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Supporting Information

Structure Efficiency Relationship in newly synthesized 4-Substituted

Donor- π -Acceptor Coumarins for Dye Sensitized Solar Cells.

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Synthetic Details

Synthesis of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde (3)

Synthesis of compound 3 was carried out according to reported protocol¹. 10 mmol of 4-Diethylaminosalicylaldehyde combined with 20 mmol of diethyl malonate in presence of 1 mL piperidine in 30 mL absolute ethanol and refluxed for 6 hours. The reaction was monitored by using TLC. After completion ethanol was evaporated under reduced pressure. The residue was collected in RB flask to which concentrated HCl (20 mL) and glacial acetic acid (20 mL) were added and refluxed for another 6 hours. The cooled reaction mass poured into 100 mL crushed ice. 40% NaOH solution was added dropwise to adjust the pH to 5 and stirred for 30 mins, the mixture was filtered, washed with water, dried, then recrystallized with toluene to give 1.70 g of compound 2 in 80.0% yield. Compound 2 was dissolved in 10 mL DMF and added as it is to a previously stirred solution of 2.3 mL DMF and 2.3 mL POCl₃. This reaction mass was stirred at 60°C for 12 h then poured on 100 gm. crushed ice. 10% NaOH was used to adjust the pH of the solution to 10.0. The crude product was filtered and washed with water and dried in an oven. The crude product was recrystallized in absolute ethanol to get 1.30 g of compound 3 in 67.7% yield.

¹H NMR (500 MHz, $CDCl_3$) δ 10.13 (s, 1H), 8.26 (s, 1H), 7.41 (d, J = 9.0 Hz, 1H), 6.64 (dd, J = 9.0, 2.5 Hz, 1H), 6.49 (d, J = 2.4 Hz, 1H), 3.48 (q, J = 7.2 Hz, 4H), 1.26 (t, J = 7.2 Hz, 6H).

¹³C NMR (125 MHz, CDCl₃) δ 187.92, 161.85, 158.92, 153.43, 145.32, 132.48, 114.37, 110.14, 108.23, 97.17, 45.25, 12.44.

Synthesis of 7-(diethylamino)-3-formyl-2-oxo-2H-chromene-4-carbonitrile (4)

Compound 4 was synthesized according to reported protocol². 6.9 mmol of compound 3 was dissolved in 10 mL DMF and cooled to 5°C. Sodium cyanide solution (7.6 mmol dissolved in 4 mL water) was added dropwise and then stirred at RT for 90 mins. After stirring reaction mass was cooled to 0°C and 10.0 mmol of liquid bromine was added dropwise. The reaction mass was stirred at RT for 30 min and filtered and dried under vacuum to afford 0.98 g of compound 4 in 52.2% yield.

¹H NMR (500 MHz, CDCl3) δ 10.18 (d, J = 1.5 Hz, 1H), 7.79 (dd, J = 9.3, 1.4 Hz, 1H), 6.77 (d, J = 9.2 Hz, 1H), 6.50 (s, 1H), 3.53 (q, J = 7.2 Hz, 4H), 1.30 (t, J = 7.1 Hz, 6H).

 ^{13}C NMR (125 MHz, CDCl3) δ 185.60, 160.13, 157.99, 154.15, 130.35, 125.35, 114.20, 112.85, 111.60, 107.94, 97.39, 45.67, 12.51.

Synthesis of 7-(diethylamino)-4-hydroxy-2H-chromen-2-one (5)

Synthesis of compound 5 and 6 was carried out according to reported protocol³. 0.108 mol of magical malonate and 0.108 mol of 3-diethylaminophenol were refluxed in 100 mL of dry toluene for 2 h. The reaction was monitored by TLC. After completion of the reaction mass was cooled to room temperature and the isolated grey solid was filtered and washed with chilled toluene. The product obtained was dried under high vacuum. (13.8 g, 50% Yield) and used as it is without further purification.

