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Solar cells based on doubly concerted companion dyes with the efficiencies modulated by inserting an ethynyl group at different positions☆

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ABSTRACT

To develop efficient sensitizers for dye-sensitized solar cells (DSSCs), we recently reported doubly concerted companion (DCC) dye **XW83** with a wrapped porphyrin sub-dye unit linked to an organic sub-dye unit through a flexible chain, which exhibits panchromatic absorption and excellent anti-aggregation ability. To further improve the absorption, we herein report **XW87** and **XW88** by inserting an ethynyl group into the organic sub-dye unit of **XW83** near the donor and acceptor, respectively. For the corresponding organic dyes **Z3** and **Z4**, the introduced ethynyl group improves their absorption, but induces aggravated charge recombination, leading to lowered power conversion efficiencies (PCEs). Similar to the organic dyes, the introduced ethynyl group improves the absorption of DCC dyes **XW87** and **XW88** as well. In addition, the ethynyl group near the acceptor of the organic sub-dye unit can be well protected by the long wrapping chains from the porphyrin unit. As a result, **XW88** affords the highest J_{SC} (21.84 mA/cm^2), V_{OC} (782 mV) and PCE (12.2%) among the DCC dyes. These results provide an effective method for developing efficient DSSC dyes by inserting an ethynyl group at a suitable position of a DCC dye.

Because of the energy crisis induced by the rapid consumption of energy sources, it has been developed as an important research topic to employ efficient photovoltaic devices for converting solar energy into electricity. Among various photovoltaic techniques [1–3], dye-sensitized solar cells (DSSCs) are relatively low-cost, colorful and environmentally friendly, and thus they have attracted considerable attention [4–6]. As one of the key components of DSSCs, dyes are used to harvest sunlight and generate excited electrons. In the past three decades, ruthenium dyes [7–9], metal-free organic dyes [10–12] and zinc porphyrin dyes [13–16] have been designed for fabricating efficient DSSCs. Among them, porphyrin dyes are promising due to their facile structural modification and excellent light-harvesting capability, showing an intense Soret band and moderate Q bands in the visible region with molar absorption coefficients higher than those of ruthenium dyes and metal-free organic dyes. Thus, many efficient porphyrin dyes have been reported [17–20]. However, porphyrin dyes exhibit weak absorption in the green light region between the Soret band and Q bands, which limits the further enhancement of the photovoltaic behavior. To address this problem, the employment of cosensitizers with absorption spectra complementary to those of the porphyrin dyes has achieved panchromatic absorption and improved efficiencies [21–23]. However, the fabrication of cosensitized devices is rather complicated and time-consuming, which requires the optimization of various dye adsorption procedures like cocktail and sequential ones as well as the dye concentrations and adsorption time to control the amounts and distribution of more than one dye on the TiO_2 film [24,25].

To address these problems, we have designed a novel class of “concerted companion” (CC) dyes by covalently linking a porphyrin sub-dye unit with an organic sub-dye unit through long flexible chains [26–28]. The CC dyes possess panchromatic absorption, affording higher efficiencies than those obtained by the corresponding cosensitization systems. For CC dyes like **XW61** which contains a doubly strapped porphyrin dye unit (Fig. 1a), the straps can suppress the aggregation of the porphyrin unit without protecting the organic sub-dye unit from aggregation. As a result, **XW61** affords a moderate V_{OC} of 763 mV and a PCE of 11.7% [28]. In order to further enhance the anti-aggregation ability of CC dyes, we have designed a class of doubly concerted companion (DCC) dyes, with the porphyrin macrocycle wrapped with four long alkoxy chains at the *ortho*-positions of the *meso*-phenyl groups [29]. For DCC dye **XW83**

☆ This paper is dedicated to the memory of Prof. Jiang Wei.

