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REVIEW ARTICLE

Atypical organic dyes used as sensitizers for efficient dye-sensitized solar cells

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Abstract Since their invention, dye-sensitized solar cells (DSSCs) have received enormous research attention from scientists with different background due to the possibility of low-cost production and fabrication on flexible substrates. One of the most important components in DSSCs is the sensitizing dye, including metal-complexes and metal-free organic dyes. The donor-π bridge-acceptor (D-π-A) structure is the mainstream in the design of organic sensitizers because it facilitates efficient charge-transfer toward the TiO_2 upon excitation. However, some sensitizers that do not follow this structure, or have some modification upon this structure, also present good efficiency when applied in DSSC devices. This review summarizes these atypical dyes in order to inspire more diverse designs toward highly efficient DSSCs.

Keywords donor- acceptor-π bridge-acceptor (D-A-π-A), donor-free, di-anchoring

1 Introduction

Over the past 20 years, dye-sensitized solar cells (DSSCs) have attracted significant interest as low-cost alternatives to conventional photovoltaic technologies. They present a record efficiency (uncertified) of ~14% under standard reporting conditions [1]. Through the years, hundreds, if not thousands of dyes have been tried as sensitizers. Among them, metal-free organic sensitizers have been developed and studied intensively for their advantages of high extinction coefficients, diverse design, potentially lower cost than metal complexes, easy preparation and purification. The overwhelming trend in designing these dyes is based on a donor-π bridge-acceptor (D-π-A) architecture [2,3]. In this case, the donor and the π spacer part will contain the highest occupied molecular orbital (HOMO) of the dye while the lowest unoccupied molecular orbital (LUMO) is distributed on the acceptor part which includes the anchoring group. Upon excitation, the electrons move from donor to acceptor through the π-bridge. This modular design allows organic dyes to show great diversity and flexibility. Each component (D, A, or π-bridge) in this architecture can be modified to tune the properties of dyes to suit the requirements for efficient DSSCs. Various donor groups have been investigated, including anthraquinone, boradiazaindacene, carbazole, coumarin, *N,N*-diakylaniline, hemicyanine, heteroanthracene, indoline, merocyanine, tetrahydroquinoline, triarylamine, squaraine, perylene and polymeric species [4]. Cyanoacrylic acid [5] and rhodamine-3-acetic acid [6] are commonly used acceptors as well as anchoring group to attach on a TiO_2 surface. Between the donor and acceptor, oligoene, coumarin, oligothiophene, fluorine and phenoxazine are often used as π-bridge [7].

Despite this mainstream focus, some sensitizers of alternative design also show good efficiency in DSSCs. The aim of this review is to highlight the dyes that break the normal trend of 'D-π-A' design and therefore to stimulate new inspiration and directions in molecular design of organic dyes for high photovoltaic performance and long-term stability of DSSCs.

2 Donor-acceptor-π bridge-acceptor (D-A-π -A) dyes

The concept of 'D-A-π-A' sensitizers was first proposed by the Zhu group [8]. Comparing to the traditional D-π-A configuration, this kind of sensitizers has an additional electron-withdrawing unit between the conventional donor and π-bridge, such as diketopyrrolopyrrole (DPP) [9–12], benzothiadiazole (BTD) [13–15], benzotriazole [16,17], benzoxadiazole (BOD) [18,19], quinoxaline [20,21],

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phthalimide [22], N-annulated perylene (NP) [23] and so on.

The introduction of an additional acceptor enables an electron transfer cascade to the acceptor/anchor group, following initial electron transfer from the donor to the internal acceptor. This has been proven by computational chemistry where it is found that the HOMO and LUMO orbitals of D-A-π-A sensitizers overlap on the additional acceptor and the π conjugated bridge. In the case of **WS-2** [14] (Fig. 1), a benzothiadiazole based D-A-π-A sensitizer, density functional theory (DFT) calculation indicates that the distributions of both HOMO and LUMO orbitals are well overlapped with the BTD unit. This is beneficial for electron transitions, which gives D-A-π-A sensitizers high extinction coefficient and good charge separation due to efficient subsequent charge transfer to the terminal acceptor group. Upon co-adsorption with deoxycholic acid (DCA), **WS-2** based DSSCs gave a high efficiency of 9%.

