

Supporting Information for:

Rigid, Conjugated Macrocycles for High Performance Organic Photodetectors

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1. Device fabrication

cP₄ and **aP_n** were synthesized according to a previously reported method.¹ PTB7-Th was purchased from 1-material. The synthesis of ZnO precursor was described elsewhere.² Prepatterned ITO-coated glass with a sheet resistance of $\sim 15\Omega/\text{sq}$ was cleaned with detergent, ultrasonicated in DI water, acetone and isopropanol for 30 min, respectively. Subsequently, we treated the substrates by UV-Ozone for 10 min. The prepared ZnO precursor was spin-cast onto the ITO substrate at 3000 rpm for 1 min, followed by annealing at 200 °C for 1 h in air, to form a thin film with approximate thickness of 20 nm. The BHJ active layer was prepared by spin-coating a mixed solution containing polymer and acceptor in chlorobenzene. The thickness of the prepared active layers is about 150 nm. Finally, a 10 nm MoO₃ layer was deposited first and then a 100 nm Al electrode were subsequently deposited through a shadow mask by thermal evaporation under a vacuum about 1×10^{-6} torr. The active area of the device was 9 mm².

2. Characterization

Absorption spectra were obtained on Shimadzu UV 1800 UV-Vis. The current-density-voltage (J - V) curves were measured by a Keithley 2635A source measure unit. EQE measurements were performed using a QEXL system from PV Measurements Inc. For linear dynamic range measurement, a light-emitting diode (625 nm) was used as light source. For cutoff frequency measurement, the LED was modulated by a function generator (Tektronix CFG253). The photodetectors were connected to an oscilloscope (Tektronix TDS 224) with an input impedance of 50 Ω .

Temperature-dependent current-voltage measurements were realized in a vacuum cryogenic probe station (Lakeshore TTP4). Computer-controlled source units were used

to apply DC potentials (Yokogawa 7651). Current measurements were obtained using a current preamplifier (Stanford Research System SR570) and a digital multimeter (Keysight 34401A). All device measurements were performed in vacuum ($P < 1 \times 10^{-4}$ Torr) at different temperatures.

In the transient absorption experiments, the pump pulse comes from an optical parametric amplifier (tunable from UV to the near IR, 100 fs pulse width, 1 KHz repetition rate). The probe pulse is a white-light supercontinuum (from 450 to 900 nm and from 850 to 1600 nm for the visible and near IR range, respectively). The detection consists of a pair of high resolution multichannel detector arrays coupled to a high-speed data acquisition system (HELIOS, Ultrafast System Inc.). In order to avoid photo degradation, we kept samples in the inert gas both in storing and during measurements.

3. Absorption spectrum

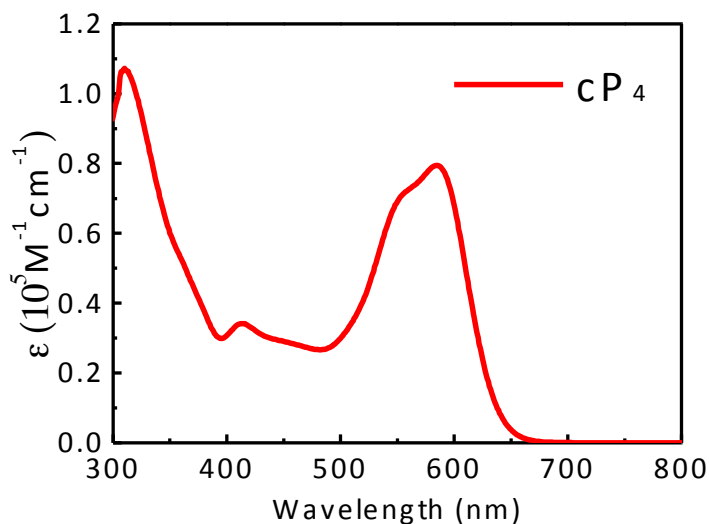


Figure S1. UV-vis absorption spectra of cP_4 (1×10^{-5} M concentration in dichloromethane with a path length $l = 1$ cm).

4. The linear dynamic range (LDR) measurement

The linear dynamic range (LDR) is expressed as $LDR=20\log(J_{\text{high}}/J_d)$, where J_{high} is the highest measurable current density in the linear response range and J_d is the dark current density.

