Supporting Information

Charge Transfer or Biradicaloid Character: Assessing TD-DFT and SAC-CI for Squarylium Dye Derivatives

G. Krishna Chaitanya [a,c,*], Avinash L. Puyad [a], K. Bhanuprakash [b]

[a] School of Chemical Sciences, S.R.T.M. University, Nanded-431 606, India

[b] Inorganic Chemistry Division, Indian Institute of Chemical Technology, Hyderabad, India.

[c] Present address: Materials Research Laboratory, University of Nova Gorica, Slovenia, SI 5000,

Table S1: diagnostic indices obtained at TD-DFT and SAC-CI methodologies for SQ derivatives

Molecule	Methodology	q^{CT} (e)	D^{CT} (Å)	μ^{CT} (Debye)	H Index (Å)	C^+/C^-
SQ-1	B3LYP	0.51	0.001	0.003	2.14	0.78
	BHandLYP	0.49	0.001	0.003	2.10	0.79
	Cam-B3LYP	0.48	0.001	0.003	2.12	0.78
	M06HF	0.42	0.001	0.003	2.13	0.81
	M062X	0.46	0.001	0.003	2.12	0.79
	WB97XD	*0.49*	0.001	0.003	2.12	0.78
	SAC-CI	*0.51*	0.001	0.003	2.05	0.81
SQ-2	B3LYP	0.36	0.001	0.002	3.42	0.98
	BHandLYP	0.43	0.001	0.002	3.38	0.98
	Cam-B3LYP	0.41	0.001	0.002	3.30	0.98
	M06HF	0.42	0.001	0.002	3.43	0.98
	M062X	0.38	0.001	0.002	3.41	0.98

	WB97XD	0.42	0.001	0.002	3.24	0.98
	SAC-CI	0.49	0.001	0.002	3.84	0.97
SQ-3	B3LYP	0.34	0.008	0.013	3.51	0.98
	BHandLYP	0.43	0.002	0.005	3.39	0.99
	Cam-B3LYP	0.41	0.002	0.004	3.33	0.99
	M06HF	0.41	0.002	0.005	3.34	0.98
	M062X	0.37	0.002	0.004	3.40	0.98
	WB97XD	0.42	0.002	0.004	3.28	0.98
	SAC-CI	0.48	0.002	0.004	3.61	0.98
SQ-4	B3LYP	0.33	0.000	0.000	3.67	0.99
	BHandLYP	0.43	0.000	0.001	3.43	0.99
	Cam-B3LYP	0.40	0.000	0.001	3.36	0.99
	M06HF	0.41	0.000	0.001	3.34	0.99
	M062X	0.37	0.000	0.001	3.45	0.99
	WB97XD	0.41	0.000	0.001	3.31	0.99
	SAC-CI	0.49	0.000	0.000	3.72	0.98
SQ-5	B3LYP	0.32	0.002	0.003	3.59	0.95
	BHandLYP	0.38	0.004	0.006	3.49	0.97
	Cam-B3LYP	0.36	0.002	0.004	3.47	0.97
	M06HF	0.37	0.002	0.003	3.40	0.98
	M062X	0.33	0.002	0.003	3.48	0.97
	WB97XD	0.38	0.002	0.003	3.44	0.97
	SAC-CI	0.36	0.001	0.001	3.39	0.98
SQ-6	B3LYP	0.29	0.011	0.016	3.85	0.96

	BHandLYP	0.36	0.003	0.005	3.78	0.98
	Cam-B3LYP	0.35	0.005	0.009	3.75	0.98
	M06HF	0.38	0.009	0.017	3.82	0.99
	M062X	0.32	0.006	0.009	3.79	0.98
	WB97XD	0.37	0.010	0.018	3.71	0.98
	SAC-CI	0.36	0.008	0.013	3.80	0.98
SQ-7	B3LYP	0.32	0.004	0.006	3.85	0.98
	BHandLYP	0.40	0.003	0.005	3.60	0.99
	Cam-B3LYP	0.38	0.003	0.005	3.57	0.99
	M06HF	0.38	0.003	0.005	3.48	0.99
	M062X	0.34	0.009	0.015	3.63	0.98
	WB97XD	0.39	0.003	0.006	3.52	0.98
	SAC-CI	0.44	0.004	0.008	3.71	0.98
SQ-8	B3LYP	0.37	0.004	0.008	3.30	0.97
	BHandLYP	0.44	0.001	0.002	3.26	0.98
	Cam-B3LYP	0.42	0.001	0.002	3.20	0.97
	M06HF	0.42	0.001	0.001	3.30	0.98
	M062X	0.39	0.002	0.005	3.28	0.98
	WB97XD	0.43	0.005	0.010	3.14	0.97
	SAC-CI	0.48	0.001	0.001	3.62	0.97
SQ-9	B3LYP	0.35	0.003	0.005	3.74	0.97
	BHandLYP	0.43	0.004	0.008	3.55	0.98
	Cam-B3LYP	0.41	0.003	0.003	3.50	0.98
	M06HF	0.41	0.004	0.009	3.43	0.98

