Electronic Supplementary Information (ESI)

Varying Numbers and Positions of Carboxylate Groups on Ru Dyes for Dye-Sensitized Solar Cells: Uptake to TiO_2, Cell Performance and Cell Stability

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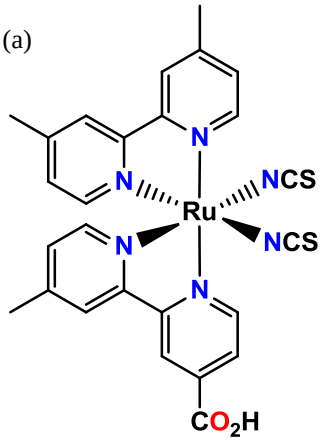
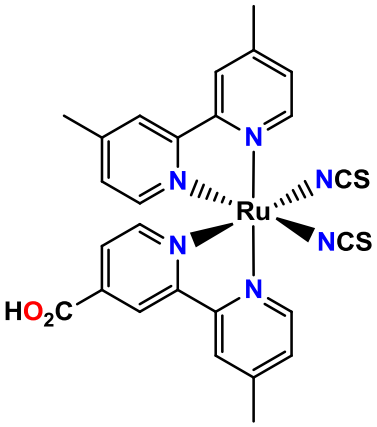
Isomers of complexes 1-4

(a)

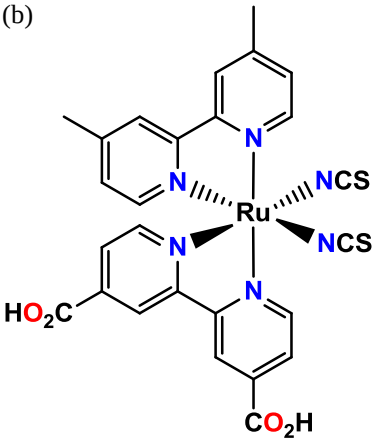


Isomer 1



Isomer 2

(b)



Isomer 1

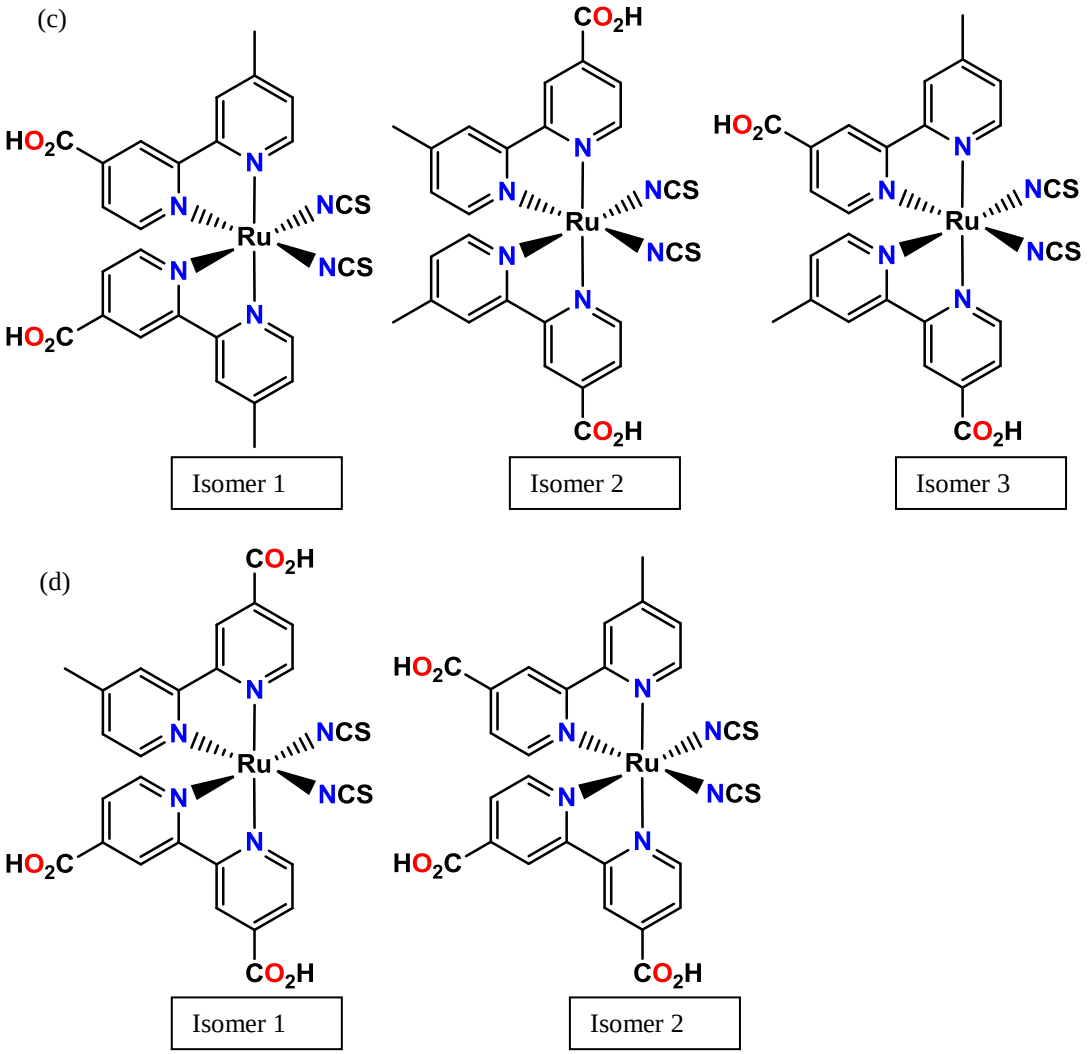


Figure S1 Geometrical isomers of (a) **1** (1:1), (b) **2**, (c) **3** (2:2:1), and (d) **4** (1:1)

Table S1 Geometrical isomerism exhibited by complexes **1-4**.

Complex	Number of Isomers	Ratio of Isomers
1	2	1:1
2	1	-
3	3	2:2:1
4	2	1:1

^{1}H NMR of Complex 3

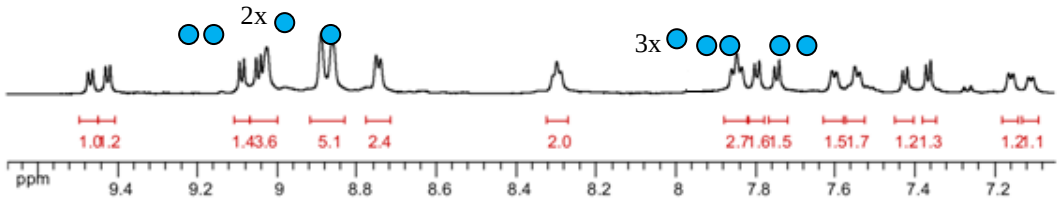


Figure S2 ^{1}H NMR spectrum of complex **3** in d_6-DMSO. The circles represent the third isomer hidden behind the other two isomers.

