Supporting Information
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An Organic Optical Transistor Operated under Ambient Conditions**
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Supporting Information

Table of Contents

1. Synthesis

2. Optical spectroscopy

3. Order of magnitude estimate of the efficiency of the photoconversions
1. Synthesis

Commercially available chemicals (Aldrich) were used as received without further purification. The solvents were dried according to standard procedures. Column chromatography was performed over Silica gel 60M (0.040-0.063 mm particle size, 230-400 mesh ASTM) purchased from Machery-Nagel. $^1$H-NMR spectra were recorded using a Bruker Avance AC 250 with TMS as internal standard. FT-IR spectroscopy was performed using a BIO-RAD Digilab FTS-40 spectrometer. Mass spectrometry was performed using an EI-MS MAT 8500, Finnigan (ionisation energy 70 eV). For cyclic voltammetry measurements, tetrabutylammonium hexafluorophosphate ($\text{Bu}_4\text{NPF}_6$, 0.1 M) was used as the conducting salt, a Pt electrode as the working electrode and Ag/AgNO$_3$ as the reference electrode. Each measurement was calibrated by the internal standard ferrocene.

The triad PBI-DCP-PBI was synthesized in a multi-step reaction starting from the commercially available 2-methylthiophene as shown in scheme below after some modifications of the published procedures.[1-3]

**Synthesis of 1,2-Bis(2-methyl-5-(4-methanoylphenyl)thiophen-3-yl)hexafluorocyclopentene (7):** 1,2-Bis(2-methyl-5-(4-formylphenyl-thiophen-3-yl)hexafluorocyclopentene (6) (931.00 mg, 1.62 mmol) was dissolved in dry toluene (40 mL) and diluted with ethanol (40 mL). Afterwards, sodium borohydride (91.63 mg, 2.42 mmol) was added in portions and stirring was continued for 2.5h at RT. Then, the solvent was evaporated. The residue was dissolved in a small amount of toluene and the product was precipitated into hexane. The solid was collected, washed with hexane and dried under vacuum. Yield: 84% (788.00 mg, 1.36 mmol), white powder. $^1$H-NMR (250 MHz, CDCl$_3$): $\delta$/ppm = 1.72 (t, 2H, f), 1.97 (s, 6H, a), 4.70 (d, 4H, e), 7.28 (s, 2H, b), 7.39 (dd, 4H, d), 7.54 (dd, 4H, c). FT-IR (KBr): $\nu$/cm$^{-1}$ = 3426, 3027, 2956, 2925, 1632, 1514, 1416, 1104, 1110, 990, 805, 739, 675. MS (70 eV): m/z = 582 (M+2, 17%), 581 (M+1, 34%), 580 (M$^+$, 100%), 565 (M-CH$_3$, 52%), 550(21%).
Supporting Scheme 1: Synthetic scheme for the PBI-DCP-PBI triad.
Synthesis of 1,2-Bis(2-methyl-5-(4-bromobenzyl)thiophen-3-yl)hexafluorocyclopentene (8)

Triphenylphosphine (1.02 g, 3.90 mmol) was suspended in dry acetonitrile (20 mL) and bromine (623 mg, 3.90 mmol) was added dropwise. Afterwards, 1,2-bis(2-methyl-5-(4-methanoylphenyl)thiophen-3-yl)hexafluorocyclopentene (7) (659.00 mg, 1.14 mmol) was also dissolved in dry acetonitrile (20 mL) and added dropwise to the triphenylphosphine suspension. Stirring was continued for 46.5 h at RT. Then, the reaction mixture was filtered and the filtrate was evaporated till dryness. The raw product was purified by column chromatography (DCM:hexane 1:1). Yield: 55% (439.00 mg, 0.621 mmol), white powder.

$^1$H-NMR (250 MHz, CDCl$_3$): $\delta$/ppm = 1.96 (s, 6H, $a$), 4.51 (s, 4H, $e$), 7.29 (s, 2H, $b$), 7.39 (dd, 4H, $d$), 7.51 (dd, 4H, $c$). FT-IR (KBr): $\nu$/cm$^{-1}$ = 3084, 3031, 2981, 2923, 2853, 1611, 1555, 1516, 1437, 826, 741, 673, 590. MS (70 eV): $m/z$ = 707 (M$^+$, 21%), 706 (M$^+$, 33%), 627 (100%), 625 (M+CH$_3$, 95%), 273 (30%).

