Supporting Information for:

Molecular Junctions Based on SAMs of Cruciform Oligo(phenylene ethynylene)s

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1. Ultraflat gold substrate.

Figure S1. (a) AFM image of E-gun evaporated gold film. Large amounts of clusters and defects are present on the surface. The roughness is about 1 nm. (b) AFM image of directly stripped gold film. This film is much flatter and the roughness has...
decreased to 0.5~0.7 nm, although some defects are still present (about 2 nm deep). (c) AFM image of the gold film stripped after annealing at 100 °C. This sample shows the lowest roughness and the surface defects are less than 1 nm deep. This method was used to get the ultraflat gold substrates for the growth of SAMs. (d) AFM image of the gold film stripped after annealing at 300 °C. This sample shows larger grains but deep boundaries. The roughness is about 0.5 nm and the surface defects are approximately 2-3 nm deep. (e) Microscopy image of the gold film stripped after annealing at 600 °C. This sample is highly discontinuous and shows very large grains. The sample is too rough to characterize with AFM measurement. (f) Height distribution diagram of the Si/SiO$_2$ template and gold films made from different methods. The widths of the peaks refer to the roughness of the surfaces. A sharper peak means smaller distribution of heights and a flatter surface. Gold films stripped after annealing at 100 °C has a peak most similar to the bare Si/SiO$_2$ template, and it yields the best result. (For AFM images a-d: 5 µm×5 µm size, height scale 5 nm)

2. UV-Vis absorption spectra, optimized molecular structures and energy gaps for the four OPEs.

![Figure S2. UV-Vis spectra of (a) OPE5s and (b) OPE3s in THF solutions.](image-url)
The structures of the isolated molecules were optimized using density functional theory with the B3LYP functional and the 6-311g** basis set in Q-Chem. The molecular orbitals for the four systems are shown in table S1 for the isolated molecules, calculated with the smaller 6-31g* basis.

Table S1. Summary of the molecular orbitals and energy gaps for the four OPEs.

<table>
<thead>
<tr>
<th>molecule</th>
<th>Molecular orbital energy (eV)</th>
<th>ΔE_{HOMO-LUMO} (eV)</th>
<th>E_g (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HOMO</td>
<td>LUMO</td>
<td></td>
</tr>
<tr>
<td>OPE5-TTF</td>
<td>-4.87</td>
<td>-2.18</td>
<td>2.69</td>
</tr>
<tr>
<td>OPE5-S</td>
<td>-5.19</td>
<td>-2.05</td>
<td>3.14</td>
</tr>
<tr>
<td>OPE3-TTF</td>
<td>-4.88</td>
<td>-1.99</td>
<td>2.89</td>
</tr>
<tr>
<td>OPE3</td>
<td>-5.31</td>
<td>-1.77</td>
<td>3.54</td>
</tr>
</tbody>
</table>

E_g refers to the optical energy gap and was calculated from the edge of the UV-Vis absorption spectra.

3. SAM thickness and DFT lengths of the four OPEs.

Two methods were used to calculate the thickness of the SAMs from XPS spectra and all the data were summarized in Table S2. The bare gold substrate used for calculation of the thickness of the layer was prepared in ultra high vacuum by argon ions bombardment with a sample current of 10 µA for 30 minutes. The resulting surface was free of carbon, oxygen and argon and the only peaks observed were from gold.

Method a: Using the gold attenuation (Figure S3a) according to the equation:

\[ d = \lambda \ln \left( \frac{I_{Au}}{I_{SAM}} \right) \]

where \( d \) is the thickness, \( \lambda \) is the attenuation length, \( I_{Au} \) is the intensity of the clean bare gold, \( I_{SAM} \) is the intensity of the gold after SAM deposition and the angle between sample and analyzer at 90°. For the attenuation length value, we used \( \lambda = 42 \) Å.
for SAM on gold.\textsuperscript{S4}

Method b:\textsuperscript{S4} The thickness can be estimated by fitting data of the Au4f\textsubscript{7/2} intensities with tilt angle (Figure S3b) according to the equation:

\[ \ln I_{\text{SAM}} = \ln I_{\text{Au}} - d/(\lambda \cos \theta) \]

where \( d \) is the thickness, \( \lambda \) is the attenuation length, \( I_{\text{Au}} \) is the intensity of the clean bare gold, \( I_{\text{SAM}} \) is the intensity of the gold after SAM deposition, and \( \theta \) is the analyzer direction (photoemission angle). The sample was tilted at 75\(^\circ\) (\( \theta=75^\circ \)).

