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Cyclic Thiourea/Urea Functionalized Triphenylamine-Based Dyes for High-Performance Dye-Sensitized Solar Cells

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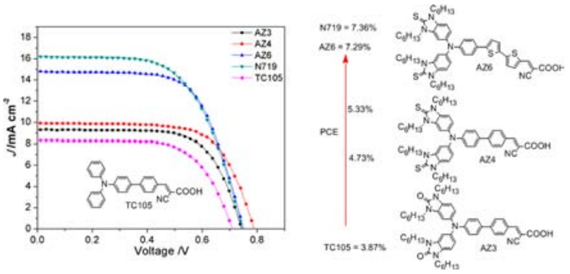
ABSTRACT



Six cyclic thiourea/urea functionalized triphenylamine-based dyes (AZ1–AZ6) containing 2-cyanoacrylic acid as an acceptor and various linkers (phenyl, biphenyl, and bithiophene) were synthesized. They exhibited high photovoltaic performance owing to an improved short-circuit photocurrent density (J_{sc}) and open-circuit voltage (V_{oc}). Among them, AZ6 bearing a cyclic thiourea group and bithiophene linker showed the highest power conversion efficiency (PCE) up to 7.29%, which was comparable to that of N719 (PCE = 7.36%).

Since the remarkable progress made by O′Regan and Grätzel in 1991, dye-sensitized solar cells (DSSCs) have aroused worldwide scientific research interest because of their easy fabrication process and low cost compared with traditional silicon-based solar cells.[1] As a key component of DSSCs, the sensitizer affects the power conversion efficiency (PCE) due to its critical function in light harvesting and electron injection. To date, several sensitizers have been developed including metal complex and organic compounds, where organic sensitizers exhibit a high PCE up to 10%,[2] which is comparable to that of metal complex sensitizers, such as a ruthenium-based complex (PCE of 11%)[3] or zinc porphyrin complex (PCE of 12%).[4] In addition, due to their inexpensive raw material and easy purification procedures, organic sensitizers have received increasing attention.[5]

Organic sensitizers are commonly composed of three units, namely the electron donor, π-conjugation linker, and electron acceptor. This structural character is favorable for optimizing DSSCs' performance by changing/modification of the different parts in the molecules.[6] Therefore, enormous efforts have been devoted toward the design and synthesis of the three units. So far, the electron acceptors have been dominated by 2-cyanoacrylic acid, but various linkers and donors have been exploited. For example, oligoene,[7] oligophenylene,[8] and oligothiophene[9] are widely used as linkers due to their prominent

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(1) (a) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737. (b) Grätzel, M. *Nature* **2001**, *414*, 338.

(2) Zeng, W. D.; Cao, Y. M.; Bai, Y.; Wang, Y. H.; Shi, Y. S.; Zhang, M.; Wang, F. F.; Pan, C. Y.; Wang, P. *Chem. Mater.* **2010**, *22*, 1915.

(3) Grätzel, M. *J. Photochem. Photobiol. A* **2004**, *164*, 3.

(4) Yella, A.; Lee, H.-W.; Tsao, H. N.; Yi, C.; Chandiran, A. K.; Nazeerudine, M. K.; Diau, E. W.-G.; Yeh, C.-Y.; Zakeeruddine, S. M.; Grätzel, M. *Science* **2011**, *334*, 629.

(5) (a) Mishra, A.; Fischer, M. K. R.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2009**, *48*, 2474. (b) Ooyama, Y.; Harima, Y. *Eur. J. Org. Chem.* **2009**, 2903.

(6) Hagfeldt, A.; Boschloo, G.; Sun, L. C.; Kloo, L.; Pettersson, H. *Chem. Rev.* **2010**, *110*, 6595.

(7) (a) Hara, K.; Kurashige, M.; Ito, S.; Shinpo, A.; Suga, S.; Sayama, K.; Arakawa, H. *Chem. Commun.* **2003**, 252. (b) Kitamura, T.; Ikeda, M.; Shigaki, K.; Inoue, T.; Anderson, N. A.; Ai, X.; Lian, T.; Yanagida, S. *Chem. Mater.* **2004**, *16*, 1806.

