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## **Propeller** *vs* **Quasi-Planar** 6-Cantilever Small Molecular Platforms with Extremely Two-Dimensional Conjugated Extension

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**Abstract:** Two exotic 6-cantilever small molecular platforms, characteristic of quite different molecular configurations of propeller and quasi-plane, are established by extremely two-dimensional conjugated extension. When applied in small molecular acceptors, the only two cases of CH25 and CH26 that could contain six terminals and such broad conjugated backbones have been afforded thus far, rendering featured absorptions, small reorganization and exciton binding energies. Moreover, their distinctive but completely different molecular geometries result in sharply contrasting nanoscale film morphologies. Finally, CH26 contributes to the best device efficiency of 15.41 % among acceptors with six terminals, demonstrating two pioneered yet highly promising 6cantilever molecular innovation platforms.

**O**rganic semiconductors, characteristic of  $\pi$ -conjugated molecular backbones, are currently the only material that could supplement inorganic semiconductors in wide application scenarios of flexibility and low-temperature processing energy-conversion devices (like solar cells),<sup>[1]</sup> photodetectors,<sup>[2]</sup> next generation of display and lighting technology,<sup>[3]</sup> etc. However, due to the nature of great flexibility in molecular skeletons and loose aggregation

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through van der Waals forces, hydrogen bonds,  $\pi$ - $\pi$  interactions, etc. rather than covalent bonds, organic semiconductors suffer from several huge challenges comparing to inorganic materials: (1) weaker intermolecular interactions; this could result in localized excitons with quite small exciton radius (<1 nm) and large binding energies (>0.3 eV; usually <0.01 eV for inorganic ones).<sup>[4]</sup> Meanwhile, the efficient diffusion of excitons through Förster and Dexter energy transfers<sup>[5]</sup> will be hindered, especially for Dexter that requires small enough intermolecular distances (  $\approx 1$  nm) to achieve sufficient overlap of molecular orbitals. Similarly, carrier transport (electrons, holes) is also to be hindered because of the large energy barrier for hoping.<sup>[6]</sup> (2) Larger structural/packing disorders; in sharp contrast to inorganic semiconductors that possess a spatial lattice with conspicuous periodicity, more structural defects and amorphous phases exist in aggregated organic semiconductors, which could serve as scattering/recombination centers for both excitons and charge carries. Therefore, the carrier mobility of organic semiconductors is usually orders of magnitude smaller comparing to inorganic semiconductors but charge recombination rates are opposite.<sup>[6]</sup>

Bearing these thoughts in mind, how to enhance molecular crystalline ordering and also strengthen intermolecular packing should be crucially important if more efficient organic photoelectric devices are expected.<sup>[7]</sup> Note that two-dimensional (2D) conjugated polycyclic aromatic hydrocarbons (PAHs) that embed sufficient heteroatoms on molecular backbones have been regarded as the most promising candidate<sup>[8]</sup> due to the following two reasons: (1) their rigid and broad framework along with high symmetry is expected to stack together more compact and orderly, thus leading to reduced molecular reorganization energies, suppressed density of states of vibration energy levels<sup>[9]</sup> and delocalized vibrational relaxation of excitons on neighboring stacked molecules;<sup>[10]</sup> (2) the sufficient heteroatoms on 2D conjugated backbones are probably involved with multiple secondary or noncovalent interactions,<sup>[11]</sup> thus strengthening intermolecular interactions and rendering facilitated carrier migrations.

In order to meet the criterion for high-performance organic semiconductors above, two exotic 6-cantilever small molecular platforms (C1 and C2) with quasi- $D_{3h}$  symmetry were established delicately by extremely two-dimensional conjugated extension (Figure 1a). On basis of different elementary units (triptycene vs. triphenylene), C1 and C2

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### Communications



*Figure 1.* (a) Chemical structures of 2D conjugated C1 and C2 employing triptycene and triphenylene as elementary units.  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  represent 2-dodecylhexadecane, 2-butyloctane, 2-decyltetradecane and n-undecane, respectively. (b) Cantor plots and energy levels of frontier molecular orbitals involving LUMOs and HOMOs.

are featured with quite different molecular configurations of propeller and quasi-plane, respectively. When applied in small molecular acceptors, six electron-deficient terminals can be successfully assembled into such broad conjugated backbones, providing the only two cases of small molecular acceptors that could contain six terminals. Finally, their distinctive but completely different molecular geometries result in sharply contrasting nanoscale morphologies and photovoltaic performances, demonstrating the pioneered yet highly promising 6-cantilever molecular innovation platforms for high-performance organic semiconductors.

