Supporting Information

Efficient non-fullerene polymer solar cells enabled by tetrahedron-shaped core based 3D-structure small-molecular electron acceptors

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† Electronic supplementary information (ESI) available: Materials and methods.

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I. Experimental section.

1. Materials and Methods.

Materials. All reagents and chemicals were purchased from commercial sources and used without further purification unless stated otherwise. Tetrahydrofuran (THF) was freshly distilled before use from sodium using benzophenone as indicator. Anhydrous chlorobenzene were purchased from Sigma-Aldrich or J&K chemicals, and used as received. PffBT4T-2DT and PDI-Br were synthesized according to literature procedure ^{1 2}. The molecular weight of PffBT4T-2DT was determined on a Polymer Laboratories PL-GPC 220 using trichlorobenzene as eluent at 170 °C vs polystyrene standards with Mn = 131 kDa and Mw = 254 kDa.

Characterizations of new compounds. ¹H and ¹³C NMR spectra were recorded on a Bruker AV-400 MHz NMR spectrometer. Chemical shifts are reported in parts per million (ppm, δ). ¹H NMR and ¹³C NMR spectra were referenced to tetramethylsilane (0 ppm) or solvent residual peak (7.26 ppm for ¹H NMR and 77.0 ppm for ¹³C NMR) as internal standard. Mass spectra were collected on a MALDI Micro MX mass spectrometer.

Electrochemical characterizations. The electrochemical cyclic voltammetry (CV) was performed in a 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) dichloromethane (DCM) solution with a scan speed at 0.1 V s⁻¹. A Pt wire and Ag/AgCl were used as the counter and reference electrodes, respectively. A ferrocene/ferrocenium redox couple was used as an external standard. The concentration of these SMs is adjusted as a 1.0×10^{-4} mol L⁻¹ solution in chromatographic pure DCM for the CV measurements. UV-Vis absorption spectra were acquired on a Gary 50 UV-Vis Spectrometer. All film samples were spincasted on ITO/ZnO substrates.

AFM analysis. AFM measurements were performed by using a Scanning Probe Microscope-Dimension 3100 in tapping mode. All film samples were spincasted on ITO/ZnO substrates.

X-Ray Diffraction. XRD data were obtained from a PANanalytical XRD instrument (model name: Empyrean) using the parallel beam mode that is recommended by the instrument manufacturer to characterize thin-film samples.

Electron mobility measurements.

The electron mobility were measured using the space charge limited current method (SCLC) method, employing a device architecture of ITO/ZnO/SM acceptor (80 nm)/Ca/Al by taking current-voltage curves and fitting the results to a space charge limited form, where the SCLC is described by:

$$J = 9\varepsilon_0\varepsilon_r \mu V^2 / 8L^3$$

Where ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, μ is the electron mobility, *V* is the voltage drop across the device and *L* is the thickness of the film.

Solar cell fabrication and testing. Pre-patterned ITO-coated glass with a sheet resistance of ~15 Ω per square was used as the substrate. It was cleaned by sequential sonications in soap deionized water, deionized water, acetone, and isopropanol for 15 min at each step. After UV/ozone treatment for 60

min, a ZnO electron transport layer was prepared by spin-coating at 5000 rpm from a ZnO precursor solution (diethyl zinc). Active layer solutions (D/A ratio 1:1.5) were prepared in CB (polymer concentration: 6.5 mg/mL). To completely dissolve the polymer, the active layer solution should be stirred on hotplate at 110 °C for at least 3 hours. Before spincoating, both the polymer solution and ITO substrate are preheated on a hotplate at about 110 °C. Active layers were spin-coated from the warm polymer solution on the preheated substrate in a N₂ glovebox at 1000 rpm to obtain thicknesses of \sim 80 nm \sim 100 nm. The polymer:SM acceptors blend films were then annealed at 100 °C for 5 min before being transferred to the vacuum chamber of a thermal evaporator inside the same glovebox. At a vacuum level of 3×10⁻⁶ Torr, a thin layer (20 nm) of V₂O₅ was deposited as the anode interlayer, followed by deposition of 100 nm of Al as the top electrode. All cells were encapsulated using epoxy inside the glovebox. Device J-V characteristics was measured under AM1.5G (100 mW cm⁻²) using a Newport solar simulator. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement) to bring spectral mismatch to unity. J-V characteristics were recorded using a Keithley 236 source meter unit. Typical cells have devices area of 5.9 mm², which is defined by a metal mask with an aperture aligned with the device area. EQEs were characterized using a Newport EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source.

