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# DDQ as an effective p-type dopant for the hole-transport material X1 and its application in stable solid-state dye-sensitized solar cells

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ABSTRACT

X1 (MeO-TPD) is an inexpensive and easily synthesized $\pi$-conjugated molecule that has been used as a hole-transport material (HTM) in solid-state dye-sensitized solar cells (ssDSSCs), achieving relatively high efficiency. In this paper, we characterize the physicochemical properties of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and show that it is a promising p-dopant in a spin-coating solution with X1 as the HTM. The doped ssDSSCs showed an increase in short-circuit current density from 5.38 mA $cm^{-2}$ to 7.39 mA $cm^{-2}$, and their overall power conversion efficiency increased from 2.9% to 4.3%. Also, ssDSSCs with DDQ-doped X1 were more stable than the undoped samples, demonstrating that DDQ can act as a p-type dopant in X1 as an HTM for highly efficient, stable ssDSSCs.



## 1. Introduction

Among all the renewable energy technologies, photovoltaic technology is considered as the most promising approach to alleviate the energy crisis. A low cost, high-efficiency solar cell based on dye-sensitized mesoporous $TiO_2$ film called dye sensitized solar cells (DSSCs) was firstly reported by Grätzel and O' Regan in 1991 [1]. Since then, the effort and research on DSSCs have been activated [2–6], to date, the overall power conversion efficiency of this type of solar cells with a co-sensitized technique was increased to 14.3% [7], which is comparable to conventional silicon solar cell. However, liquid-state DSSCs still have critical challenges such as leakage, volatilization, and corrosion of the redox-active liquid electrolytes, constraining its wide application [8].

Recently, many attempts have been made to replace the liquid electrolyte with p-type semiconductor or organic low-molecular-weight compound as the hole-transport material (HTM) to produce an all-solid-state DSSC (ssDSSC). The operation mechanism of an ssDSSC can be summarized as follows: once photons are absorbed by a sensitized dye, excited electrons in the lowest unoccupied molecular orbital (LUMO) of the sensitizer are rapidly injected into the conduction band of $TiO_2$, leaving holes in the dye molecules, forming dye cations, which are later regenerated by electrons from the HTM. The hole transporter is then restored at the counter electrode, and the circuit is finished by electron migration through an external load [9]. Hence, HTMs play an important role in ssDSSCs. Because 2,2'7,7'-tetrakis(N,N-dimethoxyphenylamine)–9,9'-spriobifluorene (Spiro-OMeTAD; Fig. S4) is quite soluble in common organic solvents, it has been widely used as HTM since 1998 [10]. ssDSSCs based on a novel quinoxaline-based sensitizer and Spiro-OMeTAD as the HTM have displayed an impressive power conversion efficiency (PCE) of 8.0% under AM 1.5 G (100 mW $cm^{-2}$) simulated solar irradiation [11]. However, its high cost, fairly low conductivity due to its twisted spiro-carbon structure, and relatively poor infiltration [12] into nanocrystalline $TiO_2$ have made alternatives desirable.

In 2013, Sun et al. produced ssDSSCs with triphenylamine-based oligomer hole-transport material named X1 (MeO-TPD; Fig. 1), which showed a power conversion efficiency of 4.8% [13]. Recently, Xu et al. developed X1 as HTM doped with silver bis(trifluoromethanesulfonyl)imide (AgTFSI), improving performance to 5.8% [14]. Because of its low cost, easy preparation and good solubility, X1 has been a promising HTM in ssDSSCs.

A simple way to enhance hole transport in HTMs is chemical doping. Many such additives have been introduced to and studied in ssDSSCs, such as $(p\text{-}BrC_6H_4)_3NSbCl_6$[10], silver bis(trifluoromethanesulfonyl)imide (AgTFSI) [15], $SnCl_4$ [16], cobalt (III) complexes [17,18], 1,1',2,2'-tetrachloroethane (TeCA) [19], and F4TCNQ [20]. Charge transfer appears to occur between the electron acceptor 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; Fig. 1) and the electron donor thiazolidine-2-thione

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**Table 1.** The conductivity of ssDSSCs with various DDQ dopant ratios (S/cm).

| | Pristine | With 0.04% DDQ | With 0.08% DDQ | With 0.16% DDQ |
|---|---|---|---|---|
| Conductivity[a] | $5.46 \times 10^{-4}$ | $1.96 \times 10^{-3}$ | $2.22 \times 10^{-3}$ | $1.04 \times 10^{-3}$ |

[a] All data of conductivity is calculated from the method of reported literature.