Synthesis of 1,2-Bis(2-methyl-5-(4-(N-(pentadecan-8-yl)-perylene-3,4:9,10-tetracarboxybismid)benzyl)thiophen-3-yl)hexafluorocyclopentene (PBI-DCP-PBI):

Under dry and oxygen-free conditions, 1,2-bis(2-methyl-5-(4-bromobenzyl)thiophen-3-yl)hexafluorocyclopentene (8) (378.00 mg, 0.535) was dissolved in dry DMF (10 mL) and N-(1-heptyloctyl)perylene-3,4:9,10-tetracarboxybismide$^{[3]}$ (707.24 mg, 1.18 mmol) was added. After stirring for 1 h at RT, the reaction mixture was heated to 70°C. Potassium carbonate (740.00 mg, 5.35 mmol) and a catalytic amount of potassium iodide were added. Stirring at 70°C was continued for 92.5 h. Then, the solvent was evaporated and the residue was dissolved in DCM, washed with water and dried over magnesium sulphate. The raw product was purified by column chromatography (THF:toluene 1:4). Yield after freeze-drying: 11% (107.00 mg, 0.0613 mmol), red powder.

$^1$H-NMR (250 MHz, CDCl$_3$): $\delta$/ppm = 0.82 (m, 12H, $f$), 1.22 (m, 40H, $i$), 1.88 (m, 10H, $h$ a), 2.17 (m, 4H, $h$), 5.19 (m, 2H, $g$), 5.38 (s, 4H, $e$), 7.21 (s, 2H, $b$), 7.47 (dd, 4H, $d$), 7.58 (dd, 4H, $c$), 8.51-8.64 (m, 16H, $f$). FT-IR (KBr): $\nu$/cm$^{-1}$ = 2963, 2928, 2857, 1698, 1659, 1596, 1514, 1439, 1098, 810, 749. MS (70 eV): $m/z$ = 603 (89%), 548 (75%), 429 (62%), 355 (82%), 281 (67%), 221 (100%). CV: HOMO$^{\text{open form}}$ = 6.13
eV, LUMO$_{\text{open form}}$ = 3.81 eV, HOMO$_{\text{closed form}}$ = 5.23 eV, (LUMO$_{\text{closed form}}$ = 3.47 eV, calculated from the optical band gap)

2. Optical spectroscopy

The absorption spectra have been recorded using Hitachi, Model U 3000 UV-VIS (pure DCP in chloroform) and Perkin Elmer Lambda 750 (pure PBI and PBI-DCP-PBI triad) spectrometers. The emission spectra of PBI-DCP-PBI in toluene, Supporting Figure 1, have been recorded using a Varian Cary Eclipse spectrometer.

![Supporting Figure 1](image)

**Supporting Figure 1**: Emission spectra of the PBI-DCP-PBI triad dissolved in toluene (concentration 1.5·10$^{-6}$ mol/l) for the open (red) and closed (blue) conformation of the DCP unit. The excitation wavelength was 520 nm. The vertical scale is valid for both traces.

For the photoconversion experiments the samples were mounted in a home-built inverted microscope and were illuminated sequentially with light of three different wavelengths, as shown in Supporting Figure 2a. The radiation in the visible spectral range is provided by an Ar ion laser (ALC 60, Laserlight Showdesign), at 514 nm, and a diode laser at 635 nm (RLT635-500-TO3, Roithner Lasertechnik; power supply ILX Lightwave LDC 3900, Laser 2000). The UV light at 300 nm results from fourth-harmonic generation that is accomplished in two consecutive steps. First a commercial frequency doubler (SHG Autotracker, APE Angewandte Physik & Elektronik GmbH) generates the second harmonic from the output of an optical parametric oscillator (OPO, APE Angewandte Physik & Elektronik GmbH) that is pumped by a pulsed Titanium:Sapphire laser (Tsunami, Spectra Physics). The quasi continuous radiation
(2.3 ps pulses at a repetition rate of 81 MHz) is frequency doubled by a type 1 beta borium borate (BBO) crystal in a home-built device. Sequential exposure of the sample with the appropriate radiation is accomplished by using electromechnical shutters that could be opened and closed with ~2 ms temporal accuracy, the timing of the three beams respect to each other is shown in Supporting Figure 2b. The conversion beams (300 nm, 635 nm) are weakly focused with a lens (f = 50 mm) resulting in spots of 0.18 mm and 0.23 mm in diameter on the sample. The probe beam is reflected via a dichroic mirror DM (Q520LP, AHF) and focused into the back focal plane of a microscope objective MO (Microthek 20×, NA=0.5) by a lens with long focal length (f = 250 mm) resulting in a spot on the sample with a diameter of 0.15 mm. The fluorescence from the sample is collected by the same objective, transmitted through the dichroic mirror and passes a by bandpass filter BPF (HQ 525 LP, transmission 525-725 nm, AHF) to suppress residual stray light. The signal is detected with a back-illuminated EMCCD camera (iXon DV877ECS, Andor), and integrated over the entire area on the sample that is illuminated with the probe beam.