(8) Im, H.; Kim, S.; Park, C.; Jang, S.-H.; Kim, C.-J.; Kim, K.; Park, N.-G.; Kim, C. *Chem. Commun.* **2010**, *46*, 1335.

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electron-transport properties, while carbazole,[10] coumarin,[11] indoline,[12] tetrahydroquinoline,[13] and triphenylamine[2,14] are adopted as donors because of their good electron-donating ability as well as excellent stability.

Despite the significant progress was achieved by organic sensitizers, much work is still desired to further improve the photovoltaic performance, for example, by expanding absorption bands and inhibiting intermolecule aggregation.[15] Here, we try to introduce cyclic thiourea/urea groups into a triphenylamine electron donor unit based on the following considerations: (1) electron transfer from the donor to the acceptor could be facilitated because sulfur/oxygen and nitrogen heteroatoms in the cyclic thiourea/urea groups tend to increase the electron-donating ability; (2) the intermolecule aggregation and undesired charge recombination are expected to be suppressed due to the long alkyl chains attached at the N-atom sites of cyclic thiourea/urea groups;[10a] (3) cyclic thiourea/urea groups may effectively delocalize the positive charges of the oxidized dyes due to sulfur/oxygen and nitrogen heteroatoms with lone pair electrons.[16]

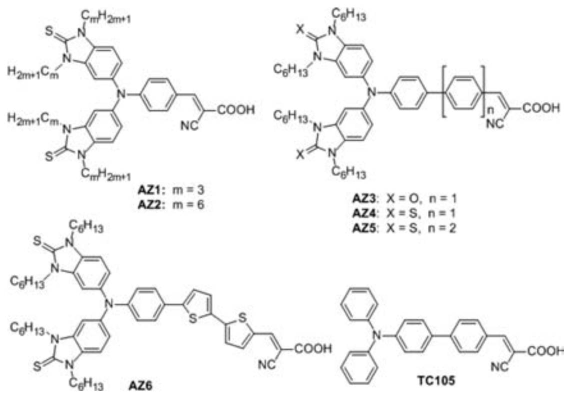

Figure 1. Structures of the cyclic thiourea/urea functionalized triphenylamine dyes **AZ1**−**AZ6** and **TC105**.

Based on aforementioned ideas, we synthesized six novel organic dyes with cyclic thiourea/urea functionalized triphenylamine as the electron donor and 2-cyanoacrylic acid as the acceptor. These donors and acceptor are directly connected (**AZ1** and **AZ2**) or bridged by oligophenylenes (**AZ3**, **AZ4**, and **AZ5**) or bithiophene (**AZ6**). Their structures are shown in Figure 1, and the synthetic protocols were described in detail in the Supporting Information. For comparison, **TC105** as a reference dye was synthesized according to the literature.[17]

The UV−vis absorption spectra of the dyes in CH_3CN solution (10^{-5} M) are illustrated in Figure 2. Their photophysical and electrochemical data are collected in Table 1. Normally, all of the dyes displayed two relatively broad absorption bands in the ranges from 290 to 400 nm and from 400 to 600 nm, respectively. The former absorption

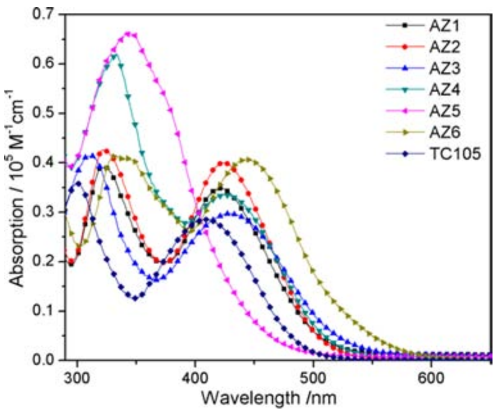

Figure 2. UV−vis absorption spectra of **AZ1**−**AZ6** and **TC105** in CH_3CN solution (10^{-5} M).

