Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Augmentation in Photocurrent through Organic Ionic Plastic Crystals as Efficient Redox Mediator for Solid-State Mesoscopic Photovoltaic Devices

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Table S1. Photovoltaic performance reported OIPC based electrolytes with various sensitizers in MPDs

Sr. No.	Dye	electrolyte	OIPC	Additives	Efficiency (%)	Ref
01	N719	$[P_{1222}][FSA]$ (4.71 M), LiI (0.78 M), I_2 (0.24M), and 4-tBP (3.92 M)	$[P_{1222}]FSA$	SiO_2	7.40	1
02	N719	$[P_{1222}][TFSA]$ (4.71 M), LiI (0.78 M), I_2 (0.24M), and 4-tBP (3.92 M)	$[P_{1222}]TFSA$	SiO_2	5.84	1
03	N719	0.600 M BII-6, 0.0300 M I_2, 0.100 M GuSCN, and 0.500 M 4-tBP in MeCN	BII-6	NiL	4.93	2
04	N719	0.600 M BII-8, 0.0300 M I_2, 0.100 M GuSCN, and 0.500 M 4-tBP MeCN	BII-8	NiL	4.06	2
05	N719	20 wt% (PMII), 0.5 M (NBB), 5 wt% (LiTFSI), and 0.05 M I_2 in $N_{44}TFSI$	$N_{44}TFSI$	Nil	5.4	3
06	Z907	$P_{12}I$/30 wt%PMII/7.5wt%CNTs/1% I_2	$P_{12}I$	CNTs	5.60	4
07	N719	DMPII:I_2:SCN	Hybrid (SCN)	DMPII	6.3	5
08	N719	BMII:I_2:SCN	Hybrid (SCN)	BMII	5.6	5
09	CdS	2-Succinonitrile/Na_2S	SN and Na_2S	Nil	1.29	6
10	MK2	40 wt% PMII and CPMPI with 0.1 M LiI and 0.10 M I_2	CPMPI	PMII	5.22	7
11	MK2	15 wt% (1 M) C_{16}MImI, 10 wt% (0.5 M) [MeIm-TEMPO][TFSI], 3 wt% (0.5 M) 4-tBP and 0.58 wt% (0.1) M $NOPF_6$	P_{12} TFSI	[MeIm-TEMPO][TFSI], C_{16}MImI	5.16	8
12	Z-907	$P_{13}I$ + 20 wt % EMII 10 wt % SiO_2, 0.2 M I_2	$P_{13}I$	SiO_2	4.90	9
13	N719	PMII and BMII in succinonitrile with a mole ratio of 2:1:125, and then $LiClO_4$ 5 wt%	PMII + BMII	$LiClO_4$	5.50	10
14	N719	MAII-SN, 0.1 M I_2, 0.5 M 4-tBP	SN	MAII	6.64	11
15	N719	EMII-SN, 0.1 M I_2, 0.5 M 4-tBP	SN	EMII	7.46	11
16	N719	SN, I_2, DMAIIs, and NMBI in a 100:1:6:0. 5mole ratio	SN	DMBI, DMAIIs	7.8	12
17	Z-907	PMII and I_2 0.1M	PMII	-	4.78	13
18	Z-907	0.2 g PMII, 0.8 g $P_{12}TFSI$ and 0.0142 g I_2 0.1M	PMII	-	3.92	13
19	Z-907	0.2 g PMII, 0.8 g $P_{12}TFSI$ and 0.0142 g I_2 (0.1M), 0.5M NBB	PMII	-	4.01	13
20	Z-907	0.2 g PMII, 0.8 g $P_{12}TFSI$ and 0.0142 g I_2 0.1M, 0.5M NBB, 0.1 M LiI	PMII	-	4.64	13

