Tetrahedron Letters 52 (2011) 3879–3882

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Novel D-π-A system based on zinc-porphyrin derivatives for highly efficient dye-sensitised solar cells

Myung Jun Lee[a], Kang Deuk Seo[a], Hae Min Song[a], Min Soo Kang[a], Yu Kyung Eom[a], Hong Seok Kang[b], Hwan Kyu Kim[a,*]

[a] Department of Advanced Materials Chemistry & Centre for Advanced Photovoltaic Materials (ITRC), Korea University, ChungNam 339-700, Republic of Korea
[b] Department of Nano & Advanced Materials, College of Engineering, Jeonju University, Hyoja-dong, Wansan-ku, Chonju, Chonbuk 560-759, Republic of Korea

ARTICLE INFO

Article history:
Received 29 March 2011
Revised 13 May 2011
Accepted 16 May 2011
Available online 23 May 2011

Keywords:
Porphyriin
Carbazole
Dye-sensitised solar cell
Quantum efficiency

ABSTRACT

We have designed and synthesised novel zinc porphyrin dyes that have a D-π-A system based on porphyrin derivatives containing a carbazole linked triphenylamine (TPA) electron-donating group as the second electron donor and a meso-substituted phenyl carboxyl anchoring group attached at the meso position of the porphyrin ring, yielding push–pull porphyrins as the most efficient green dye for DSSC applications. Under photovoltaic performance measurements, a maximum photon-to-electron conversion efficiency of 5.01% was achieved with the DSSC based on the dye **HKK-Por1** (J_{SC} = 10.7 mA/cm^2, V_{OC} = 0.67 V, *FF* = 0.70) under AM1.5 irradiation (100 mW/cm^2).

Dye-sensitised solar cells (DSSC) based on mesoporous nanocrystalline TiO_2 films have attracted significant attention due to their low cost and high sunlight-to-electric power conversion efficiencies of 10–12%.[1–5] In recent years, interest in metal-free organic dyes as an alternative to noble metal complexes has increased due to their many advantages, such as diversity of molecular structures, high molar extinction coefficient, simple synthesis as well as low cost and environmental issues.[6,7]

Porphyrins are one of the most widely studied sensitisers for DSSCs because of their strong Soret (400–450 nm) and moderate Q bands (550–600 nm).[8–10] The porphyrin-based dyes have several intrinsic advantages, such as good photostability from one kind of natural chlorophylls, their rigid molecular structures with large absorption coefficients in the visible region and their many reaction sites, that is, four meso and eight beta positions, available for functionalisation. Fine tuning of their optical, physical, and electrochemical properties thus becomes feasible.[11–15] In addition, the higher η value of porphyrin dye,[16] has been achieved up to 11% in full sunlight by Eric Diau and co-workers. To further design and develop the more efficient porphyrin dyes for DSSCs, the predominant light-harvesting abilities in visible and near-IR light of dyes are important to get a larger photocurrent response. Here, we have designed and synthesised novel zinc porphyrin dyes that have a D-π-A system based on porphyrin derivatives. To increase the electron-donating ability of the D-π-A system based on porphyrin derivatives, porphyrin with a carbazole-containing triphenylamine (TPA) moiety was designed and synthesised. Furthermore to decrease the rotation of the phenyl unit, a mesityl group was introduced at the 5, 20 position of the porphyrin, yielding push–pull porphyrins as the most efficient green dye for DSSC applications.