The synthetic routes to C1 and C2 were illustrated in Scheme S1 and S2, which are mainly involved with a triple condensation reaction.<sup>[12]</sup> The synthesized procedures and characterized data/spectra were shown in Supporting Information (SI, Figure S23-S38). Density functional theory (DFT) calculations disclosed an optimized propeller configuration for C1 but relatively planar one for C2 (Figure S1, quasi- $D_{3h}$  symmetry). For both C1 and C2, the highest occupied molecular orbitals (HOMOs) locate on the same electron-donating periphery, thus leading to similar HOMO energy levels of -4.58 eV (Figure 1b). While the lowest unoccupied molecular orbitals (LUMOs) mainly focus on triptycene and triphenylene centers. Owing to extensive  $\pi$ conjugation for triphenylene center of C2, more effective donor-acceptor architectures could be established, resulting in down-shifted LUMO energy level of -2.31 eV (-1.98 eV for C1). The tendency of energy level's evolution is roughly in accordance with that derived from cyclic voltammetry (CV) (Figure 2a and Figure S2).

The electronic absorption spectra of C1 and C2 predicted by time-dependent DFT show a featured but weak absorption band at range of 550–600 nm and two strong bands below 500 nm (Figure 2b). Due to the adequate orbital degeneracy on such 2D conjugated systems, each band is composed with transitions from multiple orbitals (Table S1), thus leading to relatively larger half-peak breadths.<sup>[13]</sup> Note that the experimental UV/Vis spectra

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**Figure 2.** (a) Energy levels derived from CV. (b) Calculated electronic spectra. Measured UV/Vis spectra for C1 (c) and C2 (d) in both solutions and solid films. (e) Time-resolved photoluminescence decay traces. (f) Exciton binding energies in pristine films.

(Figure 2c and 2d) could well replicate of the calculated absorption profiles. Almost the same absorptions in solution and solid film can be observed for C1, suggesting weak intermolecular stackings caused by its spatial structure of propeller. Whereas the maximum absorption wavelength of C2 bathochromically shifted by  $\approx 10$  nm from solution (479 nm) to solid film (489 nm), indicating the occurrence of charge transfer between adjacent molecules.<sup>[14]</sup> It is also plausible to observe quite similar lifetimes of photogenerated excitons ( $\approx 3.3$  ns) for C1 in both solution and film (Figure 2e), however, nearly double amplification for C2 in

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solid film (2.8 ns) comparing to that in solution (1.6 ns). As displayed in Figure 2f, a small exciton binding energy  $(E_{\rm b})$  of 77.1 meV is afforded by C1 in pristine film, whereas a greatly reduced one of 27.7 meV is further rendered by C2. This may be attributed to more effective exciton delocalization<sup>[10,15]</sup> and intermolecular electronic interactions<sup>[16]</sup> for C2 when considering its quasi-planar molecular geometry comparing to C1. Moreover, relatively small reorganization energies (Figure S3) for both hole (80.3 meV for C1 and 76.1 meV for C2) and electron (110.1 meV for C1 and 102.3 meV for C2) can be achieved, which is benefitting for improving charge mobility according to nonadiabatic semiclassical Marcus charge-transfer theory<sup>[17]</sup> and also demonstrates their great potentials as fundamental platforms of high-performance organic semiconductors.[18]

Organic solar cells (OSCs) are undergoing a rapid development currently, especially for small molecular acceptors (SMAs).<sup>[1c-d,19]</sup> Note that the dimer-like SMAs<sup>[20]</sup> with more than two electron-deficient terminals in one molecule have demonstrated huge potentials for achieving OSCs with both excellent efficiency and long-term stability. In a similar fashion, the only two cases of SMAs (CH25 and CH26 in Figure 3a) assembling six terminals together could be established based on 6-cantilever C1 and C2, with the aim of enhancing intermolecular stackings and limit migration of SMAs in blended films.<sup>[20e]</sup> In accordance with C1



*Figure 3.* (a) Molecular structures of CH25 and CH26. R groups are same with C1 and C2. (b) In-plane and (c) out-of-plane line cuts of 2D GIWAXS for CH25 and CH26 pristine films. (d) Exciton binding energies. (e) Histograms of charge carrier mobility of pristine films.

