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Designing triphenylamine derivative dyes for highly effective dye-sensitized solar cells with near-infrared light harvesting up to 1100 nm[†]

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Designing highly efficient sensitizers for dye-sensitized solar cells (DSSCs) is an urgent task because it is closely related to the practical application of DSSCs. In this work, we designed and screened a series of triphenylamine derivative dyes with donor- π -acceptor (D- π -A) structure using different electron donors, π bridges and electron acceptors, and further used density functional theory (DFT) and time-dependent DFT (TDDFT) approaches to investigate the molecular orbital energy levels, absorption spectra, and light harvesting efficiency of these newly designed dyes. Results indicate that the donor group in D2, π bridges in Pi10–Pi12 and the acceptor group in A7 are promising functional groups for D- π -A structure. Using the above screened functional groups as donors, π bridges and acceptors, we designed six novel D- π -A structures of BUCT1–BUCT6. The results indicate that BUCT1–BUCT6 dyes show smaller HOMO–LUMO energy gaps, higher molar extinction coefficients and obvious redshifts compared to the experimentally synthesized P0 dye. In particular, the newly designed BUCT2 dye exhibits not only a 215 nm redshift and a higher molar extinction coefficient with an increment of 32.4% compared to P0 dye, but also has an extremely broad absorption spectrum covering the entire visible range up to the near-IR region of 1100 nm. Therefore, the BUCT2 dye is a very promising candidate for highly effective DSSCs with near-infrared light harvesting up to 1100 nm. We also found that the dyes with two –CN groups and a sulfonic acid group as the electron acceptor are more efficient than dyes with one –CN group and a sulfonic acid group.

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1. Introduction

Because of the shortage of traditional fossil fuels caused by the fast consumption by a developing global society, it is an urgent task to develop renewable and clean energy sources, such as power from wind and water, biomass and solar energy. Currently, the sun provides our planet with approximately 10^4 times more energy than our global daily consumption.^{1,2} Photovoltaic cells are the most direct way to convert sunlight into electricity. Moreover, photovoltaic cells require very little maintenance because of the absence of moving components, and this makes them attractive for long term outdoor installation. Therefore, developing highly effective solar cells is very significant for the wide application of solar energy.

Since the Grätzel research group used the high specific surface area of nanoporous TiO₂ film as a semiconductor electrode to develop dye-sensitized solar cells (DSSCs) with photoelectric conversion efficiency (PCE) of 7.1% in 1991,³ DSSCs

have become a hot topic and attracted extensive attention. In 2005, Grätzel *et al.* used N719 dye as sensitizers to produce DSSCs with PCE of up to 11.18%.⁴ In 2011, they further improved the efficiency of solar cells based on porphyrin dyes to 12.3%.⁵ Recently, Grätzel⁶ and Oxford University research teams⁷ independently developed a solid-state DSSCs whose PCE exceeded 15%, further creating a new record.

In DSSCs, the dye sensitizers have been considered as one of the most important components to exhibit high performance, and various types of dyes have been explored to improve overall device performance. Ruthenium dyes have limitations for DSSCs because of the presence of noble metals and relatively large environmental pollution. Therefore, organic photosensitive dyes without noble metals have attracted considerable attention, owing to many advantages, such as low cost, variety structure, strong light-harvesting ability, convenient synthesis and minimal harm to the environment. Recently, a series of new organic dyes with donor- π -acceptor (D- π -A) structure were synthesized.^{8–14} Previous studies have shown that the D- π -A molecular structure is not only beneficial to the intramolecular charge transfer from the electron donor to the electron acceptor moiety, but also facilitated the regulation of molecule performance by modifying the donor, π bridge and acceptor groups.⁹ At present,

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investigators have identified some relatively good electron donors (such as triphenylamine, indole, dimethyl fluorene, phenothiazine) and π bridges (such as methylidyne, thiophene, furan, pyrrole and benzene).² Cyanoacrylic acid is the most widely used electron acceptor, which also acts as an anchoring group, because the dye molecule can be adsorbed on the surface of the TiO_2 nanocrystal. Currently, designing the D- π -A molecular structure to further improve the PCE of DSSC devices is still a great challenge.¹⁵

The PCE of a DSSC device is mainly determined by short circuit current density (J_{sc}), open circuit photovoltage (V_{oc}) and fill factor (FF). Improving the short circuit current density can significantly enhance the PCE of DSSCs. The most critical factor for improving the short circuit current density is to increase the electron injection (Φ_{inject})¹⁶ and the light harvesting efficiency (LHE),¹⁷ as well as the molar extinction coefficients of the dyes, and broaden the absorption spectrum scope in the visible light and near-infrared regions. Φ_{inject} is related to the driving force ΔG_{inject} of the electrons injecting from the excited states of dye molecules to the semiconductor conduction band. LHE can be calculated by the equation $\text{LHE} = 1 - 10^{-f}$, where f represents the oscillator strength of the adsorbed dye molecules.¹⁷