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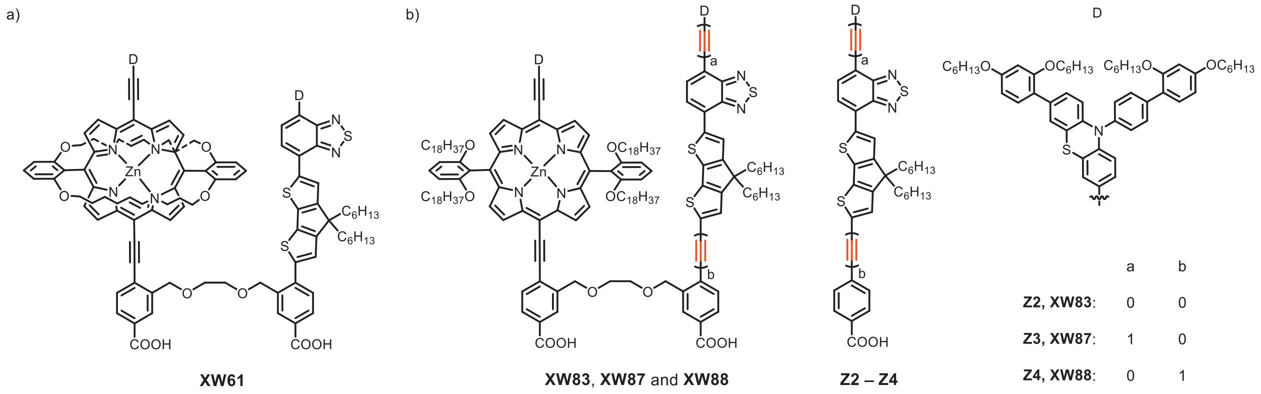
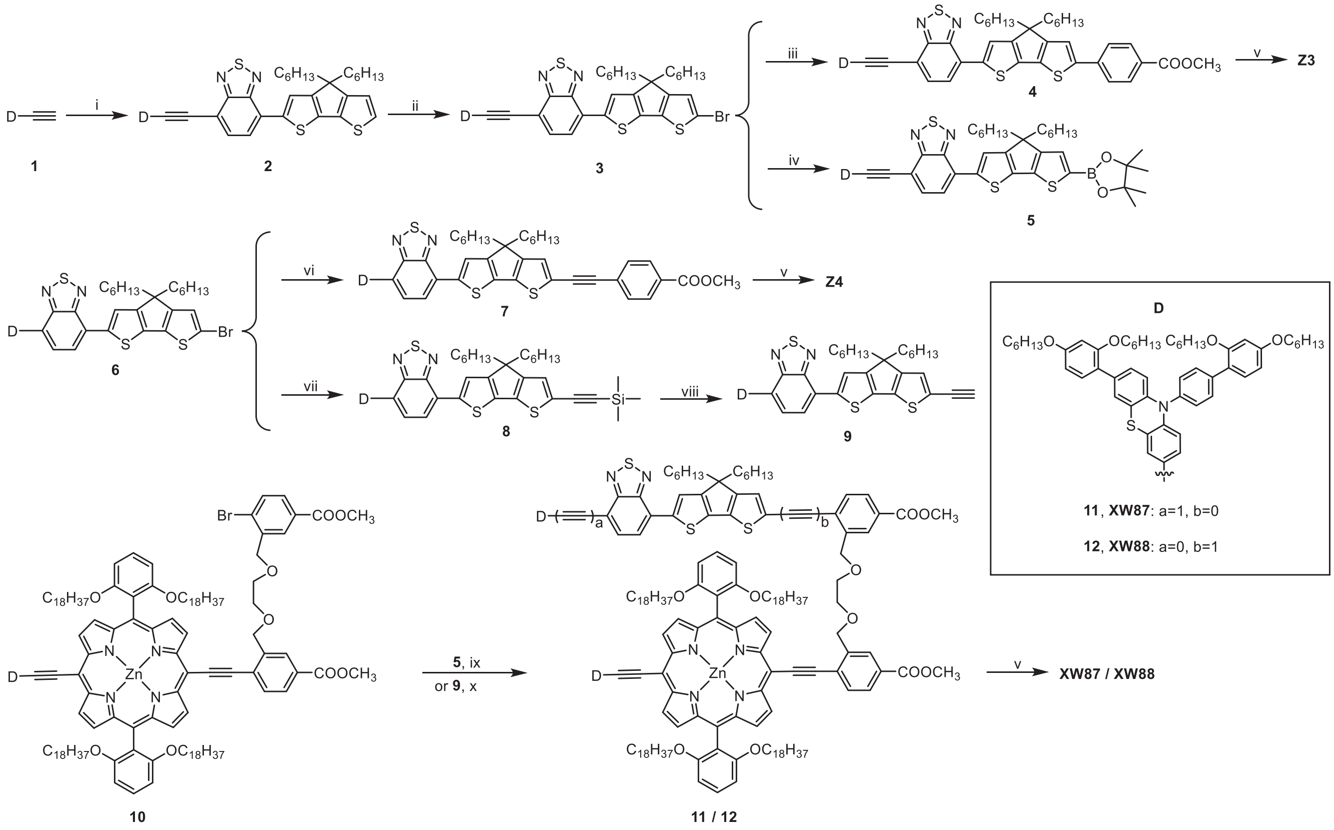


