Metal-free organic dyes for TiO_2 and ZnO dye-sensitized solar cells

Supporting Information

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1. Morphological characterization of photoanodes

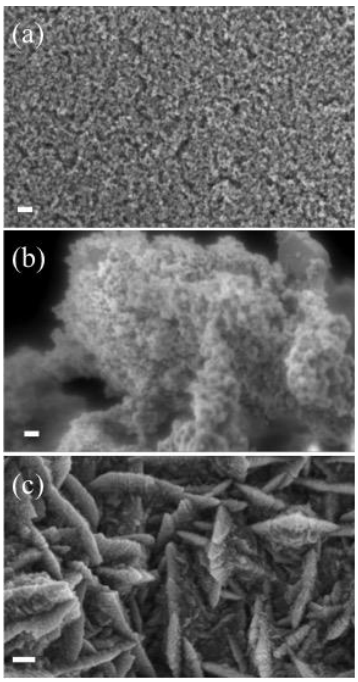

Figure S 1. Scanning electron images of (a) TiO_2 nanoparticles and (b) ZnO hierarchical structures applied as photoanodes. (c) SEM image of ZnO buffer layer. Scale bar: 100 nm.

2. Comparison of hierarchical ZnO nanocrystallites and standard mesoporous TiO_2.

2.1 Dye loading

Figure S2 shows systematic comparison of absorption spectra after the complete removal of dye molecules from the metal oxide (hierarchical structured ZnO and TiO_2) *vs* wavelength (nm).

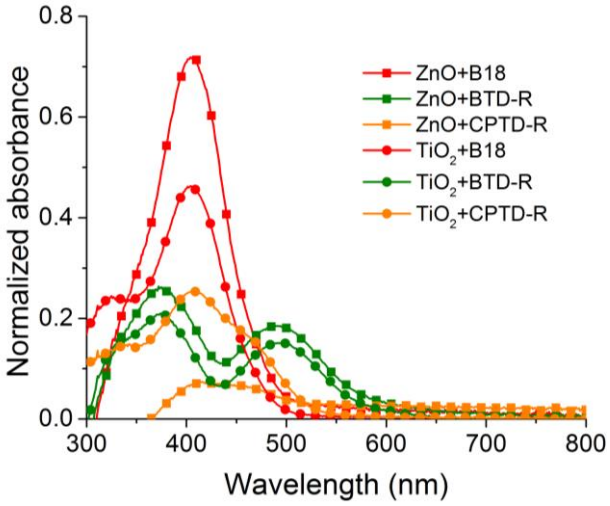

Figure S 2. Comparison of absorption spectra of dye molecules after the complete removal of the dye molecules from the metal oxide: hierarchical structured ZnO (Square) and standard mesoporous TiO_2 (Circle) by B18 (red line), BTD-R (green line) and CPTD-R (orange line).

2.2 J-V and IPCE

Figure S3 shows systematic comparison of the current density vs. photovoltage (*J-V*) curves and IPCE (%) spectra of hierarchical structured ZnO and standard mesoporous TiO_2 photoanodes of comparable thickness sensitized by the three different metal-free organic dyes. Corresponding functional parameters are reported in **Table S1**.

