Angewandte Chemie International Edition

DOI: 10.1002/anie.201204948

Organic Solar Cells

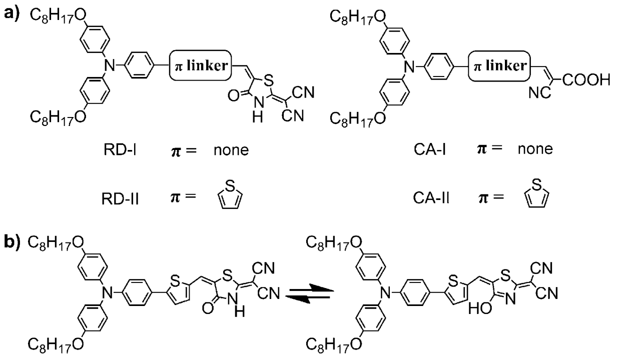
Stable Dyes Containing Double Acceptors without COOH as Anchors for Highly Efficient Dye-Sensitized Solar Cells**

Jiangyi Mao, Nannan He, Zhijun Ning, Qiong Zhang, Fuling Guo, Long Chen, Wenjun Wu, Jianli Hua, and He Tian**

Dedication to Professor Klaus Müllen on the occasion of his 65th birthday

Dye-sensitized solar cells (DSSCs) have attracted considerable attention. The sensitizer is normally regarded as the essential component of DSSCs.[1] In recent years, metal-free organic dyes have been the central topic of development of DSSCs, and they usually possess the structure of donor–π-bridge–acceptor (D-π-A).[2–8] Among donor groups, triphenylamine and its derivatives have shown promise in the development of DSSCs owing to their nonplanar structure suppressing the dye aggregation.[9] Electron acceptors have been mainly focused on carboxylic acids, cyanoacrylic acid, and rhodanine-3 acetic acid moieties as they can bind to the TiO_2. In particular, the introduction of cyanoacrylic acid as electron-accepting unit has witnessed the rapid development of organic dyes as sensitizers. This structure features evident advantages of both wide absorption spectra in the visible region and good electron injection efficiency. Based on this same electron acceptor, significant improvement in the efficiency of organic dyes has been achieved by regulating the donor and the conjugating unit. However, dyes with COOH as anchor unit will dissociate on TiO_2 surface under long irradiation times.[10] Thus, it is pivotal to increase the binding strength of the anchor unit. It was known that metal can form strong chelating bond with heterocycle ligand.[11] Recently, pyridine,[12] phosphinic acid,[13] and 8-hydroxylquinoline[10] have been explored as anchoring groups; nevertheless, the efficiencies of DSSCs based on these acceptors still lag behind that of cyanoacrylic acid counterparts. The bottleneck of this effort lies in either the low electron-injection efficiency or the limited broadening of absorption spectra.

Herein, we report a novel electron acceptor 2-(1,1-dicyanomethylene)rhodanine (DCRD), which can not only bring wide absorption spectra, but also maintain excellent electron injection efficiency owing to its following characteristics: 1) The double electron acceptors of both rhodanine and dicyanomethylene can guarantee strong electron-accepting ability;[14] 2) the O and N atoms of rhodanine in DCRD can chelate to titanium ions on the TiO_2 surface and achieve strong electron coupling between the excited-state energy level of the dyes and the conduction band of TiO_2; and 3) the anchor unit is localized on the middle acceptor, which can reduce the electron transfer distance from the donor to TiO_2. Sensitizers coded as RD-I and RD-II (Scheme 1) based on this electron acceptor were synthesized, and reference dyes CA-I and CA-II with cyanoacrylic acid were also synthesized for comparison. For this peculiar electron-acceptor DCRD, the O and N on the rhodanine unit can both form strong chelating bonds with Ti cations, furnishing enhanced stability of the dyes in comparison with COOH anchor. Both RD-I and RD-II show broadened absorption spectra than CA-I and CA-II, respectively. More importantly, these dyes based on the new electron acceptor show comparable electron injection efficiency to cyanoacrylic acid counterparts, and the overall efficiencies of RD-I and RD-II are evidently higher than CA-I and CA-II, respectively. To the best of our knowledge, this is probably the first report of dyes with alternative electron acceptor showing higher efficiency than cyanoacrylic acid counterparts.