Fig. 1. Molecular structures of dyes (a) **XW61** [28], (b) **Z2** [28], **Z3**, **Z4**, **XW83** [29], **XW87** and **XW88**.

(Fig. 1b), the long wrapping chains can suppress the aggregation of both the porphyrin unit and the organic unit. With enhanced anti-aggregation and anti-charge-recombination ability, **XW83** afforded improved V_{OC} and PCE. However, the light-harvesting ability of **XW83** within 500–600 nm still needs to be further improved. Thus, we herein report DCC dyes **XW87** and **XW88** synthesized by inserting an extra ethynyl group into the organic dye unit of **XW83** near the donor and acceptor, respectively. For comparison, the corresponding organic dyes **Z3** and **Z4** have been synthesized as well (Fig. 1b). As a result, **Z3** and **Z4** exhibit PCEs lower than that of **Z2** because of the aggravated charge recombination induced by the less compact packing resulting from the extended conjugation frameworks, as evidenced by the lowered charge recombination resistance (R_{rec}). Similarly, **XW87** affords a lower efficiency (11.5%) than that of **XW83** (11.7%). In contrast, **XW88** exhibits a higher PCE (12.2%) than that of **XW83** as the consequence of enhanced J_{SC} (21.84 mA/cm^2) and V_{OC} (782 mV). These results imply that the long wrapping chains from the porphyrin unit can protect the ethynyl group near the acceptor of the organic dye unit (**XW88**) better than that near the donor (**XW87**), which is consistent with the larger R_{rec} value observed for **XW88** and more compact packing for the optimized structure of **XW88** adsorbed on TiO_2 film, compared with **XW87**. These results indicate that the position of the ethynyl group in the organic dye unit is vital for developing efficient DCC dyes.

The synthetic routes for the dyes are summarized in Scheme 1. Dye precursors **4**, **7**, **11** and **12** were obtained *via* Suzuki or Sonogashira coupling reactions, and subsequent hydrolysis of the ester



Scheme 1. Syntheses of the dyes. (i) 4-Bromo-7-(4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*']dithien-2-yl)-2,1,3-benzothiadiazole, $Pd_2(dba)_3$, $AsPh_3$, $^tBu_3P{\cdot}HBF_4$, THF, Et_3N. (ii) NBS, THF. (iii) 4-Methoxycarbonylphenylboronic, $Pd_2(dba)_3$, Sphos, K_3PO_4, toluene. (iv) Bis(pinacolato)diboron, $Pd(PPh_3)_2Cl_2$, KOAc, 1,4-dioxane. (v) $LiOH{\cdot}H_2O$, THF, H_2O. (vi) Methyl 4-ethynylbenzoate, $Pd_2(dba)_3$, $AsPh_3$, $^tBu_3P{\cdot}HBF_4$, THF, Et_3N. (vii) Trimethylsilylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, THF, Et_3N. (viii) TBAF, THF. (ix) $Pd_2(dba)_3$, Sphos, K_3PO_4, toluene. (x) $Pd_2(dba)_3$, $AsPh_3$, $^tBu_3P{\cdot}HBF_4$, THF, Et_3N.