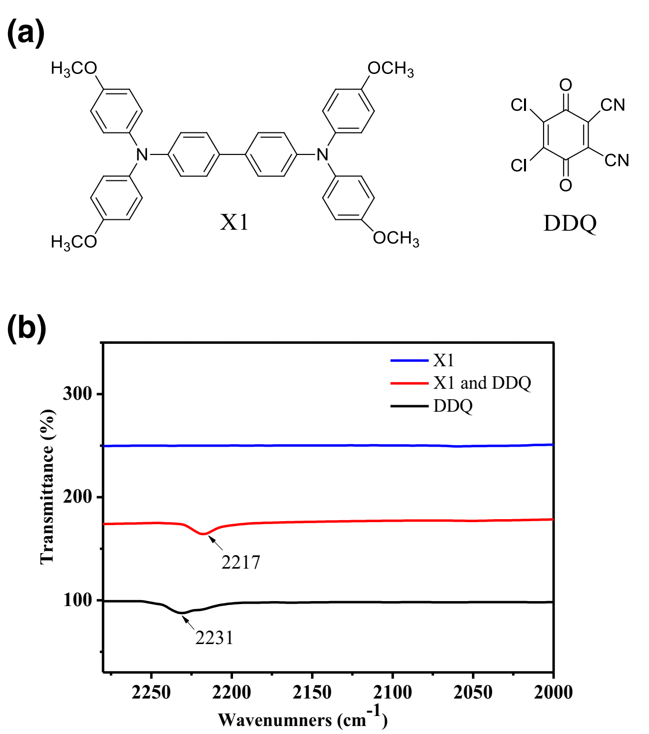


**Fig. 1.** (a) Chemical structures of X1 and DDQ. (b) FTIR spectra of X1, X1 doped with DDQ, and DDQ.

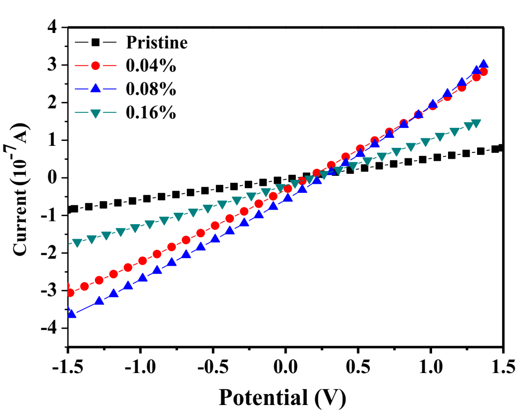


**Fig. 2.** Current–voltage plots of Ag/HTM ($TiO_2$)/Ag devices with various dopant ratios (molar ratios relative to X1).

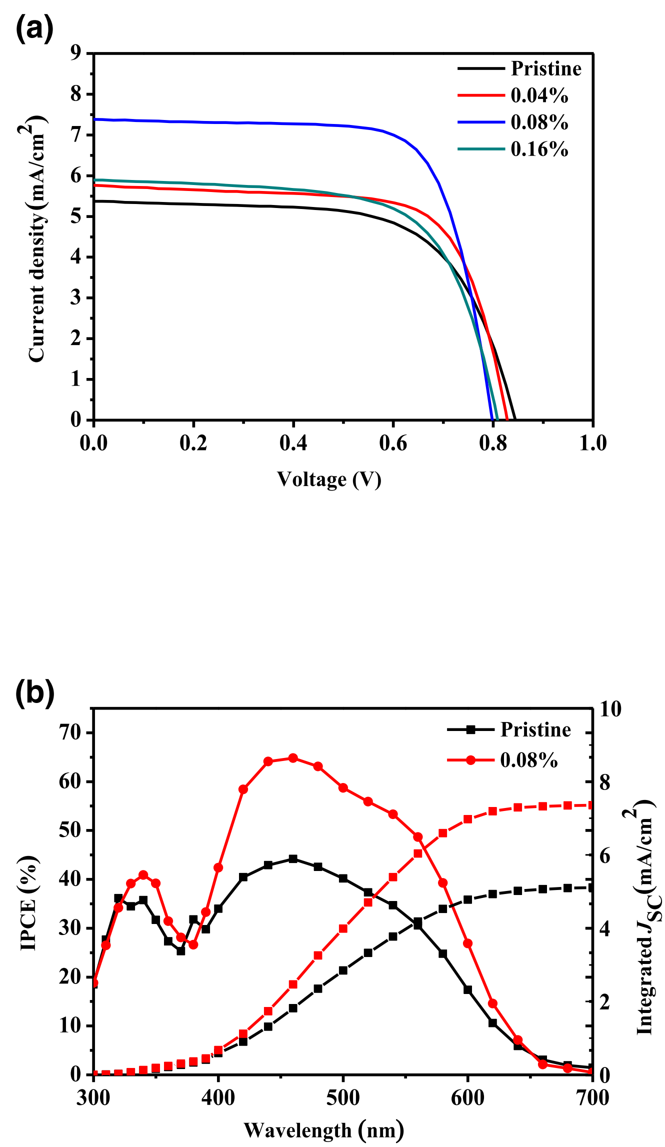


**Fig. 3.** (a) Current density–voltage characteristics of ssDSSCs with X1 as the HTM. (b) IPCE plots and integrated current-density curves of ssDSSCs with various ratios of DDQ, pristine, and 0.08%.

accompanied by the formation of a charge transfer complex [21]. Because DDQ is a strong electron acceptor, we have previous used it to dope ssDSSCs to enhance the conductivity of Spiro-OMeTAD [22]. In this paper we further utilize DDQ, using it as an effective p-type dopant for triphenylamine-based organic HTM X1 and introducing it to ssDSSCs. By adding a trace amount of DDQ into the HTM, the conductivity of X1 increased by one order of magnitude, and the overall power conversion efficiency of solid-state devices based on X1 with reasonable doping increased from 2.9% (for undoped devices) to 4.3%.

## 2. Experimental

### 2.1. Chemicals

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), chlorobenzene (CB), and acetonitrile (AN) were purchased from Aladdin Reagents Co. Ltd.; 4–tert–butylpyridine (TBP) and lithium bis(trifluoromethane)sulfonimide salt (Li-TFSI) were provided by TCI (Shanghai); and 3-{6-{4-[*bis*(2',4'-*dihexyloxybiphenyl*-4-*yl*)*amino*-]phenyl}–4,4-dihexyl-cyclopenta-[2,1-*b*:3,4-*b*]dithiphene-2-yl}–2-cyanoacrylic acid (Y123) and 18-NRT were provided by Dalian HeptaChroma SolarTech Co. Ltd.

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