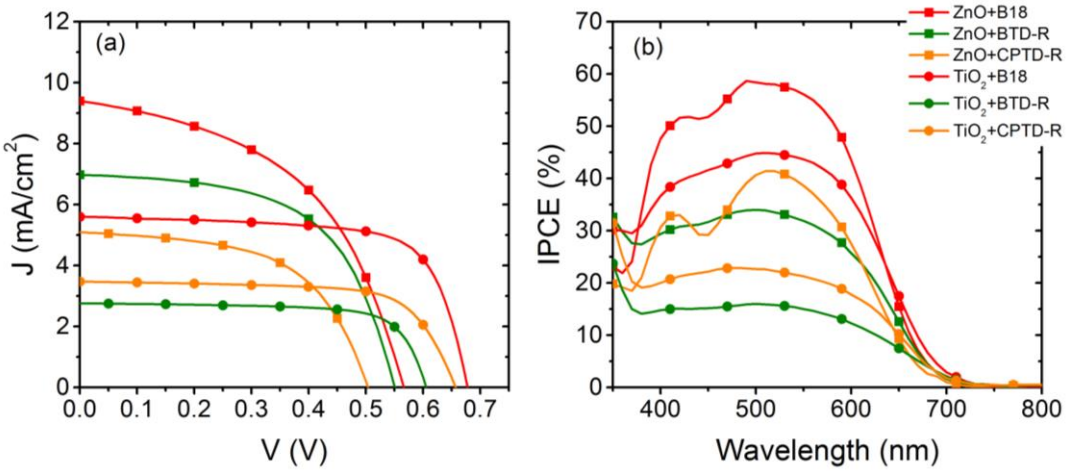

Figure S 3. Comparison of (a) Current density vs photovoltage under 1 sun illumination (AM 1.5G, 100 mW cm^{-2}); (b) IPCE spectra for hierarchical structured ZnO (Square) and standard mesoporous TiO_2 (Circle) based DSSCs sensitized by B18 (red line), BTD-R (green line) and CPTD-R (orange line).

Dye molecule	Metal Oxide	Thickness (µm)	V_{oc} (mV)	J_{sc} (mA cm^{-2})	*FF* (%)	η (%)
B18	TiO_2	11.07	679	5.60	71	2.69
	ZnO	14.44	544	9.22	54	2.71
BTD-R	TiO_2	11.02	607	2.76	73	1.22
	ZnO	13.00	539	7.64	57	2.35
CPTD-R	TiO_2	10.81	657	3.47	70	1.60
	ZnO	8.69	504	5.10	56	1.43

Table S 1. Comparison of the functional performances of TiO_2- and ZnO-based DSSCs sensitized with dye molecules B18, CPTD-R and BTD-R under AM1.5G irradiation (100 mW cm^{-2}).

2.3 Transient photocurrent and photovoltage decay measurements

Sample Code	Dye molecules	τ_R (ms) (at 3.0×10^{18}cm^{-3})	V_{oc} (V) (at 3.0×10^{18}cm^{-3})
T12	B18	24.95	0.574
T3	BTD-R	3.03	0.578
T15	CPTD-R	15.58	0.580

Table S 2. Comparison of the functional properties of TiO_2 based DSSCs sensitized with B18, BTD-R and CPTD-R calculated from transient photocurrent and photovoltage decay (TCD/TVD).

Sample Code	Dye molecules	τ_R (ms) (at 1.8×10^{18}cm^{-3})	V_{oc} (V) (at 1.8×10^{18}cm^{-3})
B22	B18	25.53	0.459
B10	BTD-R	9.10	0.531
C17	CPTD-R	5.70	0.487

Table S 3. Comparison of the functional properties of ZnO- based DSSCs sensitized with B18, BTD-R and CPTD-R calculated from transient photocurrent and photovoltage decay (TCD/TVD).

3. Effect of active layer thickness

The effect of thickness of active layer on the functional properties of all DSSCs, was investigated. Systematic comparisons of the functional performances are shown in **Figure S4** for TiO_2 photoanodes and in **Figure S5** for ZnO photoanodes. Corresponding functional parameters are reported in Table S2 and Table S3, respectively.