In order to improve the short circuit current density, Park *et al.* introduced triphenylamine as donor, benzene ring as the π bridge and cyanoacrylic acid as the acceptor to synthesize the TA-St-CA dye, and further applied it to DSSCs. The short circuit current density of the TA-St-CA-sensitized DSSC device reached 18.1 mA cm^{-2} and exhibited a PCE of 9.1%, and it has attracted significant attention because of its simple structure and outstanding photoelectric performance.¹⁸ Triphenylamine derivatives as sensitizers of DSSCs can expand the light absorption ability of the dye, and its non-planar structure can also inhibit aggregation of the dye on the TiO_2 surface.¹⁹ Triphenylamine has been widely used as an electron donor in the sensitizer. The three benzene rings of the triphenylamine group are mutually twisted, and the triphenylamine and π -conjugated groups also have certain distortion angles. Therefore, the non-planar structure of the dye molecule effectively prevents intermolecular π - π aggregation, which is beneficial because the aggregation would cause electron transfer between the molecules, which leads to loss of energy and therefore affects the PCE of DSSCs. Accordingly, triphenylamine compounds have been widely used as photovoltaic materials because of their excellent hole transport capability.^{20–39}

In order to design highly efficient photosensitive dyes, in this work, we first used density functional theory (DFT) and time-dependent DFT (TDDFT) to calculate the molecular orbital energy levels, absorption spectra, LHE and electron injection driving force of the experimentally synthesized TA-St-CA dyes.¹⁸ Using TA-St-CA dye as a prototype, we further designed and screened a series of new D- π -A structure dyes by adopting different donors, π conjugate bridges and acceptor groups. Finally, we recommended a type of novel triphenylamine derivative dyes with near-infrared light harvesting for highly effective DSSCs.

2. Computational details

2.1 D- π -A molecular models

The experimentally synthesized TA-St-CA dye is shown in Fig. 1. It is also named **P0** (R-bit of **P0** is H in Fig. 1) for simplification. The dye **P1** (also named **D5**)^{40–42} and **P2** (ref. 43) were obtained using furan and thiophene groups to replace the benzene group of **P0**. The dyes **P1** and **P2** have been experimentally synthesized and the corresponding **P1** and **P2**-sensitized DSSC devices exhibit PCEs of approximately 6.0% and 7.36%, respectively. In order to explore considerably higher efficient triphenylamine derivative dyes, we designed a series of dyes using different π -conjugated bridge groups, **Pi1–Pi12**, shown in Fig. 1. **Pi1–Pi3** were obtained by replacing the benzene group of **P0** with EDOT, bithiophene and s-DTT, respectively. Simultaneously, **Pi4–Pi9** were constructed using two combinations of benzene, thiophene, furan and EDOT to replace the π -conjugated bridge of **P0**, and **Pi10–Pi12** were designed using any two of EDOT, bithiophene and s-DTT as substituting groups. In addition, we adopted the orthogonal design to modify the donor and acceptor groups of **P0** using different electron-donating groups (*i.e.* $-\text{CH}_3$, $-\text{O}-\text{CH}_3$, $-\text{C}_4\text{H}_9$, and $-\text{NH}_2$) and different electron-accepting groups (**A1–A7**). All the abovementioned constructed D- π -A molecular structures are shown in Fig. 1.

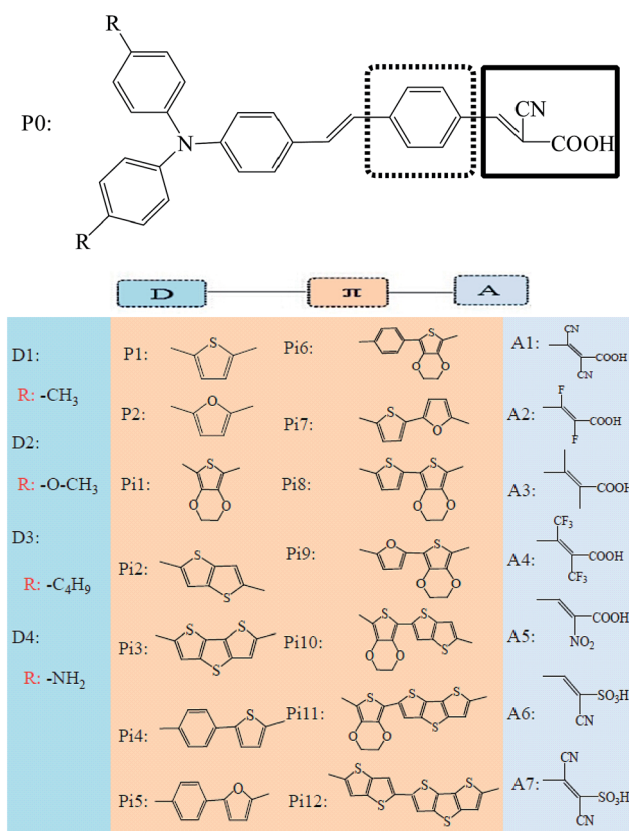


Fig. 1 Molecular structures of the triphenylamine **P0** dye and derivatives.

