Supporting Information for Interfacial electron transfer kinetics in metal-free organic dye sensitized solar cells: Combined effects of molecular structure of dyes and electrolytes

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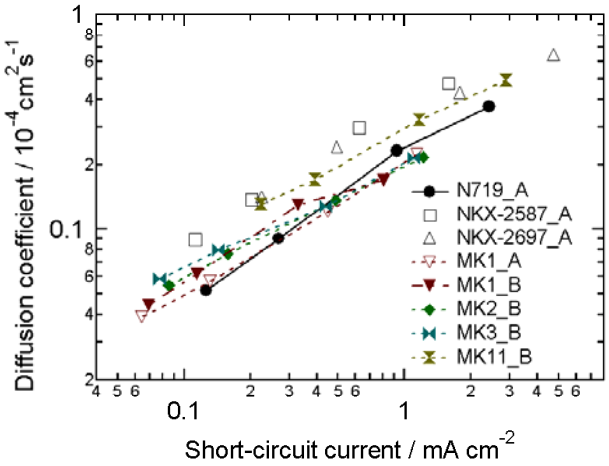
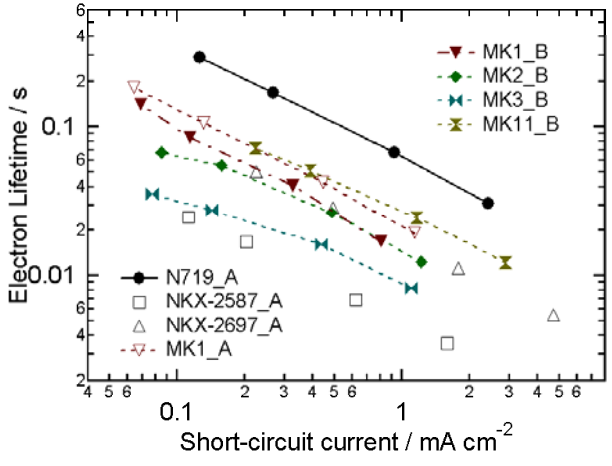
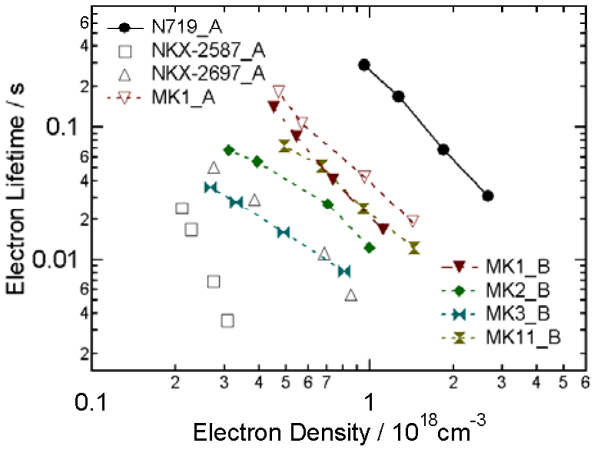
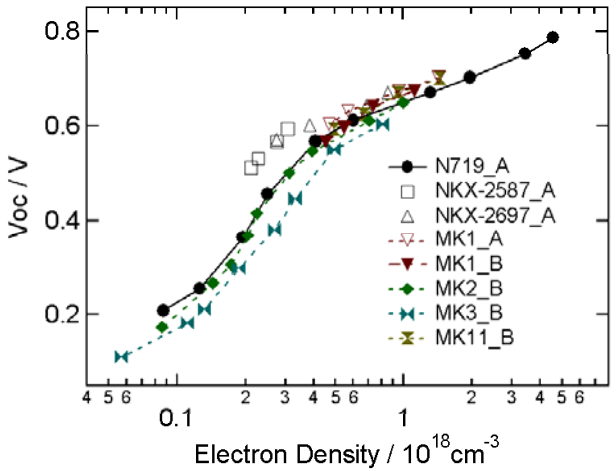
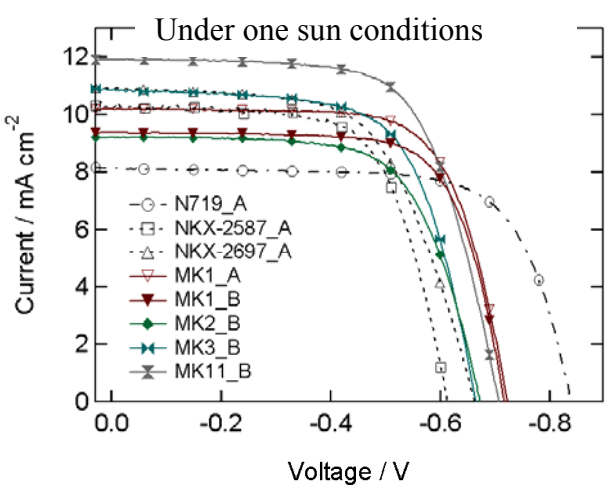
S1-1: using standard electrolyte

