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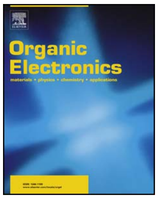

Effective photo-harvesting by dye sensitized solar cell based on dihydrothieno [3,4-b][1,4] dioxine bridge based metal free organic dye

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ABSTRACT

Here in design and synthesized new dimer organic metal free dyes based on various donor moieties along with dihydrothieno [3,4-b][1,4] dioxine and cynoacrylic acid are bridge and acceptor respectively. The influence of dye consist various donor moieties like phenothiazine (PTZ), phenoxazine (POZ) and carbazole (CBZ) studied carefully. The same donor and acceptor groups optical and electrochemical properties change when we change donor groups. The all dyes structure geometry optimization and energy levels (HOMO-LUMO) was calculated by density functional theory (DFT) with B3LYP/6-31G(d.p) basis set. It is evident from the studies that the strong electron withdrawing donor moiety based dye, POZ-102 exhibit highest short circuit current density (J_{sc}), open circuit voltage (V_{oc}) and efficiency ($\eta = 6.4\%$). The inside device electron recombination and electron lifetime was calculated by impedance spectroscopy and open circuit voltage decay techniques. In last the highest efficiency achieved POZ-102 dye based device checked long term stability up to 500hr under 100 mW/cm^2 light illumination.

1. Introduction

Owing to the fast and constant reduction of fossil fuel resources, there are nowadays severe problems that oblige the search for alternative sources of energy which will be adequate to supply for the world's growing energy necessities. Renewable solar energy, which is massive and fundamentally everlasting, has the main prospective to fulfil the future global energy requirement without substantial environmental problems [1,2]. In the last twenty years, dye-sensitized solar cells (DSSCs), a historical know-how, has been previously intensively investigated as a favourable, low-cost alternative to traditional pen junction solar cells as O'Regan and Gratzel stated functioning DSSCs in 1991 [3,4]. These devices use different types of components such as nanocrystalline semiconductors (i.e. TiO_2, ZnO, NiO, etc), photosensitive dyes (i.e. metal free and metal-based dyes), redox mediators (i.e. Iodine, Co(II/III), Bromine, sulpher, etc.) and last counter electrodes (i.e. Pt, Carbon, metal composite, etc.). Among them dye is the heart of the DSSCs device.

Metal-free sensitizers have much stronger light-harvesting ability compared to metal-based sensitizers because of their great molar extinction coefficients, ease of customized molecular design for showing wanted photo physical and photochemical properties, cheap without the need for transition metals, and environment friendliness. D-π-A dye has been successfully employed in numerous optoelectronic devices, like non-linear optics [5], electro-generated chemiluminescence [6], photovoltaic cells [7], fluorescent sensors [8] and organic light emitting diodes [2]. They are also commonly used in DSSCs [9–11] primarily due to the likelihood of fine-tuning their optical and electrochemical properties by structural changes limited only by the creativity of the designers and feasibility of the synthesis. While –CCNCOOH still remains the best acceptor group of choice, throughout years many donors were changed, among this coumarin [12,13], phenoxazine [14,15], dialkyl-aminophenyl groups [16–18], carbazole [19,20], triphenylamines [21–23], indoline [24,25] and phenothiazine are enough promising [26–29].

The thickness (of TiO_2 photoanode), composition and structure of the dye layer at the interface on TiO_2 play a vital role in the effectiveness of DSSCs [30]. If the electrolyte (iodide/triiodide) ions enter the sensitizer layer easily, the recombination rate of electrons generated at the sensitizer-TiO_2 interfaces with the electrolyte (I^-/I_3^- redox couple) will increase in the DSSC, reducing open-circuit voltage (V_{oc}) significantly. If electrolyte ions (in case of ionic liquid based electrolytes) [31,32] poorly enter into the sensitizer layer, the potential drop will extend over a larger distance on the TiO_2 photoanode, thus

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Table 1
Summary of reported dimer dyes along with photovoltaic parameters.[a]

Dyes (Donor moiety)	J_{sc} (mA cm^{-2})	V_{oc}, (V)	FF, (%)	PCE (%)	Ref.
PTZ	7.86	0.74	71	4.1	[35]
PTZ	9.29	0.75	68	4.7	
PTZ	6.98	0.74	69	3.5	
PTZ	10.9	0.71	68	5.2	
PTZ	11.9	0.74	66	5.8	[36]
PTZ	12.2	0.76	66	6.1	
IND	1.63	0.632	70	0.9	[37]
IND	1.87	0.640	72	1.0	
IND	1.91	0.692	71	1.2	
POZ	6.81	0.743	62	3.9	
DPA +CBZ	5.73	0.715	69	2.8	[38]
DPA + PTZ	8.98	0.756	69	4.6	
DPA + PTZ	10.7	0.687	70	5.2	
PTZ	9.44	0.550	63	3.2	[39]
PTZ	12.1	0.590	68	4.8	
PTZ	9.03	0.631	62	3.5	[34]
PTZ	10.3	0.628	60	3.9	
PTZ	9.8	0.570	61	3.4	[40]
PTZ	3.1	0.510	68	1.1	
PTZ	3.4	0.540	71	1.3	

[a] All dyes sensitized on TiO_2 nanocrystalline film, PTZ = phenothiazine, IND = indole, DPA = diphenylamine, POZ = phenoxazine, CBZ = carbazole.

inducing a longer electron lifetime in DSSCs [33]. Henceforth, it is obvious that the operation and performance of DSSCs will be intensely influenced by the morphology of the adsorbed sensitizer molecules, layer thickness, and chemical structure of photosensitizers [34]. In this article, we have designed and synthesis dimer of organic metal free dyes with different donor moieties (phenothiazine (PTZ), phenoxazine (POZ) and carbazole (CBZ)) based chromophores in a molecule. The –CCNCOOH acceptor property of dye on the TiO_2 photo anode surface is critical in achieving high photovoltaic efficiency in DSSCs. The concept of multiple acceptors groups in a dye was already known in ruthenium-based (N719, N3) and metal-free organic sensitizers which revealed that the multi -COOH acceptors achieved good efficiency in the DSSCs. Table 1 summarises the variously reported dimer D-π-A dye as a sensitizer in DSSCs.

