

# End-capped group manipulation of fluorene-based small molecule acceptors for efficient organic solar cells

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## ABSTRACT

Acceptor- $\pi$ -donor- $\pi$ -acceptor (A- $\pi$ -D- $\pi$ -A) type small molecule acceptors have made significant progress in organic solar cells (OSCs). To achieve high performance acceptors, three novel acceptors (s4-s6) are designed and investigated based on small molecule acceptors (s1-s3) via introduction of different end-capped groups. The quantum chemistry and Marcus theory approaches are used to calculate the electronic structures and crucial parameters dramatically related to the short-circuit current density ( $J_{SC}$ ), involving the absorption spectrum, electron-hole correlation, driving force, and electron mobility. Compared with s1-s3, s4-s6 not only yield greater red-shift and stronger and broader absorption spectra, but also exhibit much higher electron mobility, easier exciton dissociation abilities, and much better electron transfer efficiencies in active layer. Our results will offer theoretical guidelines for further design and synthesis of acceptors to enhance the performance of OSCs.

## 1. Introduction

The Bulk-heterojunction (BHJ) organic solar cells (OSCs) have become an environmentally friendly technology for transforming solar energy into electricity, and have exhibited tantalizing prospects due to their satisfying advantages of fabricating lightweight, mechanical flexibility, and low production cost [1–4]. Typical BHJ devices are consisted of electron donor and acceptor. The most widespread acceptors are fullerenes and their derivatives, such as [6, 6]-phenyl-C<sub>61</sub>/C<sub>71</sub>-butyric acid methyl ester (PC<sub>61</sub>BM/PC<sub>71</sub>BM) [5–7]. Over the past two decades, fullerene derivatives as electron acceptors are in the dominant position, and the fullerene-based OSCs have achieved a high power conversion efficiency (PCE) up to 11.7% [8]. Despite great advances in this field, the fullerene acceptors still possess some intrinsic disadvantages including weak light absorption in the visible range of the solar spectrum due to the wide band gap, and high synthesis cost [9–11]. To address these issues, non-fullerene small molecule acceptors with tunable structure, strong and broad absorption spectra, appropriate energy levels, simple synthesis method, easy purifications, and low cost have developed rapidly in last few years [5,9,12,13].

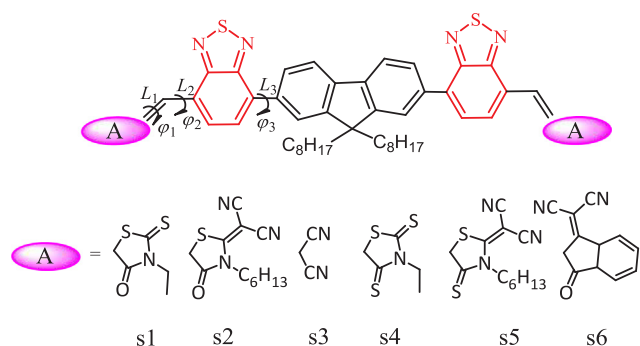
To obtain efficient non-fullerene OSCs, it is significant not only to design high-performance small molecule acceptors, but also to exploit matching donors, because the structural, optical, and electrochemical performances of both donor and acceptor play important roles in

determining photovoltaic performances of OSCs [14–18]. To date, the PCE of a single-junction OSC has exceeded 12% [19]. Design and synthesis of novel small molecule acceptors are beneficial to improve the PCEs of the OSCs. Newly, the A- $\pi$ -D- $\pi$ -A type of small molecule acceptor is one of the most hopeful and valid molecule design strategies, in which an electron-rich donor unit (D) as core building is linked with two electron-withdrawing groups (A) by two  $\pi$ -bridge units [20–23]. The absorption profiles, solubility parameters, electronic energy levels, carrier mobility, self-assembly tendencies can be easily tuned by modulating the three parts of D, A, and  $\pi$ -bridge [20,22,24,25]. So far, the popular donor units including fluorene [22,26], carbazole [24], and indacenodithiophene [21] possess a rigid coplanar structure. Meanwhile, the end-capped groups, 3-ethylrhodanine [26], dicyano-n-hexylrhodanine [6], malononitrile [24], and their derivatives [27,28] have been popularly used in the A- $\pi$ -D- $\pi$ -A molecular system. Furthermore, for A- $\pi$ -D- $\pi$ -A small molecules, a suitable electron-deficient end-capped group can successfully and effectively tune the absorption and energy levels and achieve high performance [28,29], which has also been confirmed by various experimental and theoretical scientists [30–32].

Herein, taking FBR [26] (s1), BAF-4CN [6] (s2), and FBM [24] (s3) as references, we design three novel electron acceptors (s4, s5, and s6). The small molecules s1-s6 are made up of fluorene as a rigid aromatic core, benzothiadiazole as  $\pi$ -bridge extends the conjugation, and 3-