For the attenuation length value, we used \( \lambda=42 \) Å for SAM on gold (the same as in method a).\textsuperscript{S4}

![Figure S3. (a) XPS spectra of Au4f region for bare Au and OPE SAMs on Au (method a). (b) Fitting data of the Au4f\textsubscript{7/2} intensities with photoemission angle \( \theta \) for three cruciform OPE SAMs on Au (method b).](image)

Figure S3. (a) XPS spectra of Au4f region for bare Au and OPE SAMs on Au (method a). (b) Fitting data of the Au4f\textsubscript{7/2} intensities with photoemission angle \( \theta \) for three cruciform OPE SAMs on Au (method b).

4. Calibration of \( I-V \) measurements for the molecular junctions.

The transport properties of the SAMs were measured by CP-AFM in this paper. The data were calibrated against a well-known alkanethiol SAM (dodecanethiol, C\textsubscript{12}H\textsubscript{25}-SH, which was grow from a dodecanethiol solution in ethanol). Figure S4 shows the \( I-V \) curves of the molecular junctions based on OPE5-TTF, OPE5-S and C\textsubscript{12}H\textsubscript{25}-SH SAMs under the same measuring conditions and a similar tip. The OPE5-TTF and OPE5-S SAMs had much higher currents than the C\textsubscript{12}H\textsubscript{25}-SH SAM. As we discuss in the paper, OPE5-TTF and OPE5-S SAMs are densely packed with a coverage of close to 100\% on the Au surface. However, the three compounds have different molecular areas on the surface of Au. Herein, we estimated that OPE5-TTF, OPE5-S and C\textsubscript{12}H\textsubscript{25}-SH had molecular areas of 50, 35 and 23 Å\textsuperscript{2}, respectively. An AFM tips with a radius of \( \sim25 \) nm were used in the measurements, and the contact area is estimated to \( \sim100 \) nm\textsuperscript{2}. Then, the resistance (\( R \)) of single molecule can roughly be compared. When calculated at 0.3 V, \( R_{C\text{12}H\text{25}-SH} = 65000 \times R_{\text{OPE5-TTF}}, R_{C\text{12}H\text{25}-SH} = 4600 \times R_{\text{OPE5-S}} \).
Figure S4. $I-V$ curves of the molecular junctions based on OPE5-TTF, OPE5-S and C$_{12}$H$_{25}$-SH SAMs.

5. Linear fit of resistance versus molecular length in the OPE SAMs junctions.

Figure S5. Plot of resistance versus molecular length for the two groups of OPEs.

Table S2. Molecular lengths and their SAM thickness, resistance and tunneling attenuation factor for the OPEs.

<table>
<thead>
<tr>
<th>molecule</th>
<th>DFT length (nm)</th>
<th>SAM thickness (nm)</th>
<th>Resistance ($\Omega$)</th>
<th>$\beta$ (nm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>method $a$</td>
<td>method $b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OPE5-TTF</td>
<td>3.37</td>
<td>3.10</td>
<td>1.65×10$^7$</td>
<td>1.96</td>
</tr>
<tr>
<td>OPE5-S</td>
<td>3.37</td>
<td>3.03</td>
<td>1.54×10$^8$</td>
<td>2.01</td>
</tr>
<tr>
<td>OPE3-TTF</td>
<td>2.01</td>
<td>2.36</td>
<td>1.15×10$^6$</td>
<td>1.96</td>
</tr>
<tr>
<td>OPE3</td>
<td>2.01</td>
<td>1.78$^{52}$</td>
<td>9.97×10$^6$</td>
<td>2.01</td>
</tr>
</tbody>
</table>
The DFT geometries were calculated by optimizing the structures with the B3LYP functional and the 6-311G** basis set using Q-Chem\textsuperscript{3}.\textsuperscript{3} The distances quoted above were the S-S distances in the optimized structures.