Table 1. Optical and Electrochemical Properties of the Dyes

dye	$\lambda_{max}{}^{a}$/ nm	ε/ M^{-1} cm^{-1}	$E_{ox}{}^{b,c}$/ V	$E_{0-0}{}^{d}$/ V	$E_{ox} - E_{0-0}{}^{c}$/ V
AZ1	423	34 830	0.91	2.18	−1.27
AZ2	423	39 950	0.93	2.14	−1.21
AZ3	428	29 680	0.73	2.03	−1.30
AZ4	426	33 530	0.80	2.07	−1.27
AZ5	347	66 000	0.84	2.25	−1.41
AZ6	443	40 690	0.79	1.98	−1.19
TC105	410	28 570	1.05	2.38	−1.33

[a] Measured in CH_3CN solution (10^{-5} M) at rt. [b] Measured in acetonitrile solution containing 0.1 M tetrabutylam monium hexafluorophosphate ($TBAPF_6$) as electrolyte (working electrode: glassy carbon; counter electrode: Pt (area: 0.023 cm^2); reference electrode: saturated calomel electrode (SCE)); calibrated with ferrocene/ferrocenium (Fc/Fc^+) as an external reference and converted to NHE by addition of 0.07 V.[18] [c] Values are reported versus NHE. [d] Estimated from onset wavelength in absorption spectra.

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(9) (a) Kim, S.; Lee, J. K.; Kang, S. O.; Ko, J.; Yum, J.-H.; Fantacci, S.; De Angelis, F.; Di Censo, D.; Nazeeruddin, M. K.; Grätzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 16701. (b) Liang, Y.; Peng, B.; Liang, J.; Tao, Z.; Chen, J. *Org. Lett.* **2010**, *12*, 1204. (c) Do, K.; Kim, D.; Cho, N.; Paek, S.; Song, K.; Ko, J. *Org. Lett.* **2012**, *14*, 222.

(10) (a) Koumura, N.; Wang, Z. S.; Mori, S.; Miyashita, M.; Suzuki, E.; Hara, K. *J. Am. Chem. Soc.* **2006**, *128*, 14256. (b) Lee, W.; Cho, N.; Kwon, J.; Ko, J.; Hong, J.-I. *Chem.—Asian J.* **2012**, *7*, 343.

(11) (a) Hara, K.; Sato, T.; Katoh, R.; Furube, A.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.; Sugihara, H.; Arakawa, H. *J. Phys. Chem. B* **2003**, *107*, 597. (b) Liu, B.; Wang, R.; Mi, W.; Li, X.; Yu, H. *J. Mater. Chem.* **2012**, *22*, 15379.

(12) (a) Horiuchi, T.; Miura, H.; Uchida, S. *Chem. Commun.* **2003**, 3036. (b) Wu, Y.; Zhang, X.; Li, W.; Wang, Z.-S.; Tian, H.; Zhu, W. *Adv. Energy Mater.* **2012**, *2*, 149.

(13) Hao, Y.; Yang, X.; Cong, J.; Hagfeldt, A.; Sun, L. *Tetrahedron* **2012**, *68*, 552.

(14) (a) Kitamura, T.; Ikeda, M.; Shigaki, K.; Inoue, T.; Anderson, N. A.; Ai, X.; Lian, T. Q.; Yanagida, S. *Chem. Mater.* **2004**, *16*, 1806. (b) Thomas, K. R. J.; Hsu, Y.; Lin, J. T.; Lee, K.; Ho, K.; Lai, C.; Cheng, Y.; Chou, P. *Chem. Mater.* **2008**, *20*, 1830. (c) Ning, Z. J.; Tian, H. *Chem. Commun.* **2009**, 5483.

(15) Qu, S.; Qin, C.; Islam, A.; Wu, Y.; Zhu, W.; Hua, J.; Tian, H.; Han, L. *Chem. Commun.* **2012**, *48*, 6972.

(16) Zhang, M.-D.; Pan, H.; Ju, X.-H.; Ji, Y.-J.; Qin, L.; Zheng, H.-G.; Zhou, X.-F. *Phys. Chem. Chem. Phys.* **2012**, *14*, 2809.

