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Screening Donor Groups of Organic Dyes for Dye-Sensitized Solar Cells

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Abstract

Based on the experimentally synthesized dye **D5** (also named **d01** in this work), we design and screen a series of dyes **d02-d06** with different electron donors, such as diphenyl ethylene benzene, phenothiazine and perylene and **d07-d12** by modifying the donor of **d06** using different electron-donating groups. Results indicate that the donor in **d12** is promising electron donor. Therefore, we further design six novel D-π-A structures of **BUCT7-BUCT12** by using the electron donor in **d12** as donor, any two of 3,4-ethylenedioxy thiophene (EDOT), thienothiophene and dithieno[3,2-b:2',3'-d] thiophene (s-DTT) groups as π-conjugated bridge, and dicyanovinyl carboxylic acid and dicyanovinyl sulfonic acid as acceptor. The calculated results indicate that **BUCT7-BUCT12** dyes show smaller HOMO-LUMO energy gaps, higher molar extinction coefficients and obvious redshifts compared to experimentally synthesized **d01**dye. In particular, the newly designed **BUCT8** dye exhibits not only 134 nm redshifts and higher molar extinction coefficient with increment of 74.1% compared to **d01**dye, but also the extremely broad absorption spectrum covering entire visible range up to the near-IR region of 1000 nm. In addition, we also find that the dyes with dicyanovinyl sulfonic acid as the electron acceptor are superior to the ones with dicyanovinyl carboxylic acid.

Keywords: Dye-sensitized solar cells, Absorption spectrum, Donors, Organic dyes

1. Introduction

A large challenge for our global society is to find ways to replace the slowly but inevitably vanishing traditional fossil fuels caused by fast consumption of global development. It is an urgent task to develop the renewable and clean energy sources (such as power from wind and water, biomass and solar energy)[1] to avoid negative effects from the current energy system on climate, environment and health. Actually, solar energy is playing a crucial role in a future energy resource, which provides our planet with about 10^4 times more energy than our global daily consumption.[2] The dye-sensitized solar cells (DSSCs) are the photovoltaic device that uses molecules to absorb photons and directly convert them into electric charges without the need of intermolecular transport of electronic excitation. Currently, DSSCs[3-17] are receiving significant attention due to low cost, high efficiency and relatively little maintenance. Therefore, it is very significant to develop highly effective DSSCs for wide application of renewable energy. However, there are disadvantages which limit the wide use of DSSC, such as the relatively low efficiencies and the need for the liquid electrolyte.

To date, some investigators have reported the higher power conversion efficiency (PCE) than 11% by using metal-organic sensitizers and liquid electrolyte under AM 1.5. [7, 8, 18-21] Most recently, Grätzel research teams achieved a PCE exceeding 15%, further promoting the research of solar cells.[22] Actually, the PCE of the DSSC device is mainly determined by open circuit photovoltage (V_{oc}), short circuit current density(J_{sc}) and fill factor(FF). Improving the three key factors can significantly enhance the PCE of the DSSCs. Generally, the short circuit current density (Jsc) can be increased by improving the light harvesting efficiency (LHE) (LHE can be calculated by the equation of $LHE=1-10^{-f}$, where f represents the oscillator strength of adsorbed dye molecules) [23] as well as the molar extinction coefficients of the dyes, and broaden the absorption spectrum scope in the visible light and near-infrared region.

In DSSCs, the dye sensitizers were also considered as one of the most important components to improve overall device performance. Recently, the fully organic dyes with donor-spacer-acceptor (D-π-A) structure have attracted widespread interest.[9, 11, 24] In these D-π-A structure, donor group (D) is an electron-rich unit (such as triphenylamine, indole, dimethyl fluorene, phenothiazine), linked through a conjugated bridge (π) to the electron-acceptor group (A), which is directly bound to the TiO_2 nanocrystalline surface, usually through a carboxylix or cyanoacylic group. Important features of these dyes are that they hold the strong absorption of visible light and the presence of charge transfer excited states ensuring effective charge separation. Currently, designing highly effective D-π-A structure to further improve the PCE of the DSSCs device is still a great challenge.[2]