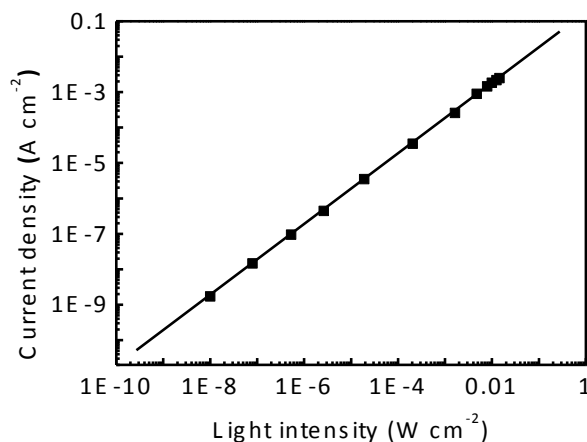


Figure S2. Linear dynamic range of the **cP₄**-based OPD. A red light emitting diode ($\lambda=625\text{nm}$) was used as the light source.

5. Frequency-dependent measurement of the cP₄-based OPD

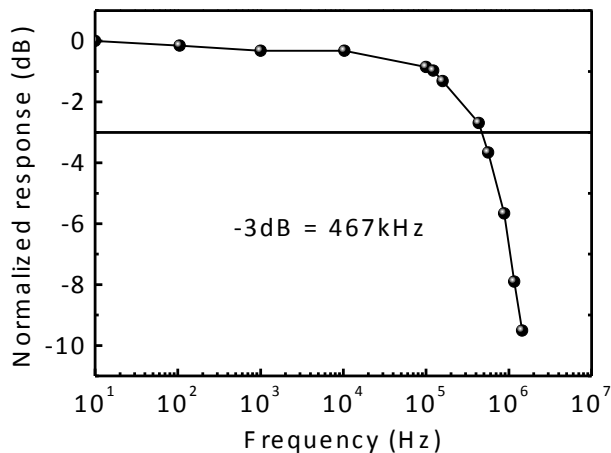


Figure S3. Frequency response of the **cP₄**-based OPD. The device area is 0.09 cm^2 .

6. Transient absorption spectra

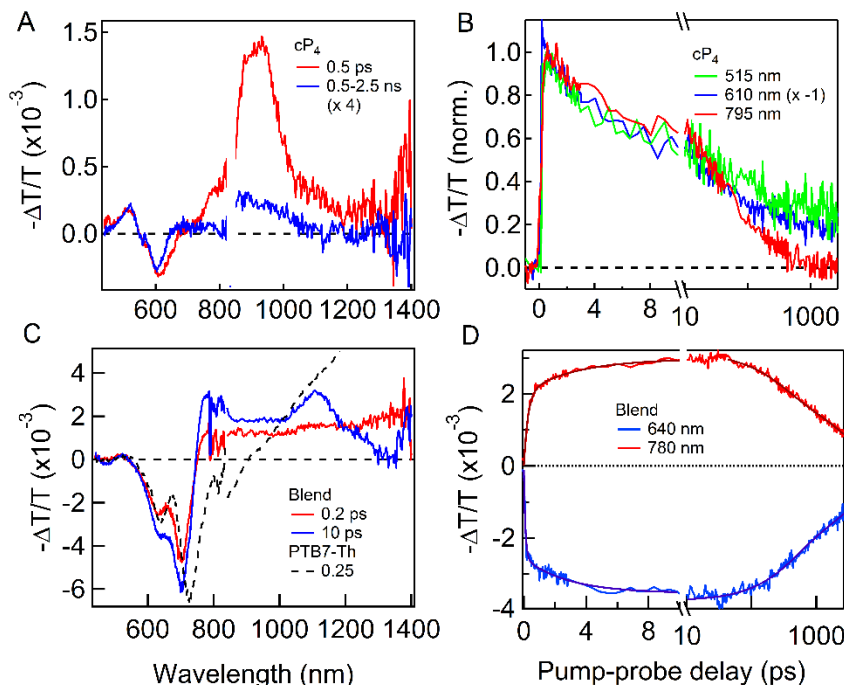


Figure S4. Transient absorption spectra and dynamics for the neat cP_4 (A, B) and the blended film of cP_4 and PTB7-Th (C,D) upon 560 nm excitation. The dashed-black curve in (C) is the spectrum from PTB7-Th upon the excitation of 710 nm. The signal from PTB7-th was scaled for comparison.

