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Highly efficient organic dyes containing a benzopyran ring as a π–bridge for DSSCs†

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A series of novel organic dyes containing a benzopyran ring as a π–bridge have been designed and applied in dye-sensitized solar cells (DSSCs). This series of dyes show the excellent DSSCs' performance, due to their efficient light-to-photocurrent conversion in the region from 380 nm to 600 nm, with the highest IPCE values exceeding 90%. Through modification of the donor units, an efficiency as high as 7.5% has been achieved under standard light illumination (AM 1.5G, 100 mW cm^{-2}) by the dye **CC103**.

Introduction

Dye-sensitized solar cells (DSSCs) have attracted much attention from researchers due to their low cost, easy fabrication, and environmentally friendly nature since O'Regan and Grätzel reported them in 1991.[1] Photosensitizers play a crucial role for highly efficient DSSCs and have been extensively investigated. Many different kinds of photosensitizers including both metal complex sensitizers and metal-free organic dyes have been designed and applied in DSSCs and the highest conversion efficiency (η) value of 12.3% has been achieved in full sunlight with the co-sensitization of porphyrin dye **YD2-*o*-C8** and metal-free dye **Y123** by Grätzel *et al.*[2] However, the porphyrin dyes (such as **YD2-*o*-C8**) are difficult to synthesize and their yield is low. Compared to metal complexes, metal-free organic dyes are a good choice due to their easier synthesis, higher molar extinction coefficients and lower cost. In order to gain effective photoinduced intramolecular charge transfer characteristics, most of the efficient organic sensitizers are modelled on the donor–(π-spacer)–acceptor (D–π–A) system. For efficient solar energy conversion, it is ideal to use dyes that possess high molar extinction coefficients and broad absorption bands extending throughout the visible regions. Organic sensitizers with long π-conjugated spacers had been shown to augment the molar extinction coefficients as well as in realize panchromatic light-harvesting, giving moderate DSSC efficiency.[3–6] Typically electron-rich systems, such as thiophene derivatives,[7–18] furan,[19] selenophene,[20] and pyrrole[21] moieties and electron-withdrawing systems, such as quinoline,[22] isoxazole,[23] and thiazole[24] moieties have been adopted as π-conjugated spacers. Herein, we report a series of organic D–π–A dyes. Their structures are composed of different tetrahydroquinoline donors and cyanoacrylic acid acceptors, bridged by an electron-rich benzopyran ring. The detailed structure is shown in Fig. 1. To clarify the effects of the new π-bridge on the photophysics, electrochemical properties and performance of DSSCs, a dye **C1-1** reported by our group previously,[25] in which a thiophene ring is employed as the π-bridge, was chosen as a reference dye.

Experimental section

Measurement

^{1}H NMR spectra were taken with a Varian INOVA 400 MHz spectrometer (USA) with the chemical shifts against tetramethylsilane. Mass spectrometry (MS) data were obtained with GCT CA156 (UK), HP1100 LC/MSD (USA), and LC/MALDI TOF

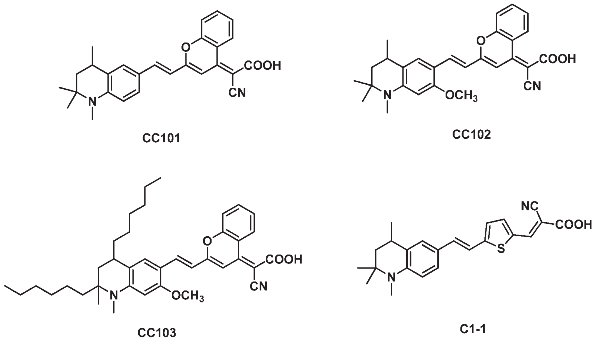

Fig. 1 Structure of sensitizers **CC101**, **CC102**, **CC103** and **C1-1**.