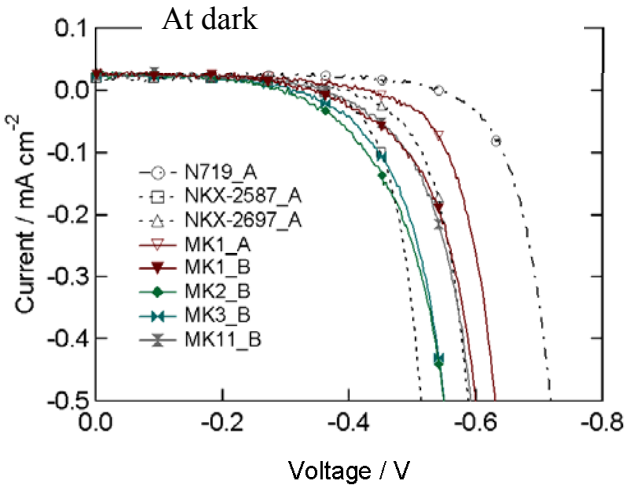






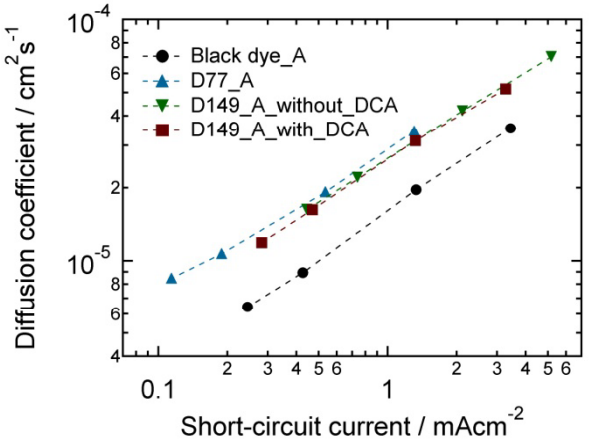


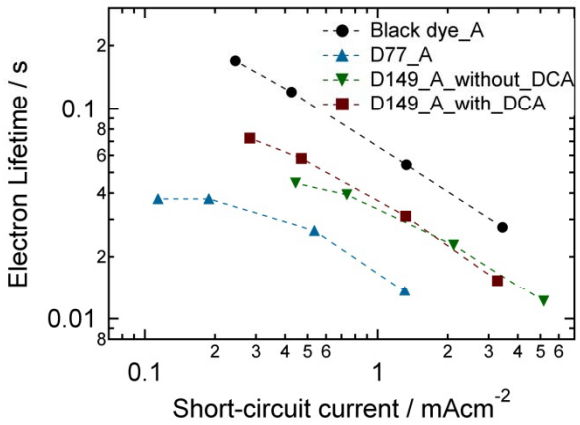


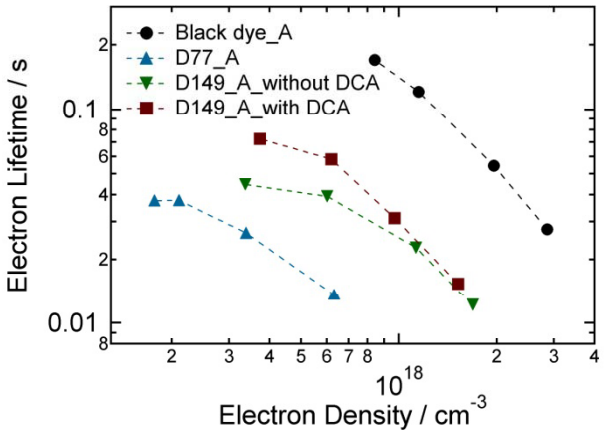


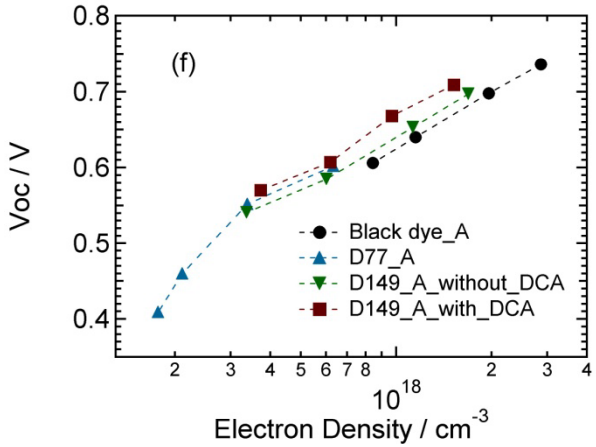
Note that when the electron density becomes lower than 2x10^{17} cm^{-3}, recombination from FTO is not negligible for the examined samples here. Under the conditions, Voc and lifetime are underestimated.