An additional electron-withdrawing unit also red-shifts the charge transfer absorption band, sometimes leading to the appearance of another absorption band. By choosing and coupling appropriate donor and acceptor together, the energy levels can be effectively tuned. For example, DPP is a strong electron-withdrawing unit due to the presence of two lactams. At the same time, it is also a chromophore. With a strong donating indoline group, **DPP17** (Fig. 1) shows superb absorption with absorption maximum at 600 nm and extinction coefficient of 69000 $M^{-1}\cdot cm^{-1}$ and yields the first example of a high-performance blue DSSC with over 10% efficiency [24].

In addition, it is known that long alkyl chains decrease intermolecular interactions, suppress aggregation and retard electron recombination. The extra acceptor allows more alkyl chains to be added on sensitizers, thus improving the open-circuit voltage and efficiency of DSSCs. In some cases, D-A-π-A structure also shows enhanced photo and thermal stability over D-π-A structure [14].

3 Donor-free oligomeric dyes

Since Hagfeldt and coworkers [25] introduced bulky alkoxy substituents into the triphenylamine-based donor of the sensitizers and obtained 6.7% efficiency with cobalt electrolyte, it becomes fashionable to make the donor part of D-π-A sensitizer bulkier and bulkier. The bulky donor is beneficial in order to reduce the electron recombination between redox electrolyte and the TiO_2 surface and to stabilize the oxidized dye. However, at the same time, the complicated structure often results in difficult synthesis with low yield. Our group designed a ‘donor-free’ cyanoacrylic end-functionalized oligo(3-hexylthiophene) sensitizer (**oligo-3HT**) and used it in both I^-/I_3^- based liquid dye-sensitized solar cells and solid-state solar cells

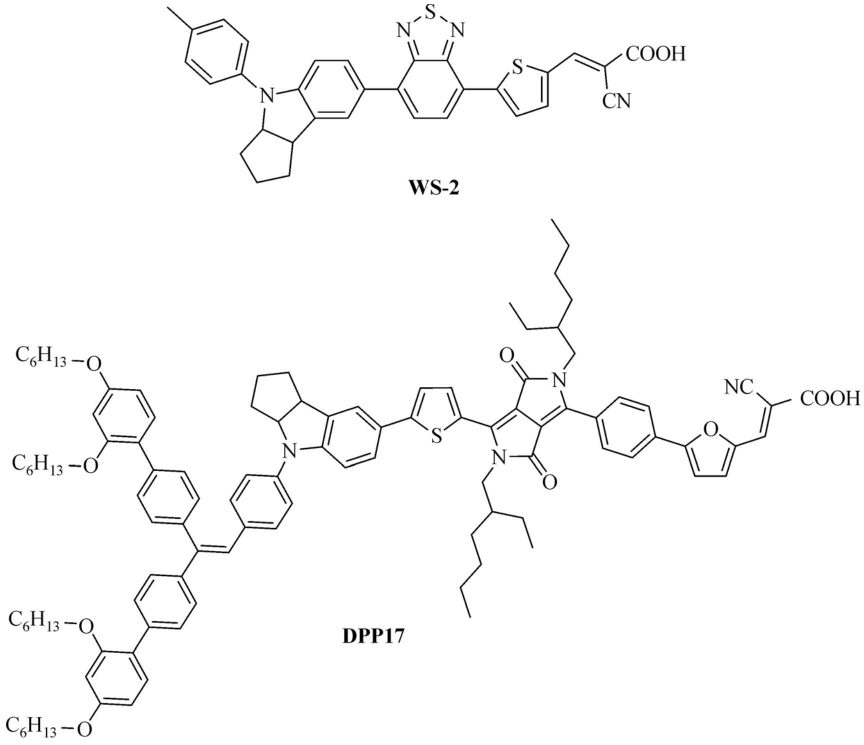
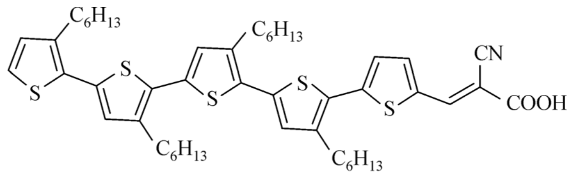
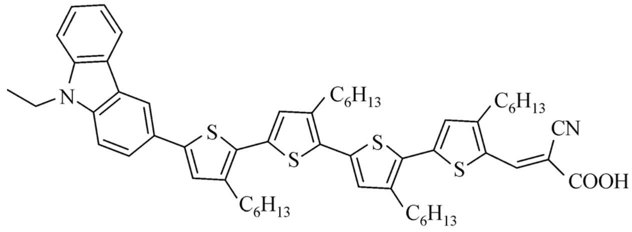