Emission Spectroscopy

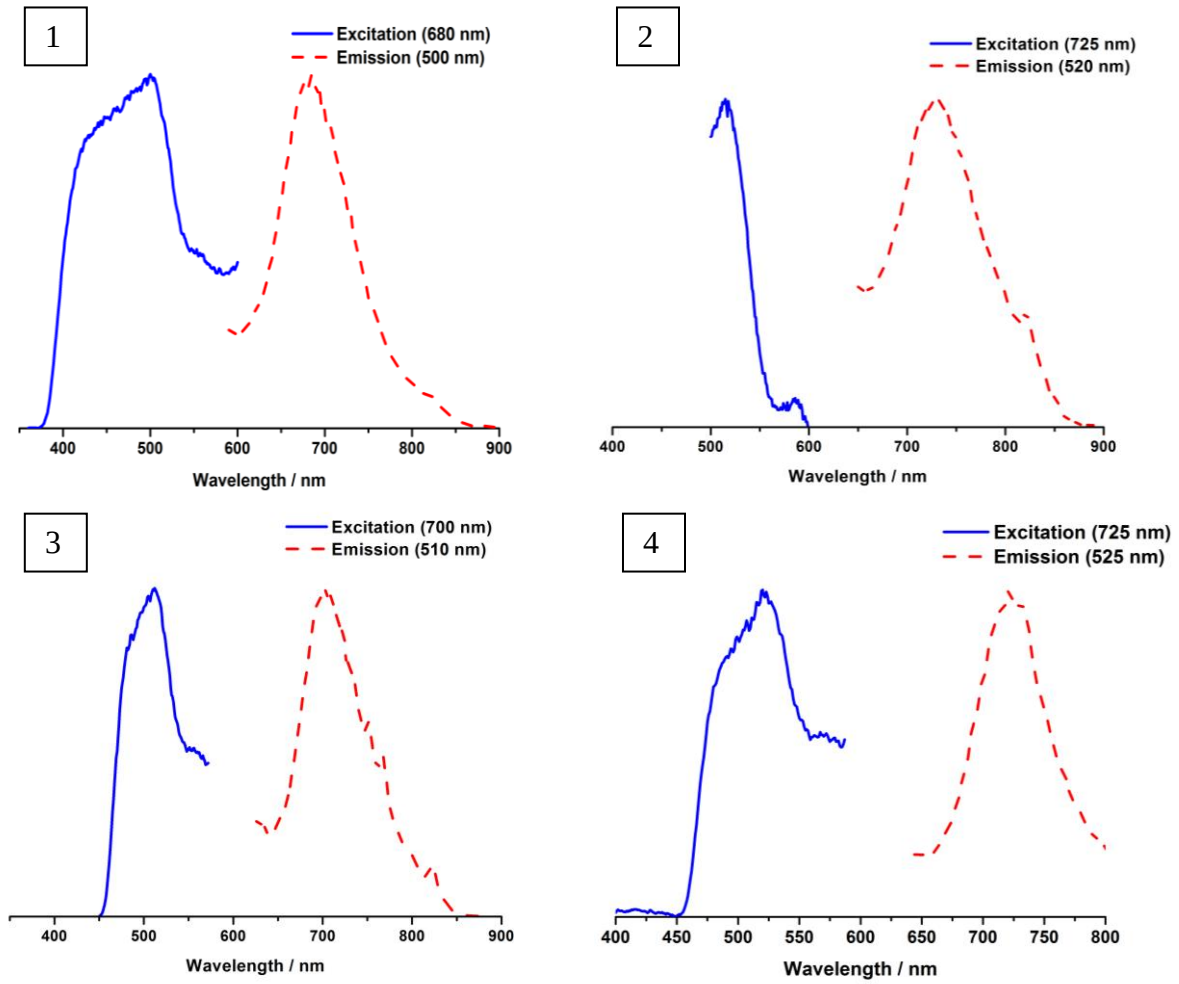


Figure S3 Excitation (blue curve) and emission (dash red curve) maxima for complexes **1-4** in DMF at 77 K.

Electrochemistry

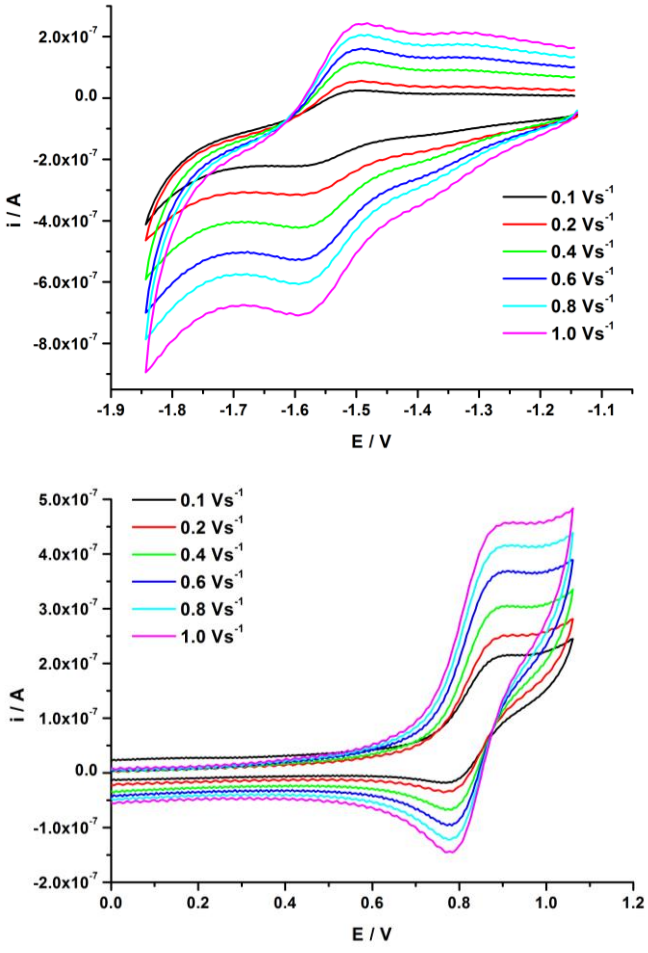
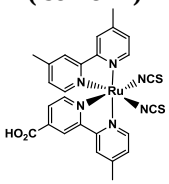


Figure S4 Cyclic voltammetry of **3** showing the reduction (top) and oxidation (bottom) peaks in 0.1M $TBABF_4$/DMF at 298 K.