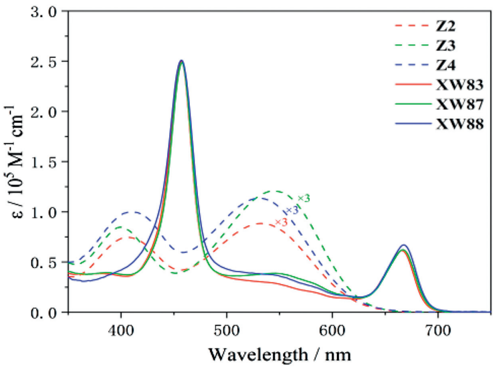


Fig. 2. Absorption spectra of dyes **Z2** [28], **Z3**, **Z4**, **XW83** [29], **XW87** and **XW88** in THF.

group under alkaline conditions afforded the target sensitizers. All the synthesized compounds have been characterized by NMR, FT-IR and mass spectra (Supporting information).

The UV–vis absorption spectra of the dyes in THF are shown in Fig. 2, with the corresponding data listed in Table S1 (Supporting information). Compared with **Z2**, the introduction of the ethynyl group enhances the absorption of **Z3** and **Z4** at around 550 nm, leading to better absorption complementarity with the porphyrin dye unit. As a result, **XW87** and **XW88** exhibit enhanced absorption within 500–600 nm relative to that of **XW83**. Upon adsorption onto the TiO_2 films, the absorption spectra of all the dyes are broadened (Fig. S2 in Supporting information), which will be favorable for sunlight-harvesting [30].

To assess the driving forces for electron injection and dye regeneration, the energy levels of the dyes were evaluated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements (Table S3, Figs. S5 and S6 in Supporting information). Thus, the highest occupied molecular orbital (HOMO) levels of **Z3**, **Z4**, **XW87** and **XW88** were assessed to be 0.84, 0.80, 0.84 and 0.81 V, respectively, *versus* the normal hydrogen electrode (NHE), which are considerably more positive than that of the I^-/I_3^- redox potential (~0.4 V *vs.* NHE), providing sufficient driving forces for dye regeneration. On the other hand, the lowest unoccupied molecular orbital (LUMO) levels range from -1.27 V to -1.01 V, obviously more negative than the conduction band of TiO_2 (-0.5 V *vs.* NHE), ensuring effective electron injection into TiO_2 from the excited dyes [31,32].

The photovoltaic performance of the dyes was investigated under simulated solar light (AM 1.5G, 100 mW/cm^2) using the I^-/I_3^- redox couple as the electrolyte. Figs. 3a and b show the photocurrent density–voltage (J–V) curves and the incident photon-to-current conversion efficiency (IPCE) spectra of the DSSCs, respectively, and corresponding photovoltaic parameters are given in Table 1.

Table 1
Photovoltaic parameters of the DSSCs based on the organic and DCC dyes under simulated AM 1.5G sunlight illumination.

Dye	V_{OC} (mV)	J_{SC} (mA/cm^2)	Fill factor (%)	PCE (%)
Z2[a]	738 ± 3	18.92 ± 0.31	69.56 ± 1.07	9.7 ± 0.2
Z3	724 ± 5	17.66 ± 0.44	70.28 ± 1.33	9.0 ± 0.1
Z4	730 ± 3	18.17 ± 0.16	70.24 ± 0.95	9.3 ± 0.2
XW83[a]	772 ± 2	21.29 ± 0.21	71.19 ± 0.85	11.7 ± 0.2
XW87	767 ± 2	21.06 ± 0.09	71.15 ± 0.45	11.5 ± 0.1
XW88	782 ± 4	21.84 ± 0.27	71.18 ± 0.27	12.2 ± 0.1

[a] The data were measured in this work. The PCEs are lower than those of reported [28,29].