Therefore, we have selected three different (CBZ, PTZ and POZ) donor moieties, which has two major advantages; (i) donor moiety is non-planar and therefore can hinder the molecular aggregation and the formation of intermolecular excimers; (ii) moiety having electron-releasing *N* and *S* heteroatoms. Moreover, the use of dihydrothieno [3,4-b][1,4] dioxine bridges [41–43] in the molecular design is not only beneficial to suppress dye aggregation, but it also helps to transfer electrons completely from donor to acceptor groups (Scheme 1).

As shown in Scheme 1, PTZ-101, POZ-102 and CBZ-103 having symmetric D-π-A chains linked by dihydrothieno [3,4-b][1,4] dioxine resulting two separate light-harvesting systems would enhance the absorption intensity and broaden the absorption range due to the absorption overlap and complement of both the donors and acceptor groups at the same time. These dimer sensitizers might be expected to depress aggregation of the dye on the TiO_2 surface to increase the electron life time since the better surface protection, which would enhance the overall performance of the DSSCs.

2. Experimental

2.1. Materials and reagents

Phenothiazine, carbazole, phenoxazine, 7-bromo-2,3-dihydrothieno [3,4-b][1,4] dioxine-5-carbaldehyde, electrolytic-copper powder, potassium carbonate, o-dichlorobenzene,Dichlorobenzene, 18-crown-6-ether were purchased from TCI chemical Ptv. Ltd. China. NBS, THF, KOAc, Bis (Pinacolato)diboron, $Pd(dppf)Cl_2$, $Pd(PPh_3)_4$, cyanoacetic acid, piperidine, CAN were purchased from Sigma-Aldrich. Meltonix tap and fluorine doped tin oxide (FTO) glass ($12\,\Omega/cm^2$) were procured from Solaronix Switzerland. The ethyl cellulose, alpha-terpineol, TiO_2nanocrystalline were purchased from Sigma-Aldrich and used as received. All the reagents were purchased from Sigma-Aldrich with 99% purity. The synthesis procedure of dimer dyes is given in Scheme 2.

2.2. Synthesis procedure

2.2.1. Synthesis compound (1a-3a)

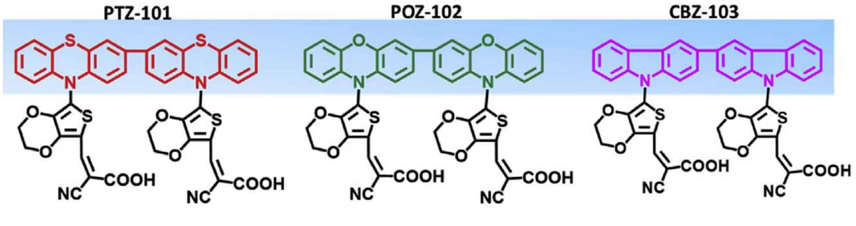
A mixture of phenothiazine (5.82 g, 29 mmol), 7-bromo-2,3-dihydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde(2.5 g, 10 mmol), electrolytic-copper powder (2.72 g, 44 mmol), potassium carbonate (11.94 g, 88 mmol) in o-dichlorobenzene (50 ml) was stirred at 180 °C for 2 days. Hot inorganic salts were filtered and under reduced pressure the solvent was removed. The purification of the crude product was performed by column chromatography via silica gel and an organic solvent as the mobile phase to yield **1a** (5.04 g, 60%) as a solid colorless powder. The same preparation-procedure of compound **1a** is followed for **2a** and **3a**, only by replacing donor moieties.

2.2.2. Synthesis compound (1b-3b)

Compound 1a (0.86 g) was dissolved in THF (15 ml) and the temperature was maintained at 0 °C. Then *N*-bromo-succinimide (NBS) (0.44 g) dissolved in THF (4 ml) was introduced gradually under nitrogen. Thin layer chromatography monitored the reaction and the temperature was set to 75 °C. The reaction mixture was lowered to room temperature after six hours and poured into the water. The product was extracted with dichloromethane (100 ml) and the organic layer was washed three times with brine solution. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated on a rotary evaporator. The purification of the final product was done by column chromatography using silica gel and HA/DCM (2:1) as the mobile phase to provide dark yellow solid (0.58 g) in 77% yield (compound **1b**). The same preparation-procedure of compound **1b** is followed for **2b** and **3b**, only by replacing donor moieties.

2.2.3. Synthesis compound (1c-3c)

The mixture of compound 1b (1 mmol), bis(pinacolato)diboron (1.3 mol) and potassium acetate (2.5 mol) was dissolved in THF solvent, using nitrogen gas; $Pd(dppf)Cl_2$ (4.5%) was put and agitated at 90 °C for 8 h. Distilled water was added and the mixture was extracted 3 times with ethyl acetate before the organic phase was washed with water and dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography (EA/HA, 0.1:2) on silica gel to yield **1c** (65% yield). The same preparation-procedure of compound 1c is followed for



Scheme 1. Chemical structure of PTZ, POZ and CBZ based dimer sensitizers.