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and C2, CH25 and CH26 exhibit propeller and quasi-planar configurations, respectively (Figure S4). However, due to the highly symmetrical molecular configurations, both CH25 and CH26 possess extremely small dipole moments (0.0055 Debye for CH25 and 0.0219 Debye for CH26) (Figure S5). As expected, the maximum molar extinction coefficients of  $\approx$  7.5\*10<sup>5</sup> L mol<sup>-1</sup> cm<sup>-1</sup> can be observed for CH25 and CH26, about three times larger than that of their monomer-like SMA (CH4 in Figure S6).<sup>[12a]</sup> Additionally, the greatly enlarged molar extinction coefficients for CH26 could be observed in solid films  $(8.5 \times 10^4 \text{ cm}^{-1})$  comparing to that of CH25 with  $4.6 \times 10^4$  cm<sup>-1</sup>, demonstrating the enhanced light harvesting capacity of CH26 with a quasi-planar configuration. In contrast to C1 and C2, enhanced intermolecular interactions for both CH25 and CH26 can be indicated by the obvious absorption variation of temperature-dependent UV/Vis spectra (Figure S7) and  $\approx 48 \text{ nm}$  redshift of the maximum absorption peaks from solutions to films (Figure S8). This should be ascribed to the six planar terminals that play a dominant role in effective intermolecular packings.[7b,12b]

The 2D grazing-incidence wide-angle X-ray scattering (GIWAXS)<sup>[21]</sup> images in Figure S9 suggest much stronger crystallinity for CH26 comparing to CH25, which is confirmed by their differential scanning calorimetry (DSC) curves in Figure S10. Moreover, CH26 prefers a favorable face-on molecular stacking rather than edge-on for CH25 (Figure 3b and 3c), accompanied by a smaller  $\pi$ - $\pi$  stacking distance of 4.08 Å than that of 4.39 Å for CH25 (Table S2). The quite different molecular packing behaviors should be caused by their contrasting propeller and quasi-planar configurations. A slightly enlarged lifetime of excitons (1.9 ns) for CH26 films can be observed with respect to that of 1.5 ns for CH25 (Figure S11), which could decrease the non-radiative recombination loss of charge transfer states in theory.<sup>[22]</sup> Additionally, the  $E_{\rm b}$ s for CH25 and CH26 films are 53.4 and 35.2 meV (Figure 3d), respectively, much smaller than that of 226 meV for the state-of-the-art Y6.[7b] Benefitting from the desirable molecular configuration and packing orientation of CH26, the greatly improved carrier mobility can be achieved comparing to CH25 (Figure 3e and S12).

When blending with an absorption complementary and energy level matched donor PM6<sup>[23]</sup> (Figure S8 and S13), CH26-based OSCs rendered an excellent power conversion efficiency (PCE) of 15.41%, featuring with a  $J_{sc}$  of 22.98 mA cm<sup>-2</sup>,  $V_{oc}$  of 0.920 V and FF of 72.7 % (Figure 4a and Table 1). However, only 2.24 % PCE was obtained by CH25-based OSCs along with an overall reduced  $J_{sc}$ ,  $V_{oc}$  and FF. The really low external quantum efficiencies (EQEs) for CH25-based OSCs (Figure 4b) suggests the inefficient photodynamic processes, which should account for the unsatisfied device performance. Among them, the exciton dissociation efficiency  $(\eta)$  for PM6:CH25-based device is only 53.5%, much lower than that of 98.1% for PM6: CH26based one (Figure 4c). In addition, the relatively lower charge carrier mobility and unbalanced hole/electron mobility ratio for PM6:CH25 blends (Figure S14) should be another crucial reason for inferior PCEs. Moreover, the

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**Figure 4.** (a) Current density-voltage curves. b) EQE spectra and integral  $J_{sc}$  (c) Steady-state photoluminescence spectra of neat and blend films. (d) EQE<sub>EL</sub> plots of CH25 and CH26-based devices. (e, f) AFM phase images. (g, h) Statistical distribution of fibril diameters (see Figure S17 for details).

