Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary material for

Artificial evolution of metal-free coumarin dyes for dye sensitized solar cells

Vishwesh Venkatraman, Sailesh Abburu, and Bjørn Kåre Alsberg

Table S1: Photovoltaic properties for the coumarin dyes investigated in this study. In the "Molecule" column, names in italics indicate test set molecules.

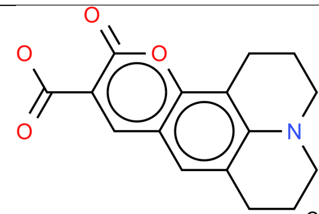
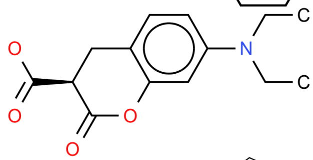
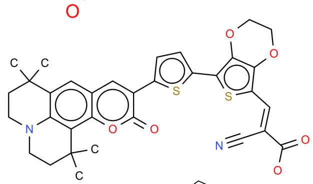
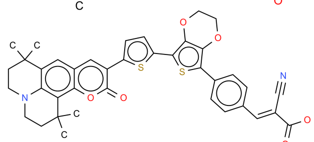
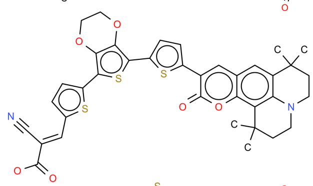
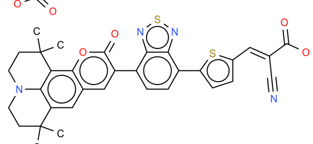
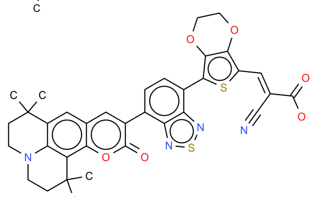
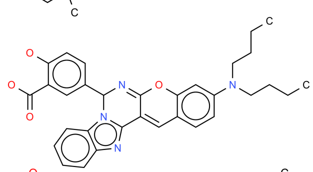
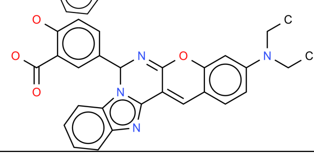
Molecule	**Structure**	J_{sc}	V_{oc}	FF	PCE	λ_{max}
C01 [5]		4.1	410	0.56	0.9	442
C02 [11]		2.18	550	0.69	1.03	445
C03 [10]		14.2	600	0.7	6.07	532
C04 [10]		10.5	620	0.57	3.73	509
C05 [10]		13.3	570	0.56	4.37	527
C06 [9]		14.3	580	0.72	5.97	507
C07 [9]		13.3	560	0.68	5.03	520
C08 [7]		2.461	491	0.635	0.767	450
C09 [7]		2.082	501	0.614	0.64	448

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Table S1 – *Continued from previous page*

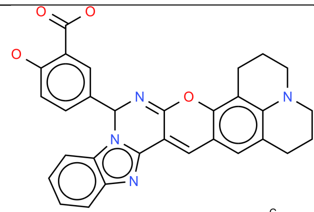
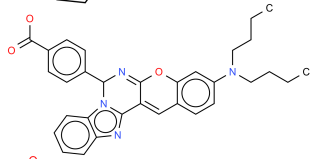
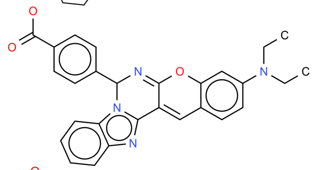
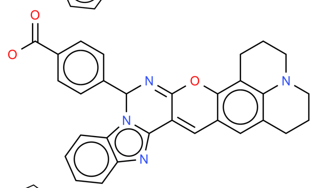
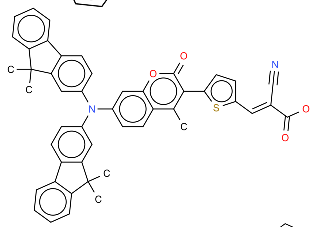
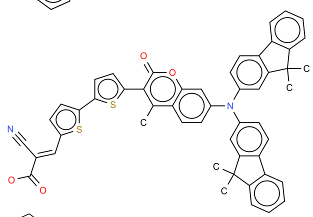
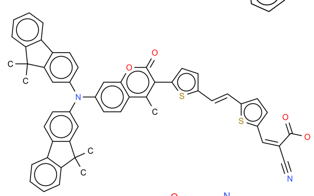
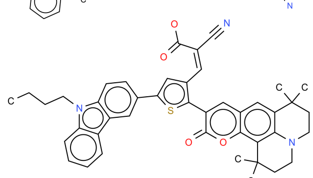
Molecule	Structure	J_{sc}	V_{oc}	FF	PCE	λ_{max}
C10 [7]		1.081	502	0.66	0.358	454
C11 [7]		1.754	441	0.683	0.528	451
C12 [7]		0.936	490	0.651	0.299	475
C13 [7]		1.912	470	0.69	0.581	454
C14 [2]		10.95	650	0.68	4.54	429
C15 [2]		9.44	650	0.7	4.34	431
C16 [2]		9.87	640	0.69	4.44	450
C17 [8]		13.47	610	0.68	5.53	507