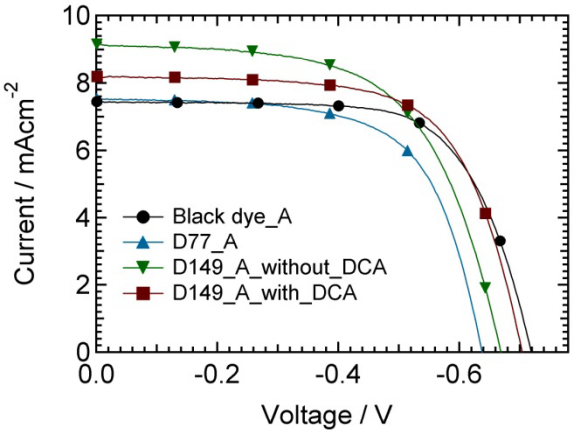
S1-2: using standard electrolyte

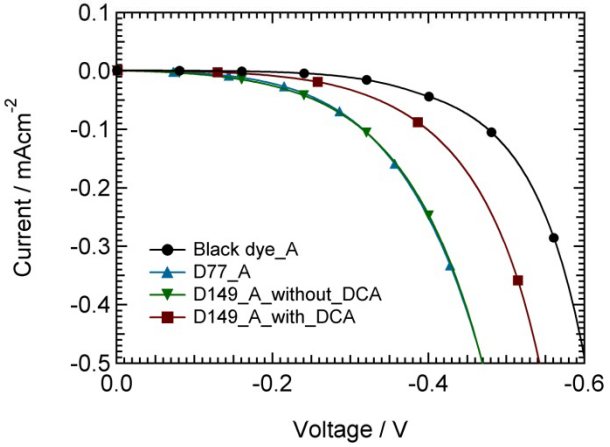




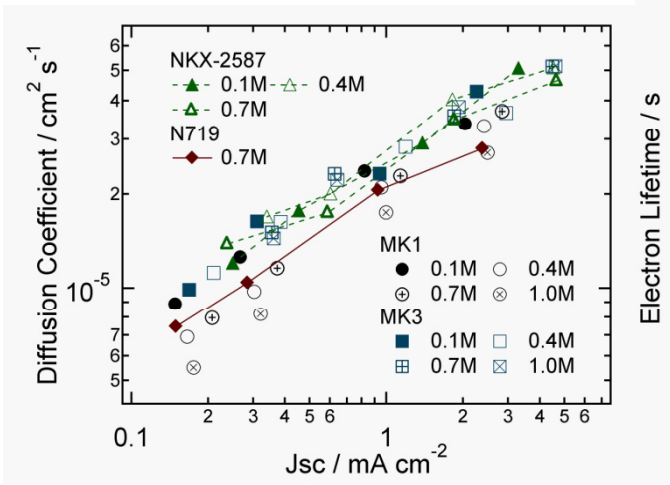


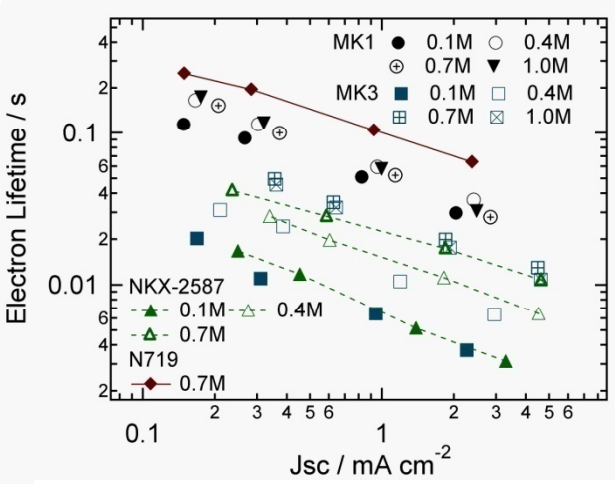


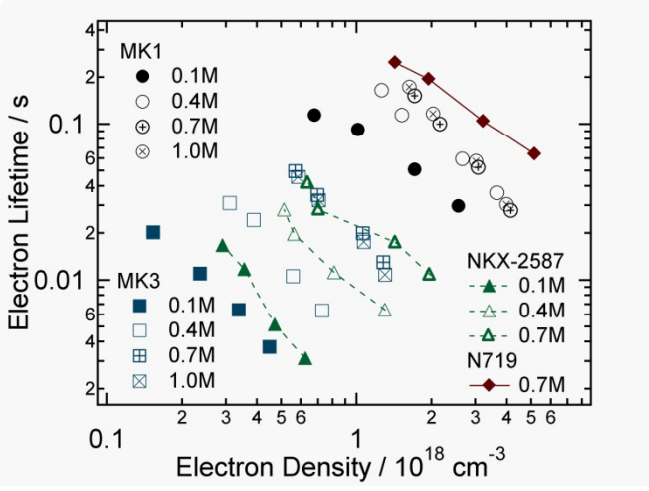


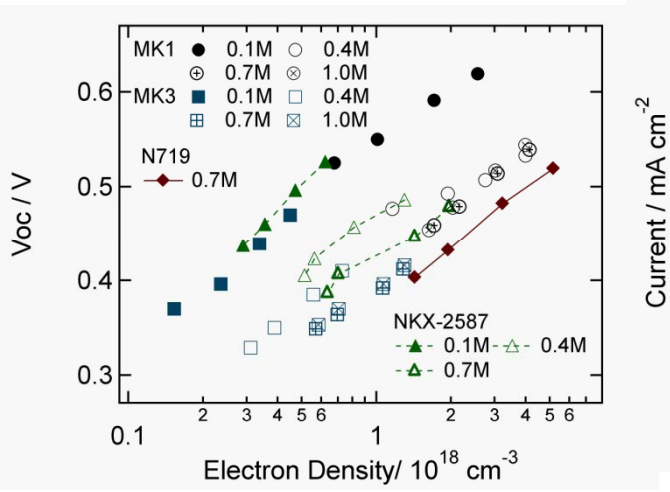


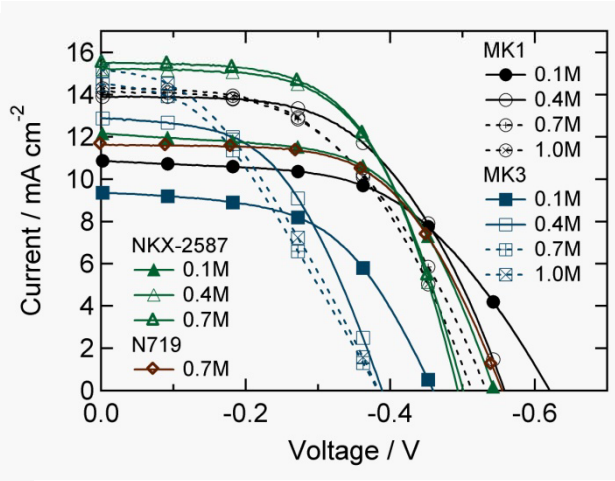
S2: with different LiI concentrations

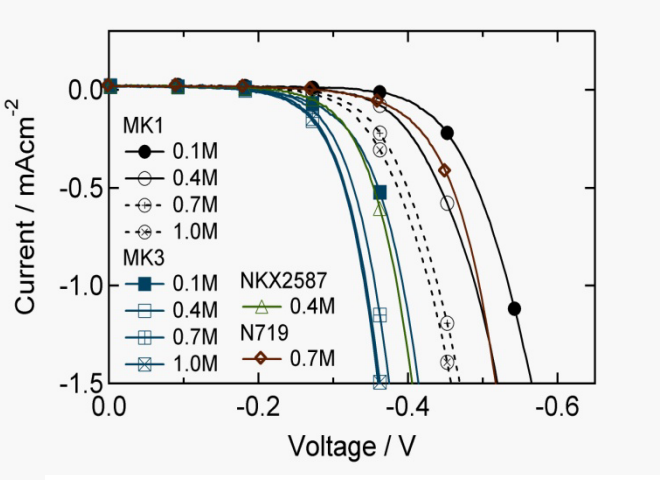








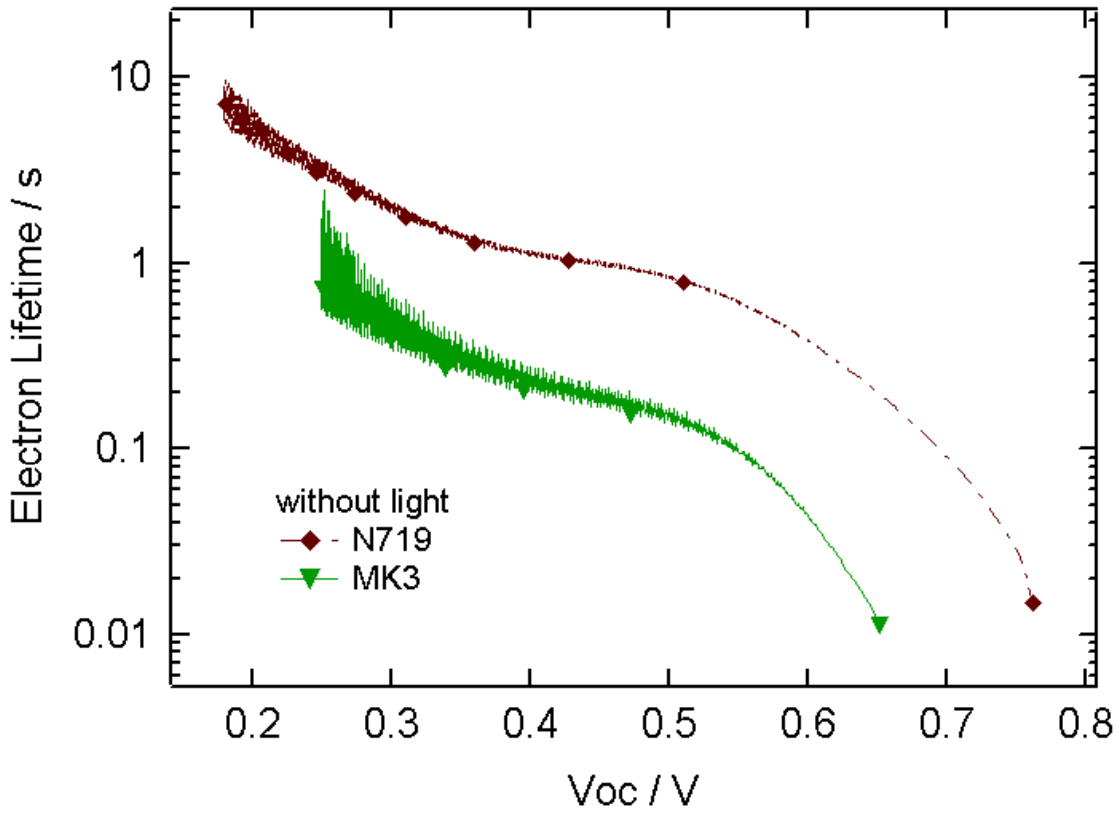




Under one sun conditions

At dark

S3: Electron lifetime obtained from open circuit voltage decay at dark conditions



Electrolytes was Standard.