Table 1 The vertical excitation energy in eV of dyes **P0**–**P2** calculated with TDDFT using different exchange–correlation functionals in acetonitrile and the experimental data

	B3LYP	CAM-B3LYP	WB97XD	Exp.
P0	2.04	2.84	2.91	3.21 (ref. 18)
P1	1.96	2.49	2.59	2.61–2.90 (ref. 40–42)
P2	1.93	2.57	2.66	2.64 (ref. 43)

2.2 Computational methods

The geometries of these dye molecules were optimized by DFT calculations using Becke's three-parameters and Lee–Yang–Parr gradient-corrected correlation hybrid functional (B3LYP) and 6-31G(d) basis sets. The vibrational frequency calculations were also carried out at the same level to confirm that the triphenylamine derivative structures are local minima (no imaginary frequencies) on potential energy surfaces.

Previous investigations indicate that TDDFT is highly efficient and accurate in the calculation of vertical excitation energy, electric properties and optical absorption.^{44,45} However, different exchange–correlation (XC) functionals for charge-transfer excitations often show significant effects. To select suitable functionals, we adopted different XC functionals, including B3LYP, CAM-B3LYP and WB97XD, in TDDFT to calculate the vertical excitation energies of **P0**, **P1** and **P2**. The calculated results and the experimental data are shown in Table 1. It was found that the vertical excitation energies of dyes were severely underestimated by the B3LYP functional, while the long range-corrected (LC) functionals, such as CAM-B3LYP and WB97XD, are in satisfactory agreement with the experimental values. Considering computational cost, we first screened the donors, π -conjugated bridges and acceptors using the CAM-B3LYP functional with 6-311+g(d, p) basis sets, combining a CPCM⁴⁶ solvation model in acetonitrile solution for these newly designed dye molecules in Fig. 1. Then, we adopted the more accurate WB97XD functional at the same level to predict the optical properties of six newly designed dyes of **BUCT1**–**BUCT6**. All the calculations were performed using a suite of Gaussian09 packages.⁴⁷

3. Results and discussion

3.1 Screening of the electron donor

Fig. 2 shows the energy levels for **P0** and **D1**–**D4** in acetonitrile solution. The results indicate that the LUMO energies of **D1**–**D4** are higher than the conduction band edge (CBE) of the TiO₂ electrode (approximately -4.0 eV),² shown as a red dashed line in Fig. 2. Thus, these excited state molecules could successfully inject electrons into the TiO₂ electrode. In addition, the HOMO energies of **D1**–**D3** are lower than the potential (approximately -4.8 eV) of the I^-/I_3^- redox electrolyte.² Therefore, those dye molecules that lose electrons could quickly obtain electrons from the electrolyte. The HOMO energy of **D4** is higher than the potential of the I^-/I_3^- redox electrolyte, and may not be suitable

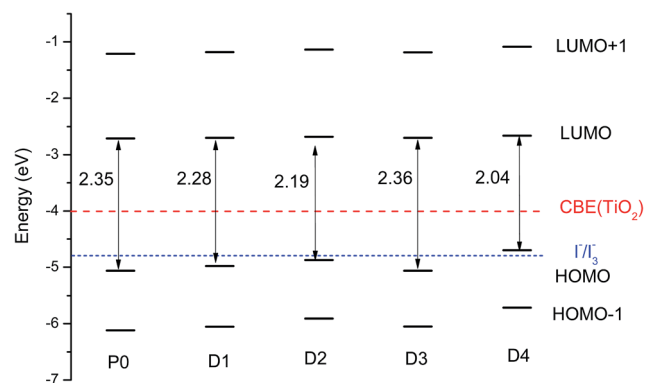


Fig. 2 Energy levels for **P0** and **D1**–**D4** dyes, where the horizontal dashed line indicates the levels (-4.0 eV) of the conduction band edge (CBE) of the anatase TiO₂ in electrolyte solutions and the redox energy level (-4.8 eV) of redox electrolyte (I^-/I_3^-).²

for sensitizer. Compared to the band gap of **P0**, **D1** and **D2** may be suitable candidates for DSSCs.