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Table S1 – *Continued from previous page*

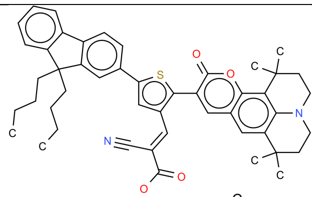
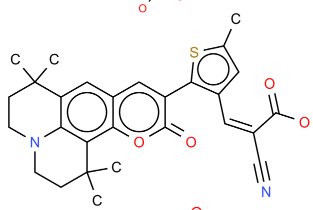
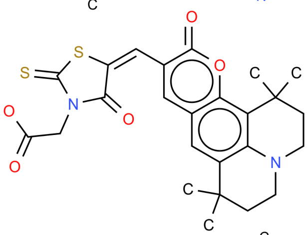
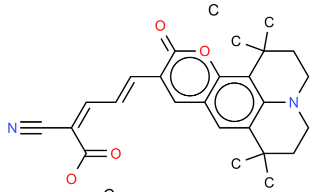
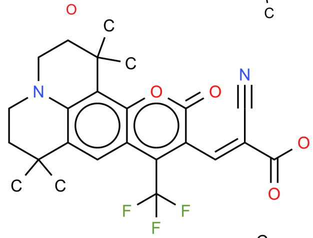
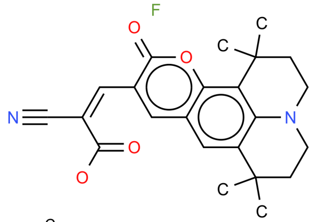
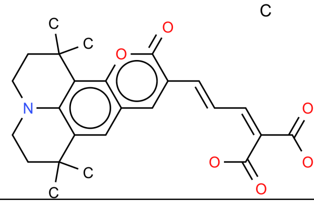
Molecule	**Structure**	J_{sc}	V_{oc}	FF	PCE	λ_{max}
C18 [8]		10.5	561	0.68	4.02	478
C19 [8]		7.61	508	0.7	2.74	467
C20 [5]		7.5	490	0.7	2.6	539
C21 [5]		15.2	550	0.62	5.2	507
C22 [5]		9.4	500	0.65	3.1	477
C23 [5]		12.9	500	0.64	4.1	493
C24 [5]		12.8	480	0.6	3.7	486

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Table S1 – *Continued from previous page*

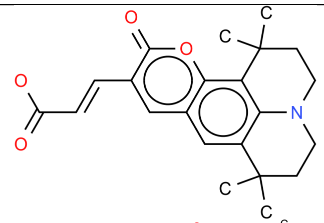
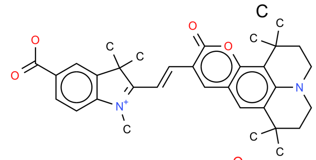
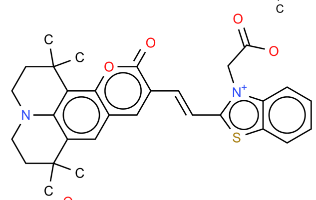
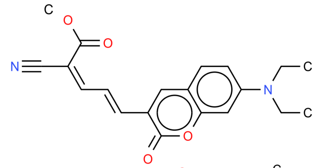
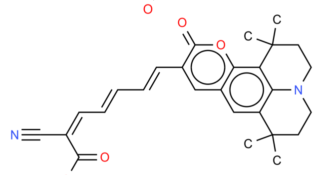
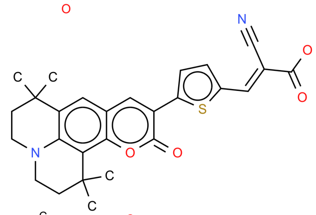
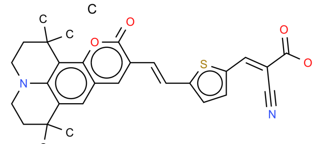
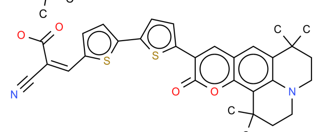
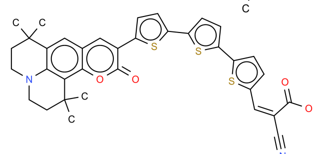
Molecule	**Structure**	J_{sc}	V_{oc}	FF	PCE	λ_{max}
C25 [5]		11.1	510	0.6	3.4	451
C26 [5]		2.7	340	0.63	0.6	616
C27 [5]		4.5	380	0.63	1.1	578
C28 [5]		13.2	530	0.67	4.7	480
C29 [5]		15.1	470	0.5	3.5	506
C30 [6]		12.1	660	0.73	5.8	507
C31 [4]		14.89	580	0.73	6.3	507
C32 [6]		15.6	660	0.7	7.2	511
C33 [6]		14.3	700	0.64	6.4	501