(17) Teng, C.; Yang, X. C.; Yang, C.; Tian, H. N.; Li, S. F.; Wang, X. N.; Hagfeldt, A.; Sun, L. C. *J. Phys. Chem. C* **2010**, *114*, 11305.

band was attributed to the localized $\pi-\pi^*$ transitions of the conjugated systems while the latter was assigned to the intramolecular charge transfer between donor and acceptor.[19] Generally, compared with **TC105** (410 nm, 28 570 M^{-1} cm^{-1}), the cyclic thiourea/urea functionalized dyes red-shifted from 10 to 40 nm with a higher molar extinction coefficient, even the dyes with a shorter bridge linker such as **AZ1** (423 nm, 34 830 M^{-1} cm^{-1}) and **AZ2** (423 nm, 39 950 M^{-1} cm^{-1}). It is worth pointing out that **AZ5** with biphenyl as the bridge linker did not show an absorption peak in the visible region while **AZ6** with bithiophene as the bridge linker red-shifted to 443 nm with a molar extinction coefficient up to 40 690 M^{-1} cm^{-1}. The main reason for this phenomenon may be the electrons of bithiophene are richer and allow better delocalization than biphenyl. The UV–vis absorption spectra demonstrated that the introduction of cyclic thiourea/urea functional groups not only broadens the absorption bands but also increases the molar extinction, which is desirable for a high-performance sensitizer with a higher short-circuit photocurrent density (J_{sc}) for DSSCs.

Cyclic voltammetry (CV) was performed in acetonitrile solutions to test first oxidation potentials (E_{ox}), corresponding to the HOMO levels of the dyes (Table 1, Figure S1). The LUMO levels of the dyes could be calculated from $E_{ox} - E_{0-0}$,[20] in which the E_{0-0} was estimated from the onset wavelength of the absorption spectra. As shown in Table 1, the HOMO levels of these dyes were more positive than the iodine/iodide redox potential value (0.4 V vs NHE), so the oxidized dye molecules could be regenerated effectively by the redox couple. The LUMO levels of these dyes were sufficiently more negative than the conduction band energy level of the TiO_2 electrode (−0.5 V vs NHE), which is energetically favorable for the electron injection from the excited dye into the conduction band of TiO_2.

The geometries of the dyes were optimized, and their frontier molecular orbitals were calculated by density functional theory (DFT) at the B3LYP/6-311G (d,p) level. Their electron distributions of the HOMO and LUMO are shown in Figure S2, and the energy levels are listed in Table S1. HOMOs were expanded from triphenylamine to the cyclic thiourea/urea functional groups, while LUMOs were mainly delocalized at the cyanoacrylic acid acceptor. This distribution of electrons will facilitate electron injection from the excited dye to the conduction band of TiO_2. The energy gaps ($\Delta E_{LUMO-HOMO}$) of **AZ3** (2.47 eV, Table S1) and **AZ4** (2.47 eV) were narrower than that of **TC105** (2.71 eV), which indicated that the introduction of thiourea/urea functional groups would facilitate the electron transfer from the donor to the acceptor. These are in line with UV–vis results.

The DSSC characteristics of dyes were evaluated under standard AM 1.5 G simulated sunlight irradiation.

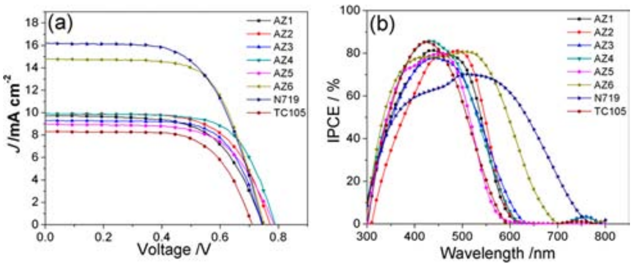

Figure 3. (a) $J-V$ curves for DSSCs based on the dyes under illumination of AM 1.5 G simulated sunlight (100 mW cm^{-2}). (b) IPCE spectra of the same DSSCs.