6. AFM images of the SAMs.

![AFM images](image1)

**Figure S6.** AFM images of the SAMs: (a) OPE5-TTF, (b) OPE5-S, (c) OPE3-TTF, (d) OPE3.

7. Synthesis of OPE5-S and OPE3-TTF.

\[ \text{1,4-Dipentylbenzene } (\text{1,4-Dichlorobenzene } \text{1}) \quad \begin{array}{c}
\text{Cl} \\
\text{C}_5\text{H}_{11}\text{MgBr, NiCl}_2(\text{dppp})_2 \\
\text{Et}_2\text{O}, 45^\circ\text{C}
\end{array} \rightarrow \begin{array}{c}
\text{C}_5\text{H}_{11} \\
\text{C}_5\text{H}_{11}
\end{array} \]

1,4-Dichlorobenzene 1 (1.00 g, 6.85 mmol) and NiCl\(_2\)(dppp)\(_2\) (103 mg, 0.19 mmol, 3 mol%) were added to dry Et\(_2\)O (15 mL) and the mixture was placed under argon. Pentylmagnesium bromide (10 mL, 20 mmol, 2M in Et\(_2\)O) was slowly added (caution: exothermic reaction) over 10 min, before the temperature was raised to 45 °C. After stirring for 5 h, the reaction mixture was diluted with Et\(_2\)O (100 mL) and washed with a cold aqueous solution of NH\(_4\)Cl (100 mL) followed by brine (100 mL). The organic layer was dried over Na\(_2\)SO\(_4\) and the solvent was removed under reduced pressure. The product was purified by flash column chromatography (SiO\(_2\), heptane) to yield the product (1.10 g, 74%) as a colorless oil. \(^1\text{H NMR (500 MHz, CDCl}_3\)): \(\delta\) 7.09 (s, 4H), 2.57 (t, \(J = 6.1\) Hz, 4H), 1.69 – 1.56 (m, 4H), 1.41 – 1.24 (m, 8H), 0.90 (t, \(J = 4.9\) Hz, 6H). \(^{13}\text{C NMR (125 MHz, CDCl}_3\)): \(\delta\) 140.1, 128.2, 35.6, 31.6, 31.3, 22.6, 14.1. GC-MS: \(m/z\) 218.3 (M\(^+\), 50), 161.3 (100), 91.2 (30).
1,4-Diiodo-2,5-dipentylbenzene 3. 1,4-Dipentylbenzene 2 (1.00 g, 4.58 mmol), NaIO₄ (0.37 g, 1.73 mmol), and iodine (1.96 g, 7.72 mmol) were dissolved in CCl₄ (3 mL) and acetic acid (11 mL). Conc. H₂SO₄ (2 mL) was added before the temperature was raised to 70 °C. After stirring for 24 h, the reaction mixture was diluted with water (70 mL) and extracted with dichloromethane (100 mL). The organic phase was washed with aqueous Na₂S₂O₃ (2 x 100 mL) and dried over Na₂SO₄. After removal of the solvent, the residue was redissolved in heptane (100 mL) and passed through a short column of silica. The product was isolated as colorless oil that solidified to white crystals (1.90 g, 88%). Mp. 34.3 – 36.0 °C.

1H NMR (500 MHz, CDCl₃): δ 7.60 (s, 2H), 2.62 – 2.56 (m, 4H), 1.61 – 1.50 (m, 4H), 1.41 – 1.31 (m, 8H), 0.92 (t, J = 7.1 Hz, 6H).

13C NMR (125 MHz, CDCl₃): δ 144.9, 139.3, 100.4, 39.8, 31.5, 29.9, 22.5, 14.0. GC-MS: m/z 470.1 (M⁺, 100), 413.0 (75), 342.9 (45), 287.1 (90). Calcd. for C₁₆H₂₄I₂: C, 40.87; H, 5.15; Found C, 41.39; H, 5.19.