Hybrid-DFT Calculations

Complex	MO	MO energy / eV	% Contribution from			
			Ru-based orbitals	Dmbpy- based orbitals	Mcbpy- based orbitals	NCS-based orbitals
1 (isomer 1) 	HOMO-8	-7.45	1.43	29.90	67.85	0.82
	HOMO-7	-7.32	1.10	69.26	28.65	0.99
	HOMO-6	-6.93	26.55	10.86	7.20	55.39
	HOMO-5	-6.79	16.73	24.12	28.39	30.76
	HOMO-4	-6.76	23.59	22.05	21.65	32.71
	HOMO-3	-6.27	0.29	6.10	7.15	86.46
	HOMO-2	-5.73	29.33	22.45	23.46	24.76
	HOMO-1	-5.69	22.11	31.32	30.51	16.06
	HOMO	-5.46	35.66	25.02	14.42	24.90
	LUMO	-2.87	4.75	45.07	46.56	3.62
	LUMO+1	-2.41	2.21	72.62	22.03	3.14
	LUMO+2	-2.16	2.14	41.44	54.45	1.97
	LUMO+3	-1.56	1.19	70.43	24.94	3.44

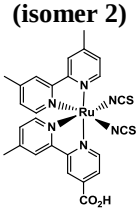
Complex	MO	MO energy / eV	% Contribution from			
			Ru-based orbitals	Dmbpy- based orbitals	Mcbpy- based orbitals	NCS-based orbitals
1 (isomer 2) 	HOMO-6	-6.91	24.42	12.04	9.22	54.32
	HOMO-5	-6.81	13.77	33.68	29.84	22.71
	HOMO-3	-6.27	0.21	7.92	9.95	81.92
	HOMO-2	-5.74	19.92	40.50	21.12	18.46
	HOMO-1	-5.69	19.79	27.62	38.01	14.58
	HOMO	-5.42	37.61	19.41	17.80	25.18
	LUMO	-2.86	4.73	38.93	53.13	3.21
	LUMO+1	-2.41	2.61	72.62	20.88	3.89
	LUMO+2	-2.16	1.81	16.38	79.84	1.97
	LUMO+3	-1.60	0.91	50.29	47.27	1.53
	LUMO+4	-1.38	0.91	58.43	38.91	1.75
	LUMO+5	-1.28	1.06	49.39	48.36	1.19

Table S2 Percentage contributions from component parts of **1** (isomer 1 - top, isomer 2 – bottom) to selected molecular orbitals, and the calculated energies for these molecular orbitals. There is little difference between both isomers with regards to the molecular orbital contributions from component parts of the molecule. Isomer 1 indicates there is a slightly higher HOMO-*n* ruthenium contribution and a lower LUMO+*n* mcbpy contribution in comparison to isomer 2.

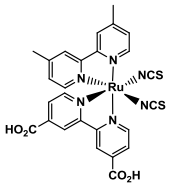
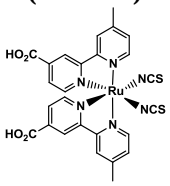
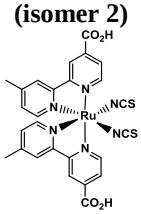
Complex	MO	MO energy / eV	% Contribution from			
			Ru-based orbitals	Dmbpy- based orbitals	Dcbpy- based orbitals	NCS-based orbitals
2 	HOMO-7	-7.36	0.97	51.81	48.53	0.63
	HOMO-6	-7.01	26.06	18.81	10.48	44.65
	HOMO-5	-6.90	19.64	33.49	20.11	26.76
	HOMO-4	-6.85	20.96	16.09	38.58	24.37
	HOMO-3	-6.31	0.27	4.74	7.75	87.24
	HOMO-2	-5.85	18.18	41.46	19.82	20.54
	HOMO-1	-5.81	20.08	23.67	38.57	17.68
	HOMO	-5.57	37.29	19.81	13.29	29.61
	LUMO	-3.10	3.81	18.57	74.40	3.22
	LUMO+1	-2.53	3.44	40.65	55.39	0.52
	LUMO+2	-2.45	2.48	54.47	40.28	2.77
	LUMO+3	-2.25	0.72	14.86	80.19	4.23
	LUMO+4	-1.58	2.52	57.39	35.33	4.76
	LUMO+5	-1.33	0.95	60.22	38.20	0.63
	LUMO+6	-0.74	2.70	46.79	50.32	0.19
	LUMO+8	-0.13	3.91	61.01	33.22	1.86

Table S3 Percentage contributions from component parts of **2** to selected molecular orbitals, and the calculated energies for these molecular orbitals. The LUMO and subsequent levels show a higher acid-bpy contribution in comparison to complex **1**, as expected due to the extra electron-withdrawing group (CO_2H).

Complex	MO	MO energy / eV	% Contribution from			
			Ru-based orbitals	mcbpy- based orbitals	mcbpy- based orbitals	NCS-based orbitals
3 (isomer 1) 	HOMO-8	-7.52	2.52	45.80	50.56	1.12
	HOMO-7	-7.47	0.55	52.36	46.46	0.63
	HOMO-6	-7.03	31.93	8.81	8.25	51.01
	HOMO-5	-6.86	20.02	22.60	26.36	31.02
	HOMO-4	-6.83	25.30	22.37	22.37	29.96
	HOMO-3	-6.30	0.25	9.30	7.57	82.88
	HOMO-2	-5.81	28.87	22.93	19.91	28.29
	HOMO-1	-5.77	20.79	29.98	31.72	17.51
	HOMO	-5.57	33.05	22.36	18.10	26.49
	LUMO	-2.99	2.16	48.51	44.93	4.40
	LUMO+1	-2.84	5.54	60.07	31.91	2.48
	LUMO+2	-2.26	0.47	51.93	45.45	2.15
	LUMO+3	-2.13	2.73	57.07	38.66	1.54
	LUMO+4	-1.47	1.11	50.69	45.24	2.96
	LUMO+5	-1.42	8.42	47.98	39.75	3.85

Complex	MO	MO energy / eV	% Contribution from			
			Ru-based orbitals	mcbpy- based orbitals	mcbpy- based orbitals	NCS-based orbitals
3 (isomer 2) 	HOMO-9	-8.38	0.31	51.37	45.65	2.67
	HOMO-8	-7.58	2.08	51.13	46.19	0.60
	HOMO-7	-7.55	0.69	49.30	49.40	0.61
	HOMO-6	-6.99	25.26	14.08	14.92	45.74
	HOMO-5	-6.91	19.32	27.39	27.60	25.69
	HOMO-4	-6.88	16.96	32.43	31.36	19.25
	HOMO-3	-6.30	0.21	9.17	9.37	81.25
	HOMO-2	-5.85	19.42	28.22	29.68	22.68
	HOMO-1	-5.82	9.54	40.95	40.12	9.39
	HOMO	-5.09	38.32	16.15	16.52	29.01
	LUMO	-2.92	1.17	25.33	71.80	1.70
	LUMO+1	-2.88	1.88	68.64	28.08	1.40
	LUMO+2	-2.28	0.36	33.87	64.97	0.80
	LUMO+3	-2.04	4.10	63.16	32.38	0.36
	LUMO+4	-1.64	0.49	42.84	55.88	0.79
	LUMO+5	-1.46	0.83	59.84	37.19	2.14