In order to obtain an excellent dye with high photocurrent, it should avoid the π-π aggregation, which will lead to intermolecular quenching or molecules residing in the system and therefore cannot be functionally attached to the TiO_2 surface. [2, 25, 26] Many organic molecules such as triphenylamine, phenothiazine are a non-planar structure which suppresses the aggregation. Sun et al. introduced triphenylamine as donor, thiophene ring as the π bridge and cyanovinyl carboxylic acid as acceptor to synthesize the **D5** dye (also named **d01**in this work), [8] and the resultant DSSC devices exhibit a PCE of 5.1% (the conventional ruthenium dye **N719**-sensitized DSSC device giving PCE about 6.1-6.4% in similar conditions,), which has attracted great attention due to its simple structure and outstanding photoelectric performance. [8, 9, 12, 24, 27-36]

In order to design outstanding dye donors with non-planar structure, we first screen a series of organic dyes with D-π-A structure by considering **d01**dye as prototype. Then, we recommend a kind of novel dye formed by the screened donor, π-conjugated bridge and acceptor groups for highly effective DSSCs with near-infrared light harvesting. [36]

2. Computational Details

Density functional theory (DFT) calculations were performed at the B3LYP level with the 6-31G(d) basis sets for the geometry optimization of these dye molecules without any symmetry constraints. The vibrational frequency calculation was also carried out in the same level to confirm that these dye structures are local minima on potential energy surfaces. The calculation results show that there is no imaginary frequency, indicating that these structures are stable in theory.

The previous investigations indicate that TDDFT is highly efficient and accurate in the calculations of the vertical excitation energy, electric properties and optical absorption. [24, 25]However, the different exchange-correlation (XC) functionals for charge-transfer excitations often show significant effects. To select suitable functional, we adopted different XC functionals, including B3LYP, CAM-B3LYP and WB97XD in TDDFT to evaluate the vertical excitation energies of **d01**. The calculated vertical excitation energies of different functionals are 1.959, 2.490 and 2.594eV with errors of 0.646, 0.115 and 0.011eV, respectively, compared to the experimental data 2.605 eV. Apparently, the vertical excitation energies of dyes were underestimated severely by B3LYP functional, and the long range-corrected (LC) functional (WB97XD) were in good agreement with the experimental values. Therefore, we adopted TD-WB97XD functional with 6-311+g(d,p) basis sets,[37, 38] and combined the conductor polarizable continuum model (CPCM)[4] in acetonitrile solution to predict the optical properties of newly designed dye molecules. All calculations were performed using a suit of the Gaussian 09 packages. [39]

3. Results and Discussion

3.1 Screening of the electron donor

The experimentally synthesized well-known organic dye **D5** is shown in Figure 1. [8]Here it is named as **d01** for simplification. The dyes **d02-d06** (Figure 1) were obtained by using indoline, phenothiazine, carbazole, tetrahydroquinoline and perylene groups as donor to replace the triphenylamine group of **d01**. It is found from the optimized geometric structures (Figure S1) that the π-conjugated bridges of **d01-d06** are the planar structure, which is greatly beneficial for the photo-induced electrons transfer from electron donor to electron acceptor. However, considering from the electron donor rather than π-conjugated bridge, we expect that its structure is non-planar, because it can effectively prevent the intermolecular π-π aggregation and the accumulation on TiO_2 surface, which causes the electron transfer between molecules and affects the PCE of DSSCs.