Compound 5. To a solution of 1,4-diiodo-2,5-dipentylbenzene 3 (0.416 g, 0.89 mmol) in dry, argon-flushed THF (12 mL) and NEt₃ (3 mL), Pd(PPh₃)₂Cl₂ (31 mg, 0.045 mmol, 5 mol%) and CuI (8 mg, 0.045 mmol, 5 mol%) were added. Then 1-(triisopropylsilyl)ethynyl-4-ethynylbenzene 4 (1.00 g, 3.54 mmol) was added and the reaction mixture was stirred for 7 h at 40 °C. The mixture was then diluted with Et₂O (50 mL) and washed with a saturated aqueous solution of NH₄Cl (50 mL) and then brine (50 mL). The organic layer was dried with Na₂SO₄ and concentrated under reduced pressure to a brown oil. The product was isolated by flash column chromatography (SiO₂, CH₂Cl₂: heptane 1:9) as a yellow oil, which solidified upon cooling to a yellow solid (0.482 g, 70%). Mp. 107.9 – 110.2 °C. 1H NMR (500 MHz, CDCl₃): δ 7.48 – 7.41 (m, 8H), 7.36 (s, 2H), 2.85 – 2.73 (m, 4H), 1.76 – 1.64 (m, 4H), 1.45 – 1.32 (m, 8H), 1.14 (s, 42H), 0.95 – 0.84 (m, 6H). 13C NMR (125 MHz, CDCl₃): δ 142.5, 132.5, 132.2, 131.4, 123.5, 123.4, 122.7, 106.8, 93.9, 93.0, 90.4, 34.3, 31.9, 30.5, 22.7, 18.8, 14.2, 11.5. MS (FAB): m/z 778.7 (M⁺). Calcd. for C₆₆H₇₄Si₂: C,
83.22; H, 9.57; Found: C, 83.24; H, 9.74.

**Compound 6.** To a solution of compound 5 (0.262 g, 0.34 mmol) in THF (10 mL) and two drops of H₂O, tetrabutylammonium fluoride (15 mg, 0.06 mmol) was added, and the reaction mixture was stirred for 20 min at rt. The solvent was then removed under reduced pressure, and the product was isolated by flash column chromatography (SiO₂, EtOAc:hexane 1:9) as a yellow solid (0.110 g, 70%) that in time underwent decomposition. Mp. 119.1 – 120.7 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.49 (d, J = 8.7 Hz, 4H), 7.46 (d, J = 8.7 Hz, 4H), 7.36 (s, 2H), 3.18 (s, 2H), 2.85 – 2.73 (m, 4H), 1.77 – 1.61 (m, 4H), 1.45 – 1.32 (m, 8H), 0.90 (t, J = 7.1 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃): δ 142.5, 132.6, 132.3, 131.5, 124.1, 122.6, 122.0, 93.6, 90.6, 83.4, 79.13 / 79.08 (doublet CCH), 34.2, 31.9, 30.5, 22.7, 14.2. MS (FAB): m/z 466.25 (M⁺). Calcd. for C₃₆H₃₄: C, 92.66; H, 7.34; Found: C, 92.22; H, 7.44.

**OPE5-S.** Compound 5 (0.200 g, 0.257 mmol) was desilylated within 30 min with tetrabutylammonium fluoride trihydrate (10 mg, 0.032 mmol) dissolved in THF (11 mL) with 2 drops of water added. The reaction mixture was then diluted with heptane (50 mL) and poured through a short column of SiO₂ using additional heptane (50 mL). Concentration under reduced pressure gave a yellow solid that was redissolved in dry, argon-flushed THF (10 mL). Then Pd(PPh₃)₂Cl₂ (16 mg, 0.026 mmol, 10 mol%) and Cul (5 mg, 0.026 mmol, 10 mol%) were added, followed by (i-Pr)₂NH (1 mL). After 5 min, p-iodothioacetylbenzene 7 (0.286 g, 1.03 mmol) was added. The reaction mixture was stirred under argon for 20 h at rt; it was then diluted with Et₂O (50 mL)
and washed with a saturated aqueous solution of NH₄Cl (25 mL) followed by brine (25 mL). The organic layer was dried with Na₂SO₄ and concentrated under reduced pressure to a yellow solid. The product was isolated by flash column chromatography (SiO₂, CH₂Cl₂:pentane 2:1) as a yellow solid (0.084 g, 43%). Mp. 176 – 178 °C. IR (neat, cm⁻¹): 2949, 2925, 2854, 1693, 1511, 1102, 834, 819, 543. ¹H NMR (500 MHz, CDCl₃): δ 7.59 (d, J = 8.5 Hz, 4H), 7.56 (d, J = 8.6 Hz, 4H), 7.53 (d, J = 8.6 Hz, 4H), 7.43 (d, J = 8.5 Hz, 4H), 7.40 (s, 2H), 2.90 – 2.76 (m, 4H), 2.43 (s, 6H), 1.79 – 1.63 (m, 4H), 1.45 – 1.36 (m, 8H), 0.92 (t, J = 7.1 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃): δ 193.8, 143.1, 135.0, 133.0, 132.6, 132.2, 132.0, 129.3, 124.7, 124.1, 123.3, 123.1, 94.2, 91.1, 91.0, 34.6, 32.3, 30.9, 30.7, 23.1, 14.4; one signal missing (overlap). MS (ESP, in MeOH): m/z 766.6 (M⁺), 789.6 (M + Na⁺) 805.5 (M + K⁺); 852.5 (M + 2MeOH + Na⁺). Calcd. for C₅₂H₄₇OₕS₈•0.5H₂O: C: 80.48, H 6.10; Found: C, 80.52; H, 6.06.