severer bimolecular and trap-assisted charge recombination have been indicated by  $\alpha$  and nkT/q values that deviating from unit (see Figure S15 for detailed discussions). This also agrees well with the enlarged non-radiative energy loss of 0.329 eV in CH25-based devices comparing to that of 0.237 eV for CH26-based one based on a detailed energy loss analysis (Figure 4d, S16 and Table S3). Note that the impeditive charge migration and aggravated recombination of CH26-based OSC consist well with its slower charge extraction and shorter electron lifetime according to tran-

Table	1:	Photovoltaic	parameters	for	OSCs. <sup>[a]</sup>
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sient photocurrent/photovoltage measurements (Figure S17).

The inferior photodynamic of CH25 should be closely related to nanoscale morphology of blended films.<sup>[12b]</sup> As displayed in Figure 4e-4 h and Figure S18. The clear fibrillar networks were observed, rendering a diameter of 8.6 nm for PM6:CH25 and 10.6 nm for PM6:CH26. Note that the larger and even-distributed fibers in PM6: CH26 blends are expected to facilitate charge carrier transport markedly.<sup>[19b]</sup> However, several obvious pinholes existed in PM6:CH25 blends, resulting in a quite larger RMS of 1.60 than that of 1.17 for PM6:CH26 (Figure S19). The pinhole microstructure in PM6:CH25 blends may result in hindered charge transport and serve as recombination centers during charge migration. Moreover, the fibrillar networks and pinholes have been further confirmed by TEM images (Figure S20). PM6: CH26 blends also demonstrate a more favorable faceon stacking comparing to that of PM6:CH25 (Figure S21), which is favor of efficient charge transport in such a vertical diode structure of OSCs. Meanwhile, the reduced Urbach energy  $(E_{\rm U})$  of 22.6 meV for PM6:CH26 blends comparing to that of 24.2 meV for PM6: CH25 also indicates its better molecular crystalline ordering, being conducive to facilitate charge migration and suppress recombination (Figure S22).<sup>[24]</sup>

To sum up, two exotic 6-cantilever small molecular platforms of C1 and C2 with high symmetry but quite different molecular configurations of propeller and quasiplane, have been established by extremely 2D conjugated extensions. The small reorganization energies, large exciton lifetimes and weak exciton binding were achieved by both C1 and C2 benefitting from their broad conjugated backbones. C2 displays a relative stronger intermolecular stacking along with more favorable face-on stacking orientation comparing to C1, because of the quasi-planar molecular geometry of C2 rather than propeller for C1. On basis of these 6-cantilever innovation platforms, the only two cases of SMAs (CH25 and CH26) that could assemble six terminals together have been explored thus far. Despite the formation of clear fibrillar networks, PM6: CH25 affords an undesirable pinhole microstructure, resulting in inferior photodynamic processes and sharply contrasting photovoltaic performance comparing to that of PM6:CH26. Consequently, CH26-based OSCs achieved the best efficiency of 15.41% among SMAs with six terminals. This work has constructed two pioneered yet highly promising 6cantilever molecular innovation platforms and will stimulate

Active Layers	V <sub>oc</sub> [V]	$J_{\rm sc}$ [mA cm <sup>-2</sup> ]	Calc. J <sub>sc</sub> <sup>[b]</sup> [mA cm <sup>-2</sup> ]	FF [%]	PCE [%]
PM6:CH25	0.840 (0.836±0.010)	4.82 (4.19±0.35)	4.33	55.4 (55.4±0.8)	2.24 (1.91±0.19)
PM6:CH26	0.920 (0.922±0.003)	22.98 (22.60±0.22)	22.49	72.7 (72.3±0.4)	15.41 (15.11±0.17

[a] The best and statistical values were out/in parentheses, respectively. The statistical values were derived from 10 devices (Table S4 and S5). [b] Current densities afforded by EQE plots.

# GDCh

their wide applications in some newly merged areas such as organic photodetectors and ferromagnetic semiconductors, etc.

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#### **Conflict of Interest**

The authors declare no conflict of interest.

#### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** 6-Cantilever Molecule · Configuration Tuning · Organic Semiconductor · Organic Solar Cells · Two-Dimensional Conjugation

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