The triphenylamine dye **d01** as sensitizer of the DSSCs can expand the light absorption ability of dye. Its non-planar donor group can also inhibit aggregation of dye on TiO_2 surface,[8] and therefore was widely used as electron donor of other sensitizer. [25, 27, [29, 31, 32, 40] The electron donor in **d02** molecule is similar as **d01**, in which the three benzene rings of **d02** donor are mutually twisted, and the benzene ring linked π-conjugated bridge in **d02** donor and π-conjugated group have little distortion angle (Figure S1). The phenothiazine donor in **d03** is a well-known heterocyclic compound with electron-rich sulfur and nitrogen heteroatoms, and the phenothiazine ring is non-planar with a butterfly conformation. Thus, phenothiazine is a potential hole-transport semiconductor in organic devices,[34, 41-44] showing unique electronic and optical properties with D-π-A structure. The electron donors in **d04** and **d06** are planar conformation, which leads to the aggregation of dye on TiO_2 surface and therefore affects the PCE of DSSC. The donor of **d05** is non-planar due to the modification by using four methyl groups. The above observation indicates that the molecular conformation of desired dye can be designed by introducing suitable electron-donating groups. Compared to the optimized donor structures of **d01**, the **d02**, **d03** and **d05** may be suitable candidates for DSSC.

Figure 2 shows the energy levels for **d01-d06** in acetonitrile solution. The results indicate that the LUMO energies of **d01-d06** are higher than the conduction band edge(CBE) of TiO_2 electrode (about -4.0eV)[28], shown as a red dashed line in Figure 2. That is to say, these excitation state molecules could inject electrons into TiO_2 electrode successfully. In addition, the HOMO energies of **d01-d06** are lower than the potential (about -4.6 eV) of the I^- / I_3^- redox electrolyte.[28] Therefore, these dye molecules that lose electrons could get electrons quickly from the electrolyte. Compared to the energy gap of **d01**, the **d05** and **d06** may be suitable candidates for DSSC. However, the HOMO of **d05** is so close to the potential of redox electrolyte that has little reduction driving force, if we increase the π-conjugated bridge length.

The UV-Visible absorption spectra of **d01-d06** dyes in acetonitrile solution are shown in Figure 3. The maximum absorption peaks of **d02-d06** are 457, 452, 455,498 and 506 nm, in which **d02-d04** exhibit 21, 26 and 23nm blueshifts while **d05-d06** exhibit 20 and 28 nm redshifts, respectively, compared to that of **d01** (478 nm). The maximum molar extinction coefficients of **d02-d06** dyes also increase greatly (see Table 1). Definitely, the optical absorption spectra redshift and the maximum molar extinction coefficient indicate that the **d06** may be a good candidate as photosensitizer for DSSC device, which is consistent with the band gap results above. However, the planar conformation of the electron donor in **d06** molecule limits its application as an excellent photosensitizer of DSSC. In order to construct a non-planar donor structure in **d06,** we designed a series of dyes of **d07-d12** by using different electron-donating groups such as amino, methoxy, butyl, phenyl, aminobenzene and methylbenzene groups, as shown in Figure 1. The optimized geometries in Figure S1 show that the donors in **d07-d09** molecules are still a planar structure, but the the electron-donating groups in **d10-d12** create a non-planar structure with twist angles of 31.3°、29.7°and 31.5° with the donor plane. So, the **d10** and **d12** may be good candidates for DSSC. Synthetically considering their energy levels and absorption spectra, we find that the properties of **d12** are slightly better than **d10**. So, we select the electron donor in **d12** as donor for further designing novel dyes.

3.2 Design of novel D-π-A dyes

On basis of the above screening for the donor structure and the screening for the π-conjugated bridges in our previous research,[36] we further design six novel dyes **BUCT7-BUCT12** by employing the electron donor in **d12** as donor, any two of 3,4-ethylenedioxy thiophene (EDOT), thienothiophene and dithieno[3,2-b:2',3'-d] thiophene (s-DTT) groups as π-conjugated bridge, and dicyanovinyl carboxylic acid and dicyanovinyl sulfonic acid as acceptor. The **BUCT7-BUCT12** structures are presented in Figure 4. Interestingly, the optimized geometric structures (Figure S1) of the π-conjugated bridges of **BUCT7-BUCT12** are the planar, which is greatly beneficial for the photo-induced electrons transferring from electron donor to electron acceptor, while their donors are non-planar, which inhibit aggregation of dyes on TiO_2 surface.