S4: less dye

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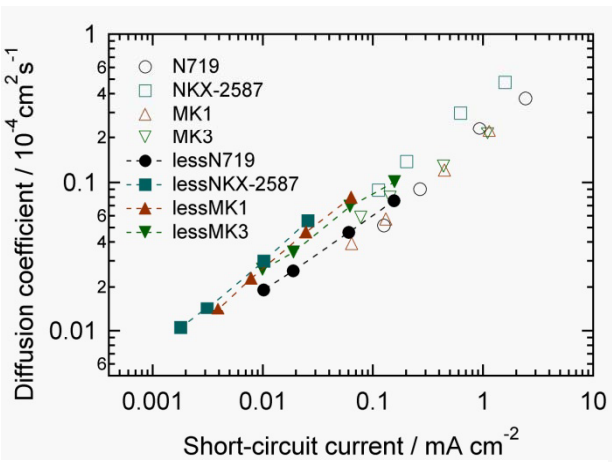

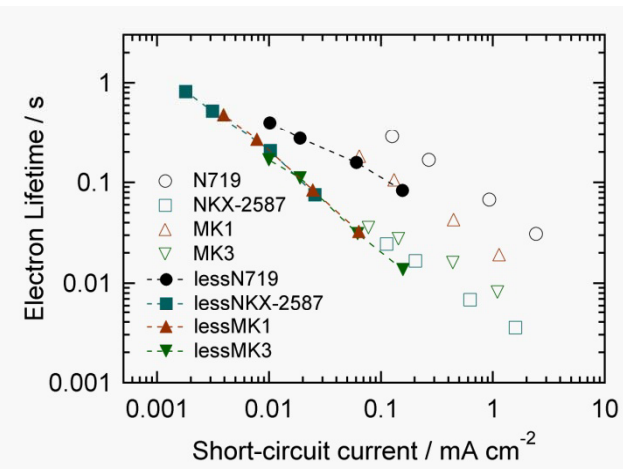

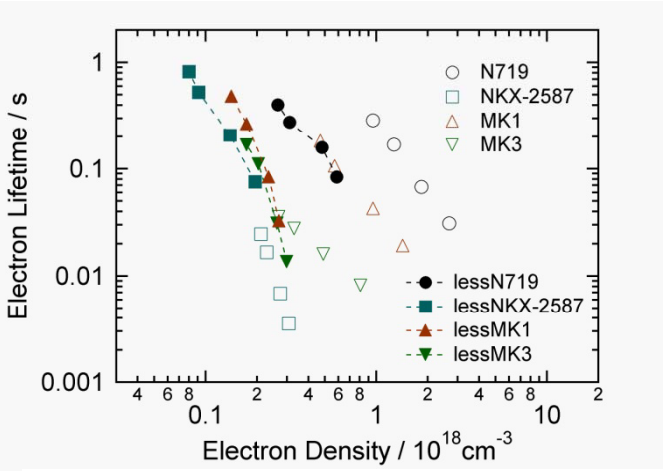

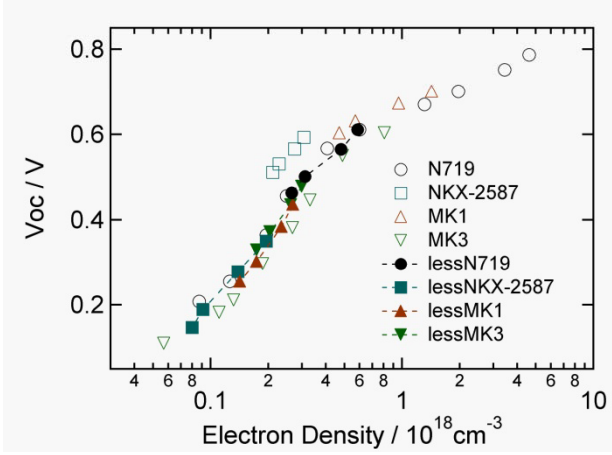

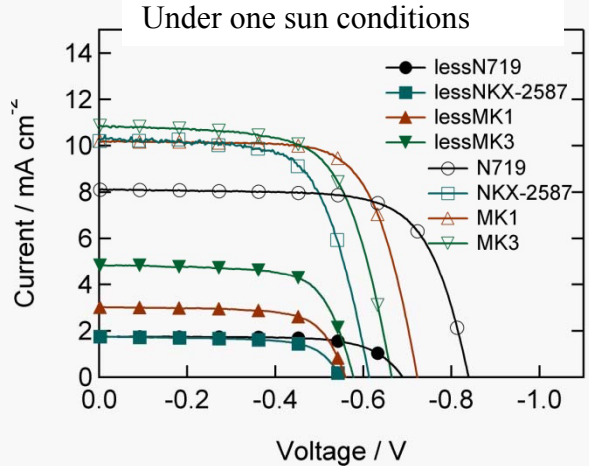

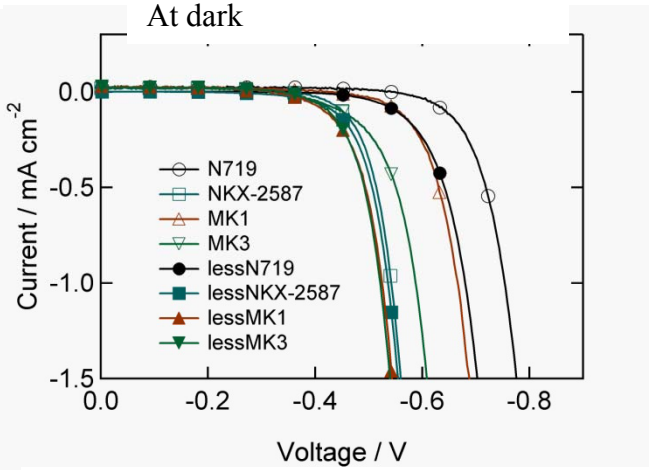

S5: with 0.7M BMImI or LiI and 0.05M I_2

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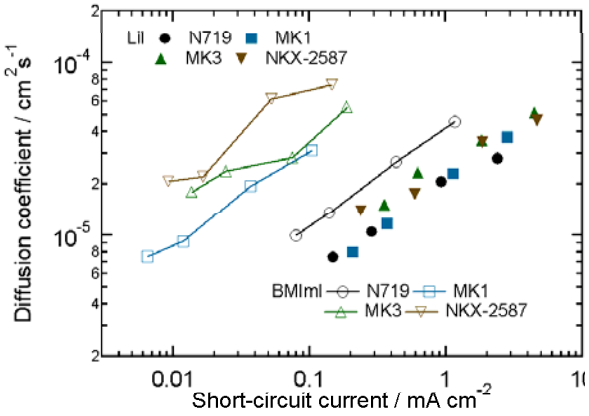