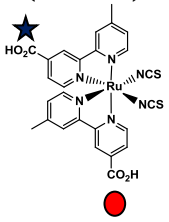
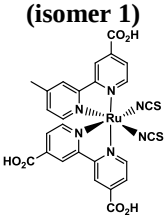
Complex	MO	MO energy / eV	% Contribution from			
			Ru-based orbitals	mcbpy- based orbitals ●	mcbpy- based orbitals ★	NCS-based orbitals
3 (isomer 3) 	HOMO-8	-7.57	1.66	68.28	29.33	0.73
	HOMO-7	-7.49	0.78	42.86	55.83	0.53
	HOMO-6	-7.01	27.54	15.23	9.11	48.12
	HOMO-5	-6.90	21.74	12.66	37.03	28.57
	HOMO-3	-6.30	0.18	8.51	23.38	67.93
	HOMO-2	-5.84	17.04	28.14	36.18	18.64
	HOMO-1	-5.80	14.42	53.25	19.58	12.75
	HOMO	-5.55	33.64	20.84	19.09	26.43
	LUMO	-2.94	2.28	75.06	20.95	1.71
	LUMO+1	-2.87	2.60	67.38	27.90	2.12
	LUMO+2	-2.28	2.21	86.19	10.68	0.92
	LUMO+3	-2.16	0.22	19.57	79.78	0.43
	LUMO+4	-1.58	1.79	30.97	65.70	1.54
	LUMO+5	-1.45	0.49	25.62	72.80	1.09
	LUMO+8	-0.12	2.11	61.04	34.47	2.38
	LUMO+9	-0.09	1.06	53.09	44.65	1.20

Table S4 Percentage contributions from component parts of **3** (isomer 1 - top, isomer 2 – middle, isomer 3 – bottom) to selected molecular orbitals, and the calculated energies for these molecular orbitals. The HOMO and HOMO-1 are relatively close in energy with a difference of 0.2 eV for isomers 1 and 3, and also a significant delocalisation over the NCS ligand. The HOMO-HOMO-1 gap is larger for isomer 2 (0.73 eV), with a significant contribution from the bipyridine ligands (HOMO-1). The HOMO energy is increased, reducing the HOMO-LUMO gap. All three isomers show similar energies for the first two LUMO energy levels, with minimal contribution from the ruthenium centre and NCS ligands.

Complex	MO	MO energy / eV	% Contribution from			
			Ru-based orbitals	Mcbpy- based orbitals	Dcbpy- based orbitals	NCS-based orbitals
4 (isomer 1) 	HOMO-8	-7.68	1.01	41.71	56.83	0.45
	HOMO-7	-7.53	0.93	49.59	48.85	0.63
	HOMO-6	-6.99	29.24	17.22	9.59	43.95
	HOMO-5	-6.97	14.31	30.53	38.73	16.43
	HOMO-4	-6.95	19.69	29.28	31.30	19.73
	HOMO-3	-6.33	0.31	7.11	7.86	84.72
	HOMO-2	-5.91	19.09	29.84	26.04	25.03
	HOMO-1	-5.89	14.42	30.17	39.64	15.77
	HOMO	-5.62	33.92	22.68	14.03	29.37
	LUMO	-3.14	4.66	24.87	65.50	4.97
	LUMO+1	-2.95	3.87	56.24	37.29	2.60
	LUMO+2	-2.57	4.34	58.93	36.14	0.59
	LUMO+3	-2.26	1.38	65.04	28.91	4.67
	LUMO+4	-2.17	2.17	47.07	49.06	1.70

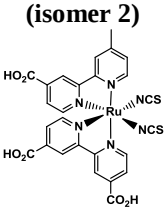
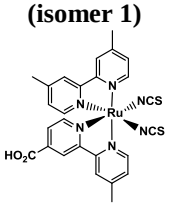
Complex	MO	MO energy / eV	% Contribution from			
			Ru-based orbitals	Mcbpy- based orbitals	Dcbpy- based orbitals	NCS-based orbitals
4 (isomer 2) 	HOMO-8	-7.69	1.38	29.58	68.36	0.68
	HOMO-7	-7.58	0.94	54.63	43.83	0.60
	HOMO-6	-7.11	25.94	23.82	15.50	34.74
	HOMO-5	-6.97	20.49	41.43	15.23	22.85
	HOMO-4	-6.92	22.97	13.17	40.57	23.29
	HOMO-3	-6.33	0.30	7.56	10.00	82.14
	HOMO-2	-5.91	17.63	35.72	23.94	22.71
	HOMO-1	-5.88	18.25	22.93	39.97	18.85
	HOMO	-5.66	35.94	10.05	21.36	32.65
	LUMO	-3.16	3.68	35.60	56.62	4.10
	LUMO+1	-2.94	4.04	73.32	19.87	2.77
	LUMO+2	-2.57	3.94	56.77	38.70	0.59
	LUMO+3	-2.33	1.22	66.94	29.72	2.12

Table S5 Percentage contributions from component parts of **4** (isomer 1 - top, isomer 2 – bottom) to selected molecular orbitals, and the calculated energies for these molecular orbitals. Both isomers have similar molecular orbital energies. The HOMO-LUMO gap is slightly smaller in comparison to that of complexes **1-3**. This is expected because increasing the number of acid groups lowers the LUMO energy level. The HOMO HOMO-1 and HOMO-2 energy levels are similar in value to one another with a significant contribution based on ruthenium and NCS ligands. The LUMO+*n* orbitals are located on the bipy ligands of the molecule.

TD-DFT Calculations

Complex	Main Visible Absorbance / nm	Main Charge Transitions MO from	MO to	Relative Contribution
1 (isomer 1) 	867	HOMO-2	LUMO	21 %
		HOMO-1	LUMO	15 %
		HOMO	LUMO	64 %
	630	HOMO-2	LUMO	38 %
		HOMO-1	LUMO	16 %
		HOMO-1	LUMO+1	10 %
		HOMO	LUMO	14 %
		HOMO	LUMO+2	22 %
	570	HOMO-2	LUMO	11 %
		HOMO-2	LUMO+1	34 %
		HOMO-1	LUMO+1	18 %
		HOMO	LUMO+2	37 %
	539	HOMO-2	LUMO	9 %
		HOMO-2	LUMO+1	22 %
		HOMO-1	LUMO	10 %
		HOMO-1	LUMO+1	12 %
		HOMO	LUMO	10 %
		HOMO	LUMO+1	9 %
		HOMO	LUMO+2	23 %
		HOMO	LUMO+3	5 %
	311	HOMO-8	LUMO	49 %
		HOMO-6	LUMO+2	18 %
		HOMO-5	LUMO+2	14 %
		HOMO-4	LUMO+2	19 %
	295	HOMO-8	LUMO	9 %
		HOMO-8	LUMO+1	24 %
		HOMO-7	LUMO+1	44 %
		HOMO-6	LUMO+2	23 %

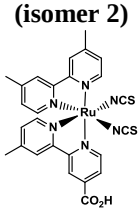
Complex	Main Visible Absorbance / nm	Main Charge Transitions MO from	MO to	Relative Contribution
1 (isomer 2) 	674	HOMO	LUMO	100 %
	539	HOMO-2	LUMO	33 %
		HOMO-1	LUMO	13 %
		HOMO	LUMO+1	54 %
	526	HOMO-2	LUMO	43 %
		HOMO-1	LUMO	15 %
		HOMO-1	LUMO+1	12 %
		HOMO	LUMO+1	30 %
	468	HOMO-2	LUMO+1	35 %
		HOMO-1	LUMO+1	17 %
		HOMO	LUMO+1	10 %
		HOMO	LUMO+2	38 %
	458	HOMO-2	LUMO	10 %
		HOMO-2	LUMO+1	26 %
		HOMO-1	LUMO+1	26 %
		HOMO	LUMO+2	38 %
	360	HOMO-6	LUMO	13 %
		HOMO-5	LUMO	23 %
		HOMO-3	LUMO+1	8 %
		HOMO-1	LUMO+3	7 %
		HOMO	LUMO+4	34 %
		HOMO	LUMO+5	15 %

Table S6 TD-DFT calculated visible absorption wavelengths for **1** (isomer 1 – top, isomer 2 – bottom), indicating the molecular orbitals involved and their relative contribution to the absorption.