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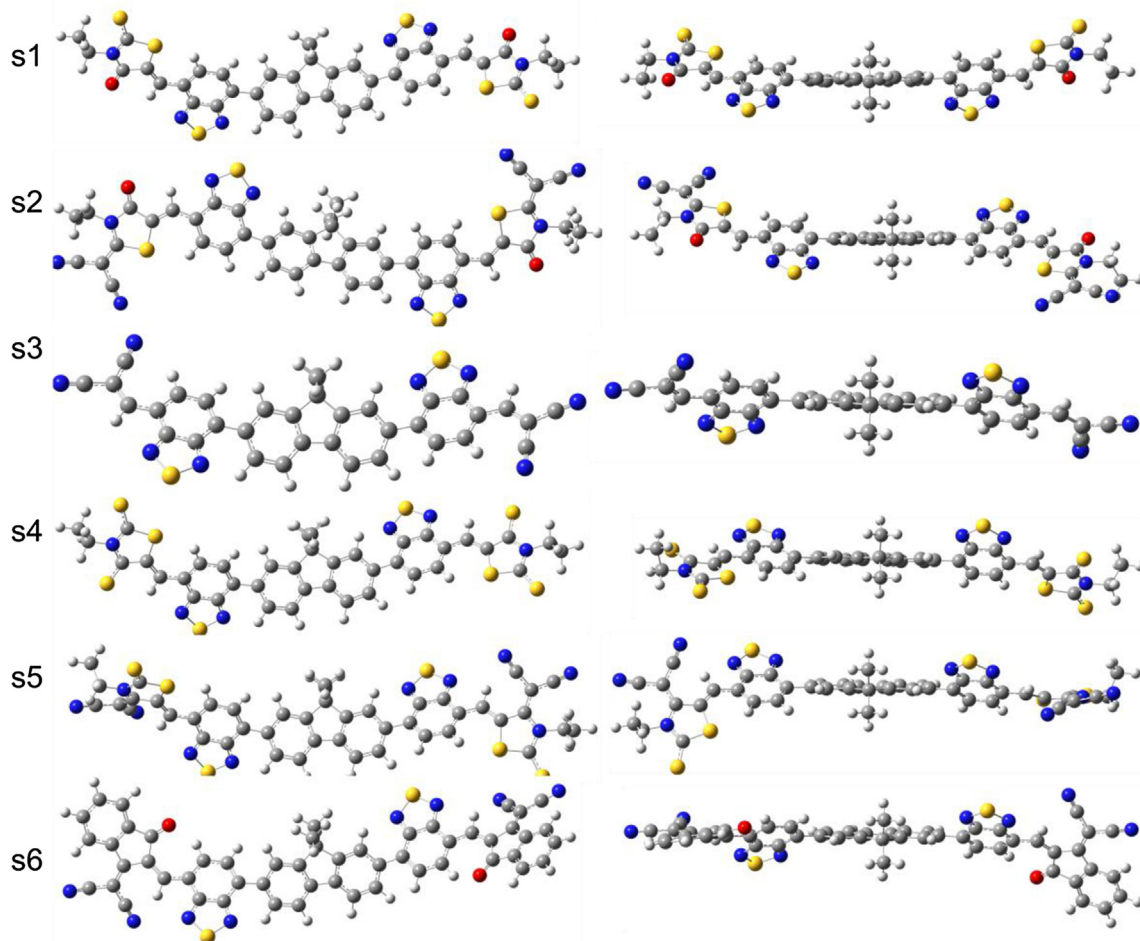
**Fig. 1.** The molecular structures of s1-s6. The key bonds ( $L_1$ ,  $L_2$ , and  $L_3$ ) and the dihedral angles ( $\varphi_1$ ,  $\varphi_2$ , and  $\varphi_3$ ) are labeled, which are described in detail in the text.

ethylrhodanine [26], dicyano-*n*-hexylrhodanine [6], malononitrile [24], 3-ethylthiazolidine-2,4-dithione, 2-(3-hexyl-4-thioxothiazolidin-2-ylidene) malononitrile, and 1,1-dicyano-methylene-3-indanone [1] as the end-capped groups, which are shown in Fig. 1. In this work, the goal is to afford molecule models to enhance the solar absorption for small molecules acceptors and to further understand the role of small molecules in electron transfer at the donor/acceptor (D/A) interface. Hence, the geometric structures, electronic capabilities, optical absorptions, and charge transports of s1-s6 were studied using quantum chemical methods and Marcus theory. Furthermore, taking PffBT4T-2OD as a donor [6] and s1-s6 as acceptors, the light absorption and electron transport in active layer were examined. Our work is expected to afford

a popular strategy for designing efficient small molecule acceptors for OSCs.

## 2. Computational methods

The ground-state ( $S_0$ ) geometries of s1 and s2 were optimized using the DFT [33] method with B3LYP [34], PBE0 [35], and HSE06 [36] functionals and the 6-311G (d, p) basis set. The optimized structures were confirmed to be minimum-energy points by vibrational analysis. The structure optimizations were carried out in dichloromethane solution with the conductor-like polarizable continuum model (C-PCM) [37], since the HOMO and LUMO energies were experimentally measured by cyclic voltammetry in dichloromethane solvent. In this work, all the alkyl branched chains were replaced by the methyl group for more efficient computations since previous work found that the long alkyl branches have little effect on the frontier molecule orbitals and the optoelectronic properties [38,39]. As shown in Table S1, the obtained HOMO/LUMO energies of s1 and s2 at the HSE06/6-311G (d, p) level [38,40,41] agree well with the experimental data while those by B3LYP and PBE0 deviate obviously. Thus, the ground-state geometries and energies of s1-s6 were calculated at the HSE06/6-311G (d, p) level. The unrestricted HSE06 method was used to optimize the ionic state geometries. The electronic affinity (EA) and reorganization energies ( $\lambda$ ) were predicted from the single point energies at the HSE06/6-311 + G (d, p) level based on the HSE06/6-311G (d, p) optimized neutral and anionic geometries. The optical properties of s1 and s2 were computed by TD-DFT using PBE0, B3LYP, HSE06, and M05 [42] functionals with the 6-311G (d, p) basis set in chloroform solution at the ground-state geometries optimized by corresponding methods. As seen in Table S2,



**Fig. 2.** The optimized configurations of s1-s6 at the HSE06/6-311G (d,p) level (left: top view; right: side view).

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