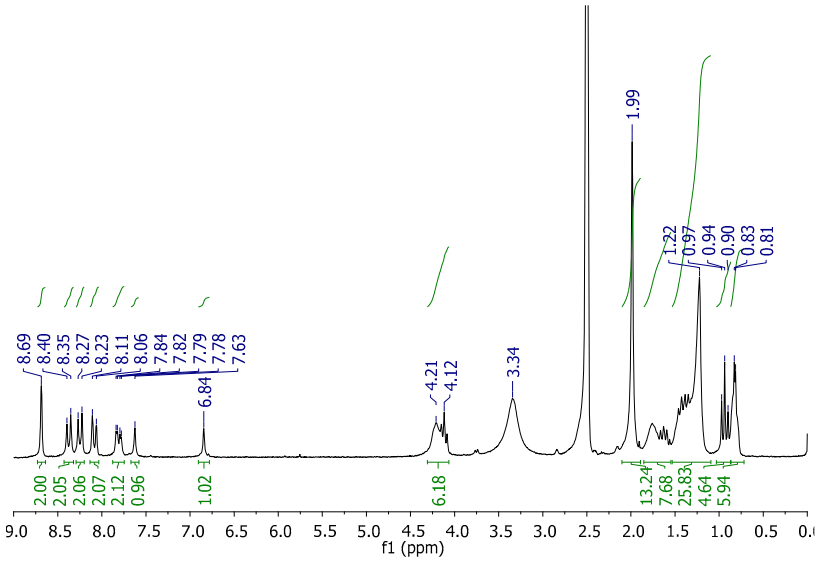

Figure S7. [1]H NMR of VG12-C8.

2. Spectroscopic Characterization

Table S1. Absorption maxima (λ_{max}) in different solvents and logε in ethanol for VG2-C8, VG3-C8, VG11-C8 and VG12-C8.

Solvent	VG2-C8	VG3-C8	VG11-C8	VG12-C8
	λ_{max} (nm)	λ_{max} (nm)	λ_{max} (nm)	λ_{max} (nm)
THF	708	714	727	733
DCM	703	708	723	728
DMSO	698	707	722	729
DMF	697	704	720	726
Acetone	697	705	718	724
ACN	692	698	713	719
EtOH	690 (5.23)	698 (5.20)	714 (5.26)	719 (5.32)
MeOH	688	694	710	715

Table S2. Emission maxima, Stokes shift, HOMO-LUMO energy gaps, lifetimes and quantum yields for **VG2** and **VG3** in different solvents.

Solvent	VG2-C8					VG3-C8				
	λ_{em} (nm)	Stokes Shift (nm)	$\Delta E_{0\text{-}0}$ (eV)	T (ns)	Φ_{fl}	λ_{em} (nm)	Stokes Shift (nm)	$\Delta E_{0\text{-}0}$ (eV)	T (ns)	Φ_{fl}
THF	724	16	1.74	3.05		731	16	1.71	2.11	
DCM	725	22	1.73	3.11		730	22	1.73	1.98	
DMSO	715	17	1.75	1.52		728	21	1.73	1.86	
DMF	710	13	1.77	1.64		725	21	1.74	1.36	
Acetone	713	16	1.76	2.28		724	19	1.74	1.47	
ACN	713	21	1.76	1.84		722	24	1.74	1.15	
EtOH	715	25	1.77	1.84	0.372	713	15	1.75	1.55	0.249
MeOH	707	19	1.77	1.92		713	14	1.76	1.02	

Table S3. Emission maxima, Stokes shift, HOMO-LUMO energy gaps, lifetimes and quantum yields for **VG11** and **VG12** in different solvents.

Solvent	VG11-C8					VG12-C8				
	λ_{em} (nm)	Stokes Shift (nm)	$\Delta E_{0\text{-}0}$ (eV)	T (ns)	Φ_{fl}	λ_{em} (nm)	Stokes Shift (nm)	$\Delta E_{0\text{-}0}$ (eV)	T (ns)	Φ_{fl}
THF	736	9	1.70	2.99		743	10	1.68	2.39	
DCM	734	11	1.70	3.01		741	13	1.70	2.20	
DMSO	733	11	1.70	2.19		742	13	1.69	1.93	
DMF	729	9	1.71	1.68		738	12	1.69	1.50	
Acetone	729	11	1.71	1.94		736	12	1.69	1.53	
ACN	726	13	1.73	1.42		732	13	1.71	1.09	
EtOH	726	12	1.73	1.96	0.315	732	13	1.71	1.73	0.320
MeOH	720	10	1.73	1.17		726	11	1.71		