	M062X	0.37	0.008	0.015	3.56	0.98
	WB97XD	0.42	0.005	0.010	3.45	0.98
	SAC-CI	0.48	0.003	0.006	3.67	0.97
SQ-10	B3LYP	0.41	0.002	0.003	3.03	0.94
	BHandLYP	0.44	0.016	0.034	2.98	0.97
	Cam-B3LYP	0.43	0.001	0.002	2.95	0.96
	M06HF	0.41	0.002	0.003	2.94	0.97
	M062X	0.40	0.001	0.002	2.96	0.96
	WB97XD	0.44	0.001	0.002	2.92	0.96
	SAC-CI	0.46	0.001	0.003	2.97	0.97
SQ-11	B3LYP	0.34	0.003	0.005	2.99	0.97
	BHandLYP	0.38	0.003	0.006	2.91	0.99
	Cam-B3LYP	0.37	0.003	0.005	2.89	0.99
	M06HF	0.36	0.003	0.004	2.87	0.99
	M062X	0.34	0.003	0.004	2.91	0.98
	WB97XD	0.38	0.003	0.006	2.87	0.98
	SAC-CI	0.38	0.003	0.005	3.00	0.99
SQ-12	B3LYP	0.34	0.003	0.005	4.62	0.98
	BHandLYP	0.42	0.004	0.008	4.13	0.99
	Cam-B3LYP	0.40	0.004	0.007	4.07	0.99
	M06HF	0.41	0.004	0.008	3.81	0.99
	M062X	0.37	0.005	0.008	4.15	0.98
	WB97XD	0.42	0.004	0.008	3.98	0.99
	SAC-CI	0.46	0.004	0.008	4.03	0.99

SQ-13	B3LYP	0.40	0.037	0.072	3.26	0.96
	BHandLYP	0.40	0.024	0.046	3.41	0.99
	Cam-B3LYP	0.39	0.023	0.043	3.37	0.99
	M06HF	0.40	0.013	0.026	3.47	0.98
	M062X	0.36	0.021	0.037	3.45	0.98
	WB97XD	0.40	0.018	0.014	3.32	0.99
	SAC-CI	0.45	0.010	0.022	3.71	0.97
SQ-14	B3LYP	0.35	0.007	0.012	3.92	0.96
	BHandLYP	0.42	0.008	0.016	3.57	0.98
	Cam-B3LYP	0.39	0.008	0.016	3.55	0.97
	M06HF	0.39	0.012	0.022	3.40	0.98
	M062X	0.36	0.011	0.019	3.61	0.97
	WB97XD	0.40	0.019	0.037	3.48	0.97
	SAC-CI	0.45	0.002	0.004	3.51	0.98

Table S2: Calculated absorption maxima (λ_{max} in nm), oscillator strength (f) and main configuration of the S0-S1 transition of cyanine dye obtained with different XC functionals with 6-311++G(d,p) basis set.

XC-functional	λ_{max}	f	Main configuration
B3LYP	445	2.324	0.720 (H→L) -0.163 (L→H)+0.060 (H-1→L+1)
BHandHLYP	436	2.423	0.702 (H→L) +0.108 (H-1→L+1)-0.097(L→H)
CAM-B3LYP	450	2.349	0.700 (H→L)+0.115 (H-1→L+1)-0.096(L→H)
M06-HF	480	2.259	0.685 (H→L)+0.113 (H-1→L+12)-0.080(H→L+7)
M06-2X	456	2.317	0.704 (H→L)-0.107 (L→H)+0.109 (H-1→L+1)
ωB97XD	452	2.346	0.696 (H→L)+0.127 (H-1→L+1)-0.081(L→H)