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† Electronic supplementary information (ESI) available: [details of synthesis of sensitizers **CC101–CC103**]. See DOI: 10.1039/c3ra41583j

MS (UK). The absorption spectra of the sensitizers in solution and adsorbed on the TiO_2 films were measured with HP8453 (USA). Electrochemical redox potentials were obtained by cyclic voltammetry (CV) on electrochemistry workstation (BAS100B, USA). The working electrode was a glass carbon disk electrode; the auxiliary electrode was a Pt wire; and Ag/Ag^+ was used as the reference electrode. $LiClO_4$ was used as supporting electrolyte in ethanol. The ferrocenium/ferrocene (Fc/Fc^+) redox couple was used as an internal potential reference. The irradiation source for the photocurrent density-voltage (J–V) measurement is an AM 1.5G solar simulator (16S-002, SolarLight Co. Ltd., USA). The incident light intensity was 100 mW cm^{-2} calibrated with a standard Si solar cell. The tested solar cells were masked to a working area of 0.159 cm^2. The J–V curves were obtained by linear sweep voltammetry (LSV) method using an electrochemical workstation (LK9805, Lanlike Co. Ltd., China). The measurement of the incident photon-to-current conversion efficiency (IPCE) was performed a Hypermono-light (SM–25, Jasco Co. Ltd., Japan). The J_{sc} was calibrated by integrating the IPCE value tuned light density of AM 1.5G against wavelength. Electrochemical impedance spectroscopy (EIS) was measured with an impedance/gain-phase analyzer (PARSTAT 2273, USA).

Fabrication of dye-sensitized solar cell

DSSCs with **CC101**, **CC102**, **CC103** and **C1-1** as sensitizers were fabricated following the literature.[26] A layer of 2 μm TiO_2 paste (TPP3, Heptachroma, China) was coated on the F-doped tin oxide conducting glass (TEC15, 15Ω/□, Pilkington, USA) by screen printing and then dried for 5 min at 125 °C. This procedure was repeated six times (12 μm) and coated by a layer of 4 μm titania paste (DHS–SLP1, Heptachroma, China) as scattering layer. The double-layer electrode (area: 6 × 6 mm) was sintered at 500 °C for 30 min in air. The sintered film was further treated with 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min, washed with water, then annealed at 500 °C for 30 min. After the film was cooled to room temperature, the film was immersed into a 2×10^{-4} M ethanol solution of dye and kept under dark conditions for 4 h. The film was then rinsed with ethanol and air dried. The hermetically sealed cells were fabricated by assembling the dye-loaded film (25 μm, Dupont). The electrolyte consisting of 0.6 M DMPII, 0.06 M LiI, 0.04 M I_2 and 0.4 M TBP in CH_3CN was introduced into the cell *via* vacuum backfilling by the hole in the back of the counter electrode. Finally, the holes were also sealed using Surlyn 1720 film.

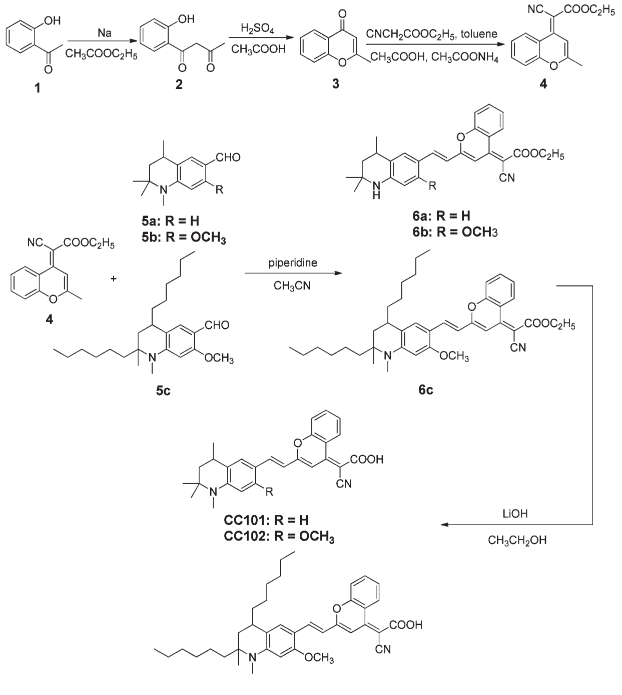
Synthesis

The synthetic route of sensitizers **CC101–CC103** is shown in Scheme 1. The specific synthesis of the compounds is described in the ESI.†

Results and discussion

Absorption properties

The absorption spectra of dyes **CC101**, **CC102** and **CC103** in ethanol solution and on TiO_2 film are shown in Fig. 2. The



Scheme 1 Synthesis of sensitizers **CC101–CC103**.

