Electronic Supplementary Information

Panchromatic Engineering for Efficient Zinc Oxide Flexible Dye-Sensitized Solar Cells Using Porphyrin and Indoline Dyes

Yu-Kai Syu,[a] Yogesh Tingare,[b] Chen-Yu Yeh,*[b] Jih-Sheng Yang[a] and Jih-Jen Wu*[a]

[a] Department of Chemical Engineering, National Cheng Kung University, Tainan, 701, Taiwan

[b] Department of Chemistry and Research Center for Sustainable Energy and Nanotechnology, National Chung Hsing University, Taichung, 402, Taiwan

*Corresponding authors.

E-mail addresses: wujj@mail.ncku.edu.tw (J.-J.W.); cyyeh@dragon.nchu.edu.tw (C.-Y.Y.)

Table S1 Absorption, fluorescence, and electrochemical data for porphyrin YD2-o-C8-TBA and YD2-o-C8[a]

Porphyrin	Absorption λ_{max}[nm]	Emission λ_{max}[nm]	HOMO (V vs. NHE)	E_{0-0} (V)	LUMO ($E_{0–0}$*) (V vs. NHE)
YD2-o-C8-TBA	448, 584, 639	665	+0.81	+1.91	-1.1
YD2-o-C8	448, 581, 645	663	+0.82	+1.90	-1.08

[a]Absorption and emission data were measured in THF at 298 K. The excitation wavelengths were 650 nm and 645 nm for YD2-o-C8-TBA and YD2-o-C8 respectively. ($E_{0–0}^* = E_{ox1} – E_{0–0}$ where $E_{0–0}^*$: excited-state oxidation potential; E_{0-0} : Zero-Zero excitation energy and E_{ox1}: First oxidation potential)

Optimization of YD2-oC8-TBA/D149 co-sensitized ZnO solar cells based on the 5-μm-thick ZnO anodes

(A) Effect of the sequence of the dye adsorption

Dye D149 adsorption was carried out by immersing the anode in a 0.5 mM acetonitrile/t-butanol (1:1) solution of D149 at room temperature (RT) for 40 min. Dye YD2-o-C8-TBA adsorption was conducted in a solution composed of 0.1 mM YD2-o-C8-TBA and 2.5 mM CDCA in ethanol at 50 ^{o}C for 15h. Electrolyte II was employed to fabricate the co-sensitized DSSCs. Figure S1 and Table S2 show the photovoltaic performances of the YD2-o-C8-TBA (first step)/D149 (second step) and D149 (first step)/YD2-o-C8-TBA (second step) co-sensitized cells. They reveal that the YD2-o-C8-TBA (first step)/D149 (second step) co-sensitized cell (named YD2-o-C8-TBA/D149 co-sensitized cell hereafter) possesses superior performances.

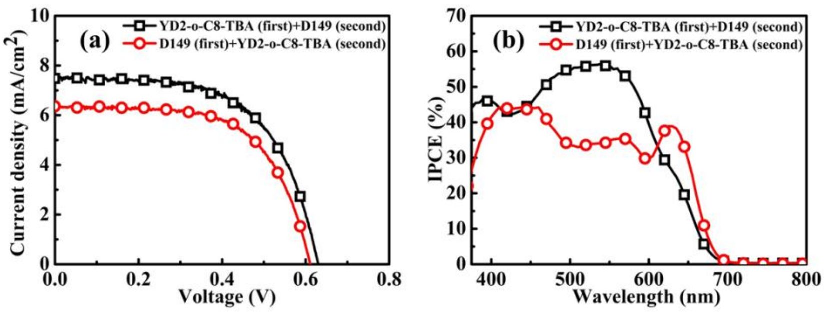

Figure S1 (a) J-V curves and (b) IPCE spectra of YD2-o-C8-TBA (first step)/D149 (second step) and D149 (first step)/YD2-o-C8-TBA (second step) co-sensitized ZnO cells.

Table S2 Photovoltaic performances of YD2-o-C8-TBA (first step)/D149 (second step) and D149 (first step)/YD2-o-C8-TBA (second step) co-sensitized ZnO cells.

Sequence of dye adsorption		Voc (V)	Jsc (mA/cm^2)	F.F.	η(%)
DSSC-1 YD2-o-C8-TBA (first) D149 (second)	Avg.	0.63±0.01	7.23±0.21	0.61±0.02	2.74±0.11
	Best	0.63	7.49	0.61	2.87
DSSC-2 D149 (first) YD2-o-C8-TBA (second)	Avg.	0.61±0.01	6.14±0.2	0.62±0.01	2.34±0.08
	Best	0.61	6.36	0.62	2.43

(B) Effect of the solvent of the dye YD2-o-C8-TBA solution

Two dye YD2-o-C8-TBA solutions were respectively prepared with 0.1 mM YD2-o-C8-TBA and 2.5 mM CDCA in ethanol and in a 1:1 volume ratio of acetonitrile and t-butanol. Dye adsorption was firstly conducted in the dye YD2-o-C8-TBA solution at RT for 1h followed by in the dye D149 solution at RT for 40 min. Electrolyte II was employed to fabricate the co-sensitized DSSCs. Figure S2 and Table S3 show the photovoltaic performances of these two YD2-o-C8-TBA/D149 co-sensitized ZnO cells. They reveal that the cell fabricated using the YD2-o-C8-TBA solution in ACN: t-BuOH possesses superior performances.

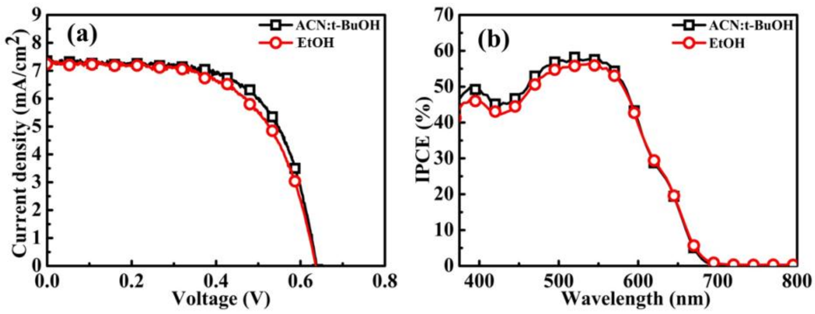

Figure S2 (a) J-V curves and (b) IPCE spectra of YD2-o-C8-TBA/D149 co-sensitized ZnO cells fabricated using YD2-o-C8-TBA solutions with different solvents.

Table S3 Photovoltaic performances of YD2-o-C8-TBA/D149 co-sensitized ZnO cells fabricated using YD2-o-C8-TBA solutions with different solvents.

Solvent of dye YD2-o-C8-TBA solution		Voc (V)	Jsc (mA/cm^2)	F.F.	η(%)
DSSC-3; Ethanol	Avg.	0.63±0.01	7.2±0.18	0.61±0.02	2.74±0.11
	Best	0.64	7.26	0.61	2.83
DSSC-4; ACN: t-BuOH (1:1)	Avg.	0.64±0.01	7.49±0.27	0.62±0.02	2.97±0.11
	Best	0.64	7.35	0.65	3.03

(C) Effect of the electrolyte

Two liquid electrolyte solutions were employed for the DSSCs in this work. Electrolyte I consisted of 0.05 M LiI, 0.05 M I_2, 1.0 M 1-methyl-3-propylimidazolium iodide (PMII), and 0.5 M 4-tertbutylpyridine (TBP) in a 85:15 volume ratio of acetonitrile and valeronitrile. Electrolyte II was composed of 0.5 M tetrapropylammonium iodide (TPAI) and 50 mM I_2 in a 1:4 volume ratio of ethylene carbonate and acetonitrile. Figure S3 and Table S4 show the photovoltaic performances of the YD2-o-C8-TBA/D149 co-sensitized ZnO cells fabricated using the two electrolytes. They reveal that the cell fabricated using Electrolyte II possesses superior performances.

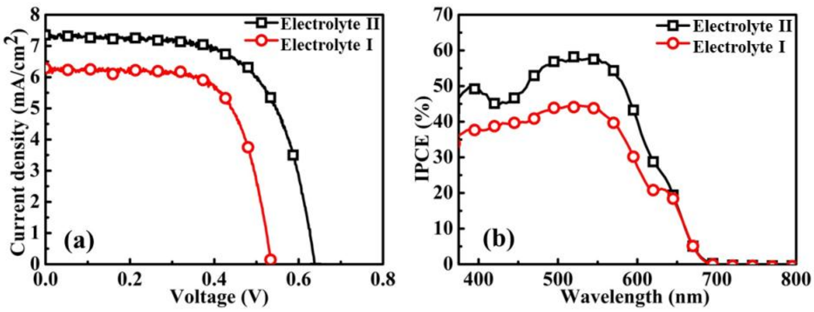

Figure S3 (a) J-V curves and (b) IPCE spectra of YD2-o-C8-TBA/D149 co-sensitized ZnO cells fabricated using different electrolytes.

Table S4 Photovoltaic performances of YD2-o-C8-TBA/D149 co-sensitized ZnO cells fabricated using different electrolytes.

Electrolyte		Voc (V)	Jsc (mA/cm^2)	F.F.	η(%)
Electrolyte I	Avg.	0.53±0.01	6.25±0.13	0.68±0.01	2.28±0.03
	Best	0.54	6.28	0.68	2.30
Electrolyte II	Avg.	0.64±0.01	7.49±0.27	0.62±0.02	2.97±0.11
	Best	0.64	7.35	0.65	3.03

IPCE linear combination model for co-sensitized DSSCs

IPCE of the DSSC is determined by three factors of light harvesting, charge injection, and charge collection efficiencies. With the same anode and electrolyte, the IPCE value can be an index to evaluate the dye performances (the combination of light harvesting and charge injection efficiencies) in the co-sensitized ZnO DSSC if intermolecular interaction between dyes is absent.

In this work, we propose an IPCE linear combination model to analyze the contributions of photoelectrons generated from YD2-o-C8-TBA and D149 dyes to the photocurrent of the co-sensitized ZnO DSSC. The IPCE values of the co-sensitized ZnO DSSC are assumed to be linear combinations of the IPCE values of the individual dye-sensitized ZnO DSSCs with the same anode thickness and electrolyte. IPCE values at 520 nm and 640 nm (i.e., the complementary wavelengths for D149 and YD2-o-C8-TBA, as shown in Figure S4(b)) are employed to set up the linear combination equations S(1) and S(2) for the estimation of the contributions of YD2-o-C8-TBA and D149 dyes to the photocurrent of the co-sensitized ZnO DSSCs.

$$a*IPCE_{YD2\text{-}o\text{-}c8\text{-}TBA,\ 520\ nm} + b*IPCE_{D149,520\ nm} = IPCE_{co\text{-}sensitization,520\ nm} \qquad S(1)$$

$$a*IPCE_{YD2\text{-}o\text{-}c8\text{-}TBA,\ 640\ nm} + b*IPCE_{D149,640\ nm} = IPCE_{co\text{-}sensitization,640\ nm} \qquad S(2)$$

where a and b are the contribution factors of YD2-o-C8-TBA and D149 dyes, respectively, to the photocurrent of the co-sensitized ZnO DSSC. With the known IPCE values, simultaneous equations S(1) and S(2) can be solved to obtain the contribution factors “a and b”.

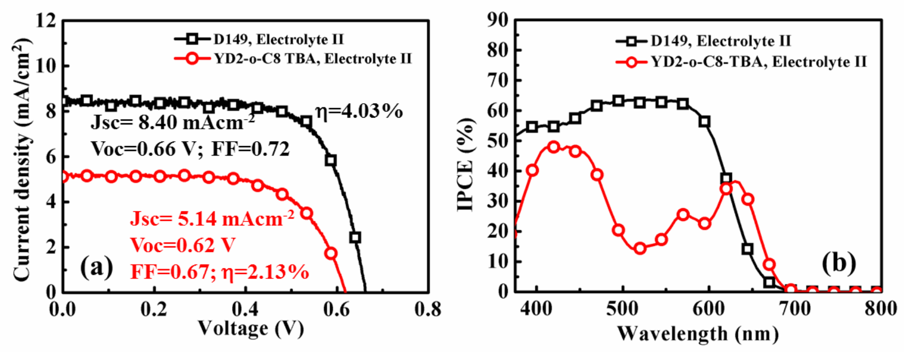

Figure S4 (a) J-V curves and (b) IPCE spectra of YD2-o-C8-TBA-sensitized and D149-sensitized ZnO cells fabricated using electrolyte II and 5-μm-thick anode.

Since the Jsc of the D149-sensitized ZnO DSSC is significantly higher than that of

YD2-o-C8-TBA as shown in Figure S4(a), the criteria for obtaining a co-sensitized ZnO DSSC with the Jsc superior to those of D149-sensitized and YD2-o-C8-TBA-sensitized DSSCs are b>a and a+b>1.

The contribution factors "a and b" as well as Jsc of the co-sensitized ZnO DSSCs fabricated using electrolyte II and the 5-μm-thick anode (shown in Figures S1 and S2) are listed in Table S5. As shown in Table S5, the values of factor b for DSSC-1, DSSC-3 and DSSC-4 are significantly larger than the factor a, which is consistent with their D149-dominated IPCE features. However, the summations of the contribution factors ("a+b") in DSSC-1, DSSC-3 and DSSC-4 are very close to unit (a+b≅1). Therefore, the Jsc of the three co-sensitized ZnO DSSCs are lower than that of D149-sensitized cell. The three co-sensitization processes are thus ineffective to improve the photocurrent of the ZnO DSSC as compared to D149-sensitized ZnO DSSC.

On the other hand, DSSC-2 (with the YD2-o-C8-TBA-dominated IPCE feature) shows the characteristics of a>b and a+b>1 as listed in Table S5. The Jsc of DSSC-2 is still lower than that of the D149-sensitized ZnO DSSC although it is improved as compared to the YD2-o-C8-TBA-sensitized ZnO DSSC.

Table S5 Jsc as well as contribution factors "a and b" of the YD2-o-C8-TBA-sensitized, D149-sensitized and co-sensitized ZnO DSSCs fabricated using electrolyte II and 5-μm-thick anode.

DSSC	Jsc ($mAcm^{-2}$)	a	b	a+b
YD2-o-C8-TBA	5.14	1	0	1
D149	8.40	0	1	1
DSSC-1	7.49	0.202	0.845	1.047
DSSC-2	6.36	0.904	0.329	1.233
DSSC-3	7.26	0.212	0.841	1.053
DSSC-4	7.35	0.179	0.885	1.064

Considering the competitive adsorption of YD2-oC8-TBA and D149 dyes on the ZnO anodes, the performance of the co-sensitized ZnO solar cell was further optimized in terms of the anode thickness. The IPCE linear combination model was employed to further analyze the contributions of photoelectrons generated from YD2-o-C8-TBA and D149 dyes to the photocurrent of the co-sensitized ZnO DSSC. Figures S5 (a) and (b) respectively show the J-V curves and IPCE spectra of YD2-o-C8-TBA-sensitized and D149-sensitized ZnO cells fabricated using electrolyte II and the 8-μm-thick anode. The J-V characteristic and IPCE spectrum of the co-sensitized ZnO DSSC are shown in Figure 3. According to the IPCE spectra shown in Figure 3(b) and Figure S5(b), the estimated contribution factors “a and b” of the co-sensitized ZnO DSSC are 0.432 and 0.970, respectively, which demonstrate the results of b>a and a+b>1. It indicates that by elongating the anode thickness to 8 μm, the co-sensitized ZnO DSSC meets the criteria for having the superior Jsc to those of the individual dye-sensitized DSSCs. Indeed, with the anode thickness of 8 μm, the performance of the co-sensitized ZnO DSSC is improved compared to those of YD2-o-C8-TBA-sensitized and D149-sensitized DSSCs as shown in Figure S5(a) and Table 1. For the ZnO DSSC fabricated using the 8-μm-thick anode with the light-scattering layer as shown in Figure 5, the estimated contribution factors “a and b” of the co-sensitized ZnO DSSC are 0.368 and 0.945, respectively, which also meets the criteria for having the improved Jsc compared to the individual dye-sensitized DSSCs.

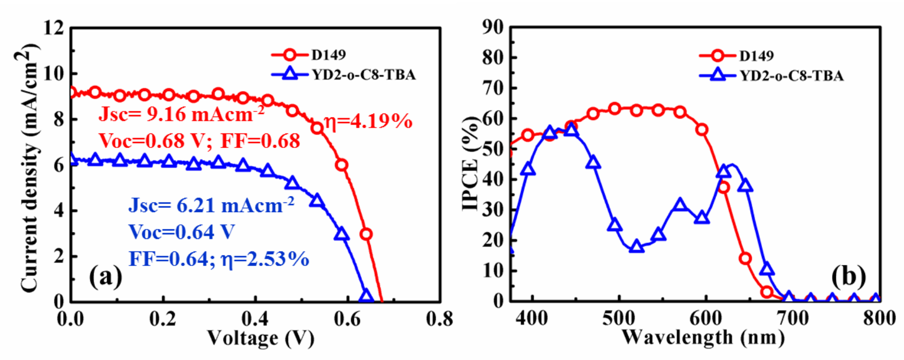

Figure S5 (a) J-V curves and (b) IPCE spectra of YD2-o-C8-TBA-sensitized and D149-sensitized ZnO DSSCs fabricated using electrolyte II and 8-μm-thick anode.