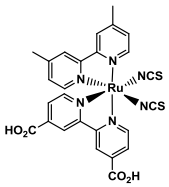
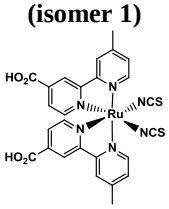
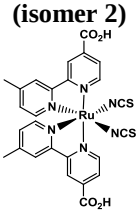
Complex	Main Visible Absorbance / nm	Main Charge Transitions MO from	MO to	Relative Contribution
2 	698	HOMO-2	LUMO	36 %
		HOMO	LUMO	9 %
		HOMO	LUMO+1	39 %
		HOMO	LUMO+2	16 %
	587	HOMO-2	LUMO	8 %
		HOMO-2	LUMO+1	9 %
		HOMO-1	LUMO+1	36 %
		HOMO-1	LUMO+2	7 %
		HOMO	LUMO+1	9 %
		HOMO	LUMO+2	31 %
	417	HOMO-5	LUMO	36 %
		HOMO-3	LUMO+2	64 %
	387	HOMO-6	LUMO	35 %
		HOMO-1	LUMO+4	30 %
		HOMO	LUMO+5	26 %
		HOMO	LUMO+8	9 %
	299	HOMO-7	LUMO+1	37 %
		HOMO-6	LUMO+3	10 %
		HOMO-4	LUMO+4	11 %
		HOMO-3	LUMO+5	14 %
		HOMO-2	LUMO+6	28 %

Table S7 TD-DFT calculated visible absorption wavelengths for **2**, indicating the molecular orbitals involved and their relative contribution to the absorption.

Complex	Main Visible Absorbance / nm	Main Charge Transitions MO from	MO to	Relative Contribution
3 (isomer 1) 	638	HOMO-2	LUMO	18 %
		HOMO-1	LUMO+1	11 %
		HOMO	LUMO	71 %
	556	HOMO-2	LUMO	46 %
		HOMO-1	LUMO+1	37 %
		HOMO	LUMO	17 %
	516	HOMO-2	LUMO+1	44 %
		HOMO-1	LUMO	17 %
		HOMO	LUMO+1	26 %
		HOMO	LUMO+3	13 %
	432	HOMO-3	LUMO	29 %
		HOMO-1	LUMO+2	33 %
		HOMO	LUMO+3	38 %
	303	HOMO-7	LUMO+1	74 %
		HOMO-6	LUMO+2	26 %
	253	HOMO-8	LUMO+2	14 %
		HOMO-7	LUMO+3	31 %
		HOMO-6	LUMO+4	13 %
		HOMO-5	LUMO+5	30 %
		HOMO-4	LUMO+4	12 %

Complex	Main Visible Absorbance / nm	Main Charge Transitions MO from	MO to	Relative Contribution
3 (isomer 2) 	657	HOMO	LUMO	100 %
	535	HOMO-2	LUMO	49 %
		HOMO-1	LUMO	15 %
		HOMO-1	LUMO+1	37 %
	471	HOMO	LUMO+2	100 %
	419	HOMO-2	LUMO+2	73 %
		HOMO-1	LUMO+3	27 %
	364	HOMO-5	LUMO+1	57 %
		HOMO-4	LUMO	12 %
		HOMO	LUMO+4	13 %
		HOMO	LUMO+5	18 %
	292	HOMO-8	LUMO	11 %
		HOMO-8	LUMO+1	19 %
		HOMO-7	LUMO+1	19 %
		HOMO-6	LUMO+3	6 %
		HOMO-5	LUMO+3	15 %
		HOMO-4	LUMO+2	6 %
		HOMO-4	LUMO+3	10 %
		HOMO-3	LUMO+4	14 %
	254	HOMO-9	LUMO+1	9 %
		HOMO-8	LUMO+3	13 %
		HOMO-7	LUMO+3	23 %
		HOMO-6	LUMO+4	22 %
		HOMO-5	LUMO+5	21 %
		HOMO-4	LUMO+5	12 %

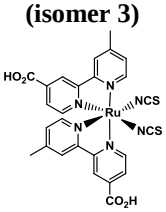
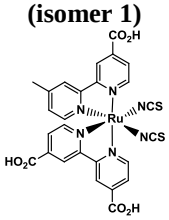
Complex	Main Visible Absorbance / nm	Main Charge Transitions MO from	MO to	Relative Contribution
3 (isomer 3) 	624	HOMO-2	LUMO+1	12 %
		HOMO-1	LUMO	15 %
		HOMO-1	LUMO+1	9 %
		HOMO	LUMO	25 %
		HOMO	LUMO+1	39 %
	546	HOMO-2	LUMO	42 %
		HOMO-1	LUMO	15 %
		HOMO-1	LUMO+1	30 %
		HOMO	LUMO	13 %
	447	HOMO	LUMO+3	100 %
	353	HOMO-6	LUMO	20 %
		HOMO-6	LUMO+1	10 %
		HOMO-5	LUMO+1	15 %
		HOMO	LUMO+4	14 %
		HOMO	LUMO+5	41 %
	293	HOMO-8	LUMO	10 %
		HOMO-8	LUMO+1	18 %
		HOMO-6	LUMO+2	9 %
		HOMO-6	LUMO+3	6 %
		HOMO-5	LUMO+2	10 %
		HOMO-5	LUMO+3	21 %
		HOMO-3	LUMO+4	7 %
		HOMO-1	LUMO+9	6 %
		HOMO	LUMO+8	13 %
	259	HOMO-8	LUMO+2	42 %
		HOMO-8	LUMO+3	8 %
		HOMO-7	LUMO+2	14 %
		HOMO-7	LUMO+3	9 %
		HOMO-6	LUMO+4	12 %
		HOMO-5	LUMO+4	15 %

Table S8 TD-DFT calculated visible absorption wavelengths for **3** (isomer 1 – top, isomer 2 – middle, isomer 3 – bottom), indicating the molecular orbitals involved and their relative contribution to the absorption.