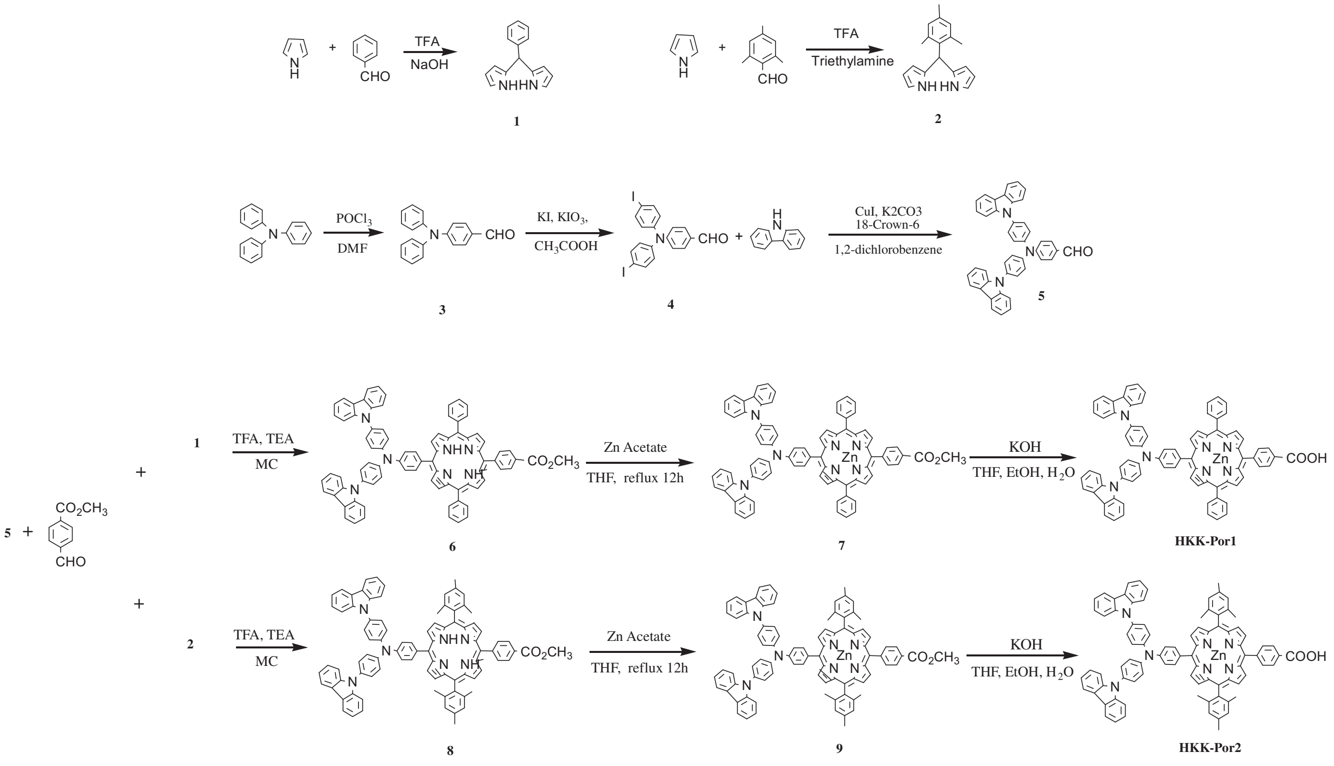
The novel zinc porphyrins were synthesised according to Scheme 1. Compounds **1** and 2 were prepared by adapting published procedures. Treatment of commercially available triphenylamine aldehyde with potassium iodide and potassium iodate in acetic acid led to intermediate compound **5**.[17] Compound **6** was synthesised according to the literature.[18] Compound **7** was synthesised by an insertion reaction of Zn(II) ion and then hydrolysed (**HKK-Por1**). **HKK-Por2** dye was synthesised by the same method. The chemical structures of the porphyrin dyes were identified by ^{1}H NMR, MALDI-TOF mass, UV–vis absorption spectroscopies (see Supplementary data for details).

Figure 1 shows the absorption and emission spectra of HKK-Por dyes measured in the THF solution; their photophysical properties are summarised in Table 1. The absorption spectrum of **HKK-Por1** displays three absorption maxima at 426.5 nm, 557.5 nm and 598.5 nm which are assigned as the π–π* transitions of the conjugated system. **HKK-Por2** also has similar behaviour to **HKK-Por1**. But, these absorption maxima of HKK-Por 1and 2 were a little red-shifted in contrast to Zn[5,-10,15-triphenyl-20(4-caboxylphenyl)-porphyrin] in our previous articles,[19] due to the tilted structure (ϕ_1: ~37.7 and ϕ_2 ~−61.1 for HKK-Por 1; ϕ_1: ~37.5 and ϕ_2 ~−60.8 for HKK-Por 2) between TPA and porphyrin unit, as shown in Figure 2. Specifically, our TD-DFT calculation shows that the charge transfer

---

* Corresponding author. Tel.: +82 41 860 1493; fax: +82 41 867 5396.
E-mail address: hkk777@korea.ac.kr (H.K. Kim).

0040-4039/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2011.05.074



Scheme 1. Chemical structures and synthesis of HKK-Por dyes.