Fig. 3 shows the UV-visible absorption spectra of **D1**–**D4** dyes. The maximum absorption peaks of **D1**–**D4** are 445, 462, 456 and 465 nm, which exhibit 7, 24, 18 and 27 nm redshifts compared to that of **P0** (438 nm), respectively. The molar extinction coefficients of these dyes also slightly increase with the exception of **D4** (see Table 2). The optical absorption spectra redshift and the molar extinction coefficient definitely indicate that **D2** may be a good candidate as a photosensitizer for a DSSC device, which is consistent with the band gap results mentioned above. This suggests that introducing the strongly electron-donating $-O-CH_3$ group into the electron donor of the dye is favorable for light absorption, which has been confirmed in previous experiments. The Grätzel research group adopted $-O-CH_3$ to replace the R-bit in **P1** to synthesize the dye **D9**,⁴² and found that the dye **D9** shows a redshift of approximately 30 nm compared to dye **P1**, and the PCE of a **D9**-sensitized device significantly increases to 6.9% from 5.9% for the **P1**-sensitized device. Both the experimental and simulation results indicate

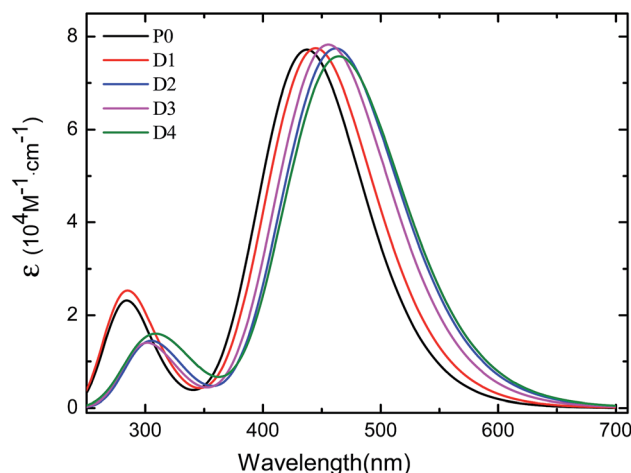


Fig. 3 The UV-visible absorption spectra of **P0** and **D1**–**D4** dyes.

Table 2 The calculated maximum absorption wavelengths λ (nm) and corresponding vertical excitation energies E_{ex} (eV) (in parentheses), molar extinction coefficient ϵ ($10^4 \text{ M}^{-1} \text{ cm}^{-1}$), oscillator strengths f and light harvesting efficiency (LHE) for triphenylamine derivative dyes

Dye	$\lambda(E_{\text{ex}})$	ϵ	f	LHE
P0	438(2.84)	7.71	1.9060	0.988
D1	445(2.79)	7.75	1.9140	0.988
D2	462(2.68)	7.75	1.9123	0.988
D3	456(2.72)	7.83	1.9326	0.988
D4	465(2.67)	7.58	1.8706	0.987
P1	498(2.49)	6.17	1.5613	0.973
P2	482(2.57)	4.40	1.0972	0.920
Pi1	483(2.56)	7.10	1.7726	0.983
Pi2	489(2.53)	9.06	2.2741	0.995
Pi3	493(2.51)	8.23	2.0311	0.991
Pi4	447(2.78)	9.19	2.2684	0.995
Pi5	447(2.78)	9.22	2.2721	0.995
Pi6	447(2.78)	9.35	2.3013	0.995
Pi7	495(2.51)	7.72	1.8811	0.987
Pi8	504(2.46)	8.21	2.0278	0.991
Pi9	504(2.46)	6.91	1.7065	0.980
Pi10	525(2.36)	10.44	2.5768	0.997
Pi11	501(2.44)	9.99	2.4570	0.997
Pi12	510 (2.43)	10.87	2.6649	0.998
A1	495(2.51)	5.44	1.3433	0.955
A2	397(3.12)	7.87	1.9437	0.989
A3	363(3.41)	7.03	1.7346	0.983
A4	375(3.30)	6.65	1.6420	0.977
A5	435(2.85)	7.05	1.7361	0.983
A6	445(2.79)	7.58	1.8705	0.987
A7	501(2.48)	6.70	1.6535	0.977
BUCT1	537(2.31)	10.82	2.6717	0.998
BUCT2	653(1.90)	10.21	2.5210	0.997
BUCT3	505(2.46)	10.52	2.5837	0.997
BUCT4	609(2.04)	7.65	1.8848	0.987
BUCT5	505(2.45)	11.36	2.778	0.998
BUCT6	592(2.09)	10.11	2.4907	0.997

that introducing the $-\text{O}-\text{CH}_3$ group into the donor of the dye may improve the J_{sc} and PCE of DSSCs.

3.2 Screening of the π -conjugated bridge

The π -conjugated bridge in D- π -A structure dye can accelerate electron transport from donor to acceptor, and thus speed up electron injection from the dye molecule to the conduction band of the semiconductor. Therefore, the π -conjugated bridge is a key factor of high performance in D- π -A structure. In order to screen excellent π -conjugated bridges of triphenylamine derivative dyes, we investigated the performance of a series of newly designed dyes (Pi1–Pi12 in Fig. 1).

