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Design strategies of metal free-organic sensitizers for dye sensitized solar cells: Role of donor and acceptor monomers

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ABSTRACT

A series of metal free organic sensitizers have been designed and their optoelectronic properties for DSSC applications have been systematically investigated using density functional theory (DFT) and time dependent density functional theory (TD-DFT) methods. The role of donor/acceptor monomers on the electron donating/withdrawing abilities has been discussed and promising donor–acceptor combinations are screened. Based on this screening, some of novel metal free sensitizers have been designed and their electronic and spectral properties have been investigated using DFT/TDDFT methods. Our results show that the designed molecules are promising candidates to provide good performances as sensitizers in the DSSC applications.

1. Introduction

Considering the environmental issues and renewable resources, more and more attentions have been paid on the solar energy utilizations. The dye sensitized solar cells (DSSCs) have attracted considerable interest after the report of O'Regan and Gratzel [1] due to the high photon-to-current conversion efficiency, easy production and cost-effective properties. In recent years, number of sensitizer molecules have been developed, which includes metal-free organic dyes [2–5], non-ruthenium metal dyes [6–9] and ruthenium (II)-polypyridly complexes [10–12] and reported their performances in the DSSC applications. At present, the state-of-the-art DSSCs are based on the ruthenium metal complexes, such as N3/N719 and black dye, which hold the record of the overall efficiencies up to 11.5% under standard (Global AM 1.5) irradiation [13–15]. However, there are some snags of ruthenium(II)-based sensitizers, for instance, containing expensive ruthenium metal, requires careful synthesis and tricky purification steps [16] which make researchers to find other possible solutions. Metal-free sensitizers are prepared rather inexpensively and compared to ruthenium-based complexes, these have larger molar extinction coefficient and higher energy absorption bands. Moreover, the major advantage of metal-free sensitizers is their tunable absorption and optoelectronic properties through suitable molecular design strategies [16].

Generally, the design of metal-free dyes is based on linking of electron donor/acceptor (D–A) systems through π-conjugated bridges (i.e., D–π–A molecular structure). Many novel D–π–A metal-free dyes with various donor moieties, such as coumarin [4,17], indoline [18], triphenylamine [3], phenothiazine [2], carbazole [19], and pyrrole [20], have been designed and used as efficient sensitizers for the DSSC applications. However, the photon-to-current conversion efficiency based on those sensitizers has been achieved up to 9.5% only, which is relatively low compared to the conventional Ru based sensitizers. In order to increase the efficiency of DSSCs, it is important to design

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the suitable dyes, which have reasonable optical properties. This could be possible if we design the sensitizer with the absorption spectrum covers visible-to-near-infrared range, have significant intra-molecular charge separation after absorbing sun light, and it should stably bind to the semiconductor surface so that electrons can inject to surface continuously [16,21,22].

Herein, we aimed to design a potential metal-free sensitizer which overcomes the flaws of existing dyes and to find an efficient way to tune optoelectronic properties. Nowadays, there are two ways in which the spectral properties of D–A or D–π–A molecules can be improved: changing the conjugation length of the sensitizer, and substituting different electron -rich and -deficient units to modify the spectrum. Previously it is reported that, some D–A oligomers have dual-band optical absorption spectra which provide broad absorption characteristics [23,24]. In general, dual-band absorption spectrum arises from two separate transitions, which lead to either charge transfer between the donor and acceptor units along with a π–π^* transition (so-called intra-molecular charge transfer, ICT) [25,26], or reorganization of molecular orbitals to produce accessible low- and high-lying energy levels spread across both donor and acceptor units (usually named as π–π^* transition to make a distinction from ICT) [27–29]. In the present study, we selected 12 monomers which are systematically varied by both in the donor and acceptor-units, to form the different π-conjugated D–A oligomers and evaluated their optoelectronic properties. The selected 12 monomers are thiophene (T), thienopyrazine (TP), dithienopyrazine (DTP), thiadiazolothienopyrazine (TDTP), 1,4-dihydro-1-phenylpyrazine (PPP), cyclopentadithiophene (CDT), dicyanomethylidene-cyclopentadithiophene (CDM), 9-phenylcyclopentadithiophene (TPAT), N,N-bis (4-methoxy-phenyl)-thiophene-2-amine (MPTA), 10-phenyl-10H-phenothiazine (PTAZ), triphenylamine (TPA), 4-methoxy-N-(4-methoxyphenyl)-N-phenyl- benzeneamine (MPBA), and 9-phenyl-9H-carbazole (PC). These monomers are derived from the several compounds [30], which are universally used in the design of D–A oligomers, namely thienopyrazine, thiophene, thiazine, carbazole, and phenylamine compounds, thus the resulting 66 D–A oligomers could be applied as a model system to represent the general classes of D–A oligomers.