Scheme 1. a) Molecular structures of dyes RD-I, RD-II, CA-I, and CA-II; b) Molecular structures of RD-II and its tautomer.

The UV/Vis absorption spectra of the four dyes in diluted solutions of CH_2Cl_2 and on thin transparent TiO_2 films (5 μm in thickness) after 12 h adsorption in CH_2Cl_2 solutions are shown in the Supporting Information, Figure S1, and their spectral data are listed in Table 1. The absorption spectra of

---

[*] J. Mao, N. He, Dr. Z. Ning, Dr. Q. Zhang, F. Guo, L. Chen, Dr. W. Wu, Prof. J. Hua, Prof. H. Tian
Key Laboratory for Advanced Materials, Institute of Fine Chemicals, East China University of Science and Technology
130 Meilong Road, Shanghai 200237 (China)
E-mail: jlhua@ecust.edu.cn
tianhe@ecust.edu.cn

[**] This work was supported by NSFC/China (2116110444, 21172073, and 21190033), the National Basic Research 973 Program (2011CB808400), the Fundamental Research Funds for the Central Universities (WJ0913001), and the Ph.D. Programs Foundation of the Ministry of Education of China (20090074110004).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201204948.

Table 1: Optical and electrochemical properties data and DSSC performance parameters of RD-I, RD-II, CA-I, and CA-II.

Dye	λ_{max}[a] [nm] (ε, 10^4 L mol^{-1} cm^{-1})	λ_{max}[b] [nm]	$E^{\circ\prime}_{ox}$[c] [V] (vs.NHE)	$E_{0\text{-}0}$[d] [eV]	$E^{\circ\prime *}$[e] [V] (vs. NHE)	Molecules cm^{-2}[f]	J_{sc} [mA cm^{-2}]	V_{oc} [mV]	FF	η [%][g]
RD-I	484 (4.42)	473	0.82	2.03	−1.21	1.16×10^{15}	9.31	742	0.72	5.00
RD-II	519 (3.14)	477	0.70	1.88	−1.18	1.20×10^{15}	13.94	746	0.68	7.11
CA-I	440 (3.79)	423	0.89	2.20	−1.31	1.23×10^{15}	8.23	789	0.72	4.69
CA-II	477 (2.36)	458	0.74	1.97	−1.23	1.25×10^{15}	11.34	804	0.70	6.39

[a] Absorption maximum in CH_2Cl_2 solution (3×10^{-5} M). [b] Absorption maximum on 5 μm TiO_2 transparent films. [c] The ground-state oxidation potential of dyes were measured in a dichloromethane with 0.1 M tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) as electrolyte (Pt working electrode, SCE reference electrode calibrated with ferrocene/ferrocenium (Fc/Fc$^+$) as an external reference, Pt counter-electrode. [d] $E_{0\text{-}0}$ was estimated from the absorption thresholds from UV/Vis absorption spectra of the dyes. [e] $E^{\circ\prime *}$ was calculated as $E^{\circ\prime}_{ox}-E_{0\text{-}0}$. [f] Adsorption amount per unit area of TiO_2 film was measured after 12 h in the dye solution. [g] The photocurrent–voltage characteristics were measured with coadsorbent (10 mM CDCA) for 13 μm thick TiO_2 film with liquid electrolyte (0.05 M I_2, 0.1 M LiI, 0.1 M DMPII, and 0.5 M TBP) at full sunlight (AM 1.5G, 100 MW cm^{-2}).

