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Photoinduced Symmetry-Breaking Charge Separation Dynamics of Perylene Diimide Dimers: A Nonadiabatic Dynamics Simulation

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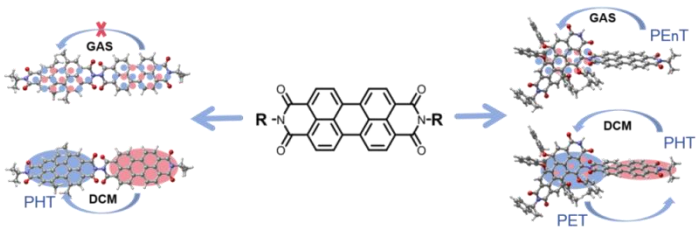
Abstract: In this work, we systematically investigate the photoinduced dynamics of two perylene diimide (PDI) dimers exhibiting symmetry breaking, namely PDI-CH_3 and PDI-iso, in both the gas phase and dichloromethane (DCM) with the combination of the optimally tuned screened range-separated hybrid (OT-SRSH) functional, the polarizable continuum model (PCM) and linear-response time-dependent density functional theory (LR-TDDFT) based nonadiabatic molecular dynamics (NAMD) simulations. The results demonstrate that both substituent effects and solvent effects influence the excited-state properties and dynamic processes of symmetry-broken PDI dimers significantly. In the gas phase, PDI-CH_3 exhibits negligible electron or hole transfer, whereas PDI-iso undergoes photoinduced energy transfer (PEnT). In DCM, the solvent effect not only reduces the excited-state energies of both structures but also alters their photoinduced dynamics by regulating the orders of different types of excitons. In short, PDI-CH_3 exhibits a photoinduced hole transfer (PHT)-dominated mechanism, while PDI-iso shifts from photoinduced energy transfer (PEnT) to concurrent hole transfer (PHT) and electron transfer (PET), facilitating the charge separation process. Moreover, this work indicates that introducing small substituents, i.e., methyl groups, at the bay positions of PDI to disrupt symmetry can also effectively modulate its photoinduced processes, providing a theoretical foundation for designing novel high-performance optoelectronic devices.



Key words: organic donor-acceptor, nonfullerene acceptor, symmetry breaking charge separation, PDI dimers, nonadiabatic dynamics simulation.

1. Introduction

The large-scale utilization of fossil fuels has led to increasingly prominent environmental issues such as atmospheric pollution and the greenhouse effect. Moreover, their non-renewable nature also continuously increases the risk of resource depletion. Consequently, the replacement of these fossil fuels with novel and renewable energy sources has become an inevitable trend [1-4]. Among various renewable energy sources, solar energy has emerged as a core alternative to traditional fossil fuels due to its ubiquitous distribution, ease of access, and virtually limitless supply [5-8]. Within the technologies for solar energy development and utilization, photovoltaic technology, which directly converts light into electricity via solar cells, has become a critical breakthrough in addressing the dual challenges of energy and environment, owing to its potential application scenarios [6,9-12].

The ability of organic solar cells to achieve photoelectric conversion fundamentally resides in their core donor-acceptor (D-A) heterojunction structure. This structure is composed of both an organic donor material and an acceptor material, and the performance compatibility between the two directly dictates the cell's charge separation efficiency and overall energy conversion performance [13-16]. Therefore, the development of donor or acceptor materials with superior properties is regarded as a fundamental strategy for enhancing the core performance of organic solar cells. In the evolution of organic solar cells, the selection of acceptor materials has undergone significant iterations and upgrades [17-19]. Fullerene-based acceptors, owing to their exceptional electron mobility, high electron affinity, and rapid photo-induced charge separation, once constituted the most widely utilized class of acceptor materials in organic solar cells [20]. However, constrained by inherent limitations such as low absorption coefficients in the visible region, difficulties in

diversifying molecular structures, and persistently high fabrication costs, fullerene-based acceptors have struggled to facilitate further breakthroughs in solar cell performance. These challenges have promoted the development of non-fullerene acceptors, which have achieved remarkable progress in recent years. Compared to traditional fullerene materials, they exhibit two distinct advantages: firstly, a broader absorption spectrum and a higher extinction coefficient, enabling more effective capture of solar photons; secondly, their unique electronic structure facilitates innovative charge separation pathways-not only electron transfer from donor to acceptor (Channel I mechanism) but also hole transfer from acceptor to donor (Channel II mechanism) [21-23]. The synergistic effect arising from this dual-channel charge generation mechanism significantly enhances charge generation efficiency, serving as a key driver for the improvement of power conversion efficiency (PCE) [24-26]. Currently, organic solar cells incorporating these materials have achieved PCEs exceeding 20%, thereby fully demonstrating their considerable potential for photovoltaic applications [27,28].