Compared with the efficiency of 9.7% obtained for **Z2** [28], the conjugation-extended dyes **Z3** and **Z4** exhibit lower photovoltaic performance despite their stronger light-harvesting capability, which may be ascribed to the aggravated charge recombination as a consequence of the less compact packing of the dyes on the TiO_2 film after the conjugation extension by introducing the ethynyl unit (*vide infra*). Due to the complementary absorption between **Z3**–**Z4** and the porphyrin dye unit, the resulting DCC dyes exhibit IPCE plateaus higher than 80% in the range of 450–700 nm. As a result, **XW87** affords J_{SC}, V_{OC} and PCE of 21.06 mA/cm^2, 767 mV and 11.5%, respectively, lower than those obtained for the reference dye **XW83**. By contrast, **XW88** gives J_{SC}, V_{OC} and PCE of 21.84 mA/cm^2, 782 mV and 12.2% respectively, higher than those obtained for **XW83** and **XW87**. These observations indicate that the unfavorable charge recombination issue owing to the introduced ethynyl group observed for **Z3**, **Z4** and **XW87** may be considerably suppressed in **XW88**, implying that the long chains from the porphyrin sub-dye unit could protect the acceptor part of the organic sub-dye unit better than the donor part, and this concerted companion protection effect is absent in **Z3** and **Z4**. To testify this hypothesis, theoretical calculations have been carried out for the DCC dyes adsorbed on TiO_2 [33]. As a result, the long chains from the porphyrin unit indeed extend to the ethynyl group near the acceptor of the organic sub-dye unit and wrap it (**XW88**). Whereas, such a protecting effect is negligible for the ethynyl group near the donor part (**XW87**), which exhibits obvious non-filled free space around the ethynyl moiety (Fig. S4 in Supporting information). Thus, the enhanced light-harvesting ability contributed by the organic sub-dye unit and the largest dye loading amount (Table S4 in Supporting information) enable **XW88** to afford the highest IPCE plateau within 450–700 nm and the highest J_{SC} among the DCC dyes. Meanwhile, the unfavorable charge recombination problem induced by the conjugation-extended organic sub-dye unit is suppressed by the concerted companion protection effect of the long chains, which also contributes to enhancing the V_{OC}, IPCE and J_{SC}. As a result, **XW88** affords the best photovoltaic performance among all the DCC dyes.

To better understand the photovoltaic behavior of the DSSCs, electrochemical impedance spectroscopy (ESI) measurements were

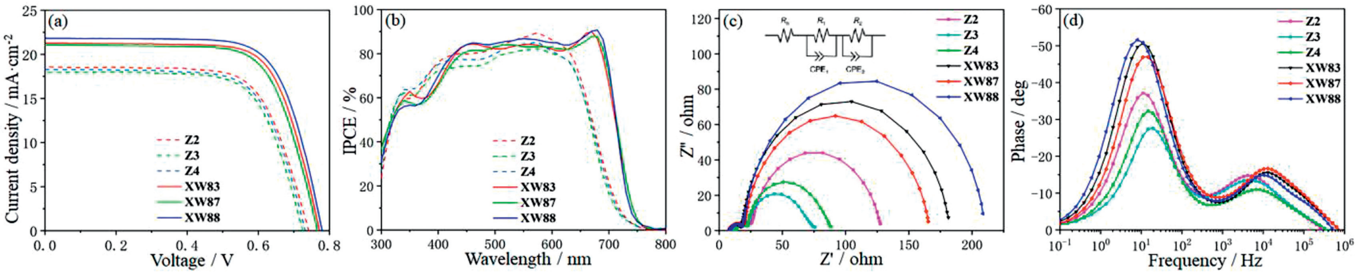


Fig. 3. (a) J–V curves, (b) IPCE spectra, (c) complex-plane plots and (d) Bode phase plots of the DSSCs based on the investigated dyes.