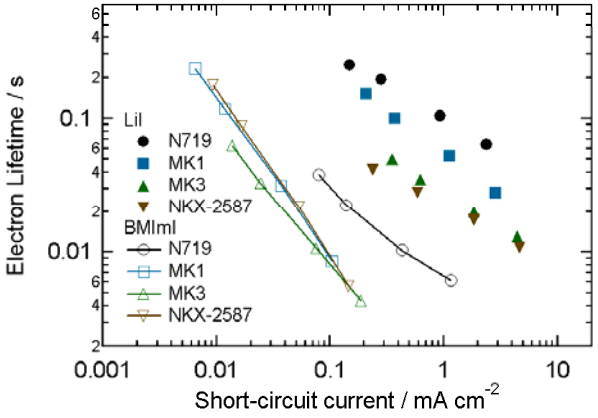

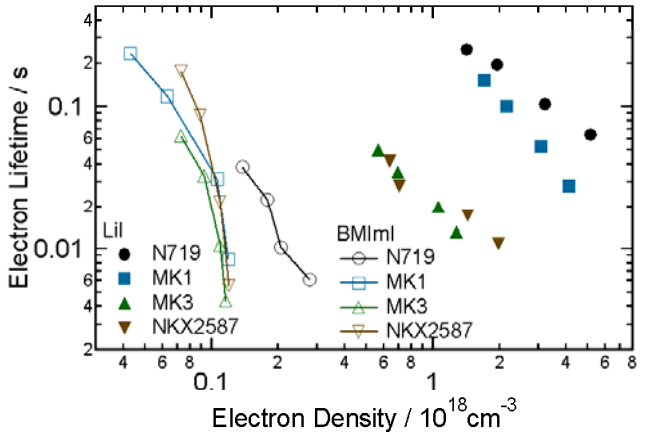

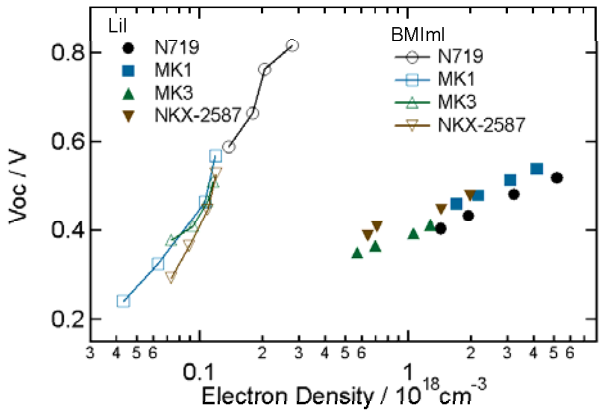

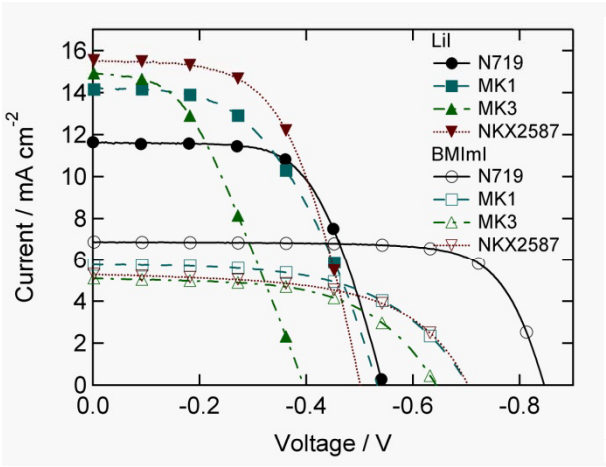

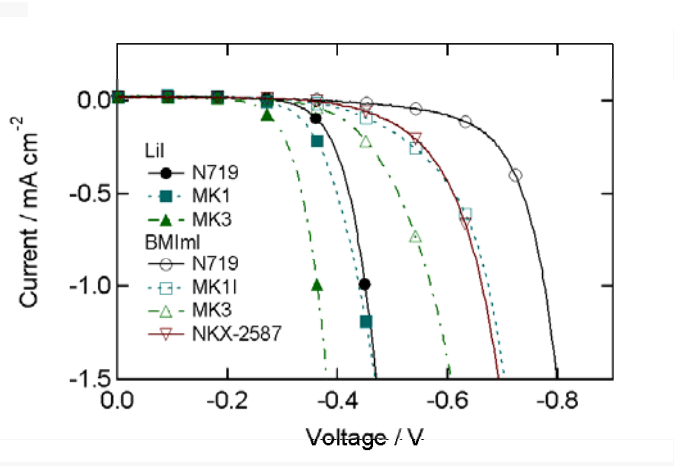

Under one sun conditions

At dark

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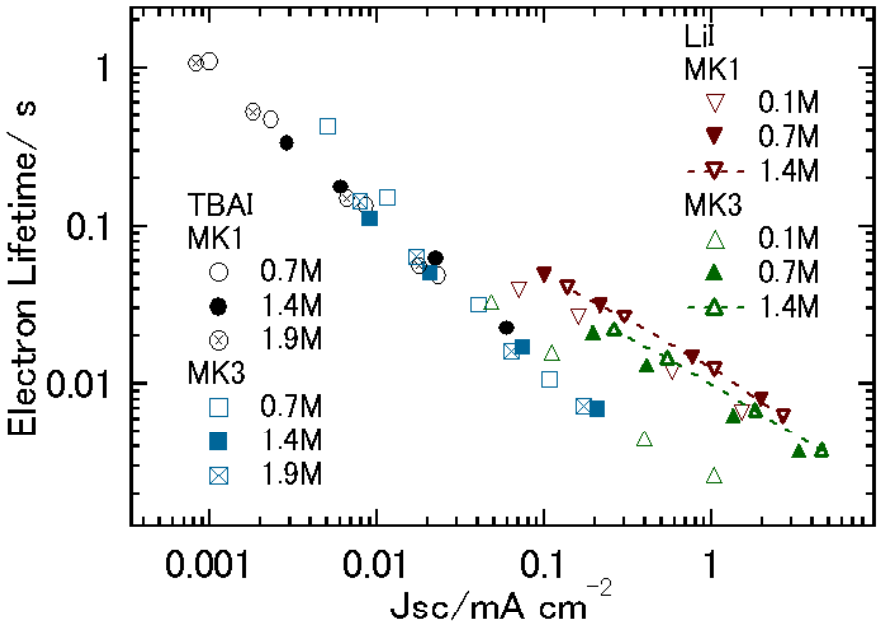
S6: Electron lifetime in DSCs using electrolyte consisting of 0.1 to 1.9 M of TBAI or LiI, 0.05M I_2