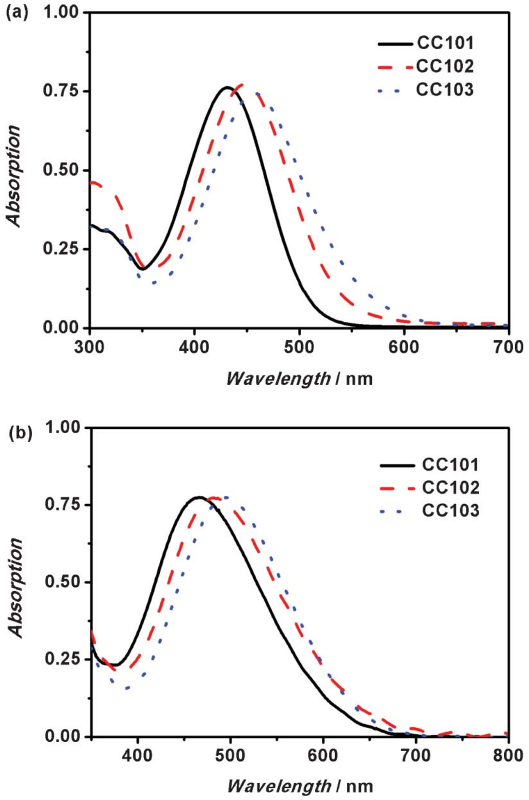


Fig. 2 Absorption spectra of **CC101–CC103** dyes in ethanol solution (a) and on TiO_2 films (b).

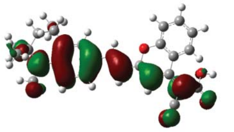
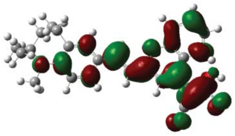
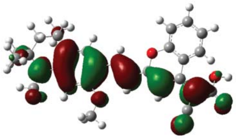
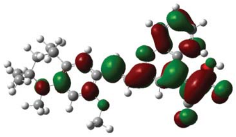
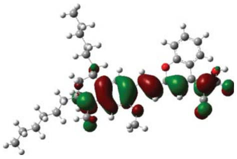
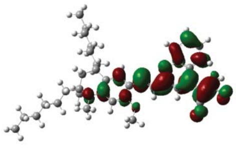
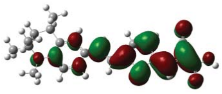
Table 1 Photophysical and electrochemical properties of **CC101**, **CC102**, **CC103** and **C1-1**

Dye	λ_{max}[a] in ethanol (nm)	ε at λ_{max} (M^{-1} cm^{-1})	λ_{max}[b] on TiO_2 (nm)	E_{0-0} (V)[c]	E_{HOMO} (V)[d] (*vs.* NHE)	E_{LUMO} (V)[e] (*vs.* NHE)
CC101	431	38 100	469	2.03	0.96	−1.07
CC102	448	38 600	486	1.91	0.87	−1.04
CC103	455	37 100	496	1.94	0.90	−1.04
C1-1	422	27 500	460	2.20	0.80	−1.40

[a] Absorption spectra were measured in CH_3CH_2OH solution (2×10^{-5} M). [b] Absorption spectra on TiO_2 film were measured with dye-loaded TiO_2 films immersed in CH_3CH_2OH solutions. [c] E_{0-0} was determined from the intersection of the tangent of absorption on TiO_2 film and the *X* axis by 1240/λ. [d] The oxidation potentials of the dyes were measured in CH_3CH_2OH solutions with $LiClO_4$ (0.1 M) as electrolyte, and ferrocene/ferrocenium (Fc/Fc^+) as an internal reference. [e] E_{LUMO} was calculated by $E_{HOMO} - E_{0-0}$.