The energy levels of **BUCT7-BUCT12** dyes in acetonitrile solution were shown in Figure 5. The results indicate that the LUMO energies of **BUCT7-BUCT12** are higher than the conduction band edge (CBE) of TiO_2 electrode (about -4.0eV),[28] shown as a red dashed line in Figure 4. That is to say, these excitation state molecules could inject electrons into TiO_2 electrode successfully. In addition, the HOMO energies of **BUCT7-BUCT12** are lower than the potential (about -4.6 eV) of the I^- / I_3^- redox electrolyte. Therefore, these dye molecules that lose electrons could get electrons quickly from the electrolyte.[28] The calculated results also indicate that **BUCT7-BUCT12** dyes show smaller HOMO-LUMO energy gaps compared to experimentally synthesized d01 dye.

Figure 6 shows the absorption spectra of **BUCT7-BUCT12** in acetonitrile solution. The maximum molar extinction coefficients of **BUCT7-BUCT12** dyes are 11.229×10^4, 11.216×10^4, 9.751×10^4, 9.658×10^4, $12.017\times10^4$and 11.878×10^4 $M^{-1}\cdot cm^{-1}$, respectively, exhibiting an increment of 49.9% ~ 86.5% compared to **d01**. The maximum absorption peaks of **BUCT7-BUCT12** are 588, 612, 574, 578, 557, and 562 nm, which show a large red-shifts ranged from 79 to 134 nm, compared to **d01**. **BUCT7-BUCT12** dyes show not only smaller HOMO-LUMO energy gaps, but also higher molar extinction coefficients and obvious redshifts compared to **d01** dye. In particular, the newly designed **BUCT8** dye exhibits not only 134 nm redshifts and higher molar extinction coefficient with increment of 74.1% compared to **d01** dye, but also the extremely broad absorption spectrum covering entire visible range up to the near-IR region of 1000 nm, which could be considered as panchromatic dyes. So, **BUCT8** dye may be a promising candidate for highly efficient DSSC devices.

In addition, we found although **BUCT8** has the same structure with **BUCT7** except the electron acceptor, **BUCT8** shows a smaller energy gap and a redshift of 24 nm compared to **BUCT7**. Similar results were observed in the comparisons of **BUCT9** and **BUCT10**, **BUCT11** and **BUCT12**. Therefore, we believe that the dyes with dicyanovinyl sulfonic acid as the electron acceptor are superior to the ones with dicyanovinyl carboxylic acid.

4. Conclusions

We have screened the series of dyes **d01-d12** and found that the donor in **d12** is promising functional electron donor. Then, we designed six novel D-π-A structures of **BUCT7-BUCT12** by using the electron donor in **d12** as donor, any two of EDOT, thienothiophene and s-DTT groups as π-conjugated bridge, and dicyanovinyl carboxylic acid and dicyanovinyl sulfonic acid as acceptor. Compared to the experimentally synthesized **d01** dye, the newly designed **BUCT7-BUCT12** dyes show smaller HOMO-LUMO energy gaps, higher molar extinction coefficients and obvious redshifts. In particular, the **BUCT8** dye exhibits not only 134 nm redshifts and higher molar extinction coefficient with increment of 74.1% compared to **d01** dye, but also the extremely broad absorption spectrum covering entire visible range up to the near-IR region of 1000 nm. In addition, we also found that the dyes with dicyanovinyl sulfonic acid as the electron acceptor are superior to the ones with dicyanovinyl carboxylic acid. It is expected that this work can provide guidance for synthesis of panchromatic dyes and also expected that the BUCT8 dye for highly efficient DSSCs can be confirmed by experiment.

Acknowledgements

This work is supported by National 863 Program (2013AA031901), NSF of China (No. 91334203, 21274011, 21121064), Outstanding Talent Funding from BUCT and Science Foundation (KYJJ2012-06-026) from CUP.