Complex	Main Visible Absorbance / nm	Main Charge Transitions MO from	MO to	Relative Contribution
4 **(isomer 1)** 	569	HOMO-2	LUMO	38 %
		HOMO-2	LUMO+1	9 %
		HOMO-1	LUMO	30 %
		HOMO	LUMO	12 %
		HOMO	LUMO+2	11 %
	520	HOMO-2	LUMO+1	44 %
		HOMO-1	LUMO+1	27 %
		HOMO	LUMO+1	9 %
		HOMO	LUMO+2	20 %
	484	HOMO-3	LUMO	10 %
		HOMO-2	LUMO	8 %
		HOMO-2	LUMO+1	12 %
		HOMO-1	LUMO	9 %
		HOMO-1	LUMO+1	8 %
		HOMO	LUMO+2	46 %
		HOMO	LUMO+3	7 %
	447	HOMO-2	LUMO+2	58 %
		HOMO-1	LUMO+2	14 %
		HOMO	LUMO+3	18 %
		HOMO	LUMO+4	10 %
	370	HOMO-6	LUMO	41 %
		HOMO-4	LUMO+1	59 %
	307	HOMO-8	LUMO	26 %
		HOMO-7	LUMO+1	20 %
		HOMO-6	LUMO+2	31 %
		HOMO-5	LUMO+3	13 %
		HOMO-4	LUMO+4	10 %

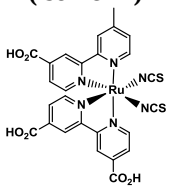
Complex	Main Visible Absorbance / nm	Main Charge Transitions MO from	MO to	Relative Contribution
4 (isomer 2) 	683	HOMO-2	LUMO	20 %
		HOMO	LUMO	80 %
	605	HOMO-2	LUMO	12 %
		HOMO-2	LUMO+1	12 %
		HOMO-1	LUMO+1	16 %
		HOMO	LUMO	9 %
		HOMO	LUMO+1	51 %
	568	HOMO-2	LUMO	43 %
		HOMO-2	LUMO+1	7 %
		HOMO-1	LUMO	12 %
		HOMO-1	LUMO+1	11 %
		HOMO	LUMO	10 %
		HOMO	LUMO+1	8 %
		HOMO	LUMO+2	9 %
	524	HOMO-2	LUMO+2	39 %
		HOMO-1	LUMO+2	26 %
		HOMO	LUMO+2	20 %
		HOMO	LUMO+3	15 %
	445	HOMO-2	LUMO+2	61 %
		HOMO-1	LUMO+2	13 %
		HOMO	LUMO+3	26 %
	365	HOMO-6	LUMO	61 %
		HOMO-6	LUMO+1	11 %
		HOMO-5	LUMO	13 %
		HOMO-4	LUMO+1	15 %
	300	HOMO-8	LUMO	15 %
		HOMO-8	LUMO+1	7 %
		HOMO-7	LUMO+1	23 %
		HOMO-6	LUMO+2	9 %
		HOMO-6	LUMO+3	22 %
		HOMO-5	LUMO+3	24 %

Table S9 TD-DFT calculated visible absorption wavelengths for **4** (isomer 1 – top, isomer 2 – bottom), indicating the molecular orbitals involved and their relative contribution to the absorption.

Solar Measurements

Dye	Dye Bath	Thickness of TiO_2	V_{OC} / mV	J_{SC} / $mAcm^{-2}$	V_{MP} / mV	J_{MP} / $mAcm^{-2}$	FF	η / %
N3	EtOH/DMSO /[TBA][DOC]	10+5 µm	680	17.37	540	15.42	0.71	8.33
N3	EtOH/DMSO /[TBA][DOC]	12+5 µm	660	17.21	510	15.44	0.69	7.87

Table S10 JV data of commercialised N3 dye using Z960 electrolyte (1M 1,3-dimethylimidazolium iodide (DMII), 0.1 M GuNCS, 0.05 M LiI, 0.03 M I_2, 0.5 M *tert*-butylpyridine and a solvent mixture (acetonitrile:valeronitrile 85:15).

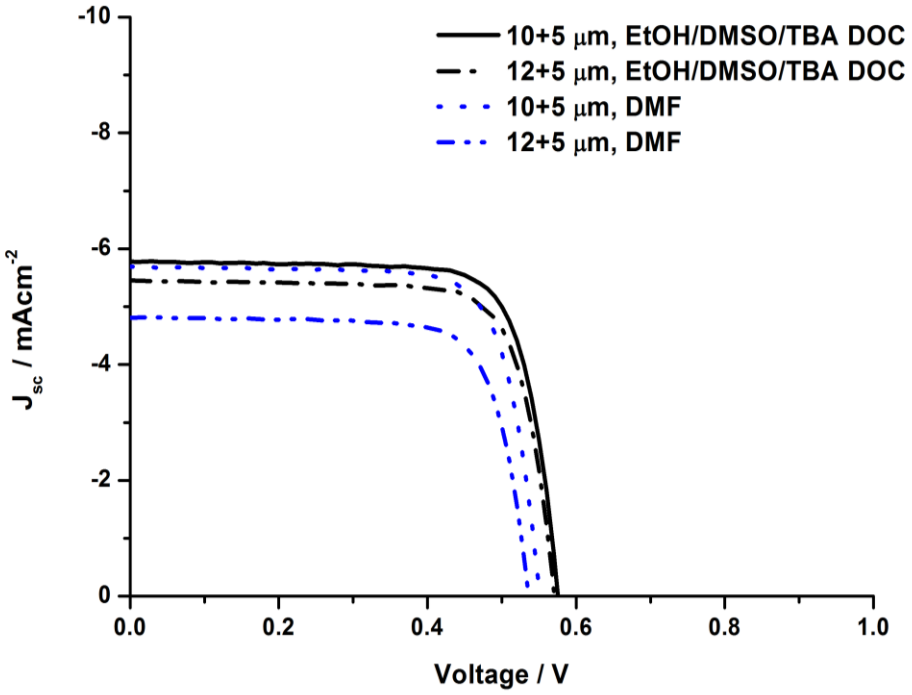


Fig. S5 JV data for **1** with varying TiO_2 thickness and solvent system (black lines: EtOH/DMSO, blue lines: DMF). Electrolyte used: 1M 1,3-dimethylimidazolium iodide (DMII), 0.1 M GuNCS, 0.05 M LiI, 0.03 M I_2, 0.5 M *tert*-butylpyridine and a solvent mixture (acetonitrile:valeronitrile 85:15).

Table S11 JV data for **1** with varying TiO_2 thickness and solvent system. The average efficiency reported is the average of three cells.

Dye Bath	Thickness of TiO_2	Voc / mV	Jsc / $mAcm^{-2}$	η / %	Average η / %
EtOH/DMSO/ [TBA][DOC]	10+5 μm	570	5.87	2.57	2.53 ± 0.04
EtOH/DMSO/ [TBA][DOC]	12+5 μm	570	5.45	2.38	2.29 ± 0.09
DMF	10+5 μm	550	5.69	2.38	2.31 ± 0.07
DMF	12+5 μm	540	4.81	1.95	1.93 ± 0.02

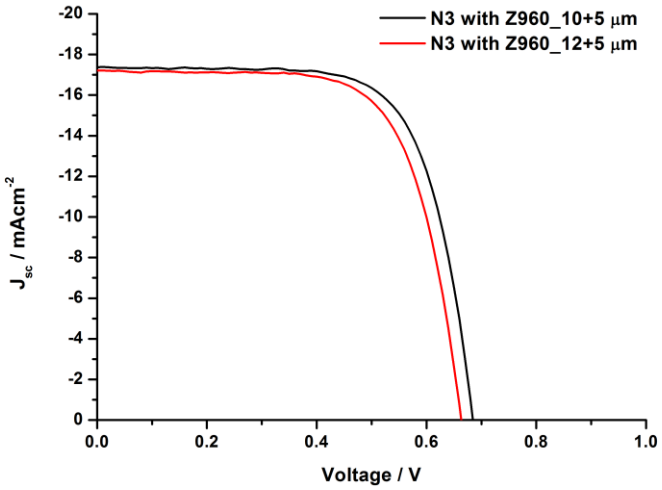


Figure S6a Photocurrent-voltage curve for N3 with varying TiO_2 film thickness.

