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ORIGINAL ARTICLE

Electro-optical and charge injection investigations of the donor-π-acceptor triphenylamine, oligocene–thiophene–pyrimidine and cyanoacetic acid based multifunctional dyes

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Abstract The corner stone of present study is to tune the electro-optical and charge transport properties of donor-bridge-acceptor (D-π-A) triphenylamine (TPA) derivatives. In the present investigation, an electron deficient moiety (pyrimidine), electron-rich moiety (thiophene) and oligocene (benzene, naphthalene, anthracene, tetracene and pentacene) have been incorporated as π-spacer between the donor TPA unit and cyanoacetic acid acceptor and anchoring group. The elongation of bridge usually affects the energy levels, i.e., higher the highest occupied molecular orbital (HOMO) while lower the lowest unoccupied molecular orbital (LUMO) thus reduces the HOMO–LUMO energy gap. The lowered LUMO energy levels of cyano-{2-[6-(4-diphenylamino-phenyl)-pyrimidin-4-yl]-tetraceno[2,3-b]thiophen-8-yl}-acetic acid (TPA-PTT4) and cyano-{2-[6-(4-diphenylamino-phenyl)-pyrimidin-4-yl]-pentaceno[2,3-b]thiophen-9-yl}-acetic acid (TPA-PPT5) dyes revealed that electron injected from dye to semiconductor surface might be auxiliary stable resulting in impediment of quenching. The broken co-planarity between the π-spacer conceiving

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LUMO and the TPA moiety would help to impede the recombination process. Moreover, it is expected that TPA derivatives with the tetracenothiophene and pentacenothiophene moieties as π-bridge would show better photovoltaic performance due to lowered LUMO energy level, higher electronic coupling constant, light harvesting efficiency and electron injection values.

1. Introduction

The compounds with the π-backbone showed prominent optoelectronic and charge transport properties in different high-tech fields, e.g., sensors (Niu et al., 2006), organic light emitting diodes (OLEDs) (Makoto Satsuki and Sadaharu Suga, 2007), organic field effect transistors (OFET) (Marks and Hersam, 2015) and photovoltaics (Chambon et al., 2013). Previously, numerous inorganic materials were studied with respect to the solar cell (Green et al., 2012) and to sense the humidity (Traversa et al., 1996; Li et al., 2004). The traditional technology (silicone), have environmental and economic issues. Moreover, metal oxides are being used in the film making of dye-sensitized solar cells, (DSCs) (O'Regan and Gratzel, 1991) and humidity sensors (Suri et al., 2002; Hsu et al., 2014). Nowadays, organic materials are being used due to their low cost, light weight, structural flexibility and fabrication simplicity. Finally, the organic dyes are favorite contenders for power conversion and sensing applications.

The power conversion efficiency (PCE) has been observed as 13% when using the porphyrin dye (Mathew et al., 2014) showing a competitive and potential renewable power generation technology. In DSCs, the dye sensitizer is a key component which has been widely designed and investigated to enhance the PCE that also harvests solar photons and starts charge separation from the excited state of the sensitizer into the conduction band of the semiconductor through photoinduced electron transfer (Bessho et al., 2009; Han et al., 2012).

Molecular engineering to model/design efficient dyes play a vital role in tuning the electro-optical and charge transport properties, i.e., light excitation should accompanyelectron injection from the light-harvesting unit toward the anchoring group. This can be attained by incorporating the strong conjugation between the donor moieties and anchoring groups as well as decent electronic coupling between the lowest unoccupied molecular orbital (LUMO) of the dye and conduction band of the semiconductor. The PCE can be improved by diminishing the aggregation of the sensitizer on the semiconductor surface. Moreover, "bulk heterojunction" (BHJ) solar cells are also gaining significant attention (Hoppe and Sariciftci, 2006). The organic π-conjugated materials are being used in DSCs, BHJ solar cells and humidity sensors.

Triphenylamine (TPA) has revealed promising properties as donor (Hagberg et al., 2007; Liang and Chen, 2013) and its propeller shape can suppress the dye aggregation (Bonhôte et al., 1999). Cyanoacetic acid showed promising characteristics as stable anchoring and strong acceptor groups (Chen et al., 2014; Zhang et al., 2015). Usually, π-spacer can directly influence the energies of the highest occupied molecular orbital (HOMO), LUMO, absorption spectrum, and the charge separation upon photoexcitation of the sensitizer (Haid et al., 2012). Thus the choice of a suitable π-spacer is very crucial. It has been proven that thiophene would be a good constitutional unit which can increase the light harvesting efficiency and charge transport properties (Zhang et al., 2009; Tian et al., 2010). Similarly, oligocenes are also being used as proficient π-spacers to tune the electro-optical and charge transport properties (Liu et al., 2014).

Quantum chemical calculations are prevailing tools (Goedecke et al., 2012) which provide guidelines for the organized and rational tuning of the dyes (Pastore et al., 2010a,b). It is well-known that density functional theory (DFT) and Time Dependent DFT (TD-DFT) are reasonable methods to calculate electronic structures, electronic excitations, predict the electro-optical and charge transport properties of organic chromophores with adequate accurateness (Cave and Castner, 2002; Persson et al., 2006; Pastore et al., 2010b). We designed systematically five new TPA derivatives to tune the electro-optical properties and dye's photoabsorption. In newly designed donor-bridge-acceptor derivatives TPA acts as electron donor, oligocenothiophene–pyrimidine as π-spacer and cyanoacetic acid as an electron acceptor and anchoring group, i.e., cyano-{2-[6-(4-diphenylamino-phenyl)-pyrimidin-4-yl]-benzo[b]thiophen-5-yl}-acetic acid (TPA-PBT1), cyano-{2-[6-(4-diphenylamino-phenyl)-pyrimidin-4-yl]-naphtho[2,3-b]thiophen-6-yl}-acetic acid (TPA-PNT2), cyano-{2-[6-(4-diphenylamino-phenyl)-pyrimidin-4-yl]-anthra[2,3-b]thiophen-7-yl}-acetic acid (TPA-PAT3), cyano-{2-[6-(4-diphenylamino-phenyl)-pyrimidin-4-yl]-tetraceno[2,3-b]thiophen-8-yl}-acetic acid (TPA-PTT4) and cyano-{2-[6-(4-diphenylamino-phenyl)-pyrimidin-4-yl]-pentaceno[2,3-b]thiophen-9-yl}-acetic acid (TPA-PPT5), see Fig. 1.

We have studied the energy levels and distribution patterns of the frontier molecular orbitals (HOMO, LUMO), excitation energies, oscillator strengths, electronic coupling constants, electron injection, light harvesting efficiencies and structure–properties relationship. The conclusions drawn from quantum chemical calculations are appreciated as guidelines for the synthesis of innovative proficient dyes (Casanova et al., 2010; Zhang et al., 2012).

2. Computational details

In previous studies it has been shown that DFT is good method to optimize the ground state geometries, particularly B3LYP/6-31G** level of theory is reasonable and precise choices for TPA sensitizers. Preat and co-workers optimized the ground state geometries of TPA based sensitizers at B3LYP/6-31G** level and found it to be a rational approach then they studied the charge transport properties (Preat et al., 2010). Moreover, in another study, they investigated the basis set effect on the properties of interests and did not find a significant effect on bond lengths (Preat et al., 2009). The structural and electronic