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# D-π-A-structured organic sensitizers with π-extended auxiliary acceptor units for high-performance dye-sensitized solar cells

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ABSTRACT

Two new D-π-A-structured dyes (SGT-160 and SGT-161) with the extension of π-conjugation in the acceptor unit have been designed and synthesized to modulate LUMO energy levels and to investigate the photophysical and electrochemical properties as well as cell performances. Based on a reference dye of SGT-130 as a platform of donor-π-bridge-BTD-phenyl-acceptor sensitizers, ethynylphenylene (T-Ph) and 2-ethynylthiophene (T-Th) moieties as an auxiliary π-spacer were introduced to replace the traditional phenylene (Ph) moiety for SGT-160 and SGT-161, respectively. It was found that the insertion of an additional ethynyl moiety into the BTD-Ph acceptor unit significantly enhanced the light-harvesting capability by extending the absorption bands and intensifying the molar absorptivity. Moreover, the π-extension in the acceptor part was beneficial for stabilizing the LUMO energy levels. The density functional theory (DFT) calculations and the partial density of states (PDOS) suggest that the variation of acceptor units affects the electronic transition between the major orbitals of the dyes. As a result, dye-sensitized solar cells (DSSCs) based on SGT-160 with a chenodeoxycholic acid (CDCA) co-adsorbent exhibited high power conversion efficiencies (PCEs) of 10.28%, while DSSCs based on SGT-161 and SGT-130 showed moderate PCEs of 8.05% and 10.06%, respectively.

## 1. Introduction

Dye-sensitized solar cells (DSSCs), as a promising alternative energy technology among next-generation photovoltaic technologies, have been attracting tremendous research interest because of their tremendous potential to convert solar and artificial light to electricity and their low cost and facile fabrication [1,2]. In particular, DSSCs are a promising technology for portable electronics and small modules, which can be applied in both indoor and outdoor conditions [3]. In 2018, Ingmar et al. [4] demonstrated the focus-induced photoresponse (FIP) technique using a solid-state DSSC as a photodetector, showing the practical application of DSSCs in ambient conditions. The unique properties of DSSCs arise mainly from the use of organic and organometallic compounds as photosensitizers, so the power conversion efficiency (PCE) development of photosensitizers has been the main field of research for DSSCs [5,6]. Recently, the PCEs of DSSCs have reached 11–14% using ruthenium complexes [7], metal-free organic dyes [8–10], and porphyrin dyes [11], and a tandem DSSC comprised of a metal-free organic dye (top cell) and a porphyrin dye (bottom cell) that reached the extremely high efficiency of 14.64% was demonstrated [12]. To reach open-circuit voltages ($V_{OC}$) over 1.0 V for boosting the PCE, copper-complex-based redox shuttles are increasingly being used in DSSCs [13–16]. Furthermore, these Cu complexes with bipyridine or phenanthroline exhibit significantly low reorganization energies for dye regeneration to proceed rapidly at a low driving force [17,18]. However, the moderate values of the short-circuit current densities ($J_{SC}$) in copper-based DSSCs have become an obstacle for achieving higher PCEs [19–23]. Overcoming the current deficiency of sensitizers with the extended long-wavelength response is a key factor to exploit the full potential of the copper redox shuttles. Therefore, various efficient metal-free organic dyes for DSSCs contain a donor-π-bridge-acceptor (D-π-A) structure because this push-pull structure can induce intramolecular charge transfer (ICT) from D to A, thereby improving the light-harvesting capability by red-shifting and broadening the absorption spectrum of the sensitizer [24,25].

The D-π-A structured organic dyes provide great possibilities for rational design and structural modification, which are vital for achieving efficient light harvesting [25]. Very recently, myriad molecular engineering strategies have been studied and developed for D-π-A structures of metal-free organic dyes [5,26]. Accordingly, numerous

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