Synthesis of 4-chloro-7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde (6)

0.0557 mol of compound 5 was added to 100 mL of anhydrous DMF. The reaction mass was heated to 100 °C until a homogeneous solution was obtained. It was then cooled to -4° C for 3 hrs. To this 0.1449 mol of POCl₃ was added drop-wise and stirred for 30 min. The reaction mass was transferred to a separating funnel and was extracted in (4 X 50 mL) of dichloromethane. The organic layer was washed with a saturated NaHCO₃ solution (3 X 50 mL) and then with brine (3 X 50 mL). The organic layer then dried over anhydrous Na₂SO₄ and concentrated under vacuum to give compound 6. (8.5 g, 55% Yield)

¹H NMR (500 MHz, CDCl₃) δ 10.27 (s, 1H), 7.82 (d, J = 9.3 Hz, 1H), 6.67 (dd, J = 9.3, 2.5 Hz, 1H), 6.41 (d, J = 2.5 Hz, 1H), 3.47 (q, J = 7.2 Hz, 4H), 1.24 (t, J = 7.2 Hz, 6H).

¹³C NMR (125 MHz, CDCl₃) δ 186.96, 159.87, 156.40, 154.00, 153.61, 129.22, 110.94, 110.50, 107.61, 96.55, 45.28, 12.40.

Synthesis of 7-(diethylamino)-2-oxo-4-(piperidine-1-yl)-2H-chromene-3-carbaldehyde (7)

0.1 mmol of compound 6 and 0.2 mmol of piperidine were stirred in 5 mL absolute ethanol in presence of 1 mL triethylamine at RT for 4 h. The reaction was monitored using TLC. After completion of the reaction, the mass was

filtered under vacuum and dried in an oven. The crude product was recrystallized from ethanol to afford 1.96 g orange color powder with 60.0% yield.

¹H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.62 (d, J = 9.3 Hz, 1H), 6.53 (dd, J = 9.5, 1.8 Hz, 1H), 6.40 (d, J = 1.7 Hz, 1H), 3.52 (s, 4H), 3.40 (q, J = 6.9 Hz, 4H), 1.80 (s, 6H), 1.20 (t, J = 7.0 Hz, 6H).

 ^{13}C NMR (100 MHz, CDCl_3) δ 187.23, 165.36, 160.69, 157.09, 151.43, 128.08, 108.43, 105.44, 101.76, 97.89, 55.13, 44.81, 26.67, 24.28, 12.47.

General procedure for Synthesis of Compound MC1-MC4

0.1 mmol of compound 3, 6, 7 and 4 were refluxed for 6 h. with 0.1 mmol of rhodanine-3-acetic acid in ethanol in presence of catalytic amount of piperidine and filtered under vacuum, sucked dried in an oven to get MC1 to MC4 compound respectively. The separated solid was purified by silica gel column chromatography using dichloromethane: methanol [9:1] as the eluent.

MC1

Yield: 66.8%

Melting Point: 230°C

¹H NMR (500 MHz, DMSO-d6) δ 8.10 (s, 1H), 7.52 (s, 1H), 7.48 (d, J = 9.0 Hz, 1H), 6.69 (dd, J = 9.1, 2.2 Hz, 1H), 6.48 (d, J = 2.2 Hz, 1H), 4.54 (s, 2H), 3.39 – 3.35 (m, 4H), 1.01 (t, J = 7.0 Hz, 6H).

 ^{13}C NMR (125 MHz, DMSO-d6) δ 194.94, 167.19, 165.17, 160.67, 157.33, 153.16, 150.16, 137.93, 132.07, 127.75, 126.63, 125.20, 109.27, 96.82, 61.60, 44.97, 12.83.

CNH Analysis calculated (percent) for C₁₉H₁₈N₂O₅S₂: C, 54.53; H, 4.34; N, 6.69: O, 19.12; S, 15.32. Found: C, 54.55; H, 4.33; N, 6.68

MC2

Yield: 61.8%

Melting Point: 215°C

¹H NMR (500 MHz, DMSO-d6) δ 7.87 (s, 1H), 7.71 (d, J = 9.4 Hz, 1H), 6.90 (dd, J = 9.5, 2.0 Hz, 1H), 6.66 (d, J = 2.0 Hz, 1H), 4.68 (s, 2H), 3.50 (d, J = 7.1 Hz, 4H), 1.12 (s, 6H).

 ^{13}C NMR (125 MHz, DMSO-d6) δ 194.60, 167.49, 167.18, 160.72, 157.13, 152.92, 147.07, 131.94, 128.58, 120.68, 112.19, 110.78, 109.19, 96.81, 48.11, 44.92, 12.84.