Supporting Figure 2: a, Schematic representation of the optical setup. The sample is illuminated sequentially by light of three different wavelengths: 635 nm (red path; conversion beam 1) from a laser diode, 300 nm (blue path, conversion beam 2) and 514 nm (green path; probe beam). The probe beam is directed to the back side of the sample via a dichroic mirror (DM) and the light is focused to the back focal plane of a microscope objective (MO). The fluorescence from the sample (orange path) is collected by the same objective, transmitted through the dichroic mirror (DM), residual stray light is suppressed by bandpass filter (BPF) and the emission is detected with a back-illuminated EMCCD camera. b, Timing of the conversion and probing beams with respect to each other. A sequence consisting of a conversion period (blue or red) followed by a probe period (green) is repeated 2×m times and referred to as a switching cycle.
3. Order of magnitude estimate of the efficiency of the photoconversions

The prerequisites for this calculation are: i) All triads within the excitation volume experience the same intensities of the conversion beams, ii) we neglect vignetting, and iii) the overall absorption of the sample does not change during the conversion process. The latter assumption is required because we have to determine the efficiencies via the change of the fluorescence signal. The first condition is fulfilled because the focal depths of about 100 µm for the conversion beams is much larger than the thickness of the samples (10 µm). The second condition is fulfilled because we work at concentrations of $1.4 \times 10^{-5}$ mol/l, which corresponds to a mean distance of 70 nm between two triads. However, since it is inherent to the experiment that the absorption of the sample is going to change during the conversion process, the last condition is fulfilled only at the very beginning of the photoconversion process.

Our goal is to estimate the number of photons, $N_{\text{conv}}^{i \rightarrow f}$, that are required to convert the triads from state $i$ to state $f$, which we define as the ratio of the number of absorbed photons, $N_{\text{abs}}$, to the number of converted triads $M_{\text{conv}}^{i \rightarrow f}$, $N_{\text{conv}}^{i \rightarrow f} = N_{\text{abs}} / M_{\text{conv}}^{i \rightarrow f}$. The number of absorbed photons is given by

$$N_{\text{abs}} = P_{\text{open} / \text{close}} M_{\text{triads}} F_\lambda \sigma_\lambda t$$

where $P_{\text{open} / \text{close}}$ refers to the fraction of triads in the open $P_{\text{open}} = M_{\text{open}} / M_{\text{triads}}$ or closed $P_{\text{closed}} = M_{\text{closed}} / M_{\text{triads}}$ state, respectively, $M_{\text{triads}}$ denotes the number of triads, $F_\lambda$ is the number of photons per time and area at wavelength $\lambda$, $\sigma_\lambda$ is the absorption cross section at that wavelength, and $t$ represents the exposure time. The total fluorescence signal from the sample is given by

$$I = (I_{\text{SM}}^{\text{(open)}} P_{\text{open}} + I_{\text{SM}}^{\text{(closed)}} P_{\text{closed}}) M_{\text{triads}}$$

where $I_{\text{SM}}$ refers to the fluorescence intensity from an individual triad in the open / closed configuration, respectively.