the dyes display the maximum absorption wavelength (λ_{max}) at 484 nm for RD-I, 519 nm for RD-II, 440 nm for CA-I, and 477 nm for CA-II, and this band is ascribed to the intramolecular charge transfer from the donor to the acceptor. The corresponding maximum molar extinction coefficients (ε) of the four dyes are 4.42×10^4, 3.14×10^4, 3.79×10^4, and 2.36×10^4 L mol^{-1} cm^{-1}, respectively. The red-shifts of the absorption band of RD-I and RD-II are approximately 40 nm in comparison to CA-I and CA-II, respectively. Furthermore, the ε values of RD-I and RD-II are higher than those of CA-I and CA-II. These results show that the rhodanine bearing the dicyanomethylene group exhibits stronger acceptor ability in the dye, thus leading to the red-shift of absorption maximum and enhancement of the extinction coefficient.

After anchoring on TiO_2 film, the λ_{max} of RD-I, RD-II, CA-I, and CA-II hypsochromically shifted to 473, 477, 423, and 458 nm, respectively, which may be ascribed to deprotonation and some type aggregates that always result in blue-shift of absorption peak. Noticeably, the absorption peak of RD-II on TiO_2 film shows a sharp shift in comparison to that in the solution of CH_2Cl_2. Cyclic voltammetric data for RD-I, RD-II, CA-I, and CA-II are listed in Table 1. The ground-state oxidation potential ($E^{\circ\prime}_{ox}$) of RD-I, RD-II, CA-I, and CA-II are 0.82, 0.70, 0.89, and 0.74 V, respectively, which are sufficiently low compared to the redox potential of the iodide/triiodide electrolyte couple, and hence dye regeneration is facilitated. On the other hand, the excited-state oxidation potentials ($E^{\circ\prime *}$) of RD-I, RD-II, CA-I, and CA-II, derived from ground-state oxidation potential and optical energy gap ($E^{\circ\prime}_{ox}-E_{0\text{-}0}$), are −1.21, −1.18, −1.31, and −1.23 V, respectively. The $E^{\circ\prime *}$ potential of the four dyes were more negative than the conduction-band edge of TiO_2 (−0.5 V vs. NHE), ensuring an efficient electron-injection process from the excited dye into the conduction band of TiO_2. Notably, the dyes RD-I and RD-II with DCRD double acceptors as the anchoring group feature relatively higher $E^{\circ\prime *}$ potentials than corresponding dyes CA-I and CA-II with cyanoacrylic acid, demonstrating stronger electron-withdrawing capability of the DCRD group.

To our knowledge, the bidentate mode is the way that the dyes with a COOH anchoring group anchor on the TiO_2 surface.[15] Regarding the anchoring mode for RD-I or RD-II, FTIR spectra of RD-I–II powders and the dyes adsorbed on TiO_2 have been measured to explore the adsorption mechanism (Supporting Information, Figure S4). For the dye powder, the characteristic multiple bands corresponding to NH stretching vibration ($\nu_{N\text{-}H}$) were observed at 3430–3200 cm^{-1}, as the amide group can bond to form dimers by intermolecular hydrogen bonding (Supporting Information, Figure S5). At the same time, the characteristic bands for the cyano group (C≡N) were clearly observed at 2205 cm^{-1}. The frequency of carbonyl (C=O) stretching vibration and N−H bending vibration ($\delta_{N\text{-}H}$) of the rhodanine were also raised to 1705 and 1660 cm^{-1} owing to the strong electron-withdrawing property of dicyanomethylene group, though the C=O and N-H absorption of amides usually occur at 1650 and 1570 cm^{-1}, respectively. When the dyes were adsorbed on TiO_2 surface, the FTIR peak for cyano group remained detected at the same frequencies while the absorption for $\nu_{N\text{-}H}$, $\delta_{N\text{-}H}$, and the C=O stretching bands disappeared. Noticeably, two new bands emerged at around 3305 and 1640 cm^{-1}, which can be attributed to the characteristic absorption of hydroxy groups. The presence of O−H vibration may be due to the residual $Ti(OH)_2$ present in the powder.[16] Based on the fact that the N and O atoms of 8-hydroxylquinoline can chelate to TiO_2,[10] we speculated that the DCRD moiety could form its tautomer (Scheme 1 b) in CH_2Cl_2, in which carbonyl heterocycle with α-hydrogen underwent equilibration with its enol tautomer.[17] Furthermore, the FTIR spectra of RD-I and RD-II adsorbed on TiO_2 nanoparticles indicated the formation of coordinate bonds between the O and N atoms of rhodanine in RD-I and RD-II tautomer and the Lewis acid sites of the TiO_2 surface (Supporting Information, Figure S6). To confirm this inference, we have also synthesized the model dye RDA-I (Supporting Information, Scheme S1) in which the hydrogen atom in lactam was substituted by butyl group. The TiO_2 film was soaked in a 3×10^{-4} M RDA-I bath in CH_2Cl_2 solution for 12 h at room temperature; no evidence of adsorption of the dye molecules RDA-I was observed. Consequently, it can be believed this is a new anchoring mode for 2-(1,1-dicyanomethylene) rhodanine moiety without COOH as the novel electron-withdrawing group for DSSCs.