CNH Analysis calculated (percent) for $C_{19}H_{17}$ ClN₂O₅S₂: C, 50.38; H, 3.78; Cl, 7.83; N, 6.18: O, 17.66; S, 14.16. Found: C, 50.39; H, 3.77; N, 6.19

MC3

Yield: 58.55%

Melting Point: 195°C

¹H NMR (500 MHz, CDCl₃) δ 9.56 (s, 1H), 7.70 (s, 1H), 7.61 (d, J = 9.2 Hz, 1H), 6.55 (d, J = 8.7 Hz, 1H), 6.43 (s, 1H), 4.67 (s, 2H), 3.56 (s, 4H), 3.42 (d, J = 6.8 Hz, 4H), 1.79 (s, 4H), 1.71 (s, 2H), 1.21 (t, J = 6.7 Hz, 6H).

 ^{13}C NMR (125 MHz, CDCl_3) δ 196.92, 171.82, 168.56, 163.96, 161.40, 156.63, 151.21, 130.68, 127.80, 120.86, 108.55, 106.22, 100.92, 97.66, 55.15, 47.52, 27.06, 24.21, 12.51.

CNH Analysis calculated (percent) for C₂₄H₂₇N₃O₅S₂: C, 57.47; H, 5.43; N, 8.38: O, 15.95; S, 12.78. Found: C, 57.45; H, 5.42; N, 8.37

MC4

Yield: 55.3%

Melting Point: 210°C

¹H NMR (500 MHz, DMSO-d6) δ 8.12 (s, 2H), 7.58 (s, 2H), 6.79 (d, J = 7.7 Hz, 2H), 6.58 (s, 2H), 4.34 (s, 4H), 3.47 (d, J = 6.2 Hz, 8H), 1.13 (s, 11H).

 ^{13}C NMR (125 MHz, DMSO-d6) δ 194.58, 167.49, 167.18, 160.72, 157.13, 152.92, 147.08, 131.94, 128.58, 120.68, 112.19, 110.78, 109.19, 96.81, 48.13, 44.92, 12.84.

CNH Analysis calculated (percent) for $C_{20}H_{17}N_3O_5S_2$: C, 54.16; H, 3.86; N, 9.47: O, 18.04; S, 14.46. Found: C, 54.17; H, 3.87; N, 9.46

Table S1: Compilation of absorption and emission data for compound MC1 to MC4 in eight solvents