Fig. 1 Examples of ‘D-A-π-A’ sensitizers

to achieve power conversion efficiency (PCE) of 7.6% and 4.4%, respectively [26]. Under the same conditions, the ‘D-π-A’ sensitizer based on a similar structure (**MK-2**) showed an efficiency of 5.1% and 2.8%, respectively (Fig. 2). In solid-state dye-sensitized solar cells, we found that without an electron donor group, a significantly-higher open-circuit voltage (V_{oc}) could be achieved while the short-circuit current (J_{sc}) remained approximately the same. With experimental and theoretical approaches, we found that in the solid-state cells **oligo-3HT** sustains a significant fraction of oxidized dye under operating conditions and enhances the open-circuit voltage through the resulting large dipole on the dye. The work challenges the fundamental premise of sensitizer design and opens a new strategy of designing highly efficient ‘donor-free’ dyes in the future. We have since designed and synthesized more ‘donor-free’ sensitizers with broader absorption and higher extinction coefficient than **oligo-3HT** [27].



oligo-3HT



MK2

Fig. 2 Example of ‘donor-free’ sensitizer and D-π-A analog for comparison

4 Bridged dyes

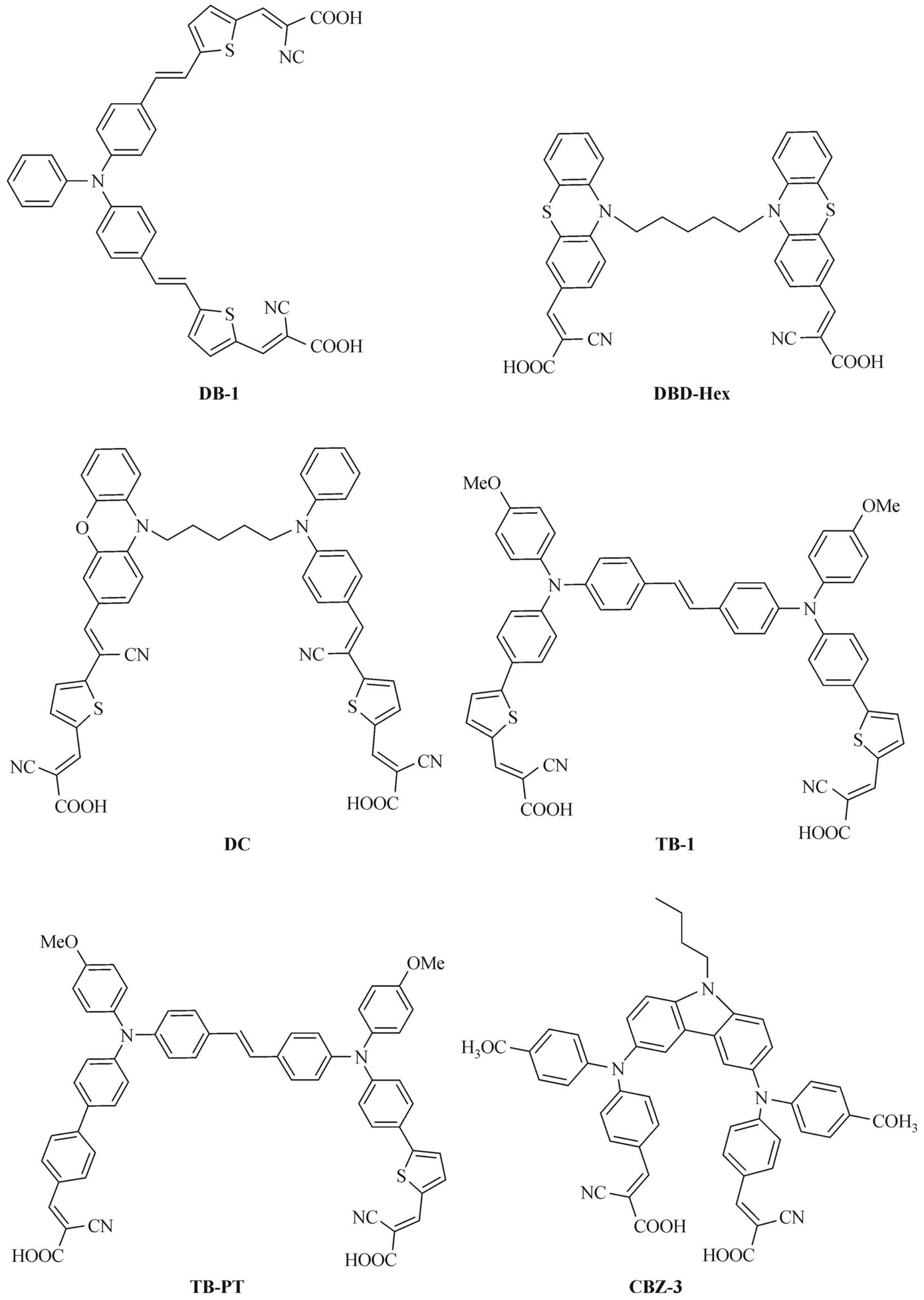
In a very restricted number of cases, branched or bridged geometries have been considered and used as sensitizers in dye-sensitized solar cells. With two acceptors and anchoring groups, these kind of sensitizers are designed to red-shift the monochromatic incident photon-to-electron conversion efficiency(IPCE) maximum and increase photocurrent, with the additional possibility of enhanced stability (Fig. 3).