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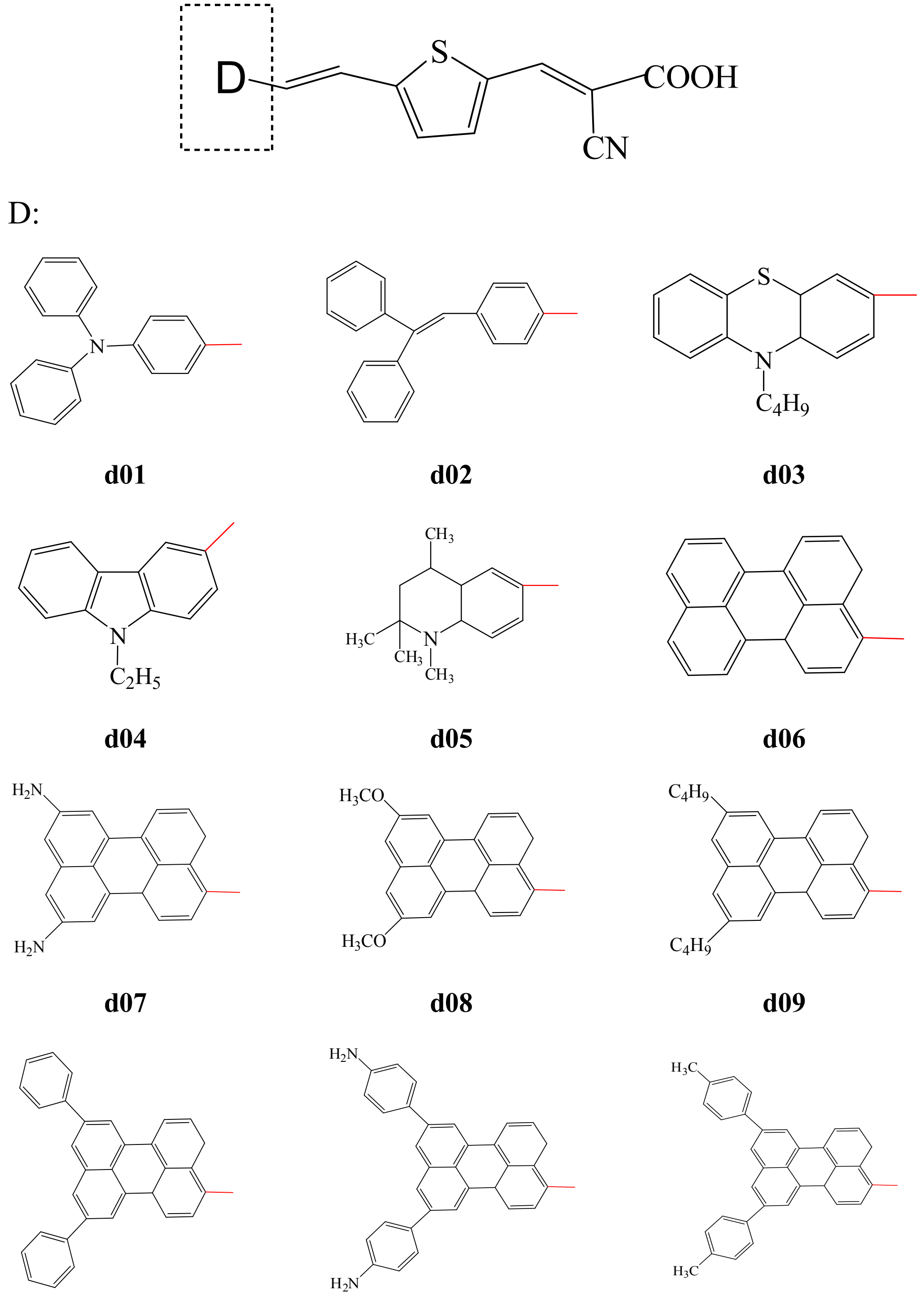
Table 1. The TDDFT calculated maximum absorption wavelengths λ (nm) , corresponding vertical excitation energies E_{ex} (eV), oscillator strengths f and the maximum molar extinction coefficient ε (10^4 $M^{-1} \cdot cm^{-1}$)