The molecular orbital energy levels of P0–P2 and Pi1–Pi12 in acetonitrile solution are shown in Fig. 4. The LUMO energies of Pi1–Pi12 are higher than the CBE (red dashed line in Fig. 4) of the TiO_2 electrode,² which ensures that the excited electrons smoothly inject into the TiO_2 electrode. Moreover, their HOMO energies are sufficiently lower than the potential of the I^-/I_3^- redox electrolyte.² Therefore, these lost electron molecules could quickly be restored by the electrolyte. The energy gaps of Pi1–Pi12 are basically smaller than that of P0, which causes the

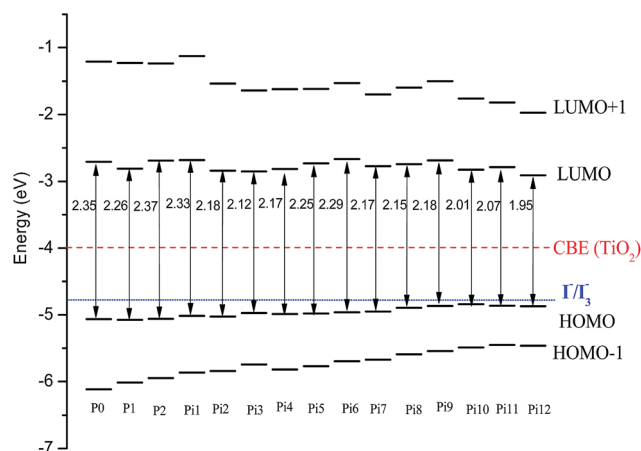


Fig. 4 Energy levels for P0–P2 and Pi1–Pi12 dyes.

redshift of absorption spectra. In particular, the energy gaps of Pi10–Pi12 are 2.01, 2.07 and 1.95 eV, respectively, which is considerably lower than that of P0.

The UV-visible absorption spectra of P1, P2 and Pi1–Pi12 dyes in acetonitrile solution are shown in Fig. 5. For clear

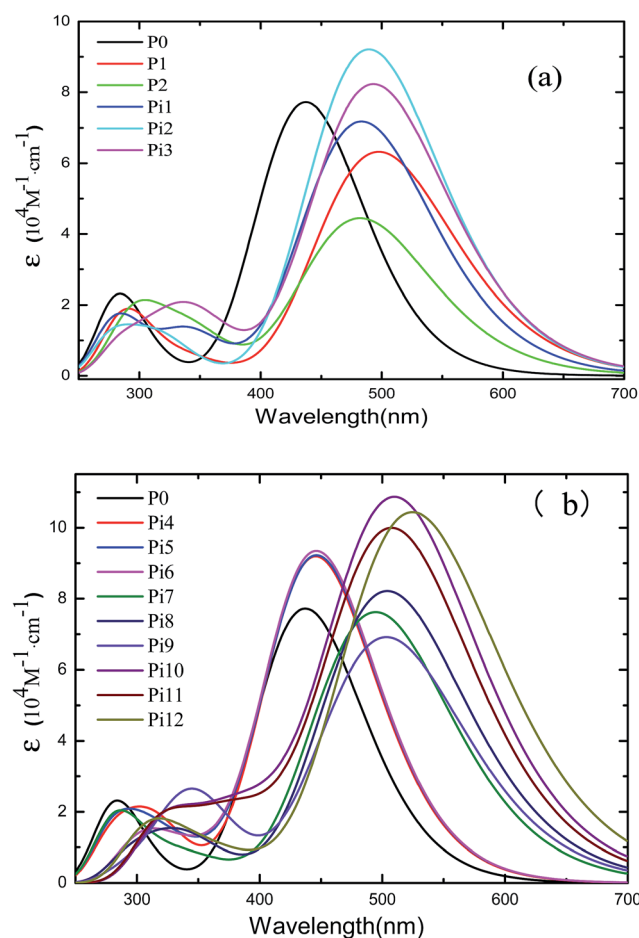


Fig. 5 The UV-visible absorption spectra of different dyes. (a) P0–P2 and Pi1–Pi3, (b) P0 and Pi4–Pi12.

observation, they are divided into Fig. 5(a) and (b). Compared to **P0**, the absorption maxima of these dyes are red-shifted 44–87 nm (see Fig. 5(a) and (b)), except that **Pi4–Pi6** exhibits a redshift of only 8 nm. Their maximal absorption wavelengths and corresponding vertical excitation energies are listed in Table 2. Compared to **P0**, the optical properties of **Pi10–Pi12** show obvious advantages. In particular, as shown in Fig. 5(b), the absorption peaks of **Pi10–Pi12** are 525, 501 and 510 nm, which exhibit redshifts of 87, 63 and 72 nm, respectively. The absorption spectra of **Pi10–Pi12** cover a broader solar spectrum, exceeding 700 nm for **Pi12**. Interestingly, it is found from the optimized geometric structures (Fig. S1†) that the π -conjugated bridges of **Pi10–Pi12** have planar structure, which is greatly beneficial for the photoinduced transfer of electrons from the electron donor to the electron acceptor.