Supporting Figures



Figure S1. The UV-Vis absorption spectra of a neat polymer film and a polymer/SM blend.



Figure S2. The XRD patterns of polymer/SM acceptor blend. The peak at ~21° was the signal of donor polymer PffBT4T-2DT.



Figure S3. The UV-Vis absorption spectra of TPC-PDI₄ in solution, casted as PS/TPC-PDI₄ film and casted as neat TPC-PDI₄. Regarding the difference of the relative intensities of 0-0 and 0-1 peak, it is probably caused by a small extent of molecular aggregation in solid state. In order to prove that, we have casted films of the SMs blended with an insulating polymer, polystyrene (PS). The results are shown in the figure bellow, the 0-1 peak intensity, as well as the degree of the red-shift exhibit a gradual change from SM solution to polystyrene/SM film and then to neat SM film. The difference of the 0-1 peak intensities could possibly be assigned to *h*-aggregation. Compared to the SM solutions, the *h*-aggregation tendency was significantly increased when we cast films with PS/SM. This tendency can be further enhanced if we cast the neat SM film. It was observed that PS could reduce the *h*-aggregation tendency in some degree. We can draw the conclusion that the SMs exhibit weak aggregation tendency when casted as neat films.

Supplementary discussion

When we compared the performances of the three SM based organic solar cells, we can find that TPGe-PDI₄ based PSC performance is much lower than the other two. We would like to note that Ge atom exhibits metallic behavior, as it is categorized as a metal in the periodic table. In our study, we found TPGe-PDI₄ decompose on silica gel column, which is possibly due to interaction between the *d*-electrons of Ge with the acidic silica gel. The reasons why the Ge-based SMs do not perform well could be possibly due to the poor stability of Ge based SM acceptor and the partial metallic properties of Ge, which could act as a trapping site for recombination. This could be related to the observed bimolecular recombination of Ge-based SM devices.

Synthesis

Tetrakis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methane (**TPC-4Bpin**), tetrakis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (**TPSi-4Bpin**), 1-bromo-N-N'-di(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylicbisimide (**PDI-Br**) were synthesized according to reported literatures. All chemicals were purchased from commercial sources and used without further purification unless otherwise specified.



General synthetic route for corresponding TPX-4Bpin, X= C, Si or Ge.

Synthesis of Tetrakis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)germane, **TPGe-4Bpin**. nitrogen atmosphere, tetrakis(4-bromophenyl)germane (1023mg, Under dry 1.47mmol), bis(pinacolato)diboron (1643mg, 6.47mmol), Pd(dppf)Cl2 · DCM (245mg, 0.3mmol) and anhydrous potassium acetate (1265mg, 12.9mmol) were mixed with 1,4-dioxane (25mL) in a 100mL Schlenk tube. The reaction mixture was heated to 80 °C for 48 hours with stirring. After cooled to room temperature, diethyl ether was added and the solution was washed with water and brine. The organic solution was dried with anhydrous sodium sulfate and the solvent was removed under reduced pressure. The remaining brown solid was dissolved in minimum amount of chloroform. The colour was removed by passing through a short silica gel column with chloroform as an eluent. The chloroform solution was collected and dried under reduced pressure. The remaining pale brown solid was further purified by dissolving in minimum amount of chloroform and precipitated out by ethanol, yielding a white powder. (724mg, 56%) ¹H NMR (400MHz, CDCl₃, 300K): δ 7.80-7.78 (d, J= 8Hz, 8H), 7.52-7.50 (d, J= 8Hz, 8H), 1.35 (s, 48H).