After irradiating the sample with 50 sequences at wavelengths of 635 nm / 514 nm we approximately assume that the initially observed fluorescence intensity, $I^{(0)}$, reflects a situation where all triads have been converted to the open state, i.e. $P_{\text{open}}^{(0)} \approx 1$ and $P_{\text{closed}}^{(0)} \approx 0$. This simplification allows us to deduce the
contribution of an individual triad to the fluorescence signal from eq.(2) as $I_{SM}^{\text{(open)}} \approx I^{(0)}/M_{\text{triads}}$. The respective fluorescence intensities $I^{(i)}$ and $I^{(f)}$ before and after the conversion process are given as

$$I^{(i)} = P_{\text{open}}^{(i)} \cdot I_{SM}^{\text{(open)}} \cdot M_{\text{triads}}$$

$$I^{(f)} = P_{\text{open}}^{(f)} \cdot I_{SM}^{\text{(open)}} \cdot M_{\text{triads}}$$

Using these relations we find for the number of converted triads

$$M_{\text{conv}}^{\text{i} \rightarrow \text{f}} = (P_{\text{open}}^{(i)} - P_{\text{open}}^{(f)}) \cdot M_{\text{triads}} = \left(\frac{I^{(i)} - I^{(f)}}{I_{SM}^{\text{(open)}}}\right) \cdot M_{\text{triads}}$$

and finally

$$N_{\text{conv}}^{\text{i} \rightarrow \text{f}} \approx P_{\text{open}/\text{close}} \cdot \frac{F_{\lambda} \cdot \sigma_{\lambda} \cdot t}{\left(\frac{I^{(i)} - I^{(f)}}{I^{(0)}}\right)}$$

The parameters used for the calculations according to eq.(5) are based on the data shown in Supporting Table 1, and the results of the calculations according to eq.(5) are summarized in Supporting Table 2. From these numbers we deduce to within an order of magnitude that the photocyclization reaction (open $\rightarrow$ close) requires about 10 photons per triad at 300 nm, and the ring-opening reaction (close $\rightarrow$ open) requires about 100 photons per triad at 514 nm and about 5000 photons per triad at 635 nm, respectively.
Supporting Table 1: Parameters used for the calculation of $N_{\text{conv}}^{i \rightarrow f}$ according to eq.(5).

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$\text{open } \rightarrow \text{ close}$</th>
<th>$\text{close } \rightarrow \text{ open}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{\text{open}}$</td>
<td>$P_{\text{open}} = 1$</td>
<td>$P_{\text{open}} = 1$</td>
</tr>
<tr>
<td>$P_{\text{close}}$</td>
<td>$P_{\text{close}} = 0.73^1$</td>
<td>$P_{\text{close}} = 0.73^1$</td>
</tr>
<tr>
<td>$F_{\lambda}$ (photons /s cm$^2$)</td>
<td>$1.24 \cdot 10^{15}$</td>
<td>$6.07 \cdot 10^{16}$</td>
</tr>
<tr>
<td></td>
<td>$2.19 \cdot 10^{15}$</td>
<td>$1.01 \cdot 10^{18}$</td>
</tr>
<tr>
<td></td>
<td>$3.30 \cdot 10^{15}$</td>
<td>$1.21 \cdot 10^{19}$</td>
</tr>
<tr>
<td></td>
<td>$8.26 \cdot 10^{15}$</td>
<td>$1.51 \cdot 10^{19}$</td>
</tr>
<tr>
<td>$\sigma_{\lambda}$ (cm$^2$)</td>
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<tr>
<td></td>
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<td>$3.24 \cdot 10^{-17}$</td>
</tr>
<tr>
<td>$t$ (s)</td>
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<td>$1.2$</td>
</tr>
<tr>
<td></td>
<td>$2.0$</td>
<td>$2.0$</td>
</tr>
</tbody>
</table>

1 After the initialization to the closed state the fluorescence drops to 27% of the initial value, from which we conclude that only 73% of the triads are in the closed conformation and able to absorb at 635 nm. Therefore the value of $P_{\text{close}} = 0.73$ is used.

Supporting Table 2: Estimated number of photons per molecule that is required to induce the ring opening/closing reaction of DCP.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$\text{Open } \rightarrow \text{ close}$</th>
<th>$\text{close } \rightarrow \text{ open}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{\text{conv}}^{i \rightarrow f}$ (# photons)</td>
<td>7</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>1300</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>3900</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3500</td>
</tr>
</tbody>
</table>

2 The absolute values of $N_{\text{conv}}^{i \rightarrow f}$ are taken because eq.(5) changes the sign in case of reversed reaction direction.

Supporting References