Figure S4A and B show the differential transmission spectra and dynamics for the neat film cP_4 upon 560 nm excitation. The negative feature centered at 600 nm is attributed to a bleaching of the ground state absorption under the presence of photo-excited excitons/charges. The positive features centered at 500 nm and from 700 nm to near IR are the excited state absorption (ESA) of the photo-excited excitons or charges. The ESA feature at 795 nm decays biexponentially with the time constants of 8 ± 0.7 ps (52%) and 122 ± 8 ps (48%) (red curve, Figure S4 B). This feature is assigned to the singlet ESA, $S_1 \rightarrow S_N$ transition, similar to that of other PDI derivative compounds. The ESA dynamics at 500 nm and ground state bleaching, however, behave differently. More than 50 % of the ESA signal at 500 nm decays with a time constant that is similarly to the

dynamics at 795 nm. The remaining signal (20%) lasts for a long time, ns time scale (green and blue curves). The long living signal can either come from photo excited charges or from triplet excitons.

At the same excitation wavelength, 560 nm, for the blend of **cP₄** and PTB7-Th, we observed the dominance of ground state bleaching from PTB7-Th at the range of 575-750 nm (Figure S4 C, the dashed-black curve is from the neat PTB7-Th pumping at 710 nm). Note that at this excitation wavelength, we excite both donor and acceptor materials. The ESA cross section and the ground state bleaching from the polymer are much stronger than that of **cP₄** resulting in the dominance feature from the polymer even we excited both materials at 560 nm. At the longer time (10 ps, Figure S4 C), the bleaching from PTB7-Th increases and the hole ESA feature in PTB7-Th at 1100 nm appears. The increase of bleaching feature from PTB7-Th indicates the hole transfers from **cP₄** to PTB7-Th. Since the ESA cross section at 780 nm for singlet in **cP₄** is very small compared to that of charge ESA (compare Figure S4 A and C), the ESA signal at this wavelength reflects the dynamics of charge generation from exciton dissociation. The fit to the dynamics at 780 nm gives two time constants, 0.2 ± 0.02 ps and 3.3 ± 0.4 ps (Figure S4 D). These time constants reflect the electron and hole transfer upon 560 nm excitation. In addition, we observed a much longer charge lifetime in the blends (on the nanosecond time scale) when compared to that of the exciton dynamics in the neat films (Figure S4 B and D). The longer charge lifetime is due to exciton dissociated into separating charges rather than charge transfer excitons.

7. Dark current-voltage characteristics

The dark current-voltage characteristics are described by $J_d = J_0 \{ \exp[e(V - JR_s)/nk_B T] - 1 \}$, where J_d is the dark current density, J_0 is the dark saturate current density, V is the applied voltage, n is the ideality factor, k_B is the Boltzmann constant, T is the temperature and e is the electron charge. The fitting method is described in ref. 3.

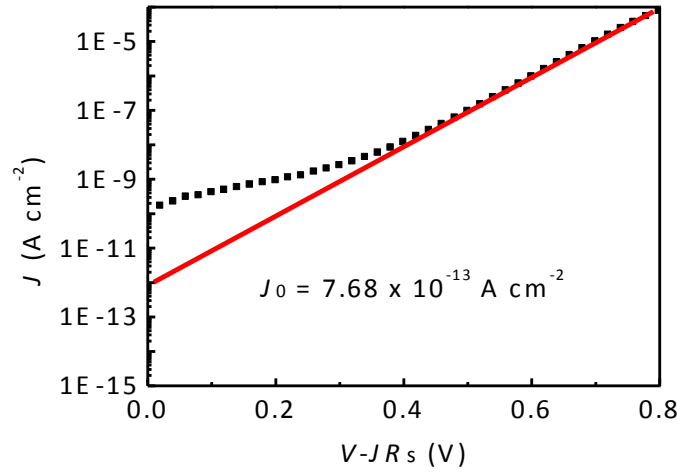


Figure S5. The device structure is ITO/ZnO/PBDTT-TT:cP₄/MoO₃/Al. The original J - V curve is shown in Fig. 2B. Plot of dV/dJ vs J^{-1} and linear fitting. (b) $\ln(J)$ vs $(V - JR_s)$ and linear fitting. The J_0 is calculated to be $7.68 \times 10^{-13} \text{ A cm}^{-2}$.