S7: Effect of $TiCl_4$ treatment

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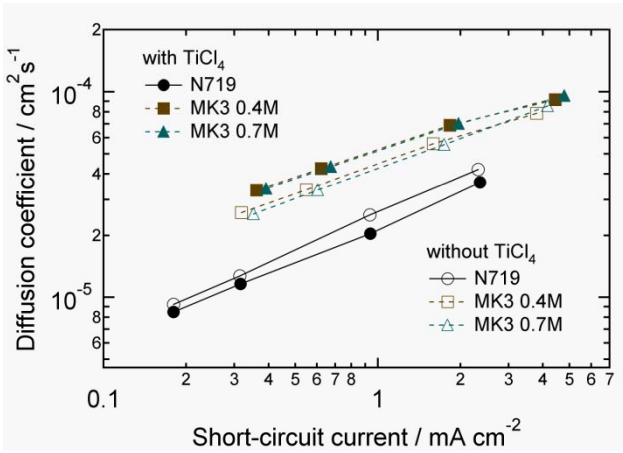
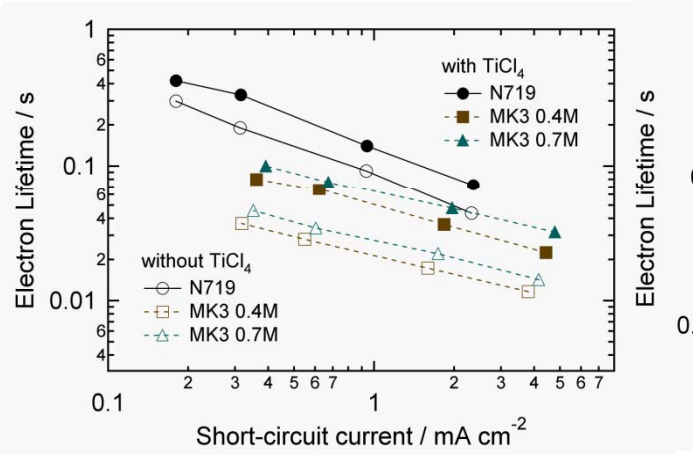
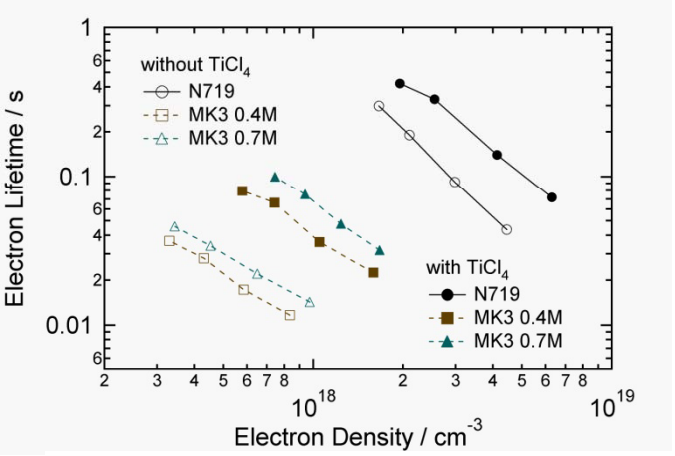
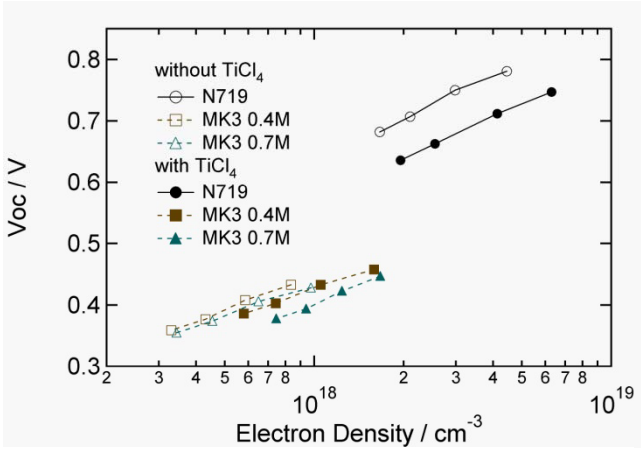
MK3 : 0.4M or 0.7M LiI and 0.05M I_2 in acetonitrile