Solvent	Abs	orption	En	nission	e Max	Stokes s	hift	F۱	мнм	f	Δµg
	(nm)	va (cm ⁻¹)	(nm)	vb (cm ⁻¹)	(mol ⁻¹ cm ⁻ 1)	Δvc (cm⁻¹)	(nm)	(nm)	(cm ⁻¹)		Ma (D)
<u>MC1</u>											
MDC	521	19193.9	565	17699.1	23500.8	1494.74	44	84	3213.4	1.3533	12.23
THF	508	19685.0	553	18083.2	17765.2	1601.86	45	83	3309.6	1.3679	12.20
EA	508	19685.0	551	18148.8	9254.0	1536.22	43	82	3288.9	1.1440	11.13
Acetone	514	19455.3	567	17636.7	22246.0	1818.57	53	92	3666.9	1.2809	11.75
Acetonitrile	509	19646.4	572	17482.5	17779.2	2163.85	63	85	3377.0	1.1842	11.31
DMF	510	19607.8	564	17730.5	32304.4	1877.35	54	85	3350.1	1.1880	11.38
DMSO	519	19267.8	576	17361.1	31878.0	1906.71	57	86	3291.0	1.1649	11.34
Ethanol	503	19880.7	577	17331.0	43767.6	2549.69	74	89	3581.2	0.3429	6.08
<u>MC2</u>											
MDC	491	20366.6	555	18018.0	10345.6	2348.58	64	78	3337.6	0.1842	4.43
THF	484	20661.2	546	18315.0	14052.8	2346.14	62	80	3526.0	0.2626	5.25
EA	483	20703.9	544	18382.4	13248.4	2321.58	61	79	3518.3	0.2428	5.04
Acetone	481	20790.0	558	17921.1	9983.2	2868.87	77	82	3630.8	0.1896	4.44
Acetonitrile	483	20703.9	563	17762.0	22947.2	2941.94	80	79	3474.0	0.4102	6.55
DMF	476	21008.4	577	17331.0	9066	3677.38	101	82	3708.7	0.1674	4.15
DMSO	496	20161.3	569	17574.7	8288.8	2586.60	73	81	3403.8	0.1506	4.02
Ethanol	475	21052.6	563	17762.0	14225.6	3290.64	88	78	3555.5	0.2551	5.12
<u>MC3</u>											
MDC	487	20533.9	556	17985.6	19035.6	2548.27	69	76	3278.1	0.3384	5.97
THF	482	20746.9	550	18181.8	13583.6	2565.07	68	78	3436.7	0.2408	5.01
EA	481	20790.0	547	18281.5	14052.8	2508.49	66	77	3428.0	0.2506	5.11
Acetone	485	20618.6	559	17889.1	16346.8	2729.47	74	78	3422.3	0.2964	5.58
Acetonitrile	487	20533.9	564	17730.5	11354.4	2803.38	77	75	3254.7	0.1989	4.58
DMF	480	20833.3	558	17921.1	14245.6	2912.19	78	80	3555.9	0.2590	5.19
DMSO	485	20618.6	567	17636.7	13935.6	2981.87	82	78	3407.9	0.2490	5.11
Ethanol	472	21186.4	563	17762.0	28596.4	3424.45	91	80	3695.3	0.5328	7.38
<u>MC4</u>											
MDC	613	16313.2	670	14925.4	24771.4	1387.84	57	110	2787.1	0.3843	7.08
THF	592	16891.9	662	15105.7	23434.2	1786.15	70	112	3222.2	0.4331	7.39
EA	591	16920.5	660	15151.5	21524	1768.96	69	140	2990.4	0.3497	6.63
Acetone	585	17094.0	676	14792.9	20553	2301.12	91	130	3433.0	0.4090	7.14
Acetonitrile	594	16835.0	671	14903.1	22244.8	1931.89	77	116	3252.1	0.4021	7.13
DMF	596	16778.5	669	14947.7	19920	1830.84	73	105	3087.7	0.3256	6.43
DMSO	604	16556.3	696	14367.8	22493	2188.48	92	106	3038.6	0.3620	6.82
Ethanol	589	16977.9	670	14925.4	10541	2052.56	81	130	3433.0	0.2463	5.56

Solvent -	Absorption	Vertical Excitation	Oscillator	Orbital Contribution
Joivent	nm	nm	Strength	%
MDC	521	496	1.5335	99.6
THF	508	495	1.5279	99.6
EA	508	492	1.5175	99.6
Acetone	514	496	1.5118	99.6
Acetonitrile	509	496	1.5058	99.6
DMF	510	500	1.5332	99.5
DMSO	519	500	1.5287	99.5
Ethanol	503	496	1.5124	99.6

Table S2 Comparison of experimental absorption and vertical excitation obtained by TD-DFTfor MC1

Table S3 Comparison of experimental absorption and vertical excitation obtained by TD-DFTfor MC2

Solvent	Absorption	Vertical Excitation	Oscillator	Orbital Contribution %	
	nm	nm	Strength		
MDC	491	515	0.9283	98.9	
THF	484	513	0.9213	98.9	
EA	483	510	0.9098	98.9	
Acetone	481	518	0.9137	98.9	
Acetonitrile	483	519	0.9103	98.9	
DMF	476	522	0.9367	98.9	
DMSO	496	522	0.9339	98.9	
Ethanol	475	519	0.9148	98.9	

Table S4 Comparison of experimental absorption and vertical excitation obtained by TD-DFTfor MC3

Solvent	Absorption	Vertical Excitation	Oscillator	Orbital	
_	nm	nm	Strength	contribution	
MDC	487	484	1.2200	99.0	
THF	482	483	1.2177	99.0	
EA	481	481	1.2111	99.1	
Acetone	485	484	1.1815	99.0	
Acetonitrile	487	485	1.1698	99.0	
DMF	480	488	1.1982	98.8	
DMSO	485	487	1.1921	98.8	
Ethanol	472	485	1.1797	98.9	