Table 2. Photovoltaic Performance Data of the Dyes[a]

dye	J_{SC}/ mA·cm^{-2}	V_{OC}/ mV	FF/ %	PCE/ %	IPCE/% (λ_{max} /nm)
AZ1	9.7	739	62.7	4.51	81 (440)
AZ2	9.9	770	65.0	4.94	81 (490)
AZ3	9.3	739	68.9	4.73	75 (450)
AZ4	9.9	780	69.0	5.33	86 (430)
AZ5	9.0	780	63.5	4.44	80 (450)
AZ6	14.8	749	65.9	7.29	81 (510)
N719	16.2	740	61.4	7.36	71 (510)
TC105	8.3	709	65.6	3.87	85 (420)

[a] Measured under AM 1.5G irradiation (100 mW cm^{-1}) with 0.25 cm^2 working area. The thickness of TiO_2 film was ~12 μm, and the electrolyte was 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 0.1 M LiI, 0.03 M I_2, 0.5 M 4-*tert*-butylpyridine, and 0.1 M guanidinium thiocyanate in acetonitrile.

The photocurrent–voltage ($J-V$) and incident photon to current efficiency (IPCE) curves are shown in Figure 3, and the corresponding photovoltaic data including J_{sc}, open-circuit voltage (V_{oc}), fill factor (FF), and PCE are listed in Table 2. Encouragingly, the cyclic thiourea/urea functionalized dyes exhibited distinctly improved PCEs (4.44–7.29%) due to the increased J_{sc} accompanied by the enhanced V_{oc} relative to **TC105** (J_{sc} = 8.3 mA cm^{-2}, V_{oc} = 709 mV, FF = 65.6%, and PCE = 3.87%). Specifically, the PCEs of **AZ1** (J_{sc} = 9.7 mA cm^{-2}, V_{oc} = 739 mV, and FF = 62.7%) and **AZ2** (J_{sc} = 9.9 mA cm^{-2}, V_{oc} = 770 mV, and FF = 65.0%) were 4.51% and 4.94%, respectively. It is worth noting that **AZ2** displayed a higher V_{oc} than **AZ1**, which may be ascribed to alkyl chains attached at thiourea groups possibly inhibiting intermolecular aggregation as well as suppressing back reactions between the injected electrons and the electrolyte.[10a] And the result seems to support that a more significant effect was obtained by the longer alkyl chains. Furthermore, the PCE of **AZ3** increased to 4.73% (J_{sc} = 9.3 mA cm^{-2}, V_{oc} = 739 mV, and FF = 68.9%), and that of **AZ4** increased to 5.33% (J_{sc} = 9.9 mA cm^{-2}, and FF = 69.0%) with a V_{oc} up to 780 mV, which increased beyond 70 mV compared with that of **TC105**. Although the V_{oc} reached 780 mV as well, a poor PCE

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(18) Yang, J.; Guo, F.; Hua, J.; Li, X.; Wu, W.; Qu, Y.; Tian, H. *J. Mater. Chem.* **2012**, *22*, 24356.

(19) Kim, S. H.; Kim, H. W.; Sakong, C.; Namgoong, J.; Park, S. W.; Ko, M. J.; Lee, C. H.; Lee, W. I.; Kim, J. P. *Org. Lett.* **2011**, *13*, 5784.

(20) Gao, P.; Tsao, H. N.; Grätzel, M.; Nazeeruddin, M. K. *Org. Lett.* **2012**, *14*, 4330.

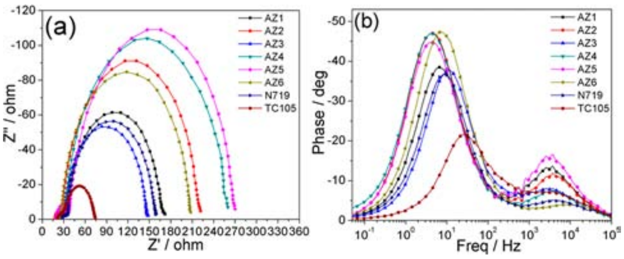

Figure 4. EIS spectra of DSSCs tested at −0.7 V forward bias in the dark: (a) Nyquist and (b) Bode phase plots.