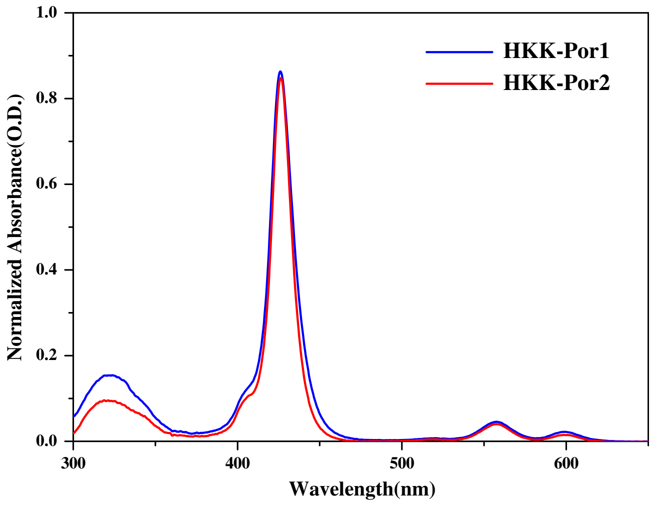


Figure 1. Absorption spectra HKK-Por dyes in THF solvent (1.0×10^{-5} M).

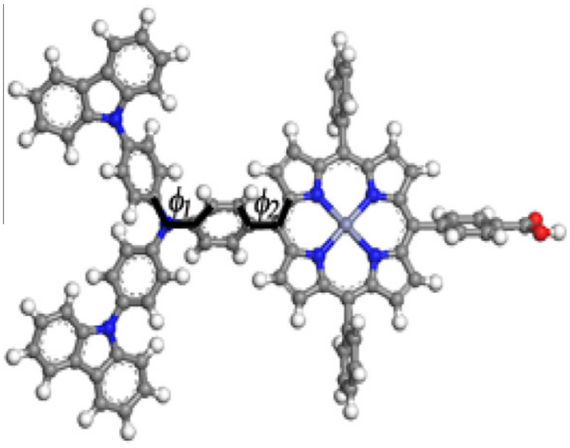


Figure 2. Optimized structure of HKK-Por dye.

transition from HOMO−4 to LUMO+2 contributes to the peak at 426.5 nm, as shown in Figure 3. The fluorescence quantum efficiency of **HKK-Por2** was slightly enhanced due to the large rotation barrier of the mesityl unit, but the extinction coefficient of **HKK-Por2** was

Table 1
Absorption/emission and electrochemical properties of HKK-Por dyes

Dye	Absorption (λ_{max}/nm)[a] (ε/$M^{-1}cm^{-1}$)	Emission (λ_{max}/nm)	E_{ox}[b]/V (vs NHE)	E_{oo}[c]/V	E_{LUMO}[d]/V (vs NHE)	Φ_f[e]
HKK-Por1	426.5(38893), 557.5(19850), 598.5 (9991)	610.0, 658.0	1.33	2.16	−0.83	0.025
HKK-Por2	427.5(38076), 557.5(17720), 599.0(7215)	612.0, 657.0	1.34	2.13	−0.79	0.034

[a] Absorption was measured in the THF solution (1.0×10^{-5} M) at room temperature.
[b] The oxidation potential of the dye was measured in methylene chloride with 0.1 M $TBAPF_6$ with a scan rate of 50 mVs^{-1}(vs NHE).
[c] E_{oo} was determined from the intersection of the absorption and emission spectra in THF.
[d] LUMO was calculated by $E_{ox}-E_{oo}$.
[e] The fluorescence quantum efficiency of chlorophyll A with $\Phi = 0.32$ (in ether) was used as the standard.

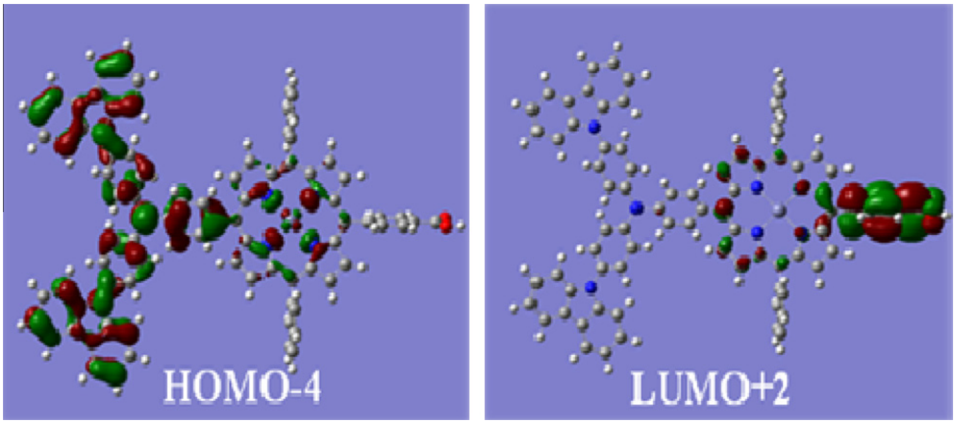


Figure 3. Plots of the isodensity surfaces (PBEPBE/6-31G*) of HOMO−4 and LUMO+2 of **HKK-Por1** dye.