RD-I and RD-II tend to aggregate when anchored on TiO_2 films, which is unfavorable for photocurrent generation. Co-adsorption of chenodeoxycholic acid (CDCA) with dye molecules has been used to prevent aggregation and improve solar cell performance. Figure 1 a shows the action spectra of incident photon-to-current conversion efficiency (IPCE) as

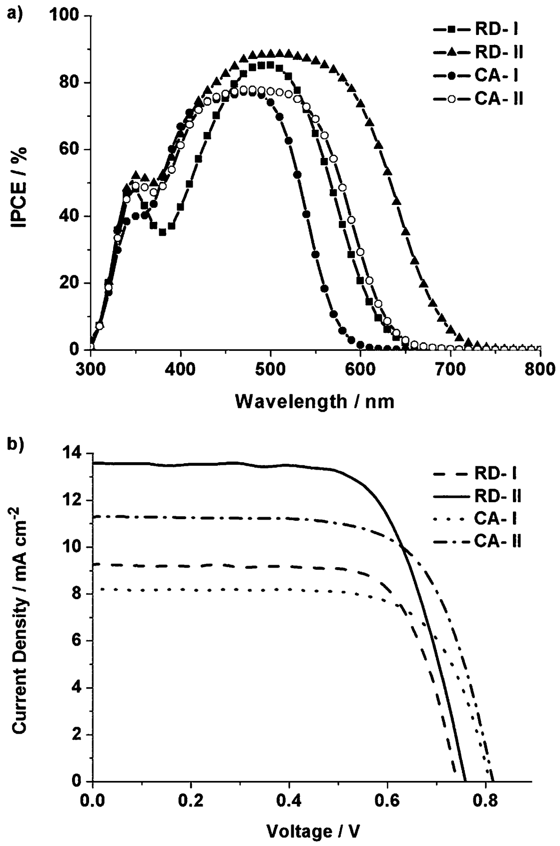


Figure 1. a) IPCE action spectra for DSSCs based on RD-I, RD-II, CA-I, and CA-II; b) Current–voltage characteristics of DSSCs based on RD-I, RD-II, CA-I, and CA-II co-adsorbed with 10 mM CDCA.