(4.44%) was obtained by **AZ5** due to its relatively lower J_{sc} (9.0 mA cm^{-2}) and FF (63.5%). Thanks to the sharply increased J_{sc}, **AZ6** yielded an exciting PCE up to 7.29% (J_{sc} = 14.8 mA cm^{-2}, V_{oc} = 749 mV, and FF = 65.9%), which was comparable to **N719** (PCE = 7.36%, J_{sc} = 16.2 mA cm^{-2}, V_{oc} = 740 mV, and FF = 61.4%). The corresponding triphenylamine dye (coded as dye **4**[14b] or **1P-PSS**[21]) was reported by Chou and Chow independently and yielded PCEs of 6.15% and 6.17%, respectively. Compared with these results, the improved photovoltaic performance of **AZ6** may originate from the introduction of cyclic thiourea functional groups. To some extent, the integral of the IPCE spectra related to the values of J_{sc} of DSSCs. The IPCE curve (Figure 3b) of **AZ6** exhibited a significantly larger area than other organic dyes and resulted in the largest J_{sc}. The IPCE spectra of other dyes basically showed consistent J_{sc} as well as PCE values.

Electrochemical impedance spectroscopy (EIS)[22] was applied to investigate the interfacial charge transfer process in DSSCs. There were two semicircles in the Nyquist plots (Figure 4a), and the larger semicircle in the low-frequency region corresponded to charge-transfer resistance (R_{rec}) at the TiO_2/dye/electrolyte interface; e.g., a larger radius indicated a larger R_{rec} and slower electron recombination. All the cyclic thiourea/urea functionalized dyes **AZ1**−**AZ6** showed a larger R_{rec} than **TC105**. In addition, the electron lifetime could be calculated from the Bode phase plots (Figure 4b)[23] and the calculated results increased in the order **TC105** (6.2 ms) < **AZ3** (13.3 ms) < **N719** (19.7 ms) < **AZ1** (21.1 ms) < **AZ6** (24.0 ms) < **AZ2** (35.1 ms) < **AZ4** (41.7 ms) < **AZ5** (42.6 ms). Both the R_{rec} and electron lifetime coincided well with V_{oc}. The enlarged R_{rec} and lengthened electron lifetime further indicated that the electron recombination between the injected electrons and the electrolyte was decreased, resulting in an increased V_{oc}.[23] **AZ4** showed a slower electron recombination than **AZ3** and resulted in a larger V_{oc}; the mechanism is unclear and still under investigation. Compared with **AZ5**, **AZ6** displayed a faster electron recombination due to a better overlap between the HOMO and the conduction band of TiO_2 (Figure S2),[24] which resulted in a decreased V_{oc}.

In summary, six novel cyclic thiourea/urea functionalized triphenylamine-based dyes were synthesized and their DSSC performances were studied as well. Compared with **TC105**, the cyclic thiourea/urea functionalized dyes **AZ1**−**AZ6** exhibited a higher J_{sc} accompanied by a larger V_{oc}, therefore obtaining improved PCEs. The improved J_{sc} may be ascribed to the broadened absorption bands as the result of the introduction of cyclic thiourea/urea functional groups, while the enhanced V_{oc} may be attributed to the intermolecular π−π aggregation and charge recombination being suppressed by long alkyl chains attached at cyclic thiourea/urea functional groups. Cyclic thiourea functionalized dye **AZ6**, in which the bithiophene is the linker bridge, yielded a satisfying PCE up to 7.29% (J_{sc} = 14.8 mA cm^{-2}, V_{oc} = 749 mV, and FF = 65.9%). This result can be in competition with **N719** (PCE = 7.36%). Overall, this work has provided evidence that the cyclic thiourea/urea functionalization is a promising approach for the further development of highly efficient organic dyes.

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Supporting Information Available. Experimental details, DSSCs device fabrication, characterization details, and calculated molecular geometries. The material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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[21] Chang, Y. J.; Chow, T. J. *Tetrahedron* **2009**, *65*, 4726.

[22] (a) Fabregat-Santiago, F.; Bisquert, J.; Garcia-Belmonte, G.; Boschloo, G.; Hagfeldt, A. *Sol. Energy Mater. Sol. Cells* **2005**, *87*, 117. (b) Wang, Q.; Moser, J. E.; Grätzel, M. *J. Phys. Chem. B* **2005**, *109*, 14945.

[23] Wan, Z.; Jia, C.; Duan, Y.; Zhou, L.; Lin, Y.; Shi, Y. *J. Mater. Chem.* **2012**, *22*, 25140.

[24] Maggio, E.; Martsinovich, N.; Troisi, A. *Angew. Chem., Int. Ed.* **2013**, *52*, 973.