OPE3-TTF. The extended TTF 8 (100 mg, 0.14 mmol) and p-iodothioacetylbenzene 7 (117 mg, 0.42 mmol) were together with [PdCl₂(PPh₃)₂] (10 mg, 0.014 mmol, 10 mol%) and CuI (5 mg, 0.026 mmol, 19 mol%) placed under an inert atmosphere of Argon. Then dry, argon-flushed THF (20 mL) and (i-Pr)₂NH (5 mL) were added. After stirring for 18 h at 40 °C, the resulting mixture was filtered through a short silica column (SiO₂, CH₂Cl₂) and the filtrate was concentrated under reduced pressure. The crude product was purified by dry column vacuum chromatography (SiO₂, 0 - 100% CH₂Cl₂ / heptanes, 5% steps, 0 - 25% EtOAc / CH₂Cl₂, 5% steps) to yield the desired compound as an orange solid (36 mg, 26%). Mp. = 178 – 180 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.60 (d, J = 8.3 Hz, 4H), 7.52 (s, 2H), 7.44 (d, J = 8.3 Hz, 4H), 6.92 (s, 2H), 4.22 (m, 8H), 2.45 (s, 6H), 1.77 – 1.69 (m, 8H), 0.98 (m, 12H). ¹³C NMR (125 MHz, CDCl₃): δ 193.5, 159.7, 159.6, 135.0, 134.4, 134.1, 132.4, 131.3, 130.1, 128.9, 128.8, 124.1, 121.5, 112.3, 95.9, 89.1, 68.5, 68.5, 30.5, 21.9, 10.5, 10.4. MS (FAB⁺): m/z 998.1 (M⁺).
References:


$^1$H NMR spectrum of 2 (calibrated relative to CHCl$_3$: 7.26 ppm)
$^{13}$C NMR spectrum of 2 (calibrated relative to CDCl$_3$: 77.16 ppm)
$^1$H NMR spectrum of 3 (calibrated relative to CHCl$_3$: 7.26 ppm)
$^{13}$C NMR spectrum of 3 (calibrated relative to CDCl$_3$: 77.16 ppm)
$^1$H NMR spectrum of 5 (calibrated relative to CHCl$_3$: 7.26 ppm)
$^{13}$C NMR spectrum of 5 (calibrated relative to CDCl$_3$: 77.16 ppm)
$^1$H NMR spectrum of 6 (calibrated relative to CHCl$_3$: 7.26 ppm)
$^{13}$C NMR spectrum of 6 (calibrated relative to CDCl$_3$: 77.16 ppm)
$^1$H NMR spectrum of **OPE5-S** (calibrated relative to CHDCl$_2$: 5.32 ppm)
$^{13}$C NMR spectrum **OPE5-S** (calibrated relative to CD$_2$Cl$_2$: 54.00 ppm)
$^1$H NMR spectrum of **OPE3-TTF** (calibrated relative to CHCl$_3$: 7.26 ppm)
$^{13}$C NMR spectrum of **OPE3-TTF** (calibrated relative to CDCl$_3$: 77.16 ppm)