a function of incident wavelength for DSSCs. In good agreement with absorption spectra, the IPCE action spectrum for DSSCs based on RD-II is broader than those of RD-I, CA-I, and CA-II. It is worth noting that the IPCE of RD-II keeps a high plateau at visible region until 710 nm. The electron injection efficiency (Φ_{inj}) of RD-I, RD-II, CA-I, and CA-II in λ_{max} calculated to be 86.7, 91.2, 78.6, and 81.0, respectively (see the Supporting Information). It was found that the Φ_{inj} values of dyes containing RD are a little higher than the dyes with CA group, indicating that these dyes based on the new electron acceptor show comparable electron injection efficiency to cyanoacrylic acid counterparts. Figure 1 b shows photocurrent-voltage (I–V) of DSSCs based on RD-I, RD-II, CA-I, and CA-II co-adsorbed with 10 mM CDCA in ethanol using 0.1 M DMPII, 0.1 M LiI, 0.05 M I_2, and 0.5 M TBP as redox electrolyte under simulated AM 1.5G irradiation (100 mW cm^{-2}), and the adsorption amounts of dyes on TiO_2 for RD-I, RD-II, CA-I and CA-II, the short-circuit photocurrent (J_{sc}), open-circuit photovoltage (V_{oc}), fill factor (FF), and overall conversion efficiency (η) are shown in Table 1. The relatively high photovoltaic performances of RD-I and RD-II are attributed to both the red-shift of absorption band and enhancement of molar extinction coefficient owing to the introduction of the strong electron-withdrawing group of DCRD. Thus, dyes RD-I and RD-II can inject electrons efficiently from DCRD to the CB of the TiO_2 electrode through the strong coordinate bonding. Interestingly, the open circuit photo-voltage of CA-II is best among RD-I–II and CA-I-based solar cells. To understand this, electrochemical impedance spectroscopy (EIS) was employed to study the electron recombination in DSSCs based on these dyes under −0.70 V bias applied voltage in the dark. The Nyquist plot and Bode plot are shown in the Supporting Information, Figure S7.[18] From the EIS measurements, the radius of the larger semicircle decreases in the order CA-II > CA-I > RD-II > RD-I, indicating that the electron recombination resistance increases from RD-I, RD-II, and CA-I to CA-II and is reflected in the improvements of V_{oc}. This result is in agreement with the observed shift in the V_{oc} values shown in Table 1.

The stability of sensitizers is an especially critical factor for the practical application of DSSCs. The stability of the dyes adsorbed on nanocrystalline TiO_2 films was tested by irradiating the sample with simulated solar light without redox mediators (Supporting Information, Figure S8 and S9). The absorbance of RD-II and CA-II remained at 95 % and 92 % of the initial value, respectively, after 30 min visible-light illumination. The stability of RD-II is a little bit higher than CA-II, indicating that DCRD is a promising acceptor to enhance the stability of the organic sensitizers. To further prove the excellent stability of the sensitizer, RD-II was used for the ionic-liquid electrolyte DSSCs using 1-butyl-3-methyl imidazolium, 1-methyl-3-trimethylsilyl imidazolium, iodine, benzimidazole, and guanidine thiocyanate (BMII/MSII/I_2/BI/GNCS = 20:20:1.67:0.67:3.33) as redox electrolyte. Figure 2 shows the photovoltaic performance during a long-term accelerated aging of a RD-II-sensitized solar cell under AM 1.5 irradiation. As shown in Figure 2, the photovoltaic parameters of RD-II-based DSSCs with ionic-liquid electrolytes obtained performance of 5.15 %. The J_{sc}, V_{oc}, and FF barely change during the 1000 h irradiation, indicating that