The maximum molar extinction coefficient is a very important factor for light-absorbing dyes, and its magnitude directly demonstrates the light absorption ability of the dye. The maximum molar extinction coefficients of **Pi1–Pi12** are listed in Table 2. It was found that the maximum molar extinction coefficients of **Pi2**, **Pi4–Pi6** and **Pi10–Pi12** show a significant increase from 17.5% to 40.9%, and other dyes also show increases except for **Pi9**. In particular, the maximum molar extinction coefficients of **Pi10–Pi12** are 10.44 , 9.99 and $10.87 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ with increases of 35.4%, 29.7% and 40.9%, respectively, compared to **P0** (Table 2). Moreover, the LHEs of the **Pi10–Pi12** dyes are also considerably higher than that of **P0**.

From the above π -conjugated bridge screening, we found that a π -conjugated bridge with planar structure enables a more efficient intramolecular charge transfer from the electron donor to the electron acceptor. By considering the energy gap, absorption spectra (including molar extinction coefficient, absorption peak redshift and the broad extent of light absorption) and LHE of **P0** and **Pi1–Pi12** we believe that the **Pi10–Pi12** may be excellent candidates for DSSC devices. This observation is in excellent agreement with previous experiments, in which the Wang research group adopted EDOT and bithiophene groups as π -conjugated bridges to synthesize dye **C217** (similar to **Pi10**),⁴⁸ and found that the dye **C217** shows a redshift of approximately 114 nm compared to dye **P0**, and that the PCE of the **C217**-sensitized device significantly increases to 9.8%. These findings are expected to provide a promising method to design new organic dyes and improve the J_{sc} and PCE of DSSCs.

3.3 Screening of the electron acceptor

Currently, researchers have mainly focused on the modifications of the electron donor and π -bridge structures for highly effective D- π -A dyes. However, the electron acceptor, which connects the dye to the semiconductor, plays an important role in anchoring on the TiO_2/ZnO semiconductor surface, optical absorption, as well as electron injection processes. Currently, cyanocyclic acid is very popular for DSSCs because its functionality largely fulfills the need of the electron acceptor.⁴⁹ It is beneficial to improve the injection efficiency by inserting the electron-withdrawing $-\text{CN}$ group into the electron acceptor. Therefore, we designed a series of dyes **A1–A7** (Fig. 1) in order to

screen acceptors by exploring the influence of electron-withdrawing chemical group substitution, such as $-\text{F}$, $-\text{CH}_3$, $-\text{CF}_3$ and $-\text{NO}_2$, and the sulfonic acid anchoring group.

The molecular orbital energy levels of **A1–A7** in acetonitrile solution are shown in Fig. 6. The LUMO energies of **A1–A7** are higher than the CBE of the TiO_2 electrode and their HOMO energies are lower than the potential of the I^-/I_3^- redox electrolyte.² The energy gaps of **A1** and **A7** are 1.76 and 1.72 eV, respectively, which are smaller than **P0** because of the significant decrease of the LUMO energy level. However, the energy gaps of **A2–A4** are larger than that of **P0**, which results in the blue shifts.

The UV-visible absorption spectra of **A1–A7** in acetonitrile solution are shown in Fig. 7. The maximum absorption peaks of **A2–A4** are blue-shifted by 41–75 nm. Thus, the visible light utilization for **A2–A4** is relatively low because the maximal absorption peaks are located in the violet light range. **A5–A6** and **P0** have very similar optical properties (Table 2). The maximum absorption peaks of **A1** and **A7** are red-shifted by 57 and 63 nm, respectively. However, the molar extinction coefficient of **A1** shows a decrease of nearly 30%, and that of **A7** is decreased by

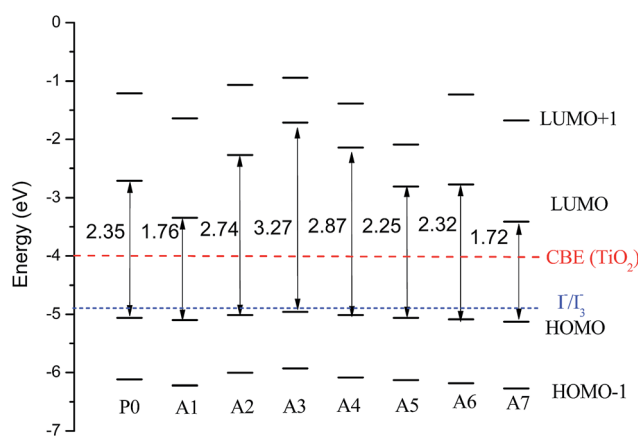


Fig. 6 Energy levels for **P0** and **A1–A7** dyes.