corresponding spectroscopic parameters are summarized in Table 1. Dyes **CC101–CC103** have a strong absorption in visible region with the absorption maxima (λ_{max}) of 431 nm (38 100 M^{-1} cm^{-1}), 448 nm (38 600 M^{-1} cm^{-1}) and 455 nm (37 100 M^{-1} cm^{-1}), respectively. All of these dyes show obvious red-shifted absorption peaks (λ_{max}) and higher extinction coefficients compared with that of reference dye **C1-1** (422 nm, 27 500 M^{-1} cm^{-1}) due to the stronger π-conjugated system, which has been proved by DFT calculations (see Table 2). The absorption maxima (λ_{max}) of dyes **CC102** and **CC103** red-shift 17 nm and 25 nm compared with that of dye **CC101**, respectively. This can be mainly attributed to the much stronger donating ability of the donor part with the introduction of a methoxy group and long alkyl chains. When attached to TiO_2, the absorption spectra of **CC101**, **CC102** and **CC103** are broadened to 700 nm and obviously bathochromically shifted (about 38–41 nm) compared to those in ethanol solution. At the same time, much wider spectra are achieved for dyes **CC102** and **CC103** compared to **CC101**. Therefore, much better performance of DSSCs can be expected for the sensitizers **CC102** and **CC103**.

Table 2 Frontier molecular orbitals (HOMO and LUMO) of the dyes calculated with DFT on a B3LYP/6-31G(d) level

Dye	HOMO	LUMO
CC101		
CC102		
CC103		
C1-1		

Electrochemical properties

The highest occupied molecular orbital (HOMO) levels of these dyes are determined by cyclic voltammetry. The lowest unoccupied molecular orbital (LUMO) is calculated from $E_{HOMO} - E_{0-0}$. The corresponding data is collected in Table 1. The HOMO levels of dyes **CC101**, **CC102**, **CC103** and **C1-1** are 0.96 V, 0.87 V, 0.90 V and 0.80 V *vs.* NHE, respectively, which are much more positive than the redox potential of I^-/I_3^- (0.42 V *vs.* NHE),[27–29] indicating that the oxidized dyes can be regenerated by the redox couple I^-/I_3^- effectively. The HOMO levels of dyes **CC102** and **CC103** are 0.09 V and 0.06 V negative than that of dye **CC101**, respectively. This is mainly due to the introduction of the 7-methoxy and long alkyl chains in the molecules of **CC102** and **CC103**, which can increase the electron-donating ability for the donor part. The LUMO levels of these dyes are sufficiently more negative than the conduction band (CB) level of TiO_2, which implies that the electron injection from the excited dyes into the CB of TiO_2 is thermodynamically permitted. Moreover, considering the big energy gap between the LUMO levels of these dyes and CB level, TBP can be added in the electrolyte to upshift the conduction band edge for obtaining higher photovoltage. Compared with the reference dye **C1-1**, all of these dyes show a much narrower energy band gap and more positive HOMO and LUMO levels.

Theoretical calculation

To get a further insight into the molecular structures and electron distribution, density functional theory (DFT) calculations were performed at a B3LYP/6-31G(d) level for the geometry optimization. As shown in Table 2, for dyes **CC101–CC103**, the HOMOs are mainly distributed along the linear system from tetrahydroquinoline ring to benzopyran ring, and the LUMOs of the dyes are mainly concentrated on the acceptor group. Consequently, the HOMO–LUMO excitation can efficiently transfer the electron from the donor part to the acceptor part, giving fast electron injection from the LUMO to TiO_2. The absorption occurring below 400 nm is due to the

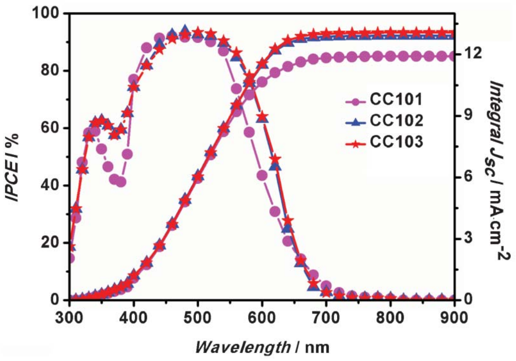


Fig. 3 IPCE spectra of the DSSCs based on **CC101**, **CC102** and **CC103**.

electronic excitation from the S_0 to S_2 state, which is insensitive to the cyanoacrylic acid units in the dye. Even with the presence of acid or base, the position of this peak is almost no change (see supporting information Fig. S1, ESI†).[30] The peak occurring above 400 nm was predicted for dyes **CC101**–**CC103** with appreciable oscillator strengths (see supporting information Fig. S2, ESI†). This originates due to the electronic excitation from the HOMO to the LUMO.