The first example of di-branched di-anchoring sensitizer **DB-1**, reported by Abbotto and coworkers in 2009, introduced two D-π-A arms into a uni-dimensional dipolar analog. This resulted in a 10% increase of photocurrent and enhanced stability compared with the corresponding monobranched, mono-anchoring dye [28]. In 2011, Cao et al. designed a symmetric double D-π-A structure architecture bridged by a nonconjugated alkyl chain (**DBD**). By connecting two phenothiazine with butyl chain, hexyl chain or benzene group, the efficiency of these DSSCs was effectively enhanced compared to the corresponding single D-A phenothiazine dye. Among them, the dye with hexyl chain showed the best performance due to a successful suppression of dye aggregation and recombination with redox couple [29]. However, due to the symmetric structure, the two units of **DBD** absorbed in the same spectral region and did not broaden the absorption range. The same authors then designed an asymmetric bridged dye **DC** with two different light-harvesting systems in one dye molecule. It was found that not only did the dye exhibit a broader and more intense absorption than the reference mono dyes, but also the efficiency of solar cells based on **DC** was superior to either mono dyes or co-sensitizing system with the two mono dyes [30]. To further expand the absorption spectrum, the hexyl bridge was replaced by a π spacer. Both symmetric (**TB-1**) and asymmetric systems (**TB-PT**) were investigated by Abbotto et al. [31,32]. The results confirmed that asymmetric systems were preferred due to the intramolecular cosensitization effect. However, the twistable π spacer led to unfavorable interaction with the TiO_2 surface. This non-optimal dye packing allowed the oxidized species in the electrolyte to approach the TiO_2 surface, thus increasing the recombination and resulting in a much lower open-circuit voltage than the corresponding unbridged dye. Kiatisevi and coworkers replaced the bridge with a donor group to extend the electron delocalization (**CBZ-3**) [33], but the additional donor group up-shifted the HOMO energy level of the dye dramatically and caused a problem for regeneration.

In summary, among all the bridged dyes, the asymmetric hexyl chain bridged sensitizer has so far proven to be the best.

5 Conclusion

Sensitizers featuring ‘donor-π spacer-acceptor’ (D-π-A) architecture have been widely used to achieve high efficiency in dye-sensitized solar cells. Meanwhile, some atypical dyes also work well, although much less attention has been paid to their synthesis and study. This review highlights the dyes that do not follow the ‘D-π-A’ design, such as ‘D-A-π-A’ dyes, ‘donor-free’ dyes and bridged dyes. This provides new directions in molecular design of organic dyes and hopefully inspires scientists to try further novel designs for DSSC sensitizers.