slightly lowered by the introduction of a mesityl group for decreasing the rotation of the phenyl unit (see Table 1), as compared with **HKK-Por1**. The electrochemical properties were investigated by cyclic voltammetry (CV) to obtain the HOMO and LUMO levels of the HKK-Por dyes. The cyclic voltammogram curves were obtained from a three-electrode cell in 0.1 M $TBAPF_6$ in CH_3CN at a scan rate of 50 mV/s, using a dye-coated TiO_2 electrode as a working electrode, a Pt wire counter electrode and an Ag/AgCl (saturated KCl) reference electrode (+0.197 V vs NHE) and calibrated with ferrocene. All of the measured potentials were converted to the NHE scale. In the case of triamine substituted porphyrin sensitizer, the conversion efficiency was very lower to other push-pull porphyrins, may be due to a slower dye regeneration arising from the raise of the HOMO level of dye.[20] HOMO values of HKK-Por dyes (1.33–1.34 V vs NHE) were more positive than the I^-/I_3^- redox couple (0.4 V vs NHE) and fulfil the requirement for effective dye regeneration. The electron injection from the excited sensitisers to the conduction band of TiO_2 should be energetically favourable because of the more negative LUMO values (-0.79 to -0.83 vs NHE) compared to the conduction band edge energy level of the TiO_2 electrode.[21]

The photovoltaic properties of the solar cells constructed from these organic dye-sensitised TiO_2 electrodes were measured under simulated AM1.5 irradiation (100 mW/cm^2). The photovoltaic performances of the HKK-Por-DSSCs are summarised in Table 2. Current density–voltage (J–V) characteristics and incident photon-to-current conversion efficiencies (IPCE) of devices are shown in Figures 4 and 5, respectively.

The onset wavelengths of the IPCE spectra for DSSCs based on HKK-Por dyes were <700 nm. IPCE values of higher than 70% were observed in the range of 400–500 nm. The maximum IPCE value of the DSSC based on **HKK-Por2** was slightly lower than the efficiencies of the DSSCs based on **HKK-Por1** due to the lower molar extinction coefficient. Under standard global AM 1.5 solar conditions, the **HKK-Por1**-sensitised cell gave a J_{SC} of 10.7 mAcm^{-2}, V_{OC} of 0.67 V, *FF* of 0.70, corresponding to, an overall conversion efficiency η of 5.01%. The **HKK-Por2**-sensitised cell gave a J_{SC} of 10.9 mAcm^{-2}, V_{OC} of 0.64 V, FF of 0.68, corresponding to an overall conversion efficiency η of 4.70%. Because of a bulky donor effect, HKK-Por dyes with a carbazole-containing TPA moiety showed a higher conversion efficiency. These results were obtained to give

Table 2
Dye-sensitised solar cell performance data of the HKK-Por dyes

Dye	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	η (%)
HKK-Por1	10.7	0.67	0.70	5.01
HKK-Por2	10.9	0.64	0.68	4.70

TiO_2 thickness of 9 µm, (5 + 4) µm, sc, $TiCl_4$; electrolyte condition 0.6 M DMPII, 0.5 M LiI, 0.05 M I_2, 0.5 M TBP in an acetonitrile solution; dye was dissolved in THF.