3. Electrochemistry

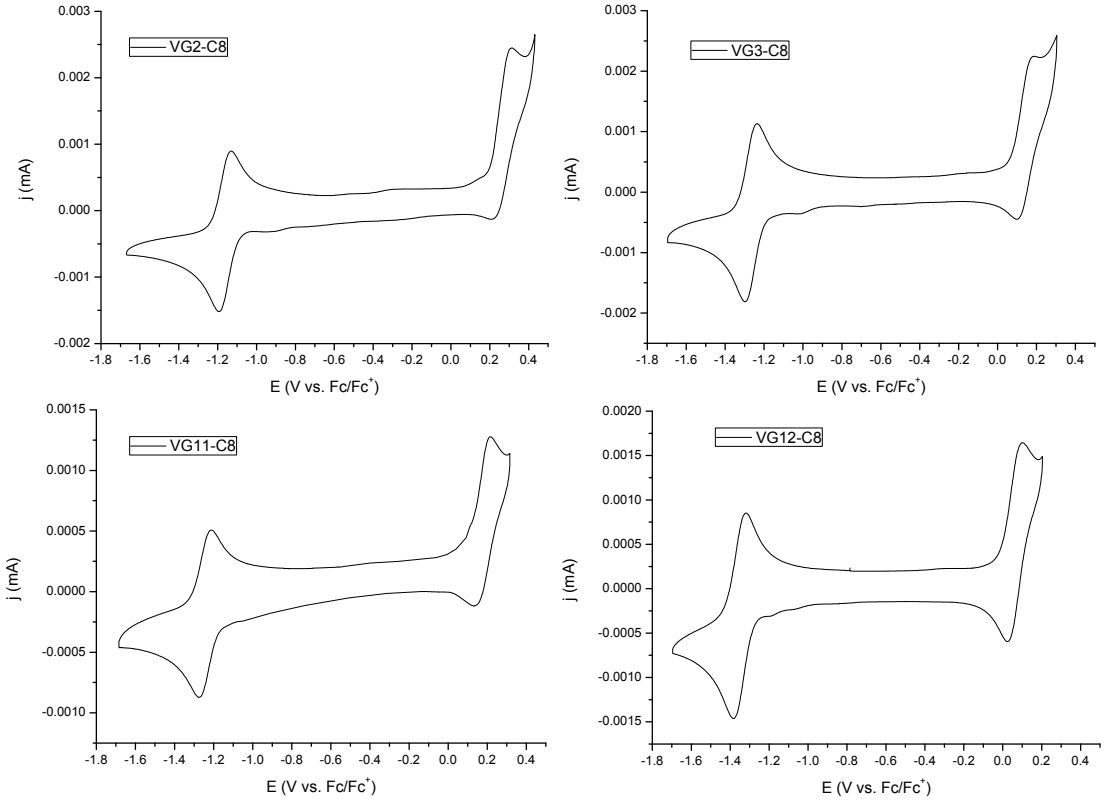

Figure S8. Cyclic voltammograms of VG2-C8, VG3-C8, VG11-C8 and VG12-C8 at scan rate 100 mV s^{-1}, 2nd scan is shown.

4. Computational Analysis of Dye Structure and Electron Distribution

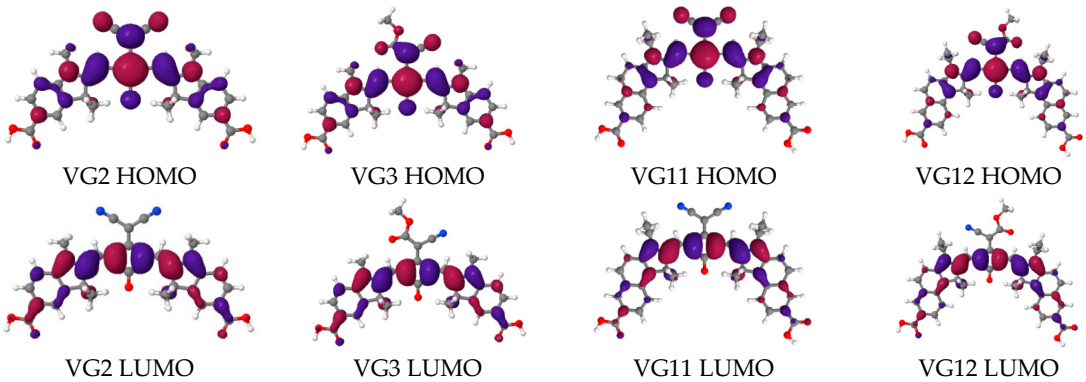

Figure S9. Upper panel HOMO, lower panel LUMO of the four dyes. In all cases the HOMO has a significant contribution from the substituent orbitals, while the LUMO is typical of squaraines.

Table S4. Vertical excitation energies (in nm) and oscillator strengths (in cm^{-1}), in parenthesis, of the functionalized squaraines, obtained from TD-DFT calculations. All calculations include the effect of tetrahydrofuran solvent by means of PCM.

State	VG2-C8	VG3-C8	VG11-C8	VG12-C8
S1	624 (1.49)	617 (1.45)	614 (1.53)	607 (1.49)
S2	347 (1.10)	339 (0.89)	336 (1.14)	328 (0.90)
S3	320 (0.16)	317 (0.0)	321 (0.19)	318 (0.50)
S4	315 (0.10)	316 (0.49)	311 (0.0)	307 (0.0)