Photovoltaic performance of DSSCs

The incident photon-to-current efficiency (IPCE) spectra and the current- voltage curves of DSSCs based on the dyes **CC101**–**CC103** are shown in Fig. 3 and Fig. 4, respectively. Dyes **CC101**–**CC103** can efficiently convert light to photocurrent in the region from 380 nm to 600 nm, with the highest IPCE values of all these dyes exceeding 90%, indicating a promising DSSCs' performance. It is also shown that the IPCE spectra of these dyes are exactly in agreement with the absorption spectra of these dyes on TiO_2 (in Fig. 2). The IPCE values of dyes **CC102** and **CC103** is a little broader than that of dye **CC101**, due to the introduction of stronger electron donors of 7-methoxy unit and long alkyl chains.

Table 3 Photovoltaic performance of DSSCs based on the **CC101**, **CC102**, **CC103** and **C1-1** dyes

Dye	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF (%)	η (%)
CC101	702	12.72	74.1	6.6
CC102	700	13.29	74.8	7.0
CC103	746	13.45	75.2	7.5
C1-1	696	12.33	69.7	6.0

As the photovoltaic properties of DSSCs based on **CC101**–**CC103** are shown in Table 3 and Fig. 4. The device sensitized by **CC101** showed an efficiency of 6.6%, with a short-circuit photocurrent density (J_{sc}) of 12.72 mA cm^{-2}, an open-circuit photovoltage (V_{oc}) of 702 mV and a fill factor (FF) of 74.1%. When a 7-methoxy group was introduced to the construct **CC102**, the efficiency of the DSSCs was improved to 7.0% (V_{oc} = 700 mV, J_{sc} = 13.29 mA cm^{-2}, FF = 74.8%). It is clear that the J_{sc} value of **CC102** was higher than that of **CC101**, due to the better light harvesting in visible region resulted from the introduction of stronger electron donor. When both a 7-methoxy group and long alkyl chains were introduced into the **CC103** structure, an efficiency of 7.5% for the **CC103** based DSSCs was obtained (V_{oc} = 746 mV, J_{sc} = 13.45 mA cm^{-2}, FF = 75.2%). **CC103** not only showed a higher J_{sc} than **CC101**, but also much higher V_{oc} due to the decreased electron recombination. This is caused by the effective steric hindrance provided by the long alkyl chains. As a result, the higher J_{sc} and V_{oc} led to a higher efficiency for **CC103** based device compared to those based on **CC101** and **CC102**. By compar-

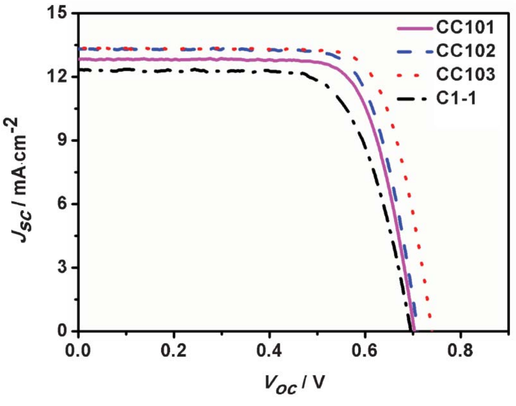


Fig. 4 *J*–*V* curves of the DSSCs based on **CC101**, **CC102**, **CC103** and **C1-1**.

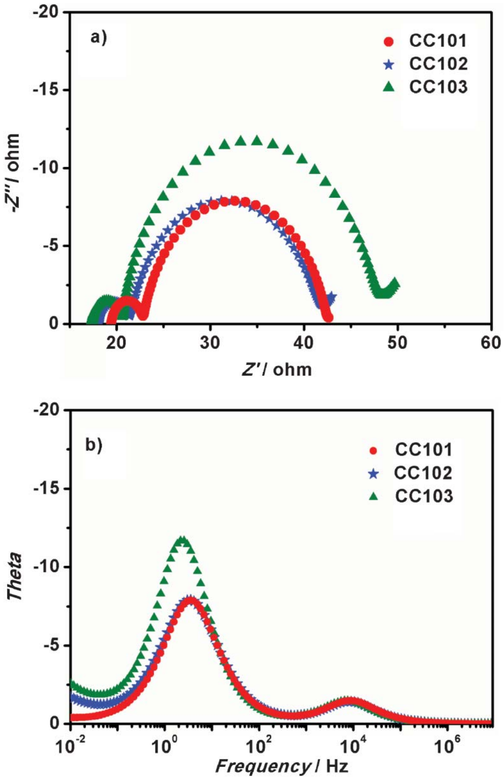


Fig. 5 The Nyquist (a) and Bode plots (b) of DSSCs based on **CC101**, **CC102** and **CC103**.