8. Dark current as a function of temperature

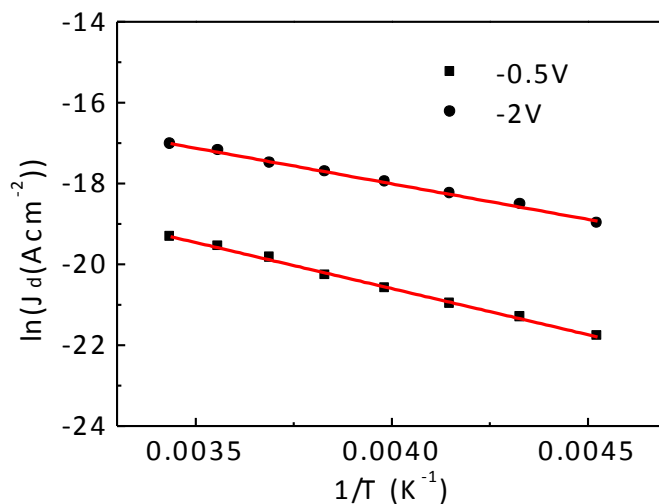


Figure S6. The dependence of the dark current density of the **cP4**-based OPD on temperature measured at -0.5 V and -2.0 V.

9. Device performance

The responsivity R was calculated from the following equation: $R = \lambda q / hc \times EQE$, where EQE is external quantum efficiency, λ the wavelength, q the electron charge, h the Planck constant, c the speed of light. When the noise current is dominated by the shot noise from the dark current, the specific detectivity (D^*) is given by $D^* = R / (2qJ_d)^{1/2}$, where R is the responsivity, q the electron charge and J_d the dark current density.

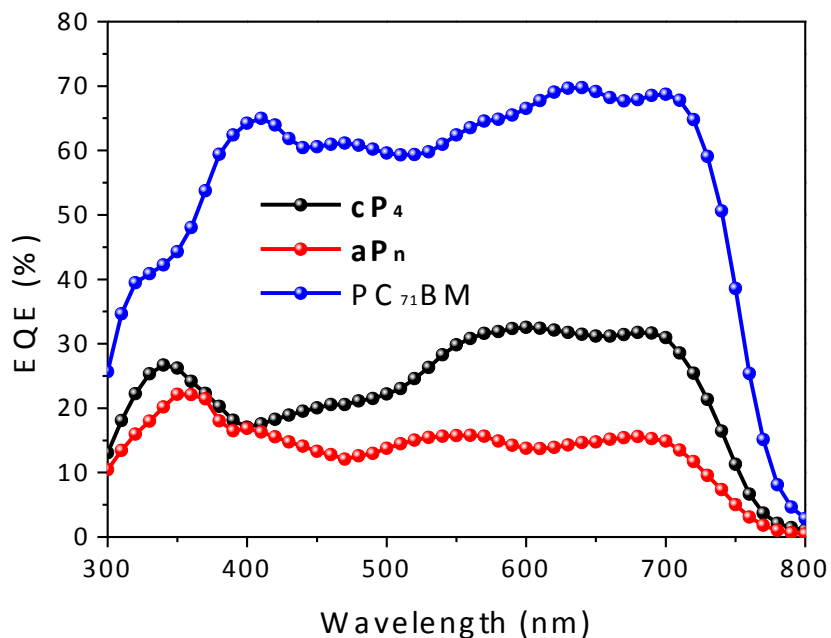


Figure S7. External quantum efficiency at different wavelength with inverted OPD structure at -0.1V .

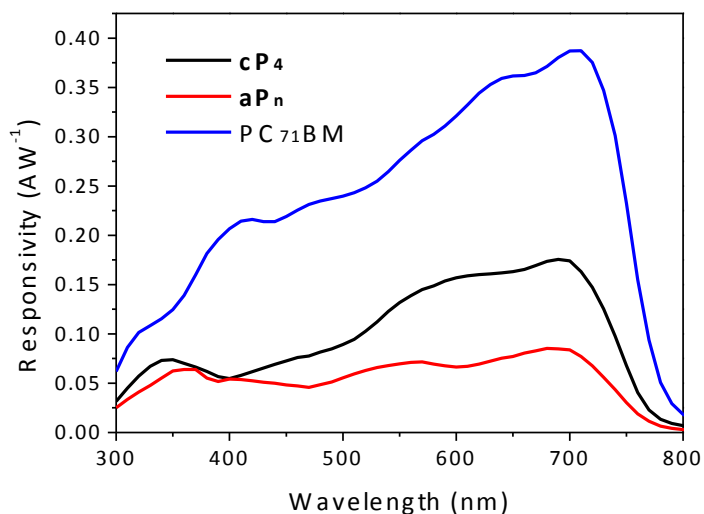


Figure S8. Calculated responsivity (R in AW^{-1}) spectra for different OPDs.

10. References and Notes

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(3) Dou, L.; Yang, Y.; You, J.; Hong, Z.; Chang, W.-H.; Li, G.; Yang, Y. *Nat. Commun.* **2014**, *5*, 5405.