carried out in the dark. For a certain electrolyte, V_{OC} is determined by the Fermi level of TiO_2 semiconductor ($E_{F,n}$), which is associated with the conduction band (E_{CB}) position and the electron density in the semiconductor, which can be reflected by the chemical capacitance (C_μ) and charge recombination resistance (R_{rec}), respectively [34–36]. The similar C_μ values obtained for the DSSCs (Table S6 in Supporting information) reveal that the small difference in E_{CB} has negligible influence on V_{OC}. Therefore, the difference in V_{OC} may be mainly related to the different R_{rec} values. Figs. 3c and d show the complex-plane plots and Bode phase plots based on a forward bias of -0.75 V. In the complex-plane plots, the small and large semicircles represent the charge transport resistance (R_{tr}) at the counter electrode/electrolyte interface and the R_{rec}, respectively. The R_{tr} values of the DSSCs are similar because of the same counter electrode and electrolyte employed (Table S6 in Supporting information). In contrast, the R_{rec} values differ considerably in the increasing order of **Z3** (50.1 Ω cm^2) < **Z4** (64.1 Ω cm^2) < **Z2** (101.4 Ω cm^2) < **XW87** (145.9 Ω cm^2) < **XW83** (163.0 Ω cm^2) < **XW88** (191.5 Ω cm^2), corresponding to the trend of increasing V_{OC}. These results are indicative of the aggravated charge recombination of **Z3** and **Z4** associated with the less compact dye packing on the TiO_2 film resulting from the extended conjugation frameworks. With respect to the organic dyes, all DCC dyes exhibit larger R_{rec} values, consistent with their higher V_{OC} values. Notably, the R_{rec} of **XW88** is much larger than that of **XW87**, indicating that the concerted companion protection effect from the long chains of the porphyrin unit is more pronounced for the acceptor part of the organic dye unit, compared with that of the donor part. This inference is consistent with the theoretical calculations (*vide supra*).

In addition to high efficiencies, stability is essential for practical application of DSSCs. Thus, we measured the adsorption stability and photostability of the DSSCs (Fig. S8 in Supporting information) [37,38]. It was found that **Z3** and **Z4** are almost quantitatively desorbed within 10 min under alkaline conditions. In contrast, more than 60% of **XW87** and **XW88** remain adsorbed after 120 min of treatment under the same conditions, indicative of stronger adsorption of the DCC dyes due to the presence of two anchoring groups. After the DSSCs were irradiated under sunlight continuously for 500 h, the PCEs of **XW87** and **XW88** remained *ca.* 91% of the initial values, higher than those of *ca.* 85% observed for **Z3** and **Z4**, revealing excellent photostability of the DCC dyes.

In summary, with the purpose to improve the light-harvesting ability, an ethynyl group has been introduced into the donor and acceptor parts of organic dye **Z2** to afford **Z3** and **Z4**, respectively. On this basis, DCC dyes **XW87** and **XW88** have been synthesized by covalently linking a porphyrin dye unit with **Z3** and **Z4**, respectively. As expected, the introduction of the ethynyl group improves the light-harvesting ability of the dyes. However, **Z3** and **Z4** afford lower photovoltaic performance than **Z2** due to their aggravated charge recombination (low R_{rec} value) resulting from the extended conjugation frameworks. For the DCC dyes, the ethynyl group near the acceptor of the organic dye unit can be wrapped better than that near the donor through the concerted companion protection by the long chains from the porphyrin unit. As a result, **XW87** exhibits decreased V_{OC}, J_{SC} and PCE, compared with those of **XW83**. In contrast, **XW88** achieves the highest PCE of 12.2% among these dyes owing to the best concerted companion protection effect and the largest dye loading amount. These results indicate that introduction of an ethynyl group in the organic dye unit at a suitable position is an effective approach for developing efficient DCC dyes with excellent absorption and concerted companion anti-charge recombination effect.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2023.109093.