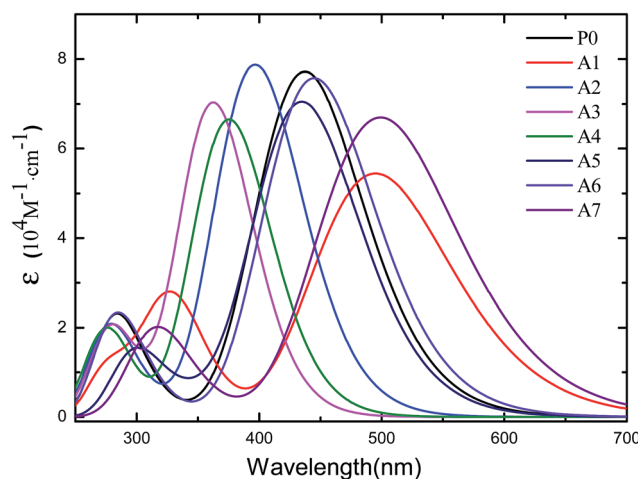


Fig. 7 The UV-visible absorption spectra of **P0** and **A1–A7** dyes.

approximately 9%. Thus, the decrease of the molar extinction coefficient of dye molecules can be effectively prevented using a sulfonic acid group to replace the carboxylic acid group as the electron acceptor.

3.4 Design of novel D- π -A triphenylamine derivatives

On the basis of the above screening of the D- π -A structure, we further designed six novel dyes, **BUCT1**–**BUCT6**, by employing 4,4'-dimethoxy triphenylamine as the electron donor, any two of EDOT, bithiophene and s-DTT groups as the π -conjugated bridge, and –CN and sulfonic acid groups as electron acceptors. The structures of **BUCT1**–**BUCT6** are presented in Fig. 8.

The molecular orbital energy levels of **P0** and **BUCT1**–**BUCT6** dyes in acetonitrile solution are shown in Fig. 9. The LUMO energies of **BUCT1**–**BUCT6** are higher than the CBE of TiO_2 .² The HOMO energies of **BUCT2** and **BUCT4** are below the I^-/I_3^- redox potential, while those of **BUCT1**, **BUCT3**, **BUCT5** and **BUCT6** are higher than the redox potential of the I^-/I_3^- electrolyte.² Thus, **BUCT1**, **BUCT3**, **BUCT5** and **BUCT6** are not suitable as sensitizers in DSSCs because they could not be quickly restored by the electrolyte after they lose their electrons and the sensitizer was oxidized. The LUMO levels of **BUCT2** and **BUCT4** are –3.45 and –3.44 eV, and the energy gaps are also reduced to 1.36 and 1.34 eV, respectively.

Fig. 10 shows the absorption spectra of **BUCT1**–**BUCT6** in acetonitrile solution. The maximum molar extinction coefficients of **BUCT2** and **BUCT4** dyes are 10.21 and $7.65 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, respectively, representing an increment of 32.4% and –0.8% compared with **P0**. The maximum absorption peaks of

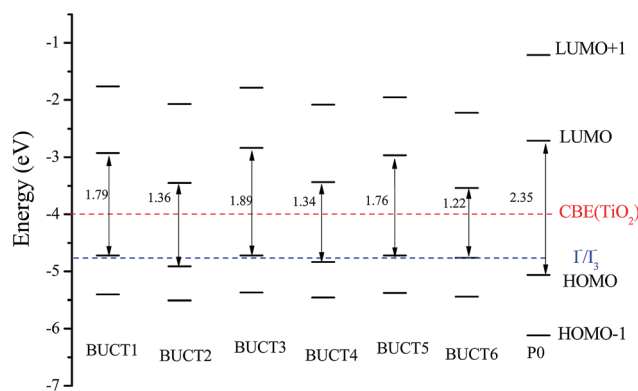


Fig. 9 Energy levels of **BUCT1**–**BUCT6** and **P0** dyes.

BUCT2 and **BUCT4** are 653 and 609 nm, which have extremely large redshifts of 215 and 171 nm, compared to **P0**. Obviously, the newly designed **BUCT2** dye has the highest molar extinction coefficient and the largest redshift among all the dyes studied. Interestingly, the absorption spectrum of **BUCT2** covers the entire visible range and extends into the near-IR region up to 1100 nm, which could be considered as a full light absorbing dye. Therefore, **BUCT2** dye is a promising candidate for panchromatic absorption, which may significantly improve the PCE of DSSC devices.

Interestingly, we find that the band gaps of **BUCT2**, **BUCT4** and **BUCT6**, where the acceptors have two –CN groups, are noticeably smaller than that of **BUCT1**, **BUCT3** and **BUCT5**, in