DB-1

DBD-Hex

DC

TB-1

TB-PT

CBZ-3

Fig. 3 Examples of bridged dyes

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References

1. Kakiage K, Aoyama Y, Yano T, Oya K, Fujisawa J, Hanaya M. Highly-efficient dye-sensitized solar cells with collaborative sensitization by silyl-anchor and carboxy-anchor dyes. Chemical Communications, 2015, 51(88): 15894–15897
2. Gabrielsson E, Ellis H, Feldt S, Tian H, Boschloo G, Hagfeldt A, Sun L. Convergent/divergent synthesis of a linker-varied series of dyes for dye-sensitized solar cells based on the D35 donor. Advanced Energy Materials, 2013, 3(12): 1647–1656
3. Yang J, Ganesan P, Teuscher J, Moehl T, Kim Y J, Yi C, Comte P, Pei K, Holcombe T W, Nazeeruddin M K, Hua J, Zakeeruddin S M, Tian H, Grätzel M. Influence of the donor size in D-π-A organic dyes for dye-sensitized solar cells. Journal of the American Chemical Society, 2014, 136(15): 5722–5730
4. Hagfeldt A, Boschloo G, Sun L, Kloo L, Pettersson H. Dye-sensitized solar cells. Chemical Reviews, 2010, 110(11): 6595–6663
5. Wang Z S, Cui Y, Hara K, Dan-oh Y, Kasada C, Shinpo A. A high-light-harvesting-efficiency coumarin dye for stable dye-sensitized solar cells. Advanced Materials, 2007, 19(8): 1138–1141
6. Liang M, Xu W, Cai F, Chen P, Peng B, Chen J, Li Z. New triphenylamine-based organic dyes for efficient dye-sensitized solar cells. Journal of Physical Chemistry C, 2007, 111(11): 4465–4472
7. Ooyama Y, Harima Y. Photophysical and electrochemical properties, and molecular structures of organic dyes for dye-sensitized solar cells. ChemPhysChem, 2012, 13(18): 4032–4080
8. Wu Y, Zhu W. Organic sensitizers from D-π-A to D-A-π-A: effect of the internal electron-withdrawing units on molecular absorption, energy levels and photovoltaic performances. Chemical Society Reviews, 2013, 42(5): 2039–2058
9. Qu S Y, Wu W, Hua J, Kong C, Long Y, Tian H. New diketopyrrolopyrrole (DPP) dyes for efficient dye-sensitized solar cells. Journal of Physical Chemistry C, 2010, 114(2): 1343–1349
10. Qu S Y, Wang B, Guo F, Li J, Wu W, Kong C, Long Y, Hua J. New diketo-pyrrolo-pyrrole (DPP) sensitizer containing a furan moiety for efficient and stable dye-sensitized solar cells. Dyes and Pigments, 2012, 92(3): 1384–1393
11. Qu S, Qin C, Islam A, Wu Y, Zhu W, Hua J, Tian H, Han L. A novel D-A-π-A organic sensitizer containing a diketopyrrolopyrrole unit with a branched alkyl chain for highly efficient and stable dye-sensitized solar cells. Chemical Communications, 2012, 48(55): 6972–6974
12. Guo F L, Qu S, Wu W, Li J, Ying W, Hua J. Synthesis and photovoltaic performance of new diketopyrrolopyrrole (DPP) dyes for dye-sensitized solar cells. Synthetic Metals, 2010, 160(15–16): 1767–1773
13. Velusamy M, Justin Thomas K R, Lin J T, Hsu Y C, Ho K C. Organic dyes incorporating low-band-gap chromophores for dye-sensitized solar cells. Organic Letters, 2005, 7(10): 1899–1902
14. Zhu W H, Wu Y, Wang S, Li W, Li X, Chen J, Wang Z, Tian H. Organic D-A-π-A solar cell sensitizers with improved stability and spectral response. Advanced Functional Materials, 2011, 21(4): 756–763
15. Wu Y Z, Zhang X, Li W, Wang Z S, Tian H, Zhu W. Hexylthiophene-featured D-A-π-A structural indoline chromophores for coadsorbent-free and panchromatic dye-sensitized solar cells. Advanced Energy Materials, 2012, 2(1): 149–156
16. Cui Y, Wu Y, Lu X, Zhang X, Zhou G, Miapeh F B, Zhu W, Wang Z S. Incorporating benzotriazole moiety to construct D-A-π-A organic sensitizers for solar cells: significant enhancement of open-circuit photovoltage with long alkyl group. Chemistry of Materials, 2011, 23(19): 4394–4401
17. Mao J, Guo F, Ying W, Wu W, Li J, Hua J. Benzotriazole-bridged sensitizers containing a furan moiety for dye-sensitized solar cells with high open-circuit voltage performance. Chemistry, an Asian Journal, 2012, 7(5): 982–991
18. Li H, Wu Y, Geng Z, Liu J, Xu D, Zhu W. Co-sensitization of benzoxadiazole based D-A-π-A featured sensitizers: compensating light-harvesting and retarding charge recombination. Journal of Materials Chemistry A, Materials for Energy and Sustainability, 2014, 2(35): 14649–14657
19. Zhu H B, Wu Y, Liu J, Zhang W, Wu W, Zhu W H. D-A-π-A featured sensitizers containing an auxiliary acceptor of benzoxadiazole: molecular engineering and co-sensitization. Journal of Materials Chemistry A, Materials for Energy and Sustainability, 2015, 3(19): 10603–10609
20. Pei K, Wu Y, Wu W, Zhang Q, Chen B, Tian H, Zhu W. Constructing organic D-A-π-A-featured sensitizers with a quinoxaline unit for high-efficiency solar cells: the effect of an auxiliary acceptor on the absorption and the energy level alignment. Chemistry-a European Journal, 2012, 18(26): 8190–8200
21. Shi J, Chen J, Chai Z, Wang H, Tang R, Fan K, Wu M, Han H, Qin J, Peng T, Li Q, Li Z. High performance organic sensitizers based on 11,12-bis(hexyloxy) dibenzo [a,c]phenazine for dye-sensitized solar cells. Journal of Materials Chemistry, 2012, 22(36): 18830–18838
22. Li W, Wu Y, Zhang Q, Tian H, Zhu W. D-A-π-A featured sensitizers bearing phthalimide and benzotriazole as auxiliary acceptor: effect on absorption and charge recombination dynamics in dye-sensitized solar cells. ACS Applied Materials & Interfaces, 2012, 4(3): 1822–1830
23. Li X, Zheng Z, Jiang W, Wu W, Wang Z, Tian H. New D-A-π-A organic sensitizers for efficient dye-sensitized solar cells. Chemical Communications, 2015, 51(17): 3590–3592
24. Yum J H, Holcombe T W, Kim Y, Rakstys K, Moehl T, Teuscher J, Delcamp J H, Nazeeruddin M K, Grätzel M. Blue-coloured highly efficient dye-sensitized solar cells by implementing the diketopyrrolopyrrole chromophore. Scientific Reports, 2013, 3: 2446
25. Feldt S M, Gibson E A, Gabrielsson E, Sun L, Boschloo G, Hagfeldt A. Design of organic dyes and cobalt polypyridine redox mediators for high-efficiency dye-sensitized solar cells. Journal of the American Chemical Society, 2010, 132(46): 16714–16724
26. Abate A, Planells M, Hollman D J, Stranks S D, Petrozza A, Kandada A R S, Vaynzof Y, Pathak S K, Robertson N, Snaith H J. An organic "donor-free" dye with enhanced open-circuit voltage in solid-state sensitized solar cells. Advanced Energy Materials, 2014, 4(13): 1400166
27. Hu Y, et al. *manuscripts in preparation*
28. Abbotto A, Manfredi N, Marinzi C, De Angelis F, Mosconi E, Yum