References

[1] X. Yang, J. Han, W. Ruan, et al., Chin. Chem. Lett. 33 (2022) 1425–1429.
[2] S.H. Kim, J.Y. Jung, R.B. Wehrspohn, et al., ACS Appl. Energy Mater. 3 (2020) 3180–3185.
[3] Y. Chang, J. Li, Y. Chang, et al., Chin. Chem. Lett. 32 (2021) 2904–2908.
[4] B. O'Regan, M. Grätzel, Nature 353 (1991) 737–740.
[5] S. Chen, H. Jia, M. Zheng, et al., Phys. Chem. Chem. Phys. 18 (2016) 29555–29560.
[6] P. Gao, H.N. Tsao, J. Teuscher, et al., Chin. Chem. Lett. 29 (2018) 289–292.
[7] A.R. Andersen, J. Halme, T. Lund, et al., J. Phys. Chem. C 115 (2011) 15598–15606.
[8] S.H. Yang, K.L. Wu, Y. Chi, et al., Angew. Chem. Int. Ed. 50 (2011) 8270–8274.
[9] Z. She, Y. Cheng, L. Zhang, et al., ACS Appl. Mater. Interfaces 7 (2015) 27831–27837.
[10] Y. Wu, X. Li, Chin. Chem. Lett. 27 (2016) 927–932.
[11] H.H. Gao, X. Qian, W.Y. Chang, et al., J. Power Sources 307 (2016) 866–874.
[12] T. Hua, K. Zhang, Z.S. Huang, et al., J. Mater. Chem. C 7 (2019) 10379–10388.
[13] T. Higashino, K. Kawamoto, K. Sugiura, et al., ACS Appl. Mater. Interfaces 8 (2016) 15379–15390.
[14] Y. Kurumisawa, T. Higashino, S. Nimura, et al., J. Am. Chem. Soc. 141 (2019) 9910–9919.
[15] C.C. Chen, J.S. Chen, V.S. Nguyen, et al., Angew. Chem. Int. Ed. 60 (2021) 4886–4893.
[16] S. Li, Y. Zhang, S. Mei, et al., ACS Appl. Energy Mater. 4 (2021) 9267–9275.
[17] S. Mathew, A. Yella, P. Gao, et al., Nat. Chem. 6 (2014) 242–247.
[18] J. Luo, M. Xu, R. Li, et al., J. Am. Chem. Soc. 136 (2014) 265–272.
[19] J.M. Ji, S.H. Kim, H. Zhou, et al., ACS Appl. Mater. Interfaces 11 (2019) 24067–24077.
[20] C.L. Wang, M.C. Tsai, K.H. Jian, et al., ACS Appl. Mater. Interfaces 13 (2021) 7152–7160.
[21] C.M. Lan, H.P. Wu, T.Y. Pan, et al., Energy Environ. Sci. 5 (2012) 6460–6464.
[22] Y. Xie, Y. Tang, W. Wu, et al., J. Am. Chem. Soc. 137 (2015) 14055–14058.
[23] H.L. Jia, Y.C. Chen, L. Ji, et al., Dye. Pigment 163 (2019) 589–593.
[24] S. Fan, X. Lu, H. Sun, et al., Phys. Chem. Chem. Phys. 18 (2016) 932–938.
[25] J. Liu, B. Liu, Y. Tang, et al., J. Mater. Chem. C 3 (2015) 11144–11150.
[26] Y. Chen, Y. Tang, J. Zou, et al., ACS Appl. Mater. Interfaces 13 (2021) 49828–49839.
[27] J. Luo, Z. Xie, J. Zou, et al., Chin. Chem. Lett. 33 (2022) 4313–4316.
[28] K. Zeng, Y. Chen, W.H. Zhu, et al., J. Am. Chem. Soc. 142 (2020) 5154–5161.
[29] J. Zou, Y. Wang, G. Baryshnikov, et al., ACS Appl. Mater. Interfaces 14 (2022) 33274–33284.
[30] Y. Wang, B. Chen, W. Wu, et al., Angew. Chem. Int. Ed. 53 (2014) 10779–10783.
[31] K. Zeng, Z. Tong, L. Ma, et al., Energy Environ. Sci. 13 (2020) 1617–1657.
[32] X. Li, P. Song, D. Zhao, et al., Materials 13 (2020) 4834.
[33] J.J.P. Stewart, J. Mol. Model. 13 (2007) 1173–1213.
[34] K. Zeng, W. Tang, C. Li, et al., J. Mater. Chem. A 7 (2019) 20854–20860.
[35] A. Usami, S. Seki, Y. Mita, et al., Sol. Energy Mater. Sol. Cells 93 (2009) 840–842.
[36] M. Lu, M. Liang, H.Y. Han, et al., J. Phys. Chem. C 115 (2011) 274–281.
[37] T. Higashino, Y. Kurumisawa, N. Cai, et al., ChemSusChem 10 (2017) 3347–3351.
[38] Y. Lu, Q. Liu, J. Luo, et al., ChemSusChem 12 (2019) 2802–2809.