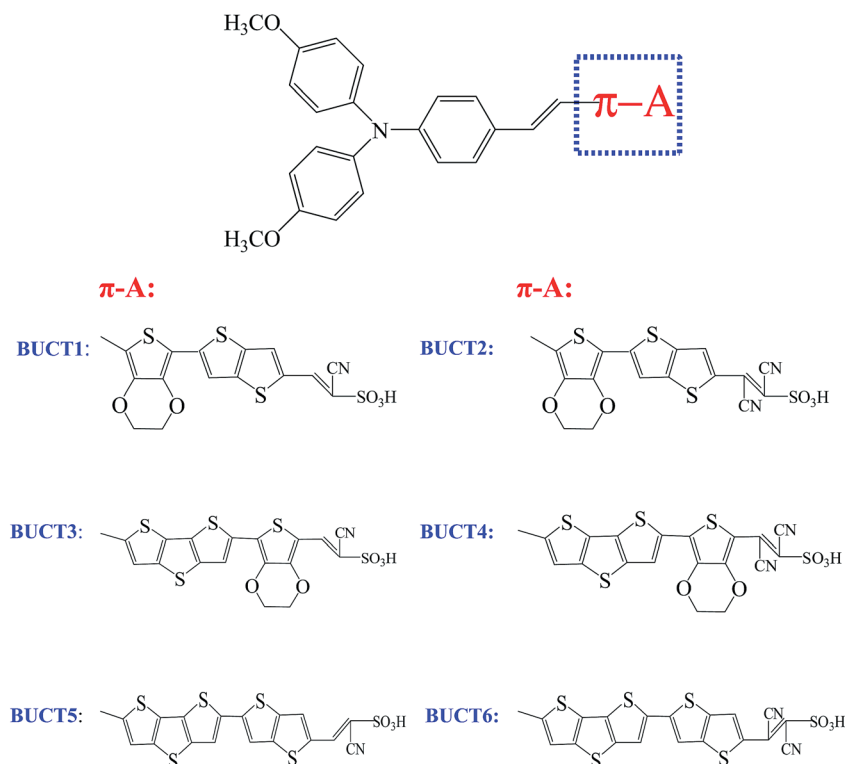


Fig. 8 Molecular structures of newly designed D- π -A triphenylamine derivatives.

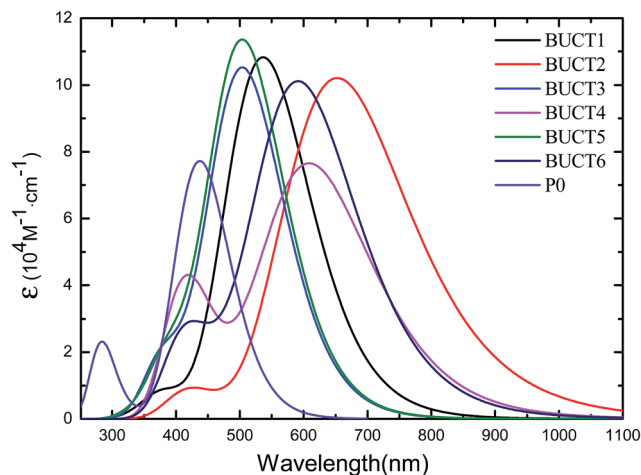


Fig. 10 Absorption spectra of BUCT1–BUCT6 dyes.

which the acceptors have only one $-\text{CN}$ group. As a result, the maximum absorption peak of dyes with two $-\text{CN}$ groups also exhibits apparent redshifts. In particular, the maximum absorption peak of **BUCT2** shows a 116 nm redshift compared to that of **BUCT1**. The maximum absorption peaks of **BUCT4** and **BUCT6** also exhibit similar phenomena compared to those of **BUCT3** and **BUCT5**. Therefore, we believe that the dyes with two $-\text{CN}$ groups and a sulfonic acid group as the electron acceptor are superior to the dyes with one $-\text{CN}$ group and a sulfonic acid group.

4. Conclusions

We have systematically investigated the molecular orbital energy levels, absorption spectra, and light harvesting efficiency of D- π -A type dyes designed by adopting different electron donors, π bridges and electron acceptors. The results indicate that the donor group in **D2**, π bridges in **Pi10–Pi12** and the acceptor group in **A7** are promising functional groups for D- π -A structure, because these functional groups significantly improve the absorption of visible light and the molar extinction coefficient of the dyes, and speed up intramolecular charge transfer from the electron donor to the electron acceptor.

By using the above screened promising functional groups as the donor, π bridge and acceptor, we reconstructed six novel D- π -A structures, **BUCT1–BUCT6**. The calculated results indicate that the **BUCT1–BUCT6** dyes show smaller HOMO–LUMO energy gaps, higher molar extinction coefficients and obvious redshifts compared to the experimentally synthesized **P0** dye. In particular, the newly designed **BUCT2** dye exhibits not only a 215 nm redshift and a higher molar extinction coefficient with an increment of 32.4% compared to **P0**, but also a extremely broad absorption spectrum covering the entire visible range up to the near-IR region of 1100 nm. Therefore, the **BUCT2** dye is a very promising candidate for highly effective DSSCs with near-infrared light harvesting up to 1100 nm. Interestingly, we also found that the dyes with two $-\text{CN}$ groups and a sulfonic acid group as the electron acceptor are more efficient than the ones

with one $-\text{CN}$ group and a sulfonic acid group. It is expected that this work can provide a new strategy for the design of new dyes for highly effective DSSCs, and can also encourage scientists to synthesize the new dyes with two $-\text{CN}$ groups and a sulfonic acid group as the electron acceptor, such as **BUCT2**, and further confirm the excellent performance of this type of the dye-sensitized device.

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