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Table S1 – *Continued from previous page*

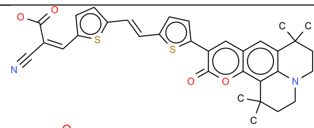
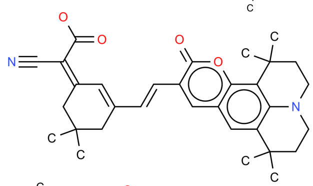
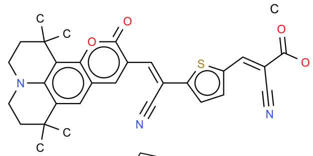
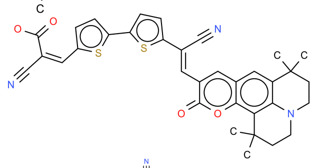
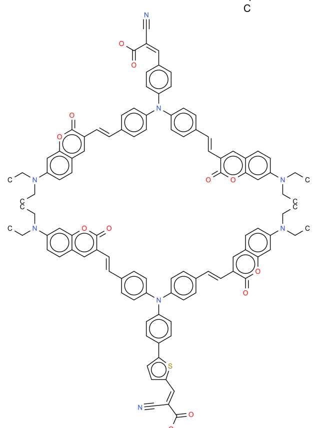
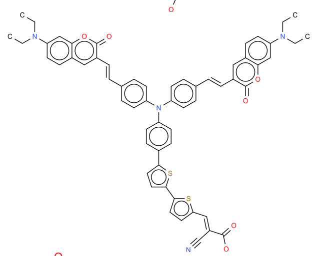
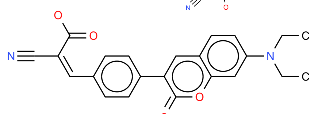
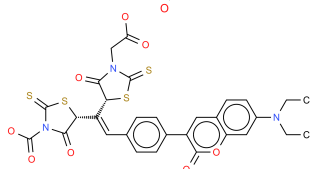
Molecule	**Structure**	J_{sc}	V_{oc}	FF	PCE	λ_{max}
C34 [12]		15	620	0.69	6.4	525
C35 [14]		16.1	600	0.69	6.7	492
C36 [13]		14.32	510	0.73	5.3	566
C37 [12]		18.8	530	0.65	6.5	553
C38 [1]		9	800	0.76	5.5	454
C39 [1]		12.2	695	0.74	6.2	460
C40 [1]		13.2	678	0.67	6	465
C41 [3]		5.63	660	0.7	2.6	420
C42 [3]		3.33	580	0.73	1.41	449

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Table S1 – *Continued from previous page*

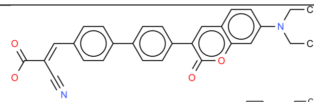
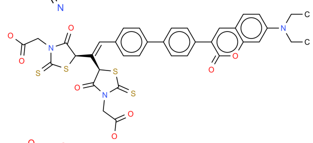
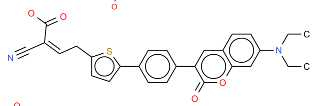
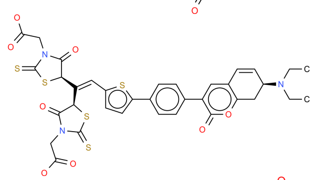
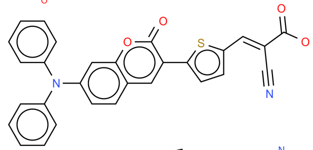
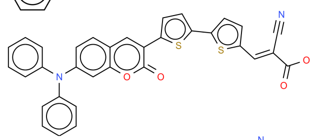
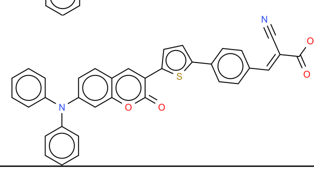
Molecule	**Structure**	J_{sc}	V_{oc}	FF	PCE	λ_{max}
C43 [3]		5.79	690	0.7	2.8	413
C44 [3]		4.03	600	0.73	1.77	425
C45 [3]		7.72	660	0.71	3.62	438
C46 [3]		3.41	560	0.73	1.39	465
C47 [15]		9.52	540	0.65	3.36	489
C48 [15]		12.91	590	0.61	4.59	492
C49 [15]		14.33	690	0.63	6.24	473

Figure F1: Scores plot for the 3 component PLSR model. The points have been coloured according to the $\mathbf{J_{sc}} \times \mathbf{V_{oc}}$ values and the size of the sphere is an indication of the magnitude.

