Resonant Transport in Single-Diketopyrrolopyrrole Junctions

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1. General Experimental Details.

The 1H and 13C NMR spectra were taken in $CDCl_3$ with TMS as an internal reference in Bruker Advance NMR spectrometer at 400 MHz frequency. The chemical shifts were reported as δ values (ppm) relative to TMS. MALDI-MS was in a Bruker Ultraflex II MALDI-TOF instrument. The optical absorption spectra of the molecules in solution were recorded with Perkin-Elmer (Lambda-35) spectrometer at room temperature.

2. Synthetic Details.

Materials and methods: All solvents were dried by standard methods. Chemicals were purchased from Aldrich, Acros Organics, S.D. fine chemicals, and Spectrochem and used without further purification. All reactions were performed in round bottomed flask equipped with argon bladder. The synthesized compounds were purified by preparative thin layer chromatography using powdered silica gel as stationary phase and 5% ethyl acetate in hexane as mobile phase.



Synthesis of DPP1: In a 50 mL round bottom flask equipped with Ar bladdar, diisopropyl amine (2.44 mmol, 0.34 mL) and n-BuLi (1.6 M in hexane) (2.44 mmol, 1.53 mL), in 10 mL anhydrous tetrahydrofuran (THF) at ice bath temperature under Ar atmosphere was stirred at room temperature for 35 minutes. It was then transferred through cannula to a solution of the parent compound (5) (0.41 mmol, 350 g) and diethyldisulfide (2.23 mmol, 0.28 mL) in 20 mL anhydrous THF at ice bath temperature. The reaction mixture was stirred for 30 minutes at ice bath temperature and then at room temperature (30 °C) for another 2 hours. The resulting mixture was extracted with dichloromethane (DCM) (3 × 100 mL), and the extracts were combined, washed with brine, and dried over Na₂SO₄. After evaporation of solvent, the residue was purified by thin layer chromatography using powdered silica gel as stationary phase and 5% ethylacetate in hexane as mobile phase to afford the final product as reddish green solid in 52% isolated yield. ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ : 8.80 (2H, d, J = 4.0 Hz), 7.16 (2H, d, J =

4.0 Hz), 3.97 (4H, d, J = 7.6 Hz), 2.97 (4H, q, J = 7.2 Hz), 1.90 (2H, br s), 1.36-1.21 (70H, m), 0.89-0.84 (12H, m); ¹³C NMR (100 MHz, CDCl₃, Me₄Si) δ : 161.7, 143.0, 139.6, 136.0, 132.1, 131.2, 107.9, 46.4, 38.0, 32.1, 32.0, 31.3, 30.2, 29.8, 29.7, 29.5, 26.4, 22.8, 14.8, 14.3. MS (MALDI): m/z calcd for C₅₈H₉₆N₂O₂S₄: 980.636 [M]⁺; found: 980.723.

Synthesis of DPP2: Compound **2** was prepared in 45% yields from the corresponding parent precursor (**6**) following the procedure as described for the synthesis of 1. ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ : 8.93 (2H, d, J = 4.0 Hz),8.86 (2H, d, J = 4.0 Hz), 7.41 (2H, d, J = 4.0 Hz), 7.17 (2H, d, J = 4.0 Hz), 4.04 (4H, d, J = 7.6 Hz), 3.99 (4H, d, J = 7.6 Hz), 2.99 (4H, q, J = 7.6 Hz),1.94 (4H, br s), 1.39-1.22 (134H, m), 0.88-0.82 (24H, m); ¹³C NMR (100 MHz, CDCl₃, Me₄Si) δ : 161.6, 161.5, 143.7, 141.0, 140.0, 139.0, 136.4, 132.0, 131.1, 130.0, 126.2, 109.3, 108.3, 46.8, 38.4, 32.6, 32.4, 31.7, 30.5, 30.1, 30.0, 29.8, 26.8, 23.1, 15.1, 14.