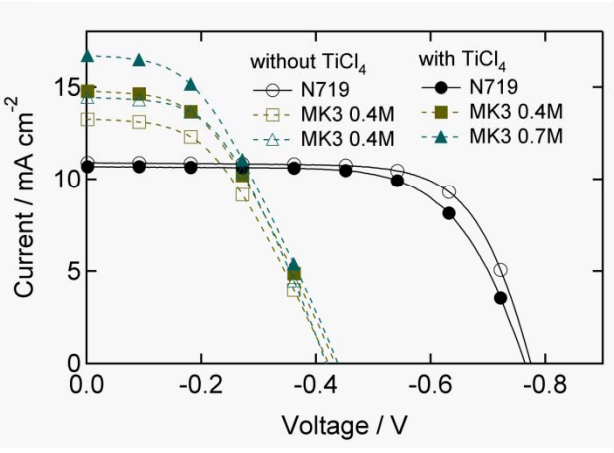
N719 : standard electrolyte

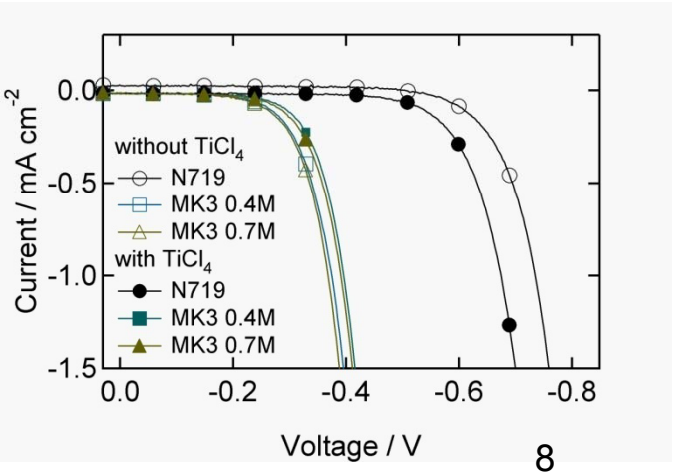












Under one sun conditions

At dark

S8: Molecular orbital calculations

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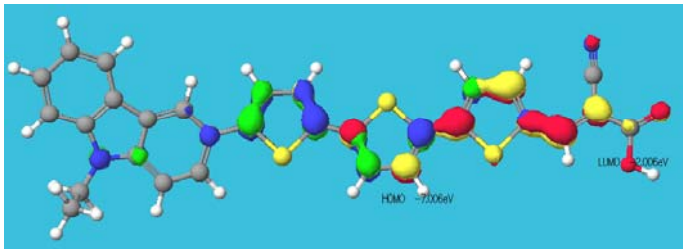
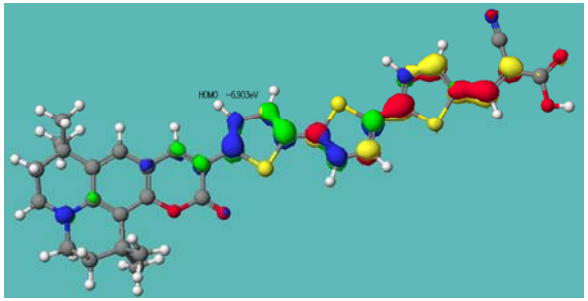
HOMO and LUMO at ZINDO level of theory

MK3



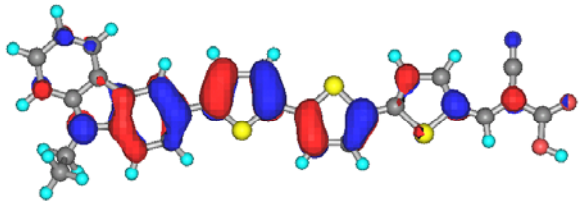
NKX2697



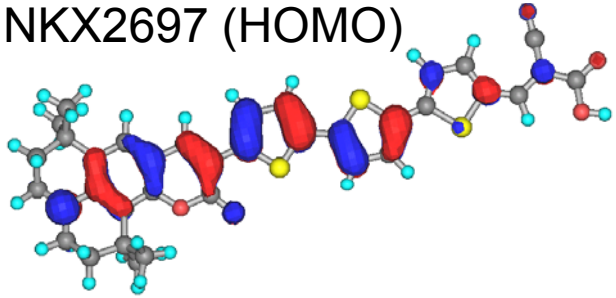
HOMO and LUMO are represented by blue, green-colored orbitals and yellow, red-colored orbitals.
Structure was optimized with 6-31G(d) by Gaussian03
Molecular orbital was calculated by CAChe 6.1.

HOMO and LUMO at B3LYP/6-311+G(d) level of theory

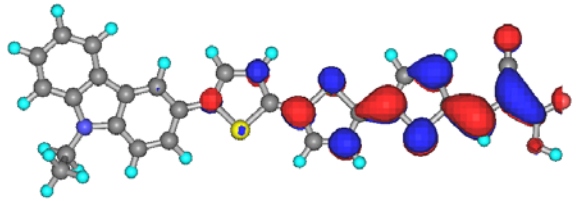
MK3 (HOMO)



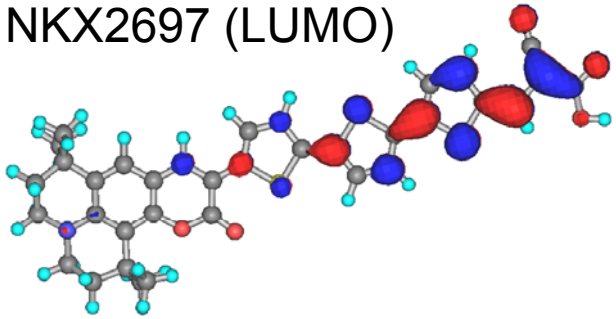
NKX2697 (HOMO)



MK3 (LUMO)

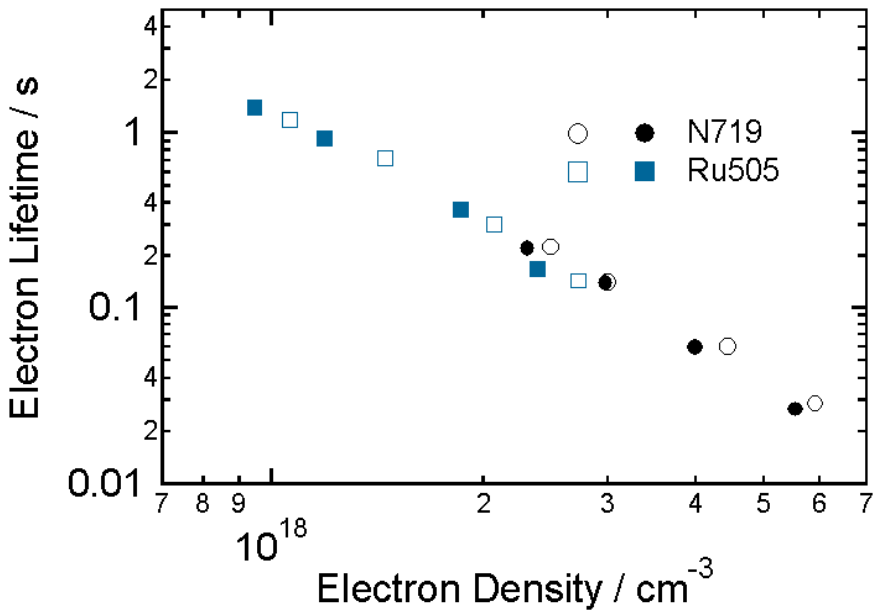


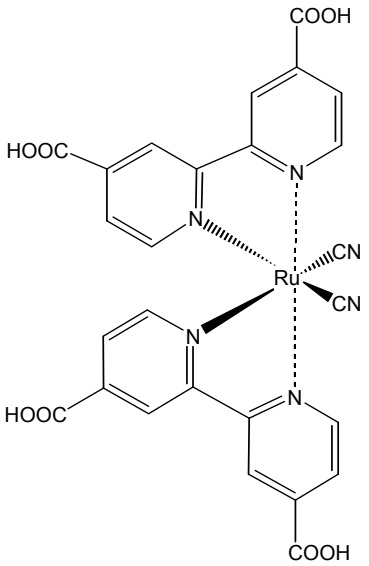
NKX2697 (LUMO)