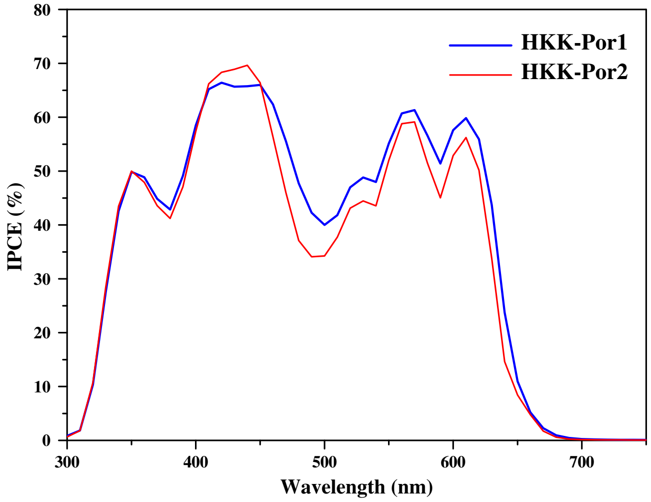


Figure 4. Typical action spectra of incident photon-to-current conversion efficiencies (IPCE) obtained for nanocrystalline TiO_2 solar cells sensitised by HKK-Por dyes.

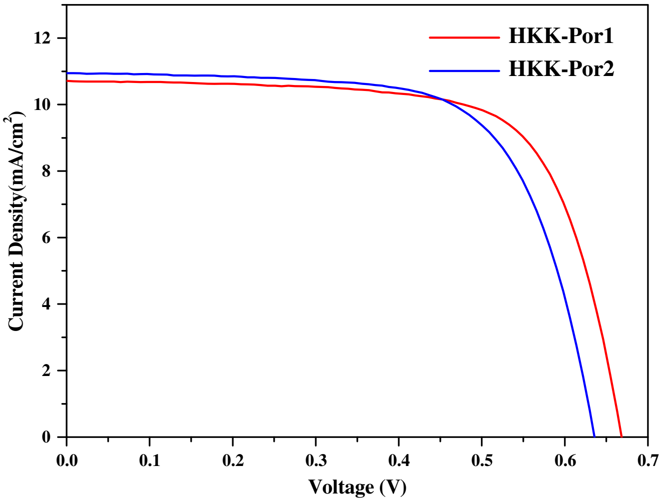


Figure 5. Photocurrent–voltage characteristics of representative TiO_2 electrodes sensitised with HKK-Por dyes.

a much poorer cell performance than other D-π-A system based on zinc-porphyrin derivatives,[16,20] due to the less π-conjugation degree between donor and acceptor units, caused by the tilted structure between TPA and porphyrin unit.

In summary, we have successfully synthesised novel HKK-Por dyes and obtained materials with interesting optical and electrochemical properties. Among the series of HKK-Por dyes, which had a different π-conjugating system and similar electron donor moieties, the ε value of **HKK-Por1** was relatively large, but the relative quantum efficiency of **HKK-Por2** was a little high. Under standard global AM 1.5 solar conditions, the **HKK-Por1** sensitiser cell gave a J_{SC} of 10.7 mAcm^{-2}, V_{OC} of 0.67 V, and *FF* of 0.70, corresponding to an overall conversion efficiency η of 5.01%. Further improvement of the power conversion efficiency of porphyrin derivative dyes can be investigated by using them as dye sensitisers instead of expensive ruthenium dye sensitisers in the near future.

Acknowledgements

This research was supported by MKE (the Ministry of Knowledge Economy), Korea, under the ITRC support programme supervised by the IITA (Institute for Information Technology Advancement) (IITA-2008-C1090-0804-0013), WCU (the Ministry of Education and Science) programme (R31-2008-000-10035-0) and by the CRC Program through the National Research Foundation of Korea (NRF) (2010K000973). Computations were performed using a supercomputer at the Korea Institute of Science and Technology Information under Contract No. KSC-2008-S03-0008.

Supplementary data

Supplementary data (detailed experimental procedures, synthesis and characterisation of all compounds as well as their TD-DFT calculation) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.05.074.