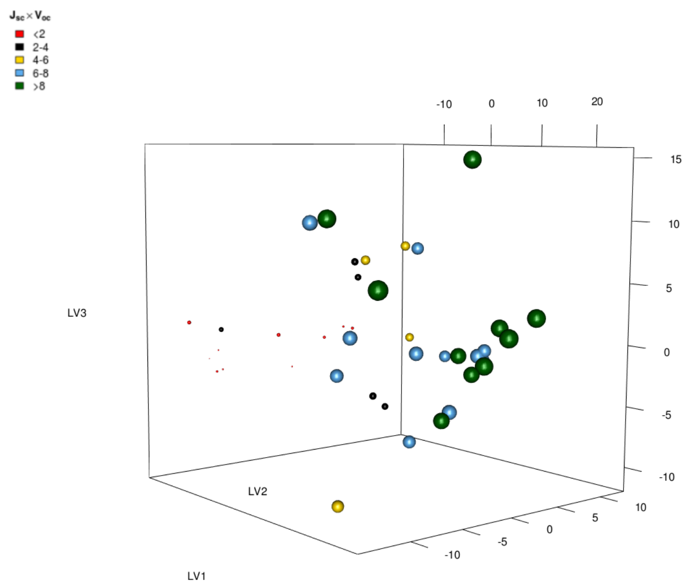
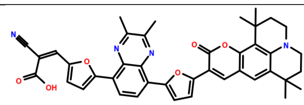
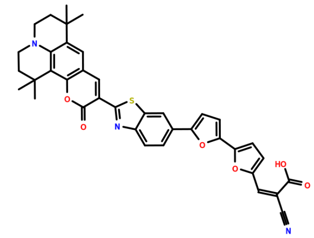
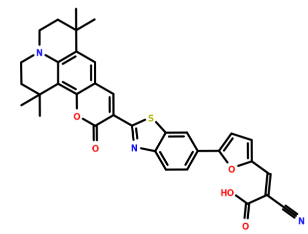


Table S2: Comparison of different TD-DFT functionals for selected coumarin molecules.

Molecule	$\lambda_{\mathbf{max}}$	**M062X/6-31G(d,p)**	**M062X/DGDZVP**	**CAM-B3LYP/DGDZVP**
C343[5]	442	364.89	371.07	369.6
JK-34[2]	429	435.35	440.88	433.87
JK-35[2]	431	454.24	461.31	459.1
JK-36[2]	450	478.25	486.09	483.66
NKX-2195[5]	539	478.37	482.36	475.21
NKX-2311[5]	507	481.7	489.9	483.98
NKX-2384[5]	477	435.29	447.23	442.66
NKX-2388[5]	493	440.66	446.65	441.93
NKX-2393[5]	486	463.8	473.14	467.22
NKX-2398[5]	451	406.54	406.54	402.34
NKX-2510[5]	480	469.47	477.48	471.85
NKX-2586[5]	506	509.87	518.67	511
NKX-2587[6]	507	474.83	481.76	477.1
NKX-2593[4]	507	517.75	529.11	521.55
NKX-2677[6]	511	503.99	512.31	507.85
NKX-2697[6]	501	519.68	530.15	526.25
NKX-2700[12]	525	532.99	545.4	538.9
NKX-2753[14]	492	488.78	496.75	487.58
NKX-2807[13]	566	391.59	398.05	385.3
NKX-2883[12]	553	397.64	404.58	406.73

Table S3: Molecular modifications made to dye M01.

Dye	$J_{sc} \times V_{oc}$	h_i
	7.99±0.52	0.03
	6.86±0.53	0.03
	7.26±0.48	0.02

References

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[3] L. Han, H. Wu, Y. Cui, X. Zu, Q. Ye, and J. Gao. Synthesis and density functional theory study of novel coumarin-type dyes for dye sensitized solar cells. *J. Photoch. Photobio., A*, 290(0):54 – 62, 2014.

[4] K. Hara, M. Kurashige, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, K. Sayama, and H. Arakawa. Design of new coumarin dyes having thiophene moieties for highly efficient organic-dye-sensitized solar cells. *New J. Chem.*, 27:783–785, 2003.

[5] K. Hara, T. Sato, R. Katoh, A. Furube, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, and H. Arakawa. Molecular design of coumarin dyes for efficient dye-sensitized solar cells. *J. Phys. Chem. B*, 107(2):597–606, 2003.

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