Table 4 Parameters obtained by fitting the EIS spectra to an electrochemical model

Dye	R_s (ohm)	R_{rec} (ohm)	R_{ce} (ohm)
CC101	19.4	21.8	3.39
CC102	18.1	20.1	3.25
CC103	17.3	27.8	3.24

ison, all of the **CC** series dyes showed higher efficiency in DSSC application than **C1-1** under the same experimental conditions.

Electrochemical impedance spectroscopy

To further study the interface charge transfer process of the DSSCs using the dyes **CC101–CC103**, the electrochemical impedance spectroscopy (EIS) was performed in the dark under −0.75 V bias applied voltage with a frequency range of 10^{-2} to 10^6 Hz, shown in Fig. 5 and Table 4. Some important parameters can be obtained by fitting the EIS spectra to an electrochemical model. R_S, R_{rec} and R_{CE} are corresponding to the series resistance, charge transfer resistance at the dye/TiO_2/electrolyte interface and counter electrode (CE), respectively. One can see that the R_{rec} of the device sensitized by dye **CC103** (R_{rec} = 27.8 Ω) is much bigger than that of the devices sensitized by **CC101** (R_{rec} = 21.8 Ω) and **CC102** (R_{rec} = 20.1 Ω), indicating an effective suppression of the electron recombination rate between the TiO_2 and the electrolyte due to the introduction of long alkyl chain. Therefore, a much higher V_{oc} was achieved by employing **CC103** as sensitizers.

Conclusion

In this study, a series of highly efficient organic dyes containing a benzopyran ring as a π–bridge were designed and developed for dye-sensitized solar cells (DSSCs) for the first time. When attached to TiO_2, the absorption spectra of the dyes **CC101–CC103** can extend to 700 nm. This series of dyes can efficiently convert light to photocurrent in the region of 380 nm–600 nm, with the highest IPCE values exceeding 90%. Through the modification of the donor units, an efficiency as high as 7.5% has been achieved under standard light illumination (AM 1.5G, 100 mW cm^{-2}), for **CC103** based DSSCs. Based on the detailed photoelectrochemical study, this series of organic dyes containing a benzopyran ring as a π–bridge will diversify dye structures with high efficiencies.