Perylene diimide (PDI) integrates a suite of advantages, including strong light absorption, high electron mobility, tunable energy levels, and excellent stability, making it one of the ideal materials for designing high-performance non-fullerene acceptors (NFAs) [29-32] (see **Figure S1** for the skeletal formula of PDI). For instance, Lin et al. reported a novel, nonplanar, star-shaped PDI acceptor using triphenylamine (TPA) as core to achieve a record high PCE for solution-processed OSCs based on non-fullerene acceptors at that time [33]. Later on, Zhong et al. designed helical PDI acceptors and further improved the PCE to ca. 6%. With the aid of femtosecond transient absorption spectroscopy, they proposed that the charge carriers are created from photogenerated excitons in both the electron donor and acceptor phases [34]. Meng et al. subsequently reported a bay-linked PDI dimer, in which selenium atoms were incorporated into the perylene core [35]. The introduction of selenium atom to the PBI core results in a high lowest unoccupied molecular orbital (LUMO) level, a twisted molecular configuration, and a high electron mobility, which are all beneficial for the photoinduced charge transfer process. After these pioneering works, a plenty of works have been conducted to explore the the relationship between molecular geometric structures of the PDI-based acceptors and OSCs performance [36-43]. Up till now, it is well established that PDI-based NFAs exhibiting twisted dimer, quasi-three-dimensional (3D), and 3D architectures usually show superior performance relative to those of the planar analogues.

Despite these achievements, the relationship between charge separation/charge recombination dynamics and the molecular geometry is complicated and still uncertain at ultrafast time scales, which motivate many time-resolved spectroscopic studies. For example, Kong et al. explored the intramolecular excited-state symmetry breaking charge separation (SB-CS) and charge recombination (CR) dynamics of two symmetric phenyl-methane-based PDI derivatives, a twist dimer PM-PDI2 (phenyl-methane-based PDI dimer) and a 3D configuration tetramer PM-PDI4 (phenyl-methane-based PDI tetramer), in different solvents with ultrafast femtosecond transient absorption spectroscopy and quantum chemical calculations. Based on the results, they concluded that the kinetics of CS and CR processes are strongly related to the molecular geometric structure, and the excited-state symmetry breaking in the 3D structure acceptor has superior photogenerated charge and photovoltaic properties [44]. Alzola et al. use transient absorption and emission spectroscopies to investigate the competition between SB-CS, fluorescence, and internal conversion in three related PDI dimers linked at the head land positions with o-, m-, and p-phenylene moieties, namely *o*-PDI2, *m*-PDI2, and *p*-PDI2 respectively. It is found that o-PDI2 exhibits SB-CS while m-PDI2 and p-PDI2 exhibit accelerated internal conversion due to the motion of the linker along with subnanosecond intersystem crossing (ISC) [45]. Very recently, Mazumder demonstrated the triplet excited-state population in a conformationally rigid perylenediimide trimer (PDI-T) via intramolecular symmetry-breaking charge separation (SB-CS) at the single-molecule level and the solvent effects are found to be important for the triplet quantum yield [46].

Apart from these experimental works, theoretical studies have also been performed to elucidate the underlying excited state mechanism for PDI based systems. However, most of them are concentrated on the static electronic structure calculations while the ultrafast dynamics remain unclear [37,38,47,48]. Until recently, nonadiabatic dynamics simulations are conducted by some groups to elucidate the photodynamics of PDI based donor-acceptor systems. For instance, Polkehn established that molecular packing determines charge separation in a liquid crystalline bisthiophene-PDI donor-acceptor material with quantum dynamical calculations using the Multi-Layer Multi-Configuration Time-Dependent Hartree (ML-MCTDH) method [49]. Recently, our group has also employed mixed-quantum-classical nonadiabatic dynamics to investigate the photoinduced dynamics of PDI based systems including the excitation wavelength-dependent charge generation dynamics in a PTB7/PDI donor-acceptor interface [50], the solvent dependent charge transfer in zinc phthalocyanine-PDI dyads [51], and the exciton dynamics in a PDI π-stack [52].

In most researches on non-fullerene acceptor materials, the construction of PDI dimers primarily relies on covalent bridging at the bay and head land position, whereas dimeric systems formed by direct N-N linkage between imide nitrogen atoms remain scarcely explored. In 2019, Fang and colleagues synthesized a series of head-to-tail PDI dimers (e.g., 1-1, 2-2). These dimers connect identical or different PDI units via N-N covalent bonds. They first conducted steady-state absorption and emission spectroscopy experiments, and the results showed that the fluorescence quantum yield of the twisted tetra-phenoxyl-substituted PDI dimer with symmetry-broken structure was significantly lower than that of the symmetric structure (0.89 vs. <0.01), suggesting that this structure might undergo ultrafast charge transfer processes leading to fluorescence quenching. Subsequent femtosecond time-resolved transient absorption spectroscopy experiments further validated this, revealing two ultrafast processes in the symmetry-broken structure with time scales of 300 fs and 14 ps. These two ultrafast processes were assigned as ultrafast energy transfer and charge separation, respectively. In contrast, no such processes were observed in the symmetric structure, where the system mainly deactivates to the ground state through fluorescence emission [53].

These results demonstrate that the introduction of substituents at the bay position, which breaks the symmetry of the PDI dimer, is the key factor enabling charge separation. Therefore, the rational design of dimer structures with tailored symmetry breaking provides a viable pathway to control the charge separation process, which plays a critical role in modulating the optoelectronic properties of the system.

To further elucidate the mechanism underlying these