Table S5 Comparison of experimental absorption and vertical excitation obtained by TD-DFTfor MC4

Solvent	Absorption	Vertical Excitation	Oscillator	Orbital	
_	nm	nm	Strength	Contribution	
MDC	613	569	1.3173	100.2	
THF	592	567	1.3080	100.2	
EA	591	564	1.2932	100.3	
Acetone	585	567	1.3102	100.3	
Acetonitrile	594	567	1.3099	100.3	
DMF	596	572	1.3356	100.2	
DMSO	604	572	1.3330	100.2	
Ethanol	589	567	1.3127	100.3	

Table S6 Excess Dipole Moment (μ_e - μ_g) values in Debye obtained from the slopes of the polarity plots.

Molecule	Solvents	Lippert- Mataga plot (D)	McRae plot (D)	Bakshive plot (D)	Reichardt- Dimroth E _T (N) (D)
	MDC	7.982	4.720	7.703	3.562
	THF	7.677	4.539	7.408	3.426
N/C1	EA	8.023	4.744	7.742	3.580
IVICI	Acetonitrile	7.962	4.708	7.683	3.553
	DMF	7.941	4.695	7.663	3.544
	DMSO	8.023	4.744	7.742	3.580
	MDC	9.573	5.601	9.095	3.649
	THF	9.335	5.462	8.869	3.558
МСЭ	EA	9.717	5.685	9.232	3.704
WICZ	Acetone	9.383	5.489	8.914	3.576
	Acetonitrile	9.240	5.406	8.779	3.522
	DMSO	9.742	5.699	9.255	3.713
	MDC	8.273	5.062	8.358	3.612
	THF	8.354	5.112	8.440	3.647
MC3	EA	8.618	5.273	8.707	3.762
WICS	Acetone	8.273	5.062	8.358	3.612
	DMF	8.476	5.186	8.563	3.700
	DMSO	8.394	5.137	8.481	3.664
	MDC	5.095	5.528	8.592	3.122
	THF	5.266	5.713	8.879	3.130
MC4	EA	5.083	5.515	8.572	3.075
	Acetonitrile	5.302	5.753	8.941	3.067
	DMF	5.180	5.620	8.736	3.130
	Ethanol	5.108	5.541	8.613	3.083



Figure S1 Absorption and emission spectra of MC2



Figure S2 Absorption and emission spectra of MC3



Figure S3 Absorption and emission spectra of MC4







Figure S5 Normalized absorption and emission spectra of MC2



Figure S6 Normalized absorption and emission spectra of MC3



Figure S7 Normalized absorption and emission spectra of MC4







Figure S9 Solvent polarity plots for MC2



Figure S10 Solvent polarity plots for MC3



Figure S11 Solvent polarity plots for MC4



Figure S12 Cyclic voltammogram of MC1-MC4 in acetonitrile.

	MC1	MC2	MC3	MC4
LUMO+1				
LUMO				
номо				
HOMO-1				

Figure S13 Graphical representation of electron density distribution at HOMO and LUMO



Figure S14. Nyquist plots of DSSC devices under dark (left side) and light (right side) condition.

Figure S14 shows a drastic difference in the mid semicircle curve of EIS under dark and light illumination condition. The high frequency semicircle curve correspond to the EIS of electron transport through the surface of counter electrode4. These semicircle curve obtained under dark condition almost similar with that in the light illumination. The similar electrochemical properties are due to same counter electrode and electrolyte used under both condition. While the mid semicircle quite smaller under light illumination, its corresponding to the charge transfer across the TiO2/dye/electrolyte interface 4,5. The resistance corresponding to the mid semicircle is known to be the resistance for recombination (Rrec), in the EIS measurement under light illumination exhibit Rrec following order MC1 (28 Ω), MC2 (31 Ω), MC3 (34 Ω) and MC4 (36 Ω).



Figure S15 ¹H NMR spectrum of MC1



Figure S16¹³C NMR spectrum of MC1



Figure S17 ¹H NMR spectrum of MC2



Figure S18 ¹³C NMR spectrum of MC2



Figure S19¹H NMR spectrum of MC3



Figure S20¹³C NMR spectrum of MC3



Figure S21 ¹H NMR spectrum of MC4



Figure S22 ¹³C NMR spectrum of MC4

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