21	Z-907	35 wt% PMII doped $P_{12}I$ and 0.2 M I_2	$P_{12}I$	PMII	4.85	14
22	N719	$[C_1mpyr][N(CN)_2]$, LiI 0.1 M and I_2 0.23 M	$[C_1mpyr][N(CN)_2$	NiL	5.1	15
23	N719	[C4mpyr][I] 0.4 M, LiI 0.1 M, I_2 0.1 M, NMB 0.2 M + 5wt% SiO_2 in SN	$[C_4mpyr][I]$	SiO_2	4.8	16
24	SK4	*0.6M OIPC-I, 0.03M* I_2*, 0.1M* 4-tBP	*OIPC -I*	NiL	7.60	This work
25	SK4	*OIPC -I*	*OIPC -I*	NiL	3.17	This work
26	SK4	*0.6M OIPC -Br, 0.03M* Br_2*, 0.1M* 4-tBP	*OIPC -Br*	NiL	5.38	This work
27	SK4	*OIPC -Br*	*OIPC -Br*	NiL	2.04	This work

Triethyl(methyl)phosphoniumbis-(trifluoromethanesulfonyl)amide $[P_{1222}]$[TFSA], triethyl- (methyl) phosphoniumbis(fluorosulfonyl)amide $[P_{1222}]$[FSA], 1,2-Bis[N-(N0-hexylimidazolium)]ethane diiodide [BII-6], 1,2-Bis[N-(N0-octylimidazolium)]ethane diiodide [BII-8], 5-azoniaspiro [4.4]nonane bis(trifluoromethanesulfonyl)imide [N_{44}TFSI], 1-ethyl-1-methyl pyrrolidinium iodide [$P_{12}I$], N-ethyl- N-methylpyrrolidinium tetrafluoroborate [$C_2mpyrBF_4$], 1,2-dimethyl-3-propyl imidazolium iodide [DMPII], 1-butyl-3-methyl imidazolium iodide [BMII], lithium iodide [LiI], iodine [I_2], 1-cyanopropyl-1-methylpyrrolidinium iodide [CPMPI], 1-propyl-3-methylimidazolium iodine [PMII], 1-ethyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl) Imide [P_{12}TFSI], 1-methyl-3-(2-oxo-2-(2,2,6,6-tetramethyl-1-oxyl-4-piperid-oxyl)butyl) imidazolium bis(trifluoromethanesulfonyl)imide [MeIm-TEMPO][TFSI], 1-hexadecyl-3-methyl imidazolium iodide [C_{16}MImI], 1-Propyl-1-methylpyrrolidinium iodine [$P_{13}I$], Succinonitrile [SN], 1-methyl-3-acetylimidazolium iodide [MAII], 1-ethyl-3-methylimidazolium iodide [EMII], 1-alkyl-2,3-dimethylimidazolium iodides [DMAIIs], N-methylbenzimidazole [NMBI], N-butylbenzimidazole [NBB], N-methyl-N-ethylpyrrolidiniumdicyanamide [C1mpyr][$N(CN)_2$], N-butyl-N-methylpyrrolidinium iodide [C_4mpyr][I], Carbon nanotubes (CNTs), 4-tert-butylpyridine (4-TBP)

Table S2. Photovoltaic performance reported for bromide/tribromide (Br^{-}/Br_3^{-}) based electrolytes with various sensitizers in MPDs