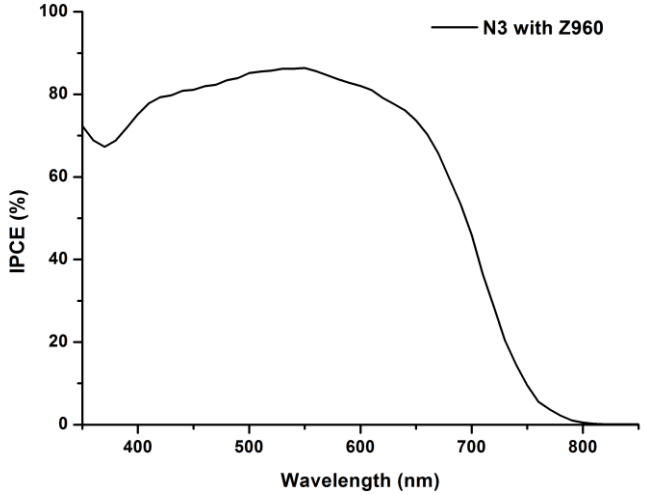


Figure S6b IPCE for N3 with 10+5 μm film thickness.

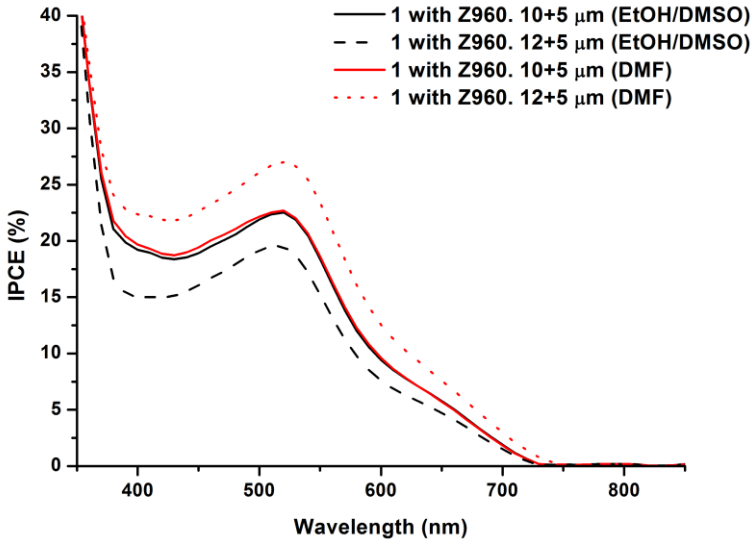


Figure S7 IPCE for **1** with Z960 electrolyte. (black solid line – 10+5 µm film thickness, EtOH/DMSO solvent, black dash line - 12+5 µm film thickness, EtOH/DMSO solvent, red solid line - 10+5 µm film thickness, DMF solvent, red dash dotted line - 12+5 µm film thickness, DMF solvent).

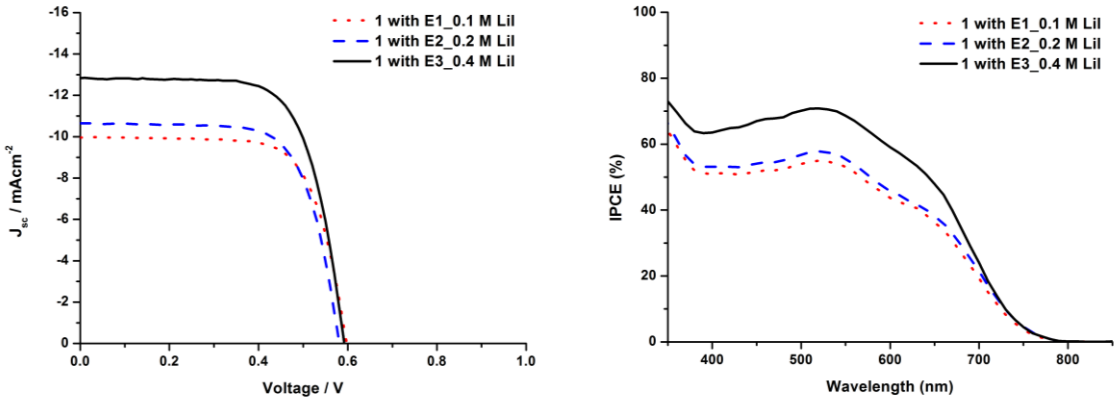


Figure S8 JV curve (left) and IPCE curve (right) of **1** with different electrolytes. (E1: 1M DMII, 0.1 M GuNCS, 0.1 M LiI, 0.03 M I_2, 0.5 M TBP, MeCN:VN (85:15), E2: 1M DMII, 0.1 M GuNCS, 0.2 M LiI, 0.03 M I_2, 0.5 M TBP, MeCN:VN (85:15), E3: 1M DMII, 0.1 M GuNCS, 0.4 M LiI, 0.03 M I_2, 0.5 M TBP, MeCN:VN (85:15)).

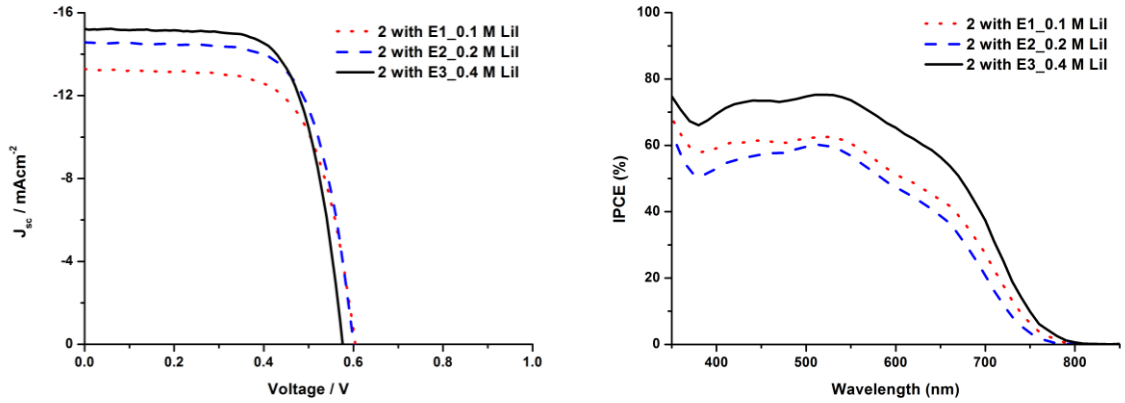


Figure S9 JV curve (left) and IPCE curve (right) of **2** with different electrolytes.