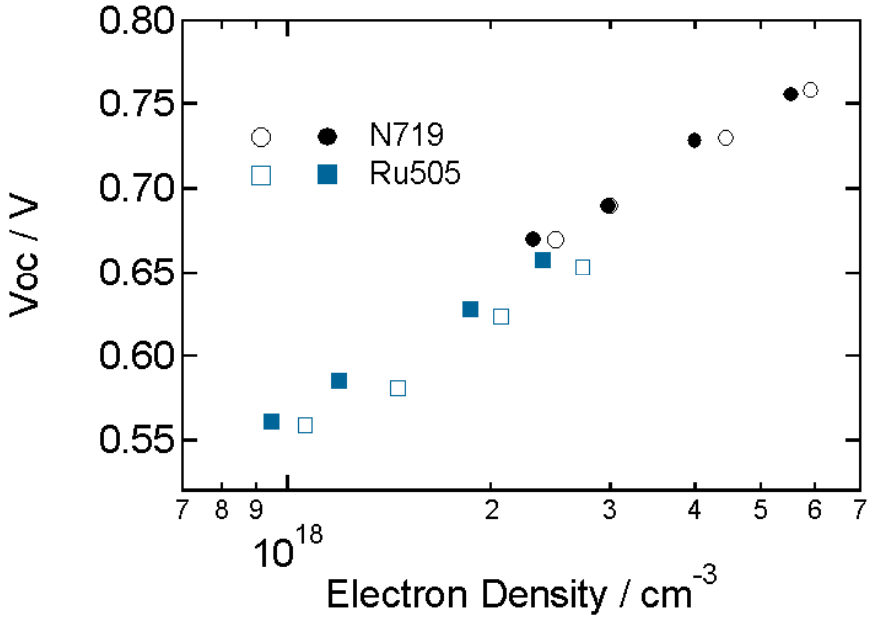
Structure was optimized with 6-31G(d) by Gaussian03.
Molecular orbital was calculated with B3LYP/6-311+G(d) by Gaussian03.

S9 Ru505 & N719 Electron Lifetime vs n, Voc vs n





Structure of Ru505



TiO_2: 18NR: sintered 450℃ for 30min

Ru505: 0.15mM immersed 25h

N719: 0.3mM immersed 18h

standard electrolyte

TiO_2 thickness: 7.2～7.5 μm

Table S1-1. I-V characteristics

S1: using standard electrolyte

sample_name	cellarea/cm^2	film_thickness/μm	Voc/V	Isc/mA cm^{-2}	fill_factor	efficiency/%
N719_A	0.189	3.7	-0.81	8.26	0.716	4.79
NKX2587_A	0.239	4.49	-0.613	10.3	0.661	4.15
NKX2697_A	0.189	3.92	-0.663	10.9	0.609	4.4
MK1_A	0.175	3.41	-0.723	10.2	0.7	5.16
MK1_B	0.164	2.89	-0.714	9.81	0.695	4.87
MK2_B	0.184	2.63	-0.671	9.22	0.664	4.11
MK3_B	0.176	3.47	-0.665	10.9	0.658	4.75
MK11_B	0.189	3.86	-0.707	11.9	0.666	5.61

A: CH_3CN : t-BuOH = 1: 1

B: CH_3CN : t-BuOH : $C_6H_5CH_3$= 1: 1: 1

S2: with different LiI concentrations

sample_name	cell area/cm2	film_thickness/μm	Voc/V	Isc/mAcm-2	fill_factor	efficiency/%
MK1_0.1M	0.242	3.12	-0.62	10.9	0.54	3.64
MK1_0.4M	0.229	3.36	-0.557	13.9	0.548	4.25
MK1_0.7M	0.197	3.52	-0.533	14.1	0.5	3.76
MK1_1.0M	0.214	3.47	-0.512	14.3	0.511	3.75
MK3_0.1M	0.229	3.09	-0.458	9.37	0.543	2.33
MK3_0.4M	0.23	3.23	-0.389	12.9	0.507	2.54
MK3_0.7M	0.207	3.54	-0.383	14.5	0.38	2.11
MK3_1.0M	0.194	3.56	-0.383	15.2	0.383	2.23
NKX2587_0.1M	0.216	3.3	-0.545	12.2	0.587	3.9
NKX2587_0.4M	0.183	3.58	-0.494	15.2	0.588	4.42
NKX2587_0.7M	0.196	3.34	-0.5	15.5	0.574	4.46
N719_0.7M	0.206	3.21	-0.555	11.6	0.591	3.82

Table S1-2. I-V characteristics

S4: less dye

sample_name	cellarea/cm^2	film_thickness/μm	Voc/V	Isc/mAcm^{-2}	fill_factor	efficiency/%
N719	0.189	3.7	-0.81	8.26	0.716	4.79
MK1	0.175	3.41	-0.723	10.2	0.7	5.16
MK3	0.176	3.47	-0.665	10.9	0.658	4.75
NKX2587	0.239	4.49	-0.613	10.3	0.661	4.15
lessN719	0.181	2.7	-0.689	1.75	0.701	0.845
lessMK1	0.168	2.68	-0.56	3.02	0.699	1.18
lessMK3	0.188	2.59	-0.578	4.85	0.693	1.94
lessNKX2587	0.178	2.71	-0.548	1.75	0.682	0.654

S5: with and BMImI and LiI

sample_name	cellarea/cm^2	film_thickness/μm	Voc/V	Isc/mAcm^{-2}	fill_factor	efficiency/%
N719_LiI	0.202	3.31	-0.543	11.6	0.626	3.96
MK1_LiI	0.196	3.52	-0.533	14.2	0.5	3.78
MK3_LiI	0.189	3.73	-0.395	14.9	0.417	2.46
NKX2587_LiI	0.196	3.34	-0.5	15.5	0.574	4.46
N719_BMImI	0.237	3.47	-0.846	6.88	0.739	4.3
MK1_BMImI	0.233	3.7	-0.701	5.76	0.561	2.27
MK3_BMImI	0.243	3.63	-0.644	5.1	0.572	1.88
NKX2587_BMImI	0.245	3.52	-0.705	5.29	0.573	2.13

Table S1-3. I-V characteristics

S5: Black dye,D77,D149

sample_name	Cell area /cm^2	film_thickness/μm	Voc/V	Isc/ $mAcm^{-2}$	fill_factor	efficiency/%
Black dye	0.156	5.45	0.718	7.45	0.683	3.65
D77	0.168	5.08	0.638	7.53	0.649	3.12
D149_without_DCA	0.151	4.92	0.669	9.15	0.605	3.7
D149_with_DCA	0.154	5.07	0.705	8.19	0.661	3.81

Table S2. Estimated solvent reorganization energy.
a: 2a was used for r. b: r was assumed from spatial distribution of HOMO.

Acceptor	r / Å	a / Å	b / Å	λ_s / eV
N3	14	7	7	0.47[a]
NKX2587	10	9	5	0.50[b]
NKX2697	10	13	5	0.39[b]
MK3	10	12.5	4.5	0.50[b]

Complete reference 26

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