Dye	Nano particle	Electrolyte	V_{oc}	Efficiency	Ref
SFD-5	Mg-doped TiO_2	0.05 M Br_2 + 0.50 M LiBr + 0.10 M BMImBr in AN/VN(9 : 1 in volume).	0.98	1.0	17
SFD-5	Mg-doped TiO_2	0.03 M Br_2 + 0.65 M BMImBr + 0.20 M TPABr + 0.07MTBP + 0.07MGuNCS in AN/VN/EC/THF (4 : 3 : 2 : 1 in volume)	1.13	1.1	17
SFD-5	Mg-doped TiO_2 (MgO, CH3COOH)	0.03 M Br_2 + 0.65 M BMImBr + 0.20 M TPABr + 0.07MTBP + 0.07MGuNCS in AN/VN/EC/THF (4 : 3 : 2 : 1 in volume)	1.21	1.2	18
TC301	TiO_2 (12+4 µm)	0.9m DMBIBr, 0.08m Br_2, and 0.5m TBP electrolytein dry CH_3CN.	1.156	3.68	19,20
TC301	TiO_2 (12+4 µm)	0.9m DMBIBr, 0.8m LiBr,0.08m Br_2, and 0.5m TBP electrolyte in dry CH3CN	1.041	3.68	19,20
TC302	TiO_2	0.9m DMBIBr, 0.08m Br_2, and 0.5m TBP electrolytein dry CH_3CN.	1.091	4.05	19
TC302	TiO_2 (12+4 µm)	0.9m DMBIBr, 0.8m LiBr,0.08m Br_2, and 0.5m TBP electrolyte in dry CH3CN	1.009	3.98	19
TC303	TiO_2 (12+4 µm)	0.9m DMBIBr, 0.08m Br_2, and 0.5m TBP electrolytein dry CH_3CN.	1.077	3.28	19
TC303	TiO_2	0.9m DMBIBr, 0.8m LiBr,0.08m Br_2, and 0.5m TBP electrolyte in dry CH_3CN	0.969	3.13	19
TC305	TiO_2 (12+4 µm)	0.9m DMBIBr, 0.08m Br_2, and 0.5m TBP electrolytein dry CH_3CN.	1.033	4.61	19
TC305	TiO_2	0.9m DMBIBr, 0.8m LiBr, 0.08m Br_2, and 0.5m TBP electrolyte in dry CH3CN	0.959	4.54	19
TC306	TiO_2 (12+4 µm)	0.9m DMBIBr, 0.08m Br_2, and 0.5m TBP electrolyte in dry CH_3CN.	0.939	5.22	19,20
TC306	TiO_2	0.9m DMBIBr, 0.8m LiBr, 0.08m Br_2, and 0.5m TBP electrolyte in dry CH_3CN	0.915	5.07	19,20
TC308	TiO_2 (12+4 µm)	0.9m DMBIBr, 0.08m Br_2, and 0.5m TBP electrolyte in dry CH_3CN.	1.045	4.06	19
TC308	TiO_2	0.9m DMBIBr, 0.8m LiBr, 0.08m Br_2, and 0.5m TBP electrolyte in dry CH_3CN	0.976	3.85	19
TC309	TiO_2 (12+4 µm)	0.9m DMBIBr, 0.08m Br_2, and 0.5m TBP electrolyte in dry CH_3CN.	1.015	3.38	19
TC309	TiO_2 (12+4 µm)	0.9m DMBIBr, 0.8m LiBr, 0.08m Br_2, and 0.5m	0.960	3.63	19

		TBP electrolyte in dry CH_3CN			
Coumarin 343	TiO_2 (6 μm)	0.4 M LiBr + 0.04 M Br_2	0.428	0.70	21
Eosin Y	TiO_2 (6 μm)	0.4 M LiBr + 0.04 M Br_2	0.813	2.61	21
N719	TiO_2 (6 μm)	0.4 M LiBr + 0.04 M Br_2	0.556	1.05	21
TC301	TiO_2 (12+4 μm)	0.05 M Br_2, 0.6 M BDMIBr	0.79	1.58	22
TC301	TiO_2 (12+4 μm)	0.05 M Br_2, 0.6 M BDMIBr with 0.5 M TBP	1.06	2.68	22
TC301	TiO_2 (12+4 μm)	0.05 M Br_2, 0.6 M BDMIBr with 0.5 M IPIN	0.95	3.30	22
TC301	TiO_2 (12+4 μm)	0.05 M Br_2, 0.6 M BDMIBr with 0.5 M PIN	0.92	2.81	22
TC302	TiO_2 (12+4 μm)	0.05 M Br_2, 0.6 M BDMIBr	0.80	1.65	22
TC302	TiO_2 (12+4 μm)	0.05 M Br_2, 0.6 M BDMIBr with 0.5 M TBP	1.00	2.99	22
TC302	TiO_2(12+4 μm)	0.05 M Br_2, 0.6 M BDMIBr with 0.5 M IPIN	0.94	3.76	22
TC302	TiO_2(12+4 μm)	0.05 M Br_2, 0.6 M BDMIBr with 0.5 M PIN	0.91	3.35	22
SK4	TiO_2(9+3 μm)	BMIBr/Br_2 + 4-TBP	0.956	3.82	This work
SK4	TiO_2(9+3 μm)	0.6M OIPC -Br, 0.03M Br_2, 0.1M 4-TBP	0.980	5.38	This work
SK4	TiO_2(9+3 μm)	OIPC-Br Single component	0.857	2.07	This work