Dye	λ	E_{ex}	f	ε	Dye	λ	E_{ex}	f	ε
d01	478	2.5890	1.5910	6.444	**d10**	505	2.4530	1.9242	7.811
d02	457	2.7107	2.0130	8.112	**d11**	509	2.4343	1.9260	7.820
d03	452	2.7419	1.8777	7.605	**d12**	506	2.4474	1.9316	7.841
d04	455	2.7250	1.9082	7.728	**BUCT7**	588	2.1089	2.7494	11.229
d05	498	2.4874	1.9284	7.810	**BUCT8**	612	2.0259	2.7544	11.216
d06	506	2.4500	1.8382	7.458	**BUCT9**	574	2.3767	2.1601	9.751
d07	510	2.4308	1.7940	7.294	**BUCT10**	578	2.145	2.2509	9.658
d08	512	2.4213	1.7947	7.305	**BUCT11**	557	2.2264	2.7933	12.017
d09	508	2.4429	1.8968	7.690	**BUCT12**	562	2.2053	2.7824	11.878



d01 **d02** **d03**

d04 **d05** **d06**

d07 **d08** **d09**

d10 **d11** **d12**

Figure 1 Molecular structures of the dyes with different donors

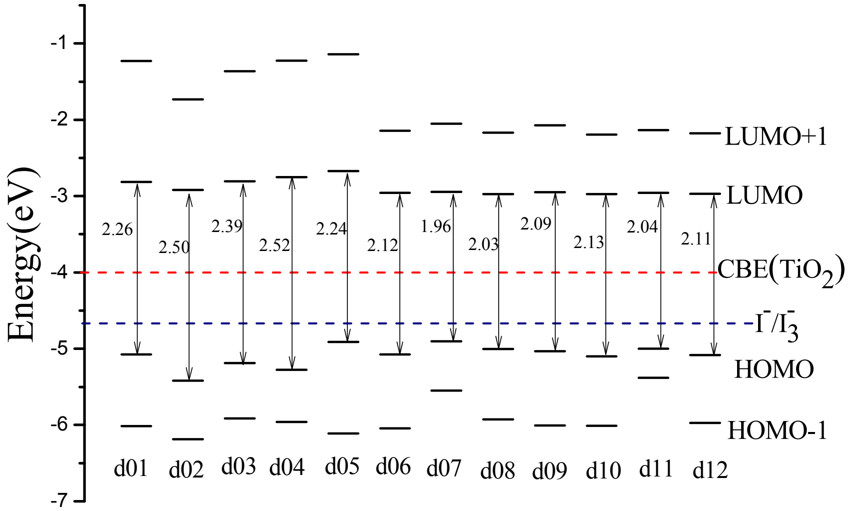


Figure 2 Energy levels for **d01-d12**dyes.