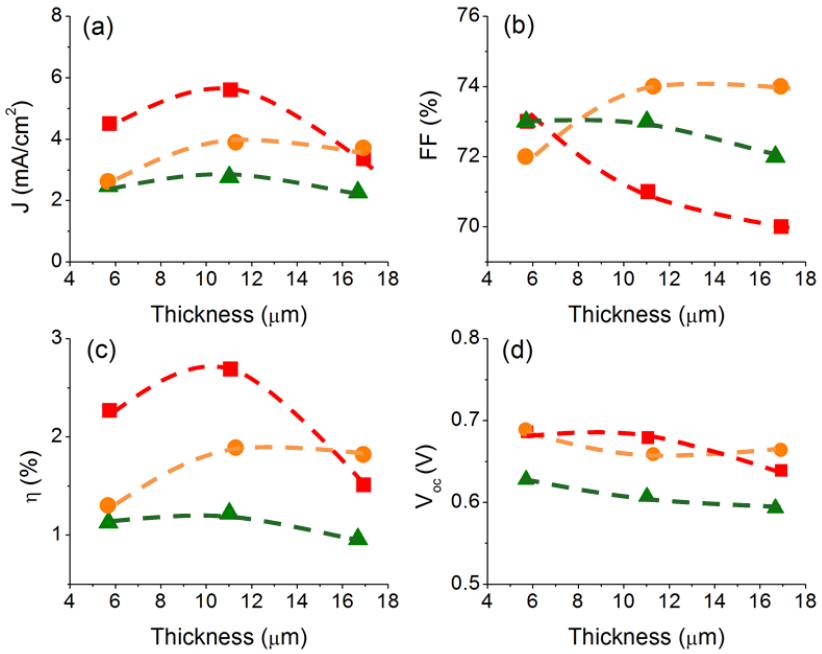

Figure S 4. Functional properties comparison of DSSCs based on standard mesoporous TiO_2 film sensitized with three different dye molecules (Red square= B18, Green triangle= BTD-R and Orange circle= CPTD-R) under AM1.5G irradiation (100 mW cm^{-2}) as a function of photoanode thickness.

Dye molecules	Thickness* (μm)	V_{oc} (mV)	J_{sc} (mA cm^{-2})	*FF* (%)	η (%)
B18	5.75	686	4.50	73	2.27
	11.07	679	5.60	71	2.69
	16.93	639	3.36	70	1.51
BTD-R	5.70	628	2.47	73	1.13
	11.02	607	2.76	73	1.22
	16.68	593	2.27	72	0.96
CPTD-R	5.68	689	2.62	72	1.30
	11.30	659	3.89	74	1.89
	16.91	664	3.71	74	1.82

Table S 4. Functional properties of standard mesoporous TiO_2 photoanodes sensitized with B18, BTD-R and CPTD-R under AM1.5G irradiation (100 mW cm^{-2}) as a function of photoanode thickness.

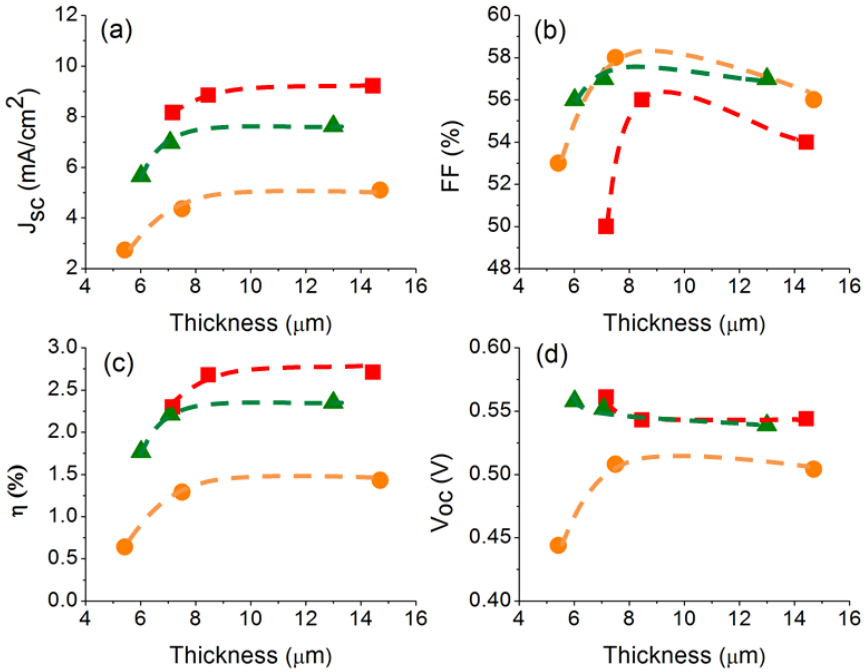

Figure S 5. Functional properties comparison of DSSCs based on hierarchical assembled ZnO nanostructures sensitized with three different dye molecules (Red square= B18, Green triangle= BTD-R and Orange circle= CPTD-R) under AM1.5G irradiation (100 mW cm^{-2}) as a function of photoanode thickness