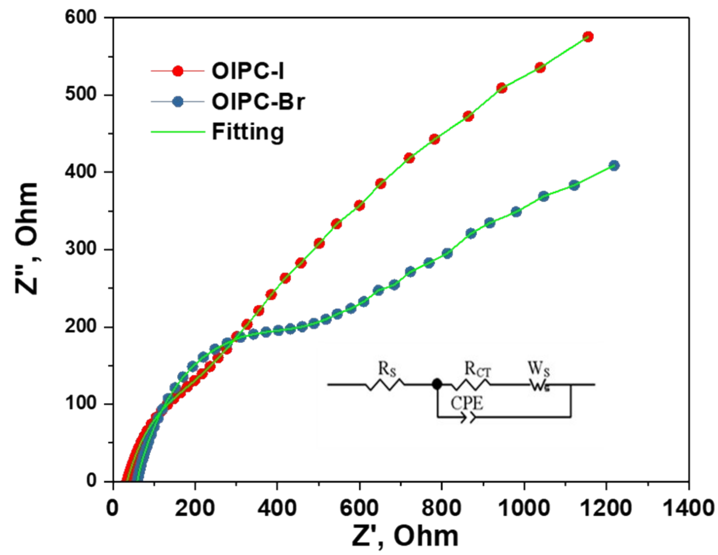

Figure S1 Nyquist plot of OIPCs between two platinum electrodes used to derive diffusion coefficient (Inset: equivalent circuit model used for fitting)

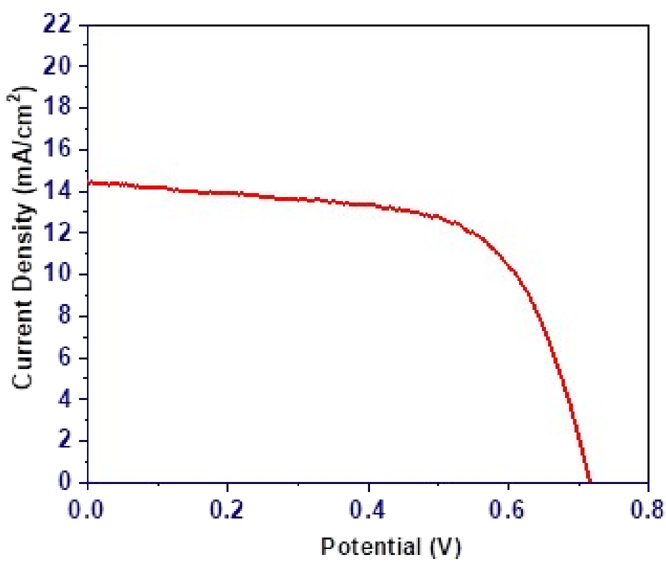

Figure S2. Performance of SK4 dye with conventional reference imidazolium-based electrolyte at 100 mW/cm^2

Calculation for TRPL parameters

The kinetic decay curves are fitted in the using following equation.

$$I(t) = \sum \alpha_i exp\left(-\frac{t}{\tau_i}\right)$$

Where, α_i is the amplitude of decay component, I possess a lifetime of τ, I is the normalized emission intensity, t is the time after pulsed laser excitation.