J H, Xianxi Z, Nazeeruddin M K, Grätzel M. Di-branched di-anchoring organic dyes for dye-sensitized solar cells. Energy & Environmental Science, 2009, 2(10): 1094–1101

29. Cao D, Peng J, Hong Y, Fang X, Wang L, Meier H. Enhanced performance of the dye-sensitized solar cells with phenothiazine-based dyes containing double D-A branches. Organic Letters, 2011, 13(7): 1610–1613
30. Hong Y, Liao J Y, Cao D, Zang X, Kuang D B, Wang L, Meier H, Su C Y. Organic dye bearing asymmetric double donor-π-acceptor chains for dye-sensitized solar cells. Journal of Organic Chemistry, 2011, 76(19): 8015–8021
31. Abbotto A, Leandri V, Manfredi N, De Angelis F, Pastore M, Yum J H, Nazeeruddin M K, Grätzel M. Bis-donor-bis-acceptor tri-branched organic sensitizers for dye-sensitized solar cells. European Journal of Organic Chemistry, 2011, 2011(31): 6195–6205
32. Leandri V, Ruffo R, Trifiletti V, Abbotto A. Asymmetric tribranched dyes: an intramolecular cosensitization approach for dye-sensitized solar cells. European Journal of Organic Chemistry, 2013, 2013(30): 6793–6801
33. Pramjit S, Eiamprasert U, Surawatanawong P, Lertturongchai P, Kiatisevi S. Carbazole-bridged double D-A dye for efficient dye-sensitized solar cell. Journal of Photochemistry and Photobiology A: Chemistry, 2015, 296(1): 1–10

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