General synthetic route for TPX-4PDI, X= C, Si, or Ge

Synthesis of **TPC-PDI**₄. Under dry nitrogen atmosphere, **TPC-4Bpin** (33mg, 0.04mmol), **PDI-Br** (139.6mg, 0.17mmol), tetrakis(triphenylphosphine)palladium(0) (9.2mg, 0.01mmol) and anhydrous potassium carbonate (55.3mg, 0.4mmol) were mixed with oxygen-free tetrahydrofuran-water-mixed solvent (tetrahydrofuran (4mL), distilled water (2mL)) in a 50mL Schlenk tube. The reaction mixture was heated to reflux for 3 days with stirring. After cooled to room temperature, diethyl ether was added and the solution was washed with water and brine. The organic solution was dried with anhydrous sodium sulfate and the solvent was removed under reduced pressure. The red solid was purified by silica gel column (eluent: 2:1 hexane :dichloromethane), yielding a red powder. (70.7mg, 53%) ¹H NMR (400MHz, CDCl₃, 395K): δ 8.79-8.58 (m, 20H), 8.15-7.99 (m, 4H), 5.24-4.71 (m, 8H), 2.33-1.74 (m, 32H), 1.39-0.94 (m, 160H), 0.86-0.79 (m, 24H), 0.71-0.64 (m, 24H).

Synthesis of **TPSi-PDI**₄. Under dry nitrogen atmosphere, **TPSi-4Bpin** (100.8mg, 0.12mmol), **PDI-Br** (419.3mg, 0.50mmol), tetrakis(triphenylphosphine)palladium(0) (27.7mg, 0.02mmol) and anhydrous potassium carbonate (248.8mg, 1.8mmol) were mixed with oxygen-free tetrahydrofuran-water-mixed solvent (tetrahydrofuran (20mL), distilled water (10mL)) in a 250mL Schlenk tube. The reaction mixture was heated to 80 °C for 2 days with stirring. After cooled to room temperature, diethyl ether was added and the solution was washed with water and brine. The organic solution was dried with anhydrous sodium sulfate and the solvent was removed under reduced pressure. The red solid was purified by silica gel column (eluent: 3:2 to 4:1 dichloromethane:hexane), yielding a red powder. (189.0mg, 47%) ¹H NMR (400MHz, CDCl₃, 395K): δ 8.72-8.65 (m, 20H), 8.20-8.14 (m, 4H), 5.23-4.90 (m, 8H), 2.27-1.71 (m, 32H), 1.31-1.06 (m, 160H), 0.83-0.80 (m, 24H), 0.70-0.67 (m, 24H).

Synthesis of **TPGe-PDI**₄. Under dry nitrogen atmosphere, **TPGe-4Bpin** (316mg, 0.36mmol), **PDI-Br** (1217mg, 1.46mmol), tetrakis(triphenylphosphine)palladium(0) (82mg, 0.07mmol) and anhydrous potassium carbonate (493mg, 3.57mmol) were mixed with oxygen-free tetrahydrofuran-water-mixed solvent (tetrahydrofuran (10mL), distilled water (5mL)) in a 250mL Schlenk tube. The reaction mixture was heated to 80 °C for 5 days with stirring. After cooled to room temperature, dichloromethane was added and the solution was washed with water and brine. The organic solution was dried with anhydrous sodium sulfate and the solvent was removed under reduced pressure. Most of the remaining red solid was dissolved in diethyl ether. The residue solid was filtered out and washed with diethyl ether, yielding a dark red powder. (949mg, 78%) ¹H NMR (400MHz, CDCl₃, 395K): δ 8.69-8.65 (m, 20H), 8.19-8.15 (m, 4H), 5.20-4.84 (m, 8H), 2.24-1.65 (m, 32H), 1.30-1.05 (m, 160H), 0.88-0.76 (m, 24H), 0.79-0.62 (m, 24H). MS spectrum (MALDI, M⁺): calculated for C₂₂₄H₂₆₂GeN₈O₁₆: 3393.9, found: 3393.7

- 1. Z. Chen, P. Cai, J. Chen, X. Liu, L. Zhang, L. Lan, J. Peng, Y. Ma and Y. Cao, *Adv Mater*, 2014, **26**, 2586-2591.
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