The average excited state lifetime values for the sample calculated by;

$$< \tau > = \sum \frac{\alpha_1 {\tau_1}^2 + \alpha_2 {\tau_2}^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2}$$

Amplitude weighted lifetime; $\tau_{amp} = \sum \alpha_1 \tau_1 + \alpha_2 \tau_2 \Big/ \sum \alpha_1 + \alpha_2$

Percentage of energy transfer efficiency; $\eta_{ET} = \left(1 - \tau_{Acceptor + Doner} \Big/ \tau_{Doner}\right) \times 100$

Electron transfer rate constants for the electron injection

$$k_{ei} = \left\{\left(\frac{1}{\tau_{SK4 + TiO2} + OIPC - I}\right) - \left(\frac{1}{\tau_{SK4 + TiO2.}}\right)\right\}$$

Table S3 TRPL calculation fitting parameter (χ), emission intensity ($\alpha_{1}, \alpha_{2}, \alpha_{3}$), excited-state lifetime ($\tau_{1}, \tau_{2}, \tau_{3}$) and average exciton lifetime (<τ>)

Dye	χ^2	α_1	α_2	α_3	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	$<\tau>$ (ns)	**Kei (ns)**	η_{ET} **(%)**
TiO_2-SK4-OIPC-I	0.998	75.589	24.411	-	0.065	0.524	-	0.294	2.48	44.8
TiO_2-SK4	1.003	40.703	37.491	21.806	0.094	0.403	1.461	0.652		

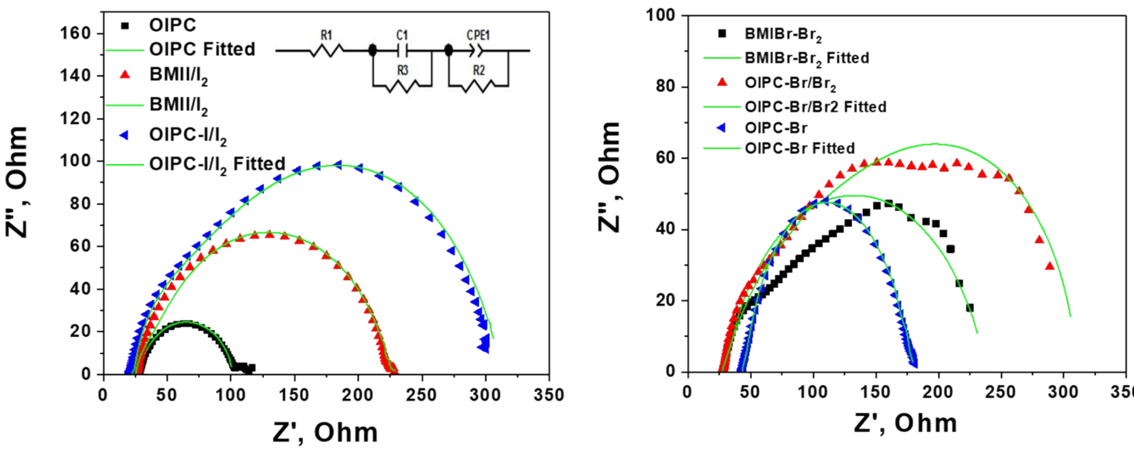

Figure S3 Nyquist plots of ss-MPDs were carried out from EIS under a dark condition with forward bias **(a)** OIPC-I based at 0.6 V and **(b)** OIPC-Br based devices at 0.9 V (Equivalent circuit for fitting of Nyquist plots)

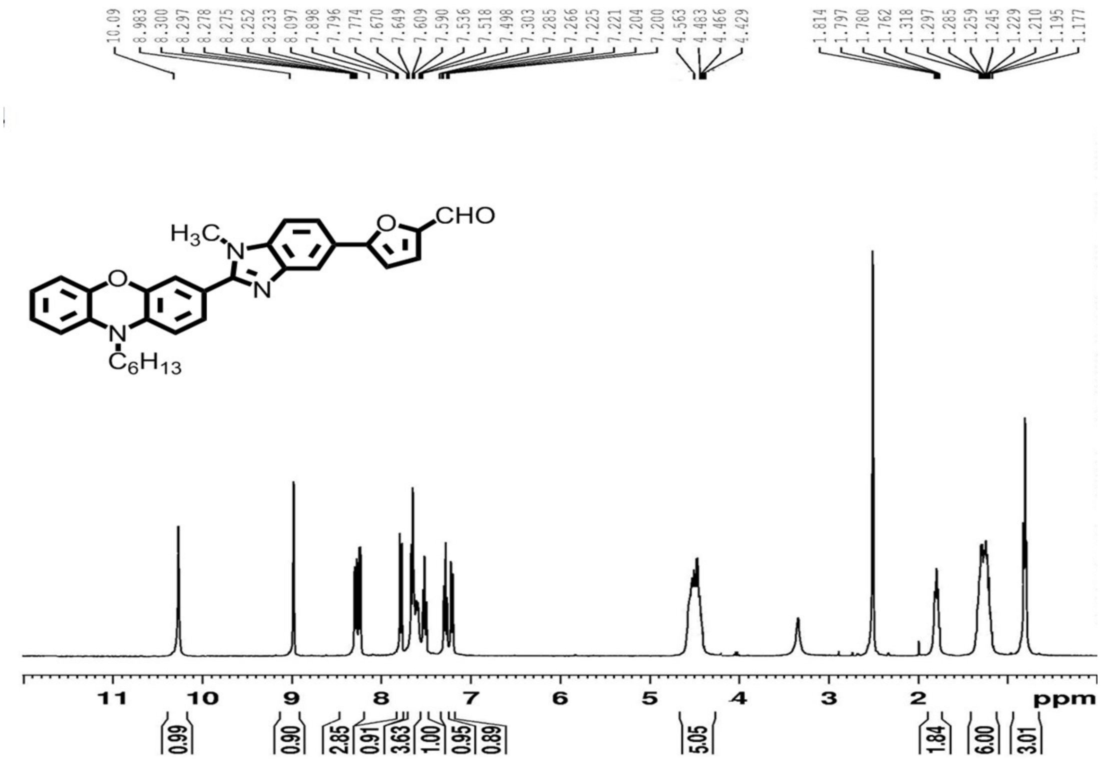

Figure S4 [1]H-NMR of compound **(i)**

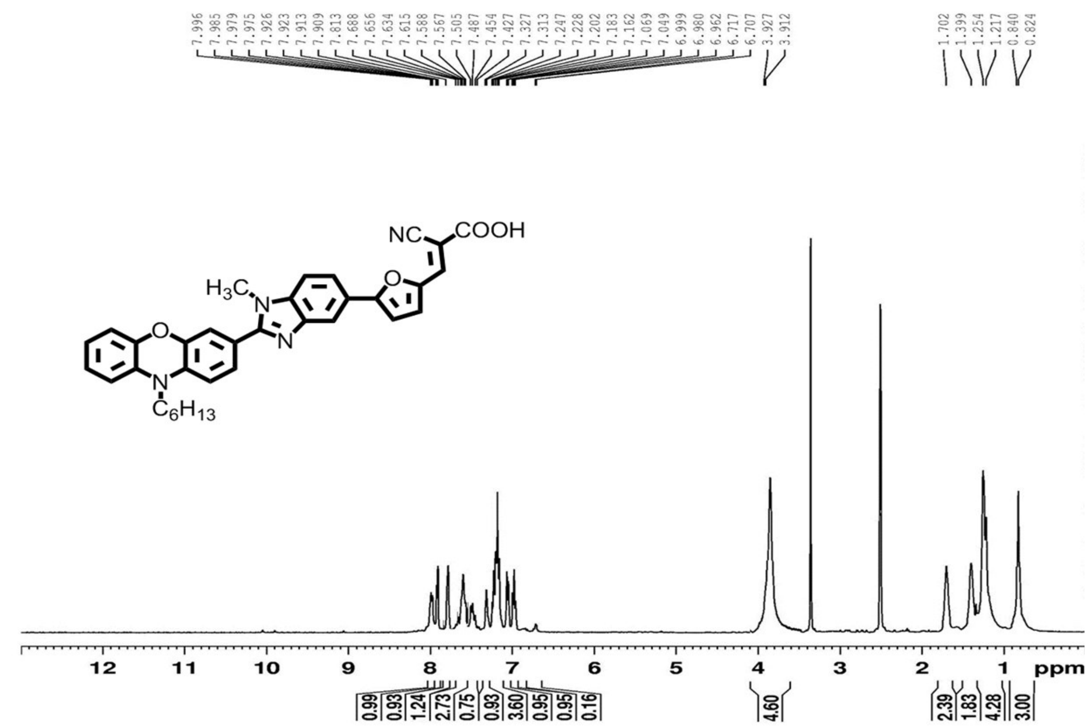

Figure S5 [1]H-NMR of SK4 dye

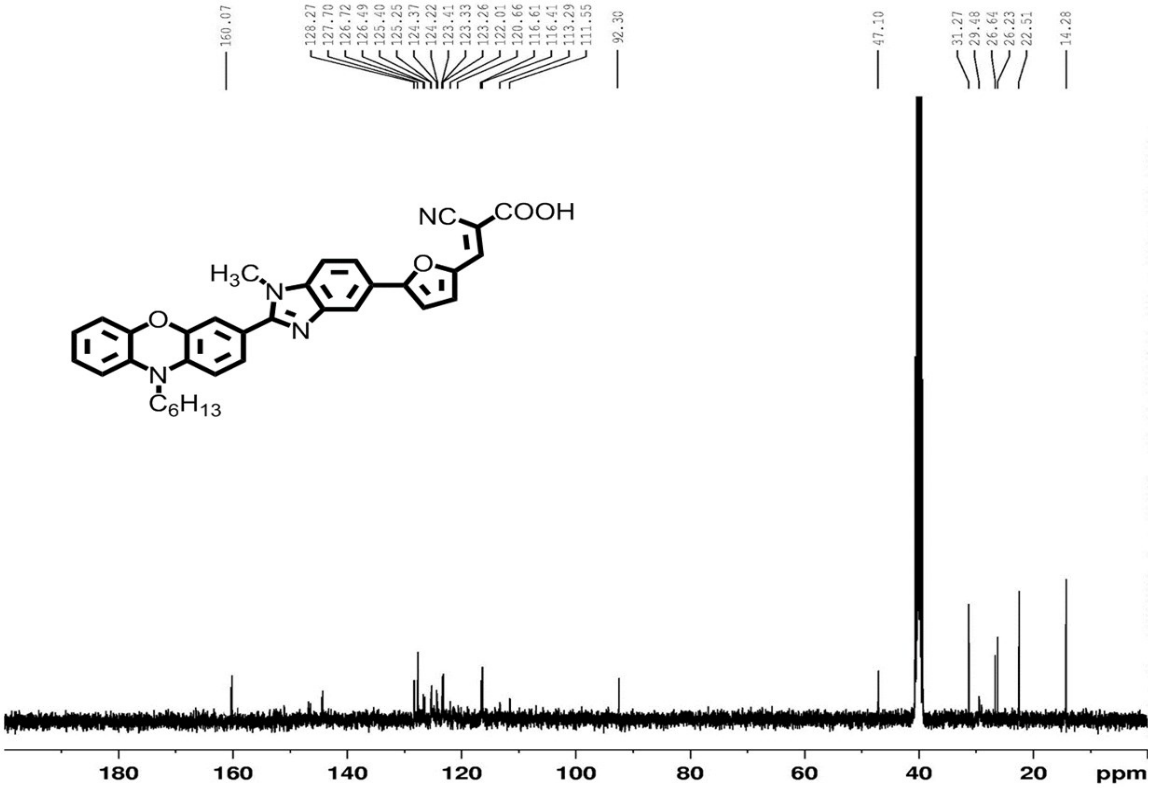

Figure S6 ^{13}C-NMR of SK4 dye

References

S1. Annkatrin Lennert, Klaudia Wagner, Ruhamah Yunis, Jennifer M. Pringle, Dirk M. Guldi, and David L. Officer, ACS Appl. Mater. Interfaces 2018, 10, 32271.

S2. Minjae Lee, Yong-Hoon Lee, Jong Hyeok Park, U Hyeok Choi, Organic Electronics, 2017, 48, 241e247.

S3. Hao Li, Shichao Li, Ye Zhang and Feng Yan, RSC Adv., 2016, 6, 346.

S4. Yun Wang, Pengfei Sun, Shan Cong, Jie Zhao, Guifu Zou, Carbon, 2015, 92, 262.

S5. Owen Byrne, Aoife Coughlan, Praveen K. Surolia and K. Ravindranathan Thampi, Prog. Photovolt: Res. Appl. 2015, 23, 417.

S6. Jialong Duan, Qunwei Tang, Benlin He and Haiyan Chen, RSC Adv., 2015, 5, 33463.

S7. Shan Cong, Yun Wang, Qinghua Yi, Jie Zhao, Yinghui Sun, Mingrong Shenand Guifu Zou, J. Mater. Chem. A, 2014, 2, 20147.

S8. Shichao Li, Lihua Qiu, Chengzhen Shi, Xiaojian Chen, and Feng Yan, Adv. Mater. 2014, 26, 1266.

S9. Chengzhen Shi, Lihua Qiu, Xiaojian Chen, Haigang Zhang, Lei Wang, and Feng Yan, ACS Appl. Mater. Interfaces 2013, 5, 1453.

S10. Junnian Chen, Tianyou Peng, Ke Fan, Renjie Li, Jiangbin Xia, Electrochimica Acta 2013, 94, 1.

S11. Xiaoming Huang, Da Qin, Xiaolu Zhang, Yanhong Luo, Shuqing Huang, Dongmei Li and Qingbo Meng, RSC Adv., 2013, 3, 6922.

S12. Daesub Hwang, Dong Young Kim, Seong Mu Jo, Vanessa Armel, Douglas R. MacFarlane, Dongho Kim, Sung-Yeon Jang, Scientific reports, 2013, 3, 3520.

S13. Qing Li, Xiaojian Chen, Jie Zhao, Lihua Qiu, Yueguang Zhang, Baoquan Sun and Feng Yan, J. Mater. Chem., 2012, 22, 6674.

S14. Qing Li, Jie Zhao, Baoquan Sun, Bencai Lin, Lihua Qiu, Yueguang Zhang, Xiaojian Chen, Jianmei Lu, and Feng Yan, Adv. Mater. 2012, 24, 945.

S15. Vanessa Armel, Maria Forsyth, Douglas R. MacFarlane, and Jennifer M. Pringle, Energy Environ. Sci., 2011, 4, 2234.

S16. V. Armel, J. M. Pringle, P. Wagner, M. Forsyth, D. L. Officer, and D. R. MacFarlane, Chem. Commun. 2011, 47, 9327.

S17. Kenji Kakiage, Toru Tokutome, Shinji Iwamoto, Toru Kyomen and Minoru Hanaya, Chem. Commun., 2013, 49, 179-180.

S18. C. Teng, X. Yang, S. Li, M. Cheng, A. Hagfeldt, L. Z. Wu and L. Sun, Chem.–Eur. J., 2010, 16, 13127.

S19. C. Teng, X. Yang, C. Yuan, C. Li, R. Chen, H. Tian, S. Li, A. Hagfeldt and L. Sun, Org. Lett., 2009, 11, 5542.

S20. Z. Wang, K. Sayama and H. Sugihara, J. Phys. Chem. B, 2005, 109, 22449.

S21. Omid Bagheri, Hossein Dehghani, and Malihe Afrooz, RSC Adv., 2015, 5, 86191.