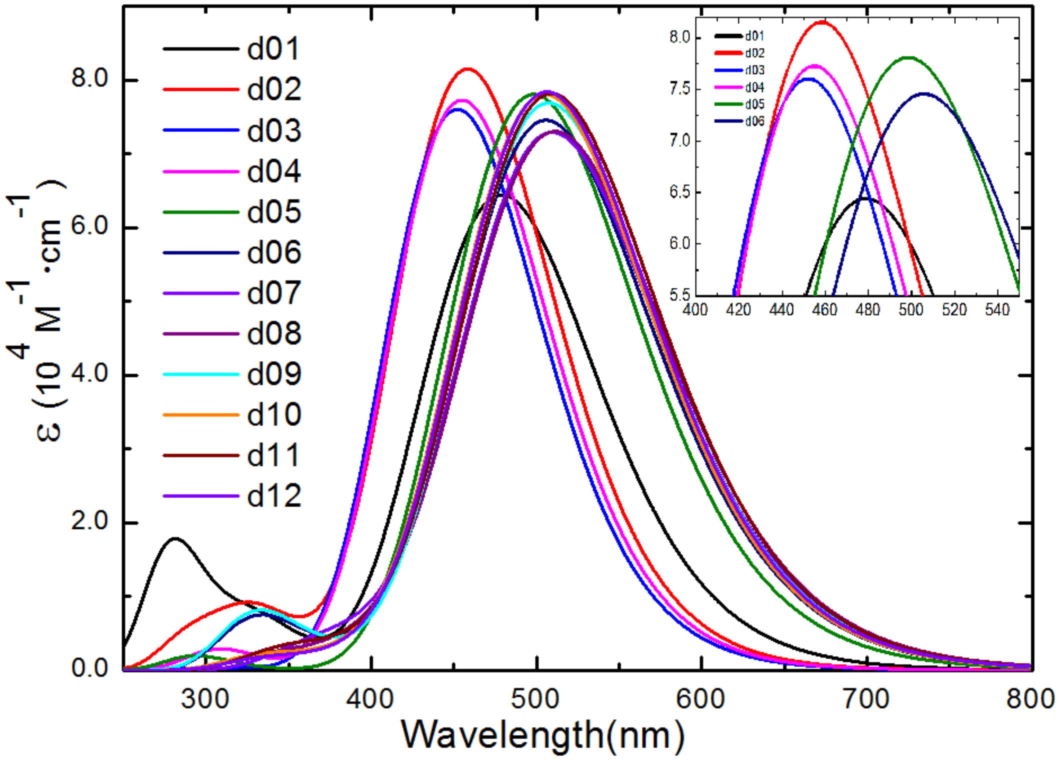


Figure 3 UV-Visible absorption spectra of **d01-d12** dyes

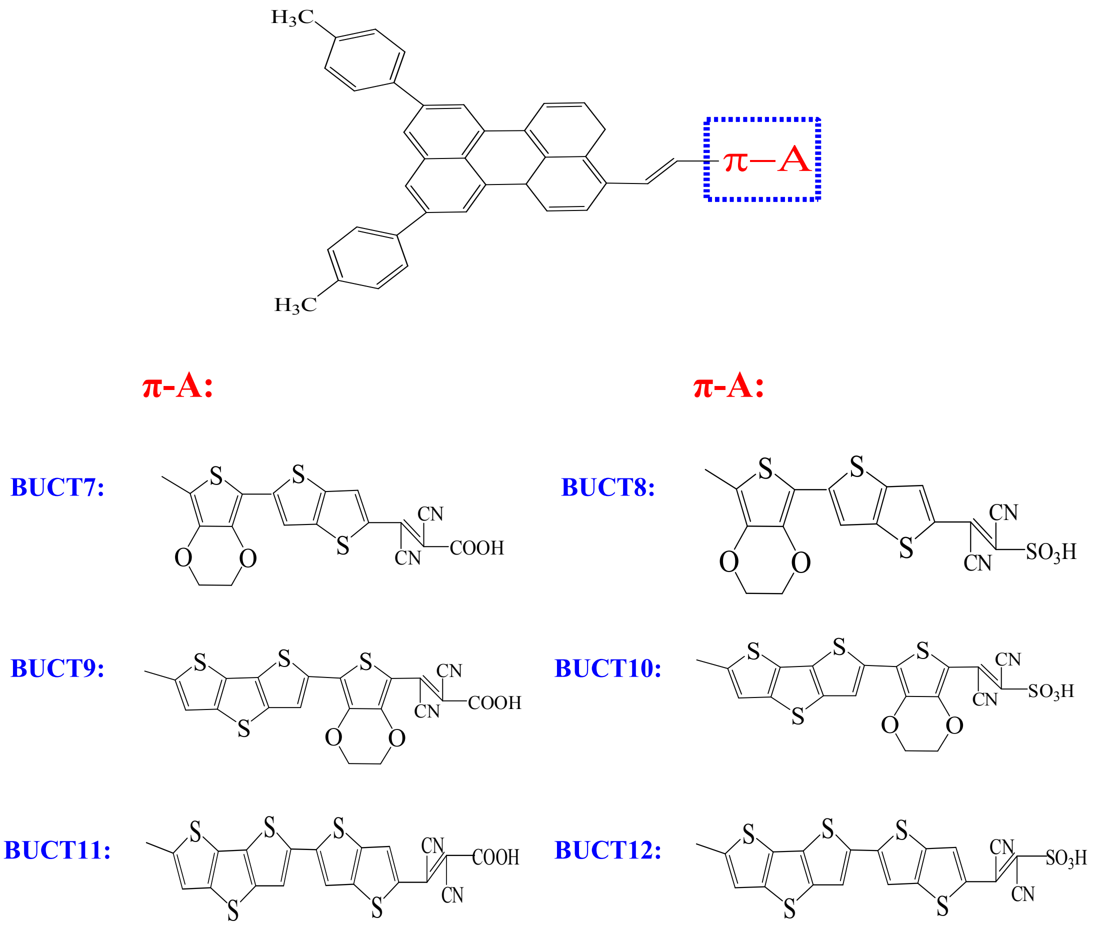


Figure4. Novel design dye structures of **BUCT7- BUCT12** dyes.