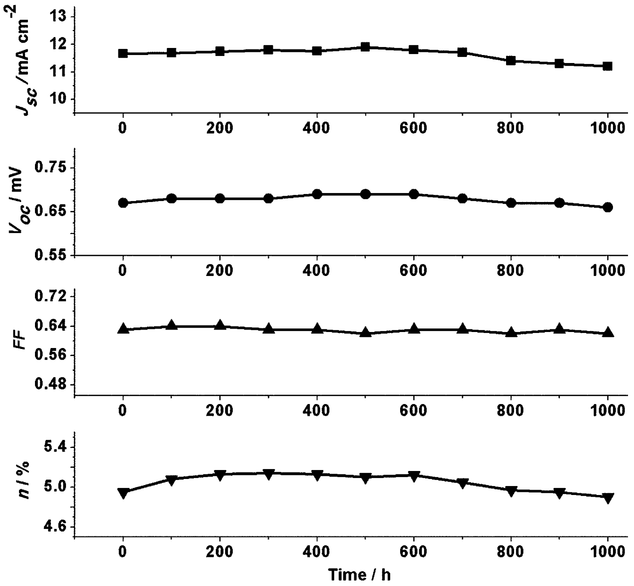


Figure 2. Variations of photovoltaic parameters (J_{sc}, V_{oc}, FF, and η) with aging time for the DSSCs device based on RD-II and ionic-liquid electrolyte under visible light soaking at 70 °C.

RD-II bond strongly to TiO_2, and it is substantially stable under working conditions.

In summary, we demonstrated for the first time that the electron acceptor 2-(1,1-dicyanomethylene) rhodanine is a promising alternative anchoring group to cyanoacrylic acid for sensitizing dyes. The double acceptor units bring a large bathochromic shift in absorption spectrum. The formation of coordinate bonds between the O and N in the middle acceptor rhodanine of RD-I and RD-II tautomers and the Lewis acid sites of the TiO_2 surface guarantee efficient electron injection from the dyes to TiO_2. RD-II-based DSSCs have obtained an overall conversion efficiency of 7.11 %, which is considerably higher than dyes with cyanoacrylic acid as electron acceptor. Furthermore, these dyes show remarkable stability under long-term irradiation. Thus, this finding may pave the way to develop novel high efficiency and stable metal-free organic sensitizers.

Received: June 25, 2012

Keywords: acceptors · anchoring groups · dye-sensitized solar cells · rhodanines

---

[1] a) B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737; b) K.-L. Wu, S.-T. Ho, C.-C. Chou, Y.-C. Chang, H.-A. Pan, Y. Chi, P.-T. Chou, *Angew. Chem. Int. Ed.* **2012**, *51*, 5642.

[2] a) N. Robertson, *Angew. Chem.* **2006**, *118*, 2398; *Angew. Chem. Int. Ed.* **2006**, *45*, 2338; b) N. Robertson, *Angew. Chem.* **2008**, *120*, 1028; *Angew. Chem. Int. Ed.* **2008**, *47*, 1012.

[3] a) Y. Ooyama, Y. Harima, *Eur. J. Org. Chem.* **2009**, 2903; b) A. Listorti, B. O'Regan, J. R. Durrant, *Chem. Mater.* **2011**, *23*, 3381.

[4] a) W. H. Zhu, Y. Z. Wu, S. T. Wang, W. Q. Li, X. Li, J. Chen, Z. S. Wang, H. Tian, *Adv. Funct. Mater.* **2011**, *21*, 756; b) J. X. He, F. L. Guo, X. Li, W. J. Wu, J. B. Yang, J. L. Hua, *Chem. Eur. J.* **2012**, *18*, 7903; c) S. Y. Qu, C. J. Qin, A. Islam, Y. Z. Wu, W. H. Zhu, J. L. Hua, H. Tian, L. Y. Han, *Chem. Commun.* **2012**, *48*, 6972.

[5] A. Mishra, M. K. R. Fischer, P. Bäuerle, *Angew. Chem.* **2009**, *121*, 2510; *Angew. Chem. Int. Ed.* **2009**, *48*, 2474.

[6] a) A. Hagfeldt, G. Boschloo, L. C. Sun, L. Kloo, H. Pettersson, *Chem. Rev.* **2010**, *110*, 6595; b) J. Y. Liu, J. Zhang, M. F. Xu, D. F. Zhou, X. Y. Jing, P. Wang, *Energy Environ. Sci.* **2011**, *4*, 3021; c) J. N. Clifford, E. Martínez-Ferrero, A. Viterisi, E. Palomares, *Chem. Soc. Rev.* **2011**, *40*, 1635; d) M. Planells, L. Pellejà, J. N. Clifford, M. Pastore, F. D. Angelis, N. López, S. R. Marder, E. Palomares, *Energy Environ. Sci.* **2011**, *4*, 1820.