2. Computational details

All the calculations in this study were performed with Gaussian 09 package [31]. The geometries of neutral monomers and metal-free sensitizers were optimized using B3LYP exchange correlation functional [32] combined with the standard double-ζ plus polarization basis set, 6-31G(d) [33]. Different basis sets and functionals in gas phase did not affect the structural parameters much, but it influences the optoelectronic properties such as excitation energies and intensities. Hence, we have performed a benchmark calculation in order to find the most suitable method for simulating UV–Vis absorption. For this, we considered four DFT methods such as, PBE0, B3LYP, BHandHLYP and CAM-B3LYP to calculate the UV–Vis absorption spectra for TC-1 [34], T2-1 [2] and I-1 [35] molecules of D–A type and L1 [36], TA–St–CA [3] and MK2 [19] molecules of D–π–A type. We used 6-31G (d) basis set for all the benchmark calculations and the calculated excitation energies of D–A type and D–π–A type molecules are shown in Table 1.

Compared with the experimental values of D–A and D–π–A types of molecules, the calculated results show that the absorption energy from B3LYP was more accurate for D–A system and BHandHLYP method show perfect agreements for D–π–A system which contains longer conjugated length. Considering that D–π–A backbone molecules are main structures in real DSSCs, therefore, we choose BHandHLYP functional to calculate the optoelectronic properties of D–π–A molecules including 20-lowest excitation energies and intensities of all the metal-free sensitizers considered here.

The optoelectronic properties were transformed, using the SWizard program [37,38], into simulated spectra as described before, using Gauss functions with half-widths of 4000 cm^{-1}, as shown in following equation:

$$\varepsilon(\omega) = c_1 \sum_1 \frac{f_I}{\Delta_{1/2,I}} \exp\left(-2.773 \frac{(\omega - \omega_1)^2}{\Delta^2_{1/2,I}}\right) \quad (1)$$

where ε is the molar extinction coefficient given M^{-1} cm^{-1} in unit; the energy ω of all the allowed transitions included in Eq. (1), is expressed in cm^{-1}; f_I and $\Delta_{1/2}$ are the oscillator strength and the half-bandwidths, respectively.

3. Results and discussion

3.1. The classification of donor- and acceptor-monomers

The molecular structures of 12 selected monomers considered in this study are summarized in Fig. 1. These selected monomers are then classified whether they belong to donor- or acceptor-monomer and then, every possible combination of different donor- and acceptor-unit is combined together to form 66 D–A oligomers. This classification is made on the basis of their vertical ionization potential (IP_v), vertical electron affinity (EA_v), and HOMO/LUMO energy levels. As described by Dixon et al. [39], stronger donor has smaller IP_v (easy to lose an electron) and higher HOMO level that would lose electrons easily; and stronger acceptor has more negative value of EA_v (easily to gain an electron) and lower LUMO level which would accept electrons strongly. Therefore, we have calculated

Table 1
The calculated UV–Vis absorption energies (in nm) for D–A and D–π–A sensitizers using different DFT methods.

Sensitizers	PBE0	B3LYP	BHandHLYP	CAM-B3LYP	Exptl.[a]
TC-1	451.7	401.7	354.3	359.0	400
T2-1	441.6	461.7	367.2	370.2	452
I-1	435.9	453.3	374.4	381.6	483
L1	482.4	506.9	405.8	404.3	405
TA–St–CA	504.5	534.2	409.3	403.0	410
MK2	575.2	612.8	481.5	472.6	480

[a] Taken from Refs. [2,3,19,34–36].