Acknowledgements

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References

1 B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737.
2 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.
3 W. Zeng, Y. Cao, Y. Bai, Y. Wang, Y. Shi, M. Zhang, F. Wang, C. Pan and P. Wang, *Chem. Mater.*, 2010, **22**, 1915.
4 G. Zhang, Y. Bai, R. Li, D. Shi, S. Wenger, S. M. Zakeeruddin, M. Grätzel and P. Wang, *Energy Environ. Sci.*, 2009, **2**, 92.
5 G. Zhang, H. Bala, Y. Cheng, D. Shi, X. Lv, Q. Yu and P. Wang, *Chem. Commun.*, 2009, 2198.
6 H. Choi, I. Raabe, D. Kim, F. Teocoli, C. Kim, K. Song, J. H. Yum, J. Ko, M. K. Nazeeruddin and M. Grätzel, *Chem.–Eur. J.*, 2010, **16**, 1193.
7 S. Kim, J. K. Lee, S. O. Kang, J. Ko, J.-H. Yum, S. Fantacci, F. De Angelis, D. Di Censo, M. K. Nazeeruddin and M. Grätzel, *J. Am. Chem. Soc.*, 2006, **128**, 16701.
8 H. Choi, C. Baik, S. O. Kang, J. Ko, M.-S. Kang, M. K. Nazeeruddin and M. Grätzel, *Angew. Chem., Int. Ed.*, 2008, **47**, 327.
9 N. Koumura, Z.-S. Wang, S. Mori, M. Miyashita, E. Suzuki and K. Hara, *J. Am. Chem. Soc.*, 2006, **128**, 14256.
10 Z.-S. Wang, N. Koumura, Y. Cui, M. Takahashi, H. Sekiguchi, A. Mori, T. Kubo, A. Furube and K. Hara, *Chem. Mater.*, 2008, **20**, 3993.
11 K. R. J. Thomas, Y.-C. Hsu, J. T. Lin, K.-M. Lee, K.-C. Ho, C.-H. Lai, Y.-M. Cheng and P.-T. Chou, *Chem. Mater.*, 2008, **20**, 1830.
12 J. H. Yum, D. P. Hagberg, S. J. Moon, K. M. Karlson, T. Marinado, L. Sun, A. Hagfeldt, M. K. Nazeeruddin and M. Grätzel, *Angew. Chem., Int. Ed.*, 2009, **48**, 1576.
13 H.-Y. Yang, Y.-S. Yen, Y.-C. Hsu, H.-H. Chou and J. T. Lin, *Org. Lett.*, 2010, **12**, 16.
14 Z.-S. Wang, N. Koumura, Y. Cui, M. Miyashita, S. Mori and K. Hara, *Chem. Mater.*, 2009, **21**, 2810.
15 M. Xu, R. Li, N. Pootrakulchote, D. Shi, J. Guo, Z. Yi, S. M. Zakeeruddin, M. Grätzel and P. Wang, *J. Phys. Chem. C*, 2008, **112**, 19770.
16 H. Qin, S. Wenger, M. Xu, F. Gao, X. Jing, P. Wang, S. M. Zakeeruddin and M. Grätzel, *J. Am. Chem.Soc.*, 2008, **130**, 9202.
17 W.-H. Liu, I.-C. Wu, C.-H. Lai, C.-H. Lai, P.-T. Chou, Y.-T. Li, C.-L. Chen, Y.-Y. Hsu and Y. Chi, *Chem. Commun.*, 2008, 5152.
18 Y. Liang, B. Peng, J. Liang, Z. Tao and J. Chen, *Org. Lett.*, 2010, **12**, 1204.
19 J. T. Lin, P.-C. Chen, Y.-S. Yen, Y.-C. Hsu, H.-H. Chou and P. M.-C. Yeh, *Org. Lett.*, 2009, **11**, 97.
20 R. Li, X. Lv, D. Shi, D. Zhou, Y. Cheng, G. Zhang and P. Wang, *J. Phys. Chem. C*, 2009, **113**, 7469.
21 Y.-S. Yen, Y.-C. Hsu, J. T. Lin, C.-W. Chang, C.-P. Hsu and D.-J. Yin, *J. Phys. Chem. C*, 2008, **112**, 12557.
22 H. Choi, H. Choi, S. Paek, K. Song, M.-S. Kang and J. Ko, *Bull. Korean Chem. Soc.*, 2010, **31**, 125.

23 Y.-T. Li, C.-L. Chen, Y.-Y. Hsu, H.-C. Hsu, Y. Chi, B.-S. Chen, W.-H. Liu, C.-H. Lai, T.-Y. Lin and P.-T. Chou, *Tetrahedron*, 2010, **66**, 4223.

24 C.-H. Chen, Y.-C. Hsu, H.-H. Chou, K. R. J. Thomas, J. T. Lin and C.-P. Hsu, *Chem.–Eur. J.*, 2010, **16**, 3184.

25 R. Chen, X. Yang, H. Tian, X. Wang, A. Hagfeldt and L. Sun, *Chem. Mater.*, 2007, **19**, 4007.

26 M. Cheng, X. Yang, J. Li, C. Chen, J. Zhao, Y. Wang and L. Sun, *Chem.–Eur. J.*, 2012, **18**, 16196.

27 C. Qin, A. Islam and L. Han, *J. Mater. Chem.*, 2012, **22**, 19236.

28 Y. Cui, Y. Wu, X. Lu, X. Zhang, G. Zhou, F. B. Miapeh, W. Zhu and Z. Wang, *Chem. Mater.*, 2011, **23**, 4394.

29 K. Pei, Y. Wu, W. Wu, Q. Zhang, B. Chen, H. Tian and W. Zhu, *Chem.–Eur. J.*, 2012, **18**, 8190.

30 G. D. Sharma, J. A. Mikroyannidis, M. S. Roy, K. R. J. Thomas, R. J. Ball and R. Kurchania, *RSC Adv.*, 2012, **2**, 11457.