References and notes

1. Nazeeruddin, M. K.; De Angelis, F.; Fantacci, S.; Selloni, A.; Viscardi, G.; Liska, P.; Ito, S.; Takeru, B.; Grätzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 16835.
2. Pe′chy, P.; Renouard, T.; Zakeeruddin, S. M.; Humphry-Baker, R.; Comte, P.; Liska, P.; Cevey, L.; Costa, E.; Shklover, V.; Spiccia, L.; Deacon, G. B.; Bignozzi, C. A.; Grätzel, M. *J. Am. Chem. Soc.* **2001**, *123*, 1613.
3. Mishra, A.; Fischer, M. K. R.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2009**, *48*, 2474.
4. Ning, Z.; Fu, Y.; Tian, H. *Energy Environ. Sci.* **2010**, *3*, 1170.
5. (a) Baek, N. S.; Yum, J.-H.; Zhang, X.; Kim, H. K.; Nazeeruddin, M. K.; Grätzel, M. *Energy Environ. Sci.* **2009**, *2*, 1082; (b) Seo, K. D.; Song, H. M.; Lee, M. J.; Pastore, M.; Anselmi, C.; De Angelis, F.; Nazeeruddin, M. K.; Gräetzel, M.; Kim, H. K. *Dyes and Pigments* **2011**, *90*, 304.
6. Liang, Y.; Peng, B.; Liang, J.; Tao, Z.; Chen, L. *Org. Lett.* **2010**, *12*, 1204.
7. Velusamy, M.; Thomas, K. R. J.; Lin, J. T.; Hsu, Y. C.; Ho, K. C. *Org. Lett.* **2005**, *7*, 1899.
8. Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Muller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382.
9. (a) Mozer, A. J.; Griffith, M. J.; Tsekouras, G.; Wagner, P.; Wallace, G. G.; Mori, S.; Sunahara, K.; Miyashita, M.; Earles, J. C.; Gordon, K. C.; Du, L.; Katoh, R.; Furube, A.; Officer, D. L. *J. Am. Chem. Soc.* **2009**, *131*, 15621; (b) Park, J. K.; Lee, H. R.; Chen, J.; Shino kubo, H.; Osuka, A.; Kim, D. *J. Phys. Chem. C* **2008**, *112*, 16691.
10. (a) Cherian, S.; Wamser, C. C. *J. Phys. Chem. B* **2000**, *104*, 3624; (b) Watson, D. F.; Marton, A.; Stux, A. M.; Meyer, G. J. *J. Phys. Chem. B* **2003**, *107*, 10971; (c) Watson, D. F.; Marton, A.; Stux, A. M.; Meyer, G. J. *J. Phys. Chem. B* **2004**, *108*, 11680; (d) Rochford, J.; Chu, D.; Hagfeldt, A.; Galoppini, E. *J. Am. Chem. Soc.* **2007**, *129*, 4655; (e) Rochford, J.; Galoppini, E. *Langmuir* **2008**, *24*, 5366.
11. Victoria, M. M.-D.; Torre, G. D. L.; Torres, T. *Chem. Commun.* **2010**, *46*, 7090.
12. Imahori, H.; Umeyama, T.; ITO, S. *Acc. Chem. Res.* **2009**, *42*, 1809.
13. Walter, M. G.; Rudine, A. B.; Wamser, C. C. *J. Porphyrins Phthalocyanines* **2010**, *14*, 759.
14. Liu, Y.; Lin, H.; Dy, J. T.; Tamaki, K.; Nakazaki, J.; Nakayama, D.; Uchida, S.; Kubo, T.; Segawa, H. *Chem. Commun.* **2011**, *47*, 4010.
15. Imahori, H.; Matsubara, Y.; Iijima, H.; Umeyama, T.; Matano, Y.; Ito, S.; Niemi, M.; Tkachenko, N. V.; Lemmetyinen, H. *J. Phys. Chem. C* **2010**, *114*, 10656.
16. Bessho, T.; Zakeeruddin, S. M.; Yeh, C.-Y.; Diau, E. W.-G.; Grätzel, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 6646.
17. Ning, Z.; Chen, Z.; Zhang, Q.; Yan, Y.; Zian, S.; Cao, Y.; Tian, H. *Adv. Funct. Mater.* **2007**, *17*, 3799.
18. Kang, M. S.; Oh, J. B.; Seo, K. D.; Kim, H. K.; Park, J. H.; Kim, K. K.; Park, N. G. *J. Porphyrins Phthalocyanines* **2009**, *13*, 798.
19. (a) Nah, M. K.; Oh, J. B.; Kim, H. K.; Choi, K. H.; Kim, Y. R.; Kang, J.-G. *J. Phys. Chem. A* **2007**, *111*, 6157; (b) Oh, J. B.; Kim, Y. H.; Nah, M. K.; Kim, H. K. *J. Lumin.* **2005**, *111*, 255.
20. Hsieh, C.-P.; Lu, H.-P.; Chiu, C.-L.; Lee, C.-W.; Chuang, S.-H.; Mai, C.-L.; Yen, W.-N.; Hsu, S.-J.; Diau, E. W.-G.; Yeh, C.-U. *J. Mater. Chem.* **2010**, *20*, 1127.
21. Hagfeldt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49.