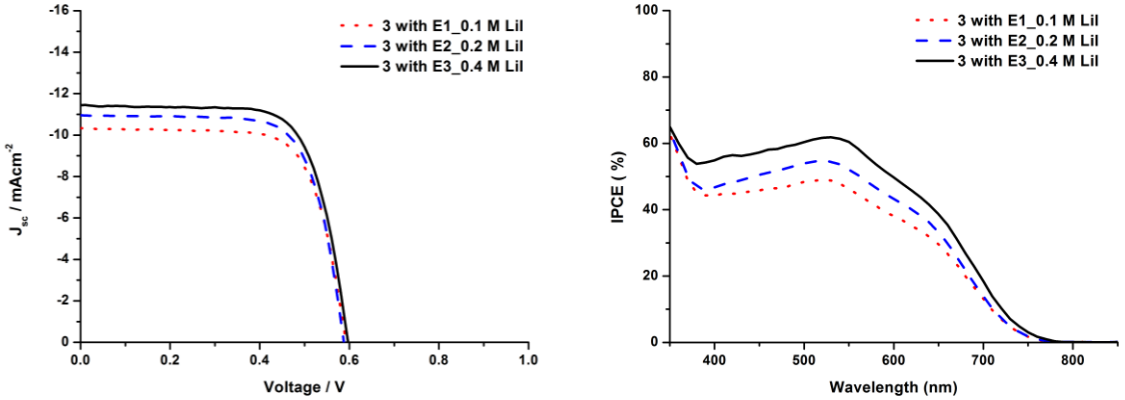


Figure S10 JV curve (left) and IPCE curve (right) of **3** with different electrolytes.

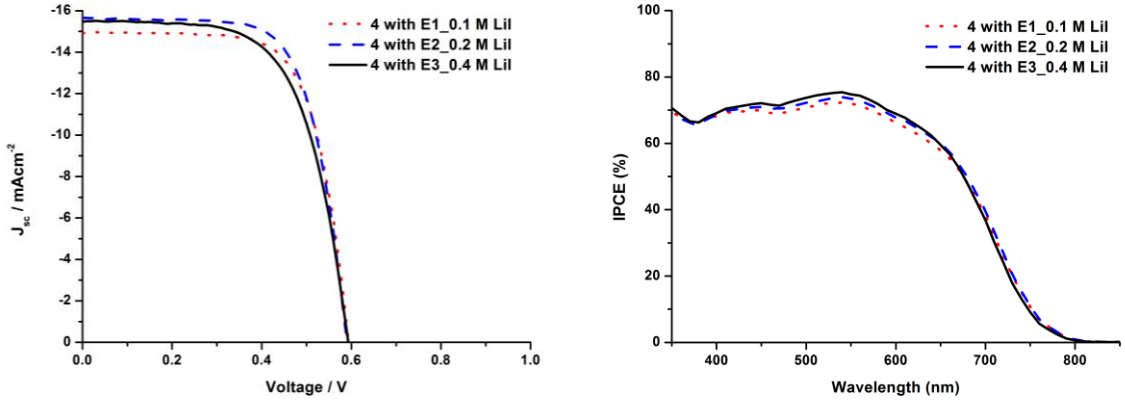


Figure S11 JV curve (left) and IPCE curve (right) of **4** with different electrolytes.

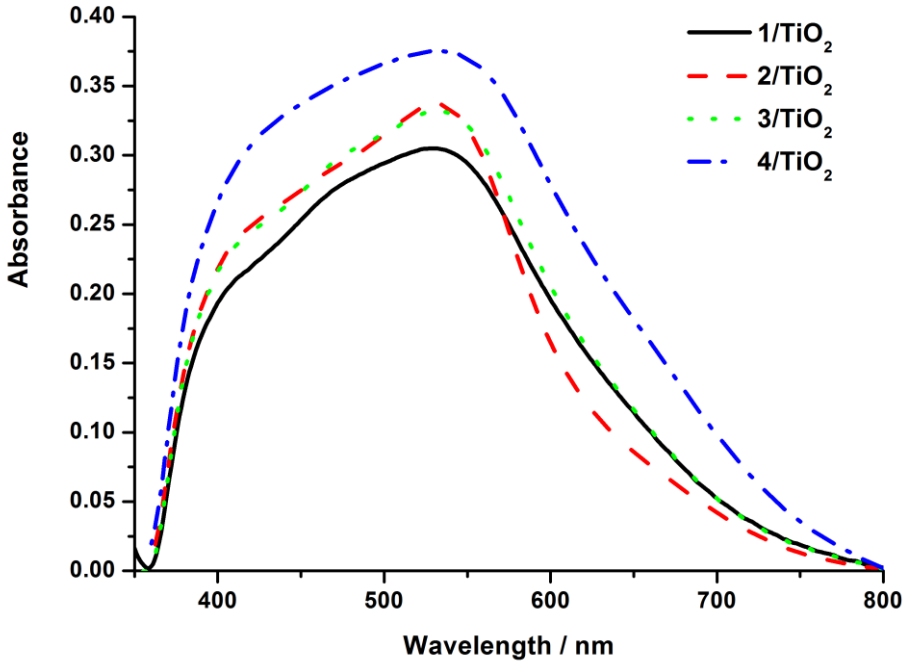


Figure S12 UV-Vis spectra of dye bound to TiO_2. Solid black line = **1**, red dash line = **2**, green dotted line = **3** and blue dash/dot line = **4**. Each dye was dissolved in 0.3 mM EtOH/DMSO and adsorbed to TiO_2 for 24 hours.

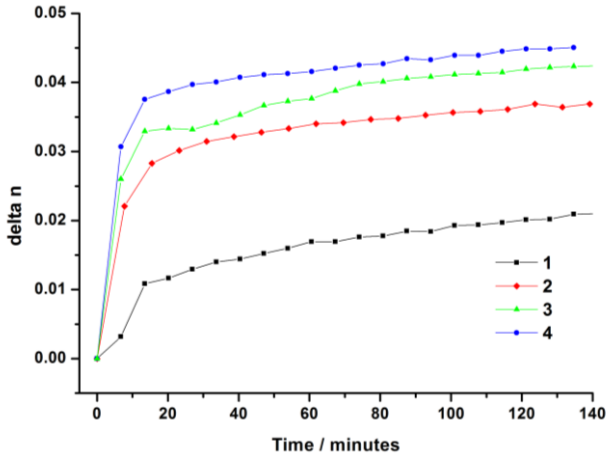


Fig.S13 Change in refractive index within the film for the first 140 minutes.

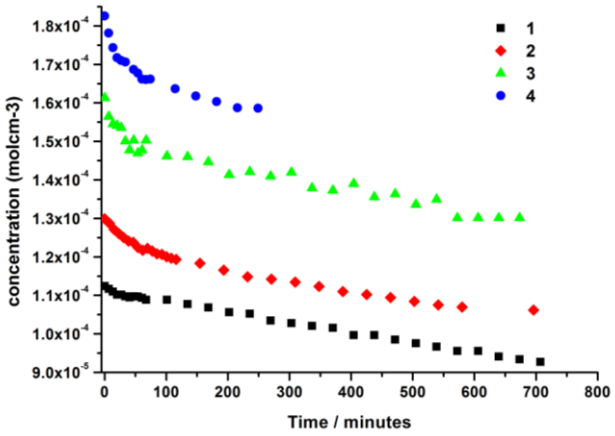


Fig.S14 Changes in concentration of dye in the film during the initial rinsing stage.