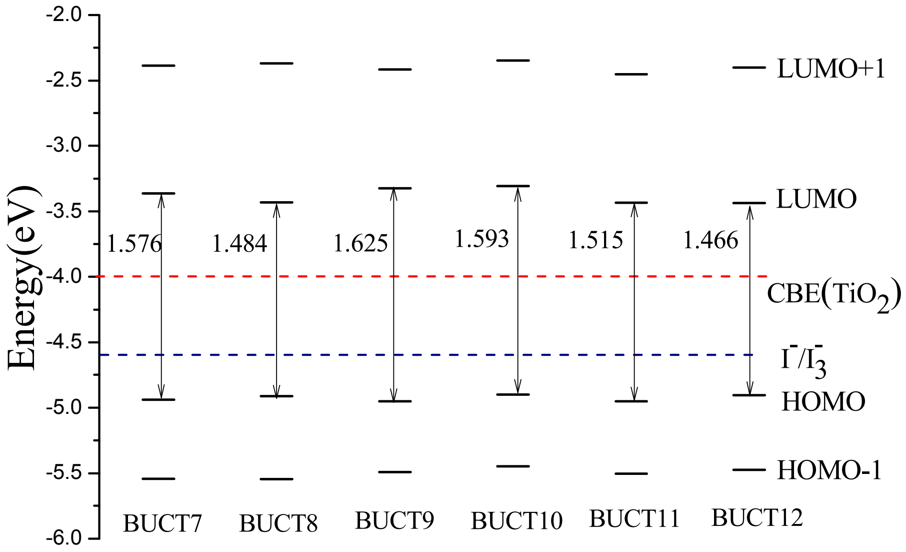


Figure 5. Energy levels for **BUCT7- BUCT12** dyes.

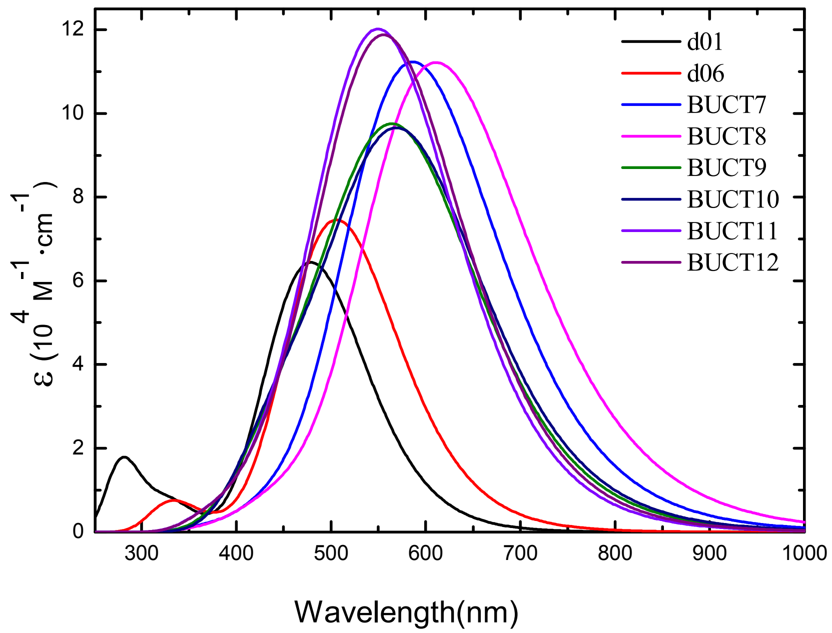


Figure 6. UV-visible absorption spectra of for **BUCT7- BUCT12** dyes