Dye molecules	**Thickness (μm)**	V_{oc} **(mV)**	J_{sc} **(mA cm^{-2})**	***FF*** **(%)**	η **(%)**
B18	7.16	561	8.16	50	2.30
	8.46	543	8.85	56	2.68
	14.44	544	9.22	54	2.71
BTD-R	6.01	558	5.67	56	1.77
	7.07	552	6.98	57	2.21
	13.00	539	7.64	57	2.35
CPTD-R	5.42	444	2.73	53	0.64
	7.50	508	4.36	58	1.29

	14.70	504	5.10	56	1.43

Table S 5. Functional properties of hierarchical assembled ZnO nanostructured photoanodes sensitized with B18, BTD-R and CPTD-R under AM1.5G irradiation (100 mW cm^{-2}) as a function of photoanode thickness.

4. Reproducibility of the effect of blocking layer

Functional performances of hierarchically self-assembled ZnO nanocrystallites photoanodes with and without ZnO blocking layer (BL) are presented in **Figure S6** and **Table S6**.

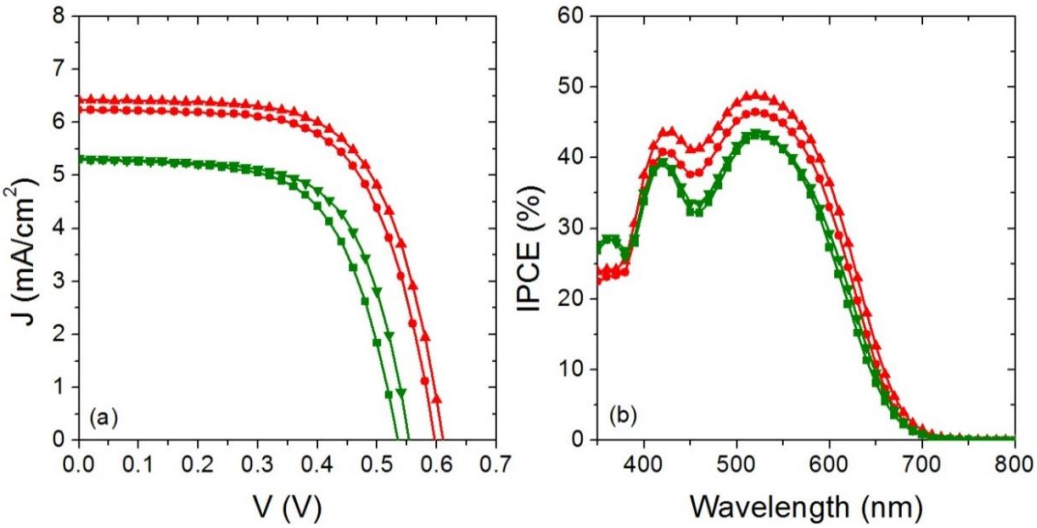

Figure S 6. Comparison of (a) current density vs photovoltage curves; (b) IPCE spectra, for DSSCs with and without blocking layer between FTO and active layer (red line: with BL; green line: without BL).

Sample Code	BL	Thickness* (μm)	V_{oc} (mV)	J_{sc} (mA cm^{-2})	*FF* (%)	η (%)
A6	Yes	8.31	613	6.43	64	2.52
A7	Yes	8.16	601	6.24	64	2.39
B11	No	9.04	557	5.32	64	1.90
C8	No	12.46	538	5.30	62	1.77

*Thickness includes BL (as thick as 0.8 μm)

Table S 6. Functional properties of ZnO-based DSSCs with and without blocking layer

Sample Code	BL	τ_R (ms) (at 0.56 V)	τ_R (ms) (at 1 mA cm^{-2})	τ_R (ms) (at $13.5\times10^{18}cm^{-3}$)	V_{oc} (V) (at $13.5\times10^{18}cm^{-3}$)
A5	Yes	20.41	11.00	27.93	0.548
B11	No	5.57	6.00	4.23	0.568

Table S 7. Comparison of functional properties of B18 sensitized hierarchical assembled ZnO nanostructured based DSSCs with and without blocking layer calculated by transient photocurrent and photovoltage decay (TCD/TVD)