[7] a) H. Choi, I. Raabe, D. Kim, F. Teocoli, C. Kim, K. Song, J.-H. Yum, J. Ko, M. K. Nazeeruddin, M. Grätzel, *Chem. Eur. J.* **2010**, *16*, 1193; b) A. Yella, H. W. Lee, H. N. Tsao, C. Y. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W. Diau, C. Yeh, S. M. Zakeeruddin, M. Grätzel, *Science* **2011**, *334*, 629.

[8] J. H. Yum, E. Baranoff, S. Wenger, M. K. Nazeeruddin, M. Grätzel, *Energy Environ. Sci.* **2011**, *4*, 842.

[9] a) Z. Ning, H. Tian, *Chem. Commun.* **2009**, 5483; b) Y. Liang, B. Peng, J. Chen, *J. Phys. Chem. C* **2010**, *114*, 10992.

[10] H. S. He, A. Gurung. L. P. Si, *Chem. Commun.* **2012**, *48*, 5910.

[11] a) X. M. Zhang, M. L. Tong, X. M. Chen, *Angew. Chem.* **2002**, *114*, 1071; *Angew. Chem. Int. Ed.* **2002**, *41*, 1029; b) Y.-L. Rao, S. Wang, *Inorg. Chem.* **2011**, *50*, 12263.

[12] Y. Ooyama, S. Inoue, T. Nagano, K. Kushimoto, J. Ohshita, I. Imae, K. Komaguchi, Y. Harima, *Angew. Chem.* **2011**, *123*, 7567; *Angew. Chem. Int. Ed.* **2011**, *50*, 7429.

[13] I. López-Duarte, M. Wang, R. Humphry-Baker, M. Ince, M. V. Martínez-Díaz, M. K. Nazeeruddin, T. Torres, M. Grätzel, *Angew. Chem.* **2012**, *124*, 1931; *Angew. Chem. Int. Ed.* **2012**, *51*, 1895.

[14] a) T. Horiuchi, H. Miura, K. Sumioka, S. Uchida, *J. Am. Chem. Soc.* **2004**, *126*, 12218; b) A. Insuasty, A. Ortiz, A. Tigreros, E. Solarte, B. Insuasty, N. Martín, *Dyes Pigm.* **2011**, *88*, 385.

[15] a) M. K. Nazeeruddin, R. Humphry-Baker, P. Liska, M. Grätzel, *J. Phys. Chem. B* **2003**, *107*, 8981; b) Z. S. Wang, K. Hara, Y. Danoh, C. Kasada, A. Shinpo, S. Suga, H. Arakawa, H. Sugihara, *J. Phys. Chem. B* **2005**, *109*, 3907.

[16] K. Vignesha, A. Suganthia, M. Rajarajanb, R. Sakthivadivel, *Appl. Surf. Sci.* **2012**, *258*, 4592.

[17] a) V. Enchev, I. Petkov, S. Chorbadjiev, *Struct. Chem.* **1994**, *5*, 225; b) D. Tahmassebi, *J. Mol. Struct.: THEOCHEM.* **2003**, *638*, 11; c) A. G. Al-Sehemi, T. M. El-Gogary, *J. Mol. Struct.: THEOCHEM.* **2009**, *907*, 66; d) G. V. Baryshnikov, B. F. Minaev, V. A. Minaeva, A. T. Podgornaya, *Chem. Heterocycl. Compd.* **2012**, *47*, 1268.

[18] a) F. S. Francisco, G. B. Germà, M. S. Iván, J. Bisquert, *Phys. Chem. Chem. Phys.* **2011**, *13*, 9083; b) J. Y. Mao, F. L. Guo, W. J. Ying, W. J. Wu, J. Li, J. L. Hua, *Chem. Asian J.* **2012**, *7*, 982.