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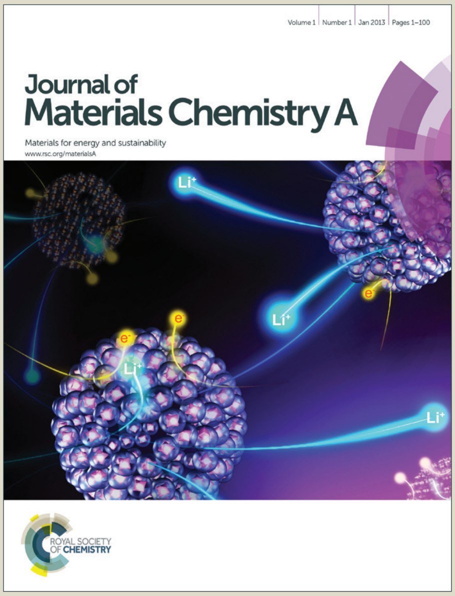

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Panchromatic Co-sensitization for Porphyrin-sensitized Solar Cells To Harvest Near-infrared Light Beyond 900 nm

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We designed a dimeric porphyrin dye (LDD1) based on an efficient push-pull zinc porphyrin (LD14) with extended π-conjugation through coupling of two zinc porphine cores via an acetylene bridge at the *meso* position of the porphyrin to extend the absorption spectrum effectively into the near infrared region. The effect of dye aggregation among porphyrin molecules was significantly suppressed when the LDD1 and LD14 dyes were co-sensitized on a nanocrystalline TiO_2 film in a dye-sensitized photovoltaic system. The light-harvesting ability of the device exhibits a panchromatic feature covering a broad spectral region from 400 nm to 900 nm, which results in a short-circuit current density 21.3 mA cm^{-2} and power conversion efficiency 10.4 % in an iodine-based solar cell.

Solar energy is an abundant, clean and ultimate source of power. The development of materials with the ability to tune the energy levels for maximal efficiency to convert solar energy remains one of society's important challenges. Dye-sensitized solar cells (DSSC) that fulfill this requirement become prospective new-generation photovoltaic systems with the advantages of low cost, convenient fabrication based on solution, and versatile design for the light absorbers. Among the photosensitizers of varied types, zinc porphyrins became promising candidates to harvest solar energy efficiently for DSSC.[1-6] For example, YD2-oC8 co-sensitized with organic dye Y123 using a cobalt electrolyte outperformed others with a power conversion efficiency (PCE) 12.3 %.[7] Further modification of the porphyrin dye with a benzothiadiazole spacer raised the device performance to PCE 13 %.[8,9] Although the absorption spectra of these highly efficient porphyrin dyes exhibit a panchromatic spectral feature to cover the entire visible absorption region, 400–700 nm, a strategy to design a new porphyrin sensitizer with a light-harvesting ability beyond 700 nm into the near infrared region is encouraged to further promote the device performance for a porphyrin-sensitized solar cell (PSSC).[1]

We designed and synthesized a near-infrared porphyrin dye (LD31)[10] in which the porphyrin core was coupled with an anthracene moiety based on a well-known porphyrin (LD14)[11] with a donor-π-acceptor structure. The resulting device made of the LD31 dye extends the spectrum of efficiency to convert incident photons to current (IPCE) toward 800 nm with a short-circuit current density (J_{SC}) exceeding 20 mA cm^{-2}. In the present work, we show that the ability of a PSSC to harvest light is significantly enhanced with a new dimeric porphyrin sensitizer (LDD1) in which the two zinc porphyrin cores are linked with ethynyl, similar to the molecular design of LD14 and LD31; the molecular structures of LD14 and LDD1 are shown in Figure 1. The device made of LDD1 co-sensitized with LD14 in an iodine-based electrolyte attained PCE 10.4 % with the onset of the IPCE action spectrum reaching 900 nm. The superior light-harvesting ability of this LDD1 dye towards the near-infrared region is a remarkable feature because it might be adopted into the system of perovskite solar cells to improve the device performance.[12-15]

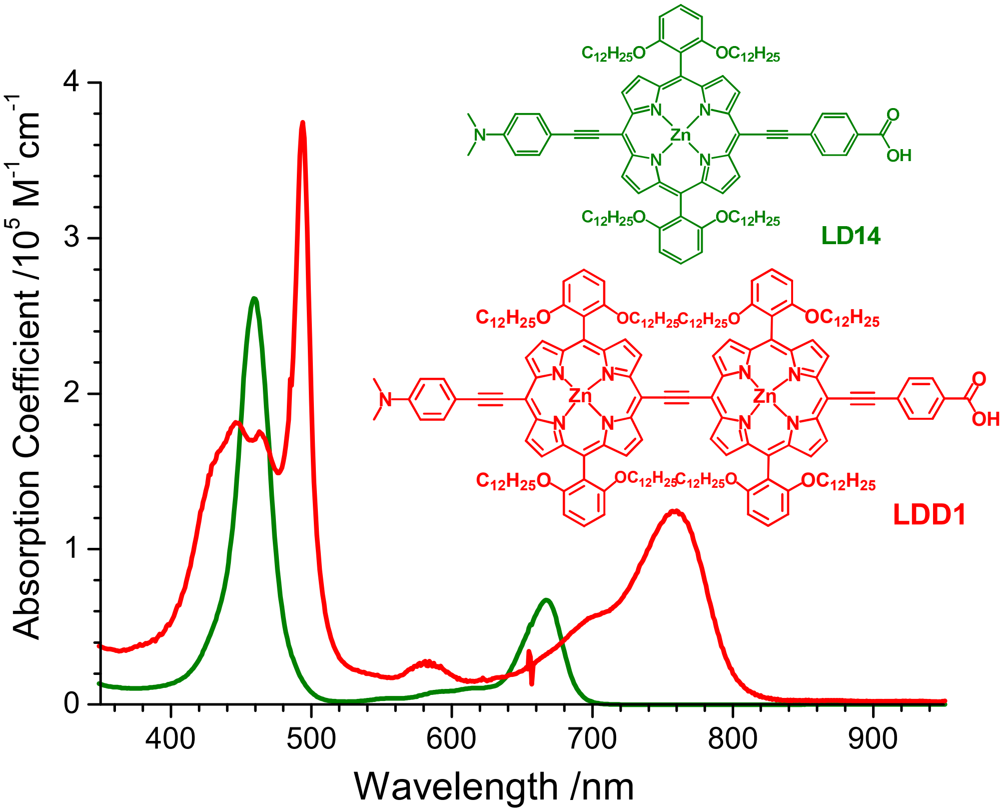

Figure 1. Absorption spectra of LDD1 (red) and LD14 (olive) in THF solution. The corresponding molecular structures are indicated.

The details of the synthesis and characterization of LD14 are reported elsewhere[11] and those of LDD1 are provided in Electronic Supplementary Information (ESI). Figure 1 shows the absorption spectra of LD14 and LDD1 in THF. The spectrum of LD14 shows an absorption feature typical of a zinc porphyrin with B (Soret) and Q bands in the visible spectral region (400-700 nm) but with a large spectral gap between these two absorption bands.[16] Consistent with an acetylenyl bridged porphyrin dimer,[17] B-band absorption of LDD1 shows broadened features centered about 450 nm and with a maximum located at 500 nm. The Q-band absorptions are broadened, intensified and extended beyond 800 nm in solution. Because of the push-pull design, the B and Q bands of LDD1 are much red-shifted from those of a non-push-pull system.[17] The B-bands of LDD1 fill the gap between the two absorptions of LD14, and the Q-bands of LDD1 extend toward the near-infrared region. With these important spectral properties, co-sensitization of the LDD1 dye with the LD14 dye creates a panchromatic and efficient PSSC system with light-harvesting ability reaching 900 nm.

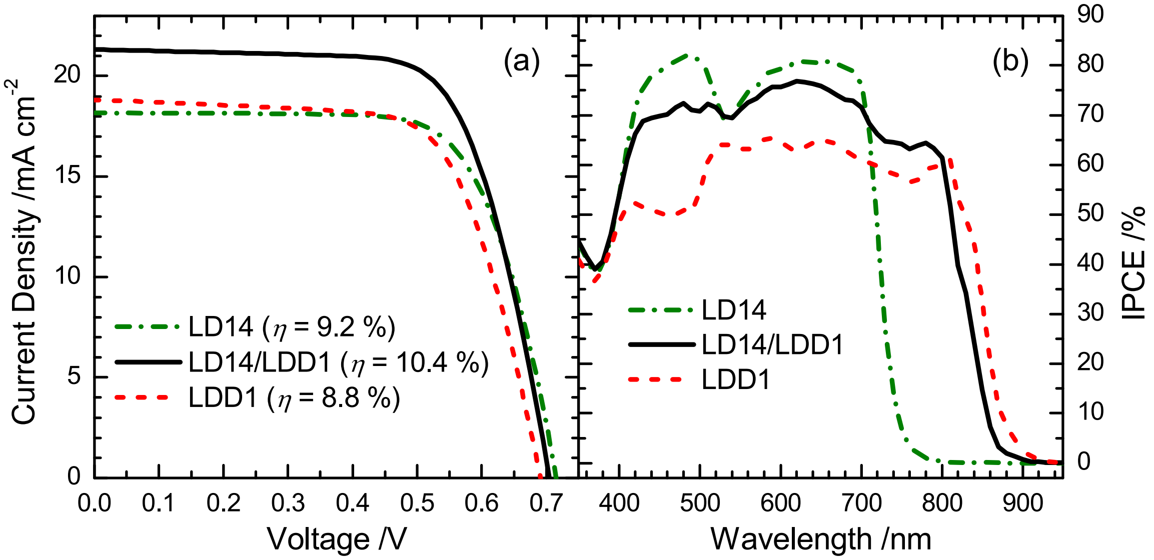

Figure 2. Photovoltaic properties of (a) current–voltage curves and (b) corresponding IPCE action spectra of devices made of the co-sensitized LD14/LDD1 system and individual dyes (LD14 and LDD1).

Table 1. Photovoltaic parameters of devices fabricated with varied porphyrin-based or co-sensitized systems and a perovskite solar cell under AM 1.5G one-sun irradiation.

Systems	J_{SC} /mA cm^{-2}	V_{OC} /mV	FF	η /%	References
LD14	18.2	716	0.704	9.2	This work
LDD1	18.8	692	0.677	8.8	This work
LD14/LDD1	21.3	705	0.692	10.4	This work
LD31/AN-4	20.3	704	0.718	10.3	10
YD2-oC8/CD4/YDD6	19.3	753	0.719	10.4	18
Perovskite	19.8	924	0.663	12.1	23

Our devices of PSSC were fabricated according to the procedures summarized in ESI. Figures 2a and b display the current-voltage characteristics and IPCE action spectra, respectively. Corresponding photovoltaic parameters are listed in Table 1 for devices made of LD14 dye alone, LDD1 dye alone, and the LD14/LDD1 co-sensitized system. For the co-sensitized system, the two-dye cocktail solutions contained LD14 and LDD1 in molar ratios of 10/1, 5/1 and 1/1, for which the 5/1 system gave the best photovoltaic performance as shown in Figure 2. The IPCE values of the LD14 device reached 80 % almost throughout the visible region except a dip located about 540 nm.[10,11] In contrast, the LDD1 device exhibited excellent light harvesting to extend the IPCE spectrum beyond 900 nm. Dye aggregation seemed significant among these porphrin dimers:[18] the IPCE values of the LDD1 device decreased to ~60 %. As a result, both the single-dye devices attained similar J_{SC} values above 18 mA cm^{-2}. Co-sensitization of LD14 with LDD1 in a cocktail solution containing LD14/LDD1 (molar ratio 5/1) significantly enhanced the IPCE values in the entire region up to 900 nm. In this way, the co-sensitized LD14/LDD1 device attained a remarkable J_{SC} (21.3 mA cm^{-2}), an intermediate V_{OC} (705 mV) and FF (0.692), rendering an overall device performance to attain η = 10.4 %. Note that the IPCE spectra of the devices sensitized with a black dye also showed broad spectral feature extending to 900 nm,[19] but the IPCE values of black dye significantly decreased in the near IR region (700 – 900 nm). In contrast, the LD14/LDD1 cell featured panchromatic light-harvesting ability not only in the visible spectral region, but also broadly extended toward the near IR region due to the contribution of the Q-band absorption of the dimeric porphyrin co-sensitizer.

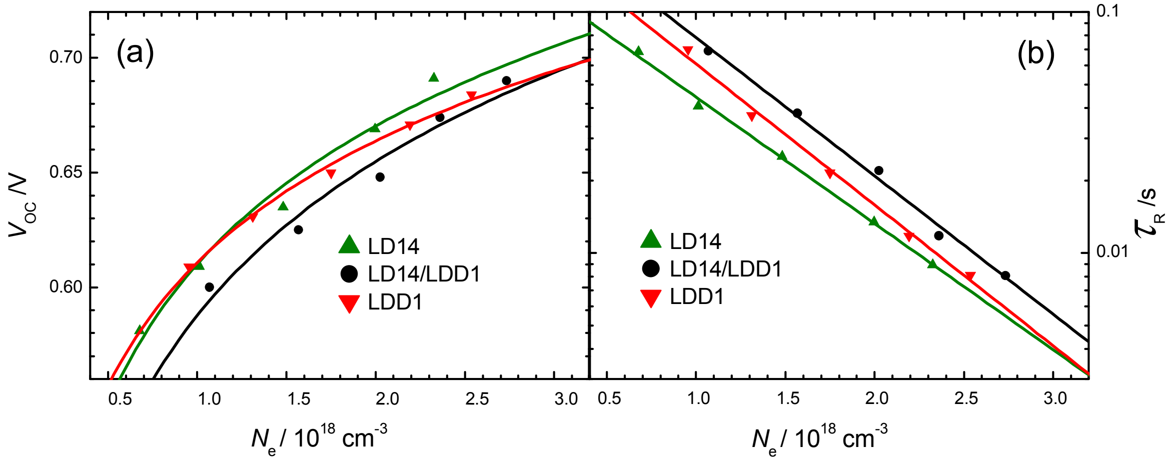

Figure 3. Plots of (a) V_{OC} vs. charge density (N_e) and (b) electron lifetime (τ_R) vs. N_e for devices made of individual dyes LD14 and LDD1 and their co-sensitized LD14/LDD1 system.

We measured the charge extraction (CE) and intensity-modulated photovoltage spectra (IMVS) at five intensities of white-light irradiation according to procedures reported elsewhere;[10, 20] the CE and IMVS results are shown in Figures 3a and b, respectively. The CE results show that the potential band edges of TiO_2 are similar for the LD14 and the LDD1 devices, but that of the co-sensitized LD14/LDD1 system shifts downwards slightly. V_{OC} of the LDD1 device is smaller than that of the LD14 device (0.716 V vs 0.692 V), possibly due to the effect of dye aggretaion. The extent of dye aggregation seemed, however, less severe for the LDD1 system than for the YDD6 system because more electrons can be extracted from the former than from the latter: V_{OC} of LDD1 (0.692 V) is thus greater than that of YDD6 (0.671 V).[18] Co-sensitization of LD14 with LDD1 decreased the electron lifetime (τ_R); this retardation of charge recombination was observed also for other co-sensitization systems.[18-22]

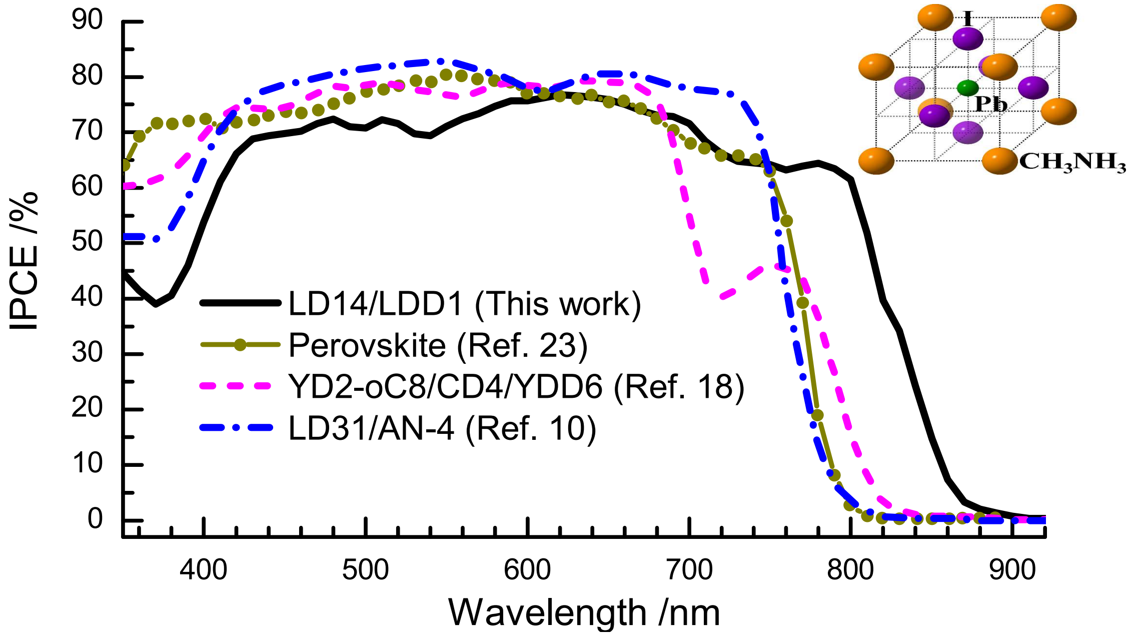

Figure 4. Comparison of IPCE action spectra of devices made of co-sensitized systems LD14/LDD1 (this work), YD2oC8/CD4/YDD6[18] and LD31/AN-4[10] with respect to that of a typical solid-state perovskite solar cell.[23] The up-right corner shows a molecular structure for the unit cell of perovskite crystal with a chemical formula $CH_3NH_3PbI_3$.

In conclusion, we designed a new dimeric porphyrin sensitizer, LDD1, with a panchromatic spectral feature to harvest solar energy up to 900 nm. When co-sensitizing LDD1 with LD14 in a liquid-type iodine-based PSSC, the device performance became optimized to attain PCE 10.4 %. In Figure 4, we compare the light-harvesting abilities of varied co-sensitized systems for YD2-oC8/CD4/YDD6,[18] LD31/AN-4[10] and LD14/LDD1 with respect to a typical *n*-type solid-state perovskite (PSK) solar cell.[23] The IPCE action spectra exhibit a systematic trend of light-harvesting coverage, LD14/LDD1 > LD31/AN-4 ~ PSK > YD2-oC8/CD4/YDD6. The IPCE spectral edge of the LD14/LDD1 cell is red-shifted, remarkably, ~100 nm more than for the YD2-oC8, LD31 and PSK devices. As a result, the values of J_{SC}/mA cm^{-2} increased from 19.3 (YD2-oC8/CD4/YDD6), 19.8 (PSK), 20.3 (LD31/AN-4) to 21.3 in a LD14/LDD1 co-sensitized system. The superior light-harvesting capability of the LDD1 dye is an important feature to be considered as a prospective bi-functional material to incorporate into a PSK system for enhanced photovoltaic performance.

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References

1. L.-L. Li and E. W.-G. Diau, *Chem. Soc. Rev.*, 2013, **42**, 291–304.
2. K. Kurotobi, Y. Toude, K. Kawamoto, Y. Fujimori, S. Ito, P. Chabera, V. Sundström and H. Imahori, *Chem.-Eur. J.*, 2013, **19**, 17075–17081.
3. J. Luo, M. Xu, R. Li, K.-W. Huang, C. Jiang, Q. Qi, W. Zeng, J. Zhang, C. Chi, P. Wang and J. Wu, *J. Am. Chem. Soc.*, 2014, **136**, 265–272.
4. Y. Wang, B. Chen, W. Wu, X. Li, W. Zhu, H. Tian and Y. Xie, *Angew. Chem. Int. Ed.*, 2014, **53**, 10779–10783.
5. J. Lu, X. Xu, K. Cao, J. Cui, Y. Zhang, Y. Shen, X. Shi, L. Liao, Y. Cheng and M. Wang, *J. Mater. Chem. A*, 2013, **1**, 10008–10015.
6. S. Rangan, S. Coh, R. A. Bartynski, K. P. Chitre, E. Galoppini, C. Jaye and D. Fischer, *J. Phys. Chem. C*, 2012, **116**, 23921–23930.
7. A. Yella, H. W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W.-G. Diau, C. Y. Yeh, S. M. Zakeeruddin and M. Grätzel, *Science*, 2011, **334**, 629–634.
8. A.Yella,, C.-L Mai,. S. M.Zakeeruddin, S.-N.Chang, C.-H.Hsieh, C.-Y.Yeh and M.Grätzel, *Angew. Chem. Int. Ed.*, 2014*,* **53**, 2973–2977.

9. S.Mathew, A.Yella, P.Gao, R.Humphry-Baker, B. F. E.Curchod, N.Ashari-Astani, I.Tavernelli, U.Rothlisberger, M. K.Nazeeruddin and M.Grätzel, *Nature Chemistry*, 2014, **6**, 242–247.
10. C.-L.Wang, J.-Y. Hu, C.-H. Wu, H.-H. Kuo, Y.-C. Chang, Z.-J. Lan, H.-P. Wu, E. W.-G. Diau and C.-Y. Lin, *Energy Environ. Sci.*, 2014, **7**, 1392–1396.
11. Y.-C. Chang, C.-L. Wang, T.-Y. Pan, S.-H. Hong, C.-M. Lan, H.-H. Kuo, C.-F. Lo, H.-Y. Hsu, C.-Y. Lin and E. W.-G. Diau, *Chem. Commun*., 2011, **47**, 8910–8912.
12. J. H. Rhee, C. C. Chung and E. W.-G. Diau, *NPG Asia Materials*, 2013, **5**, e68.
13. J. Burschka, N. Pellet, S. J. Moon, R. Humphry-Baker, P. Gao, M. K.Nazeeruddin and M. Grätzel, *Nature*, 2013, **499**, 316–319.
14. M. Liu, M. B. Johnston and H. J. Snaith, *Nature*, 2013, **501**, 395–398.
15. H. Zhou, Q. Chen, G. Li, S. Luo, T. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu and Y. Yang, *Science*, 2014, **345**, 542–546.
16. M.Gouterman, *J. Mol. Spectrosc.*, 1961*,* **6**, 138–163.
17. V. S.-Y. Lin, S. G. DiMagno and M. J. Therien, *Science*, 1994, **264**, 1105–1111.
18. H.-P. Wu, Z.-W. Ou, T.-Y. Pan, C.-M.Lan, W.-K. Huang, H.-W. Lee, N. M. Reddy, C.-T. Chen, W.-S. Chao, C.-Y. Yeh and E. W.-G. Diau, *Energy Environ. Sci.*, 2012, **5**, 9843–9848.
19. S. Zhang, X. Yang, Y. Numata and L. Han, *Energy Environ. Sci.*, 2013, **6**, 1443–1464.
20. L.-L .Li, Y.-C. Chang, H.-P. Wu and E. W.-G. Diau, *Int. Rev. Phys. Chem*., 2012, **31**, 420–467.
21. C.-M. Lan, H.-P. Wu, T.-Y. Pan, C.-W. Chang, W.-S. Chao, C.-T. Chen, C.-L.Wang, C.-Y. Lin and E. W.-G.Diau, *Energy Environ. Sci*., 2012, **5**, 6460–6464.
22. S. Chang, H. Wang, Y. Hua, Q. Li, X. Xiao, W.-K. Wong, W. Y. Wong, X. Zhu and T. Chen, *J. Mater. Chem. A*, 2013, **1**, 11553–11558.
23. Q. Chen, H. Zhou, Z. Hong, S. Luo, H.-S. Duan, H.-H. Wang, Y. Liu, G. Li and Y. Yang, *J. Am. Chem. Soc.*, 2014, **136**, 622–625.