All-Solid-State Dye-Sensitized Solar Cells with Alkyloxy-Imidazolium Iodide Ionic Polymer/SiO₂ Nanocomposite Electrolyte and Triphenylamine-Based Organic dyes

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Table S1. Absorption, Emission, and Electrochemical Properties of TPAR14 and TC15 Dyes

Dye	Adsorption			Emission	Oxidation potential		
	λ_{\max} [nm] ^[a]	<i>E</i> _{max}	λ_{\max} [nm]		E_{0-0} [V]	$E_{\text{S+/S}}$ [V]	$E_{S+/S^*}[V]$
		$[M^{-1} cm^{-1}]$	(on TiO ₂)	$\lambda_{\rm em} [\rm nm]^{[a]}$	(Abs/Em) ^[c]	(vs. NHE) ^[d]	(vs. NHE) [e]
TPAR14	486	39200	487	616	2.34	1.15	-1.19
TC15	486	34100	451	571	2.33	1.11	-1.22

[a] Absorption and emission spectra measured in dichloromethane solution $(5 \times 10^{-5} \text{ M})$ at room temperature. [b] Absorption spectra of dye-adsorbed TiO₂ films sensitized from dichloromethane

solution. [c] The zero-zero transition E_{0-0} estimated from the intersection of the normalized absorption and emission spectra. [d] Cyclic voltammogram of the oxidation behavior of the dyes measured in dry dichloromethane solution containing 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte (scanning rate: 100 mV/s; working electrode: glassy carbon; reference electrode: Ag/AgCl calibrated with ferrocene/ferrocenium (Fc⁺/Fc) as an internal reference; counter electrode: Pt wire). [e] E_{S+/S^*} gained from the difference of the $E_{S+/S}$ and E_{0-0} values.

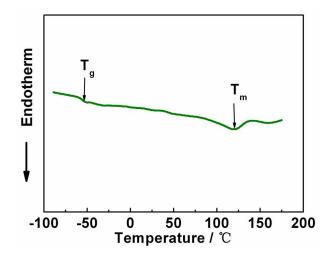


Figure S1. Differential scanning calorimetry thermogram of the optimal electrolyte, which is composed of I_2 (with mole ratio of $I_2/O = 0.9$), DMPImI (with mole ratio of DMPImI/O = 0.6), and SiO₂ (1 wt %) in AIIP.

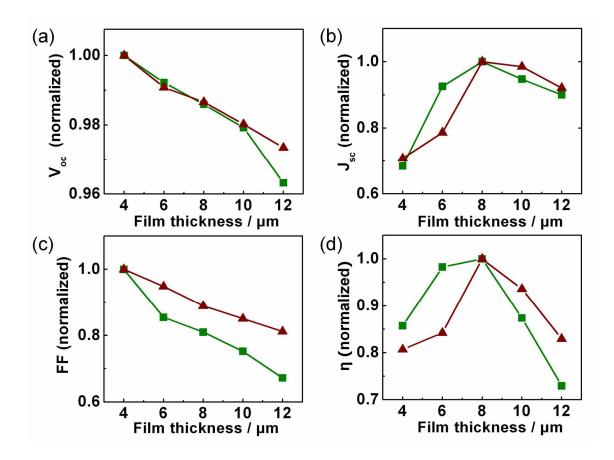


Figure S2. Normalized photovoltaic performance of all-solid-state solar cells sensitized by TPAR14 (red triangles) and TC15 (green squares) as a function of the nanocrystalline TiO₂ film thickness: (a) open-circuit voltage, V_{oc} ; (b) short-circuit photocurrent density, J_{sc} ; (c) fill factor, FF; (d) energy conversion efficiency, η .

The correlation between the nanocrystalline TiO₂ film thickness and the photovoltaic performance of the all-solid-state solar cells sensitized by TPAR14 or TC15 is depicted in Figure S2. The changes of V_{oc} (Figure S2a), J_{sc} (Figure S2b), FF (Figure S2c), and η (Figure S2d) for both the TPAR14- and TC15-based cells as a function of thickness of the TiO₂ film are similar. The J_{sc} increases firstly and peaks at 8 μ m. The V_{oc} gradually decreases as the film thickness is increased. The increase of the film thickness can augment the surface area of the photoanode and provide additional charge-recombination sites, consequently lowering their quasi-Fermi level and reducing V_{oc} .^{S1} In the mean time, the transport resistance of electrons in the TiO₂ particles is increased with increasing thickness of film, leading to the

decrease of FF.^{S1} The TiO₂ film thickness of these all-solid-state DSCs is optimized to be 8 μ m because the maximum η value is attained at this thickness.

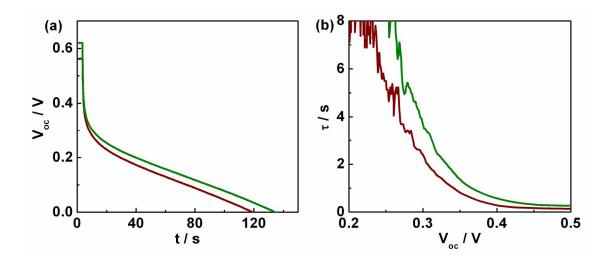


Figure S3. (a) Open-circuit voltage-decays of cell A (red line) and cell B (green line) after switching off the light. (b) Calculated electron lifetime vs V_{oc} .

The electron lifetime τ can also be measured by the open-circuit voltage-decays (OCVD) of DSCs. Figure S3a shows the decay of V_{oc} that follows after witching off the light.^{S2} The electron density falls when the illumination is interrupted due to the back reaction between the injected electrons and I_3^- ions at the TiO₂/electrolyte interface, leading to the decay of the photovoltage. The electron lifetime, τ , can be calculated from eq :^{S3,S4}

$$\tau = -\frac{k_{\rm B}T}{e} \left[\frac{\mathrm{d}V_{\rm oc}}{\mathrm{d}t} \right]^{-1} \tag{1}$$

The electron lifetime as a function of the V_{oc} is displayed in Figure S3b, in which, the lifetime increases approximately exponentially with decreasing V_{oc} . The electron lifetime of cell B is larger than that of cell A.

References

(S1) Ito, S.; Zakeeruddin, S. M.; Humphry-Baker, R.; Liska, P.; Charvet, R.; Comte, P.; Nazeeruddin,

M. K.; Péchy, P.; Takata, M.; Miura, H.; Uchida, S.; Grätzel, M. Adv. Mater. 2006, 18, 1202-1205.

(S2) Brown, P.; Takechi, K.; Kamat, P. V. J. Phys. Chem. C 2008, 112, 4776-4782.

(S3) Bisquert, J.; Zaban, A.; Greenshtein, M.; Mora-Seró, I. J. Am. Chem. Soc. 2004, 126, 13550-13559.

(S4) Shankar, K.; Bandara, J.; Paulose, M.; Wietasch, H.; Varghese, O. K.; Mor, G. K.; LaTempa, T.

J.; Thelakkat, M.; Grimes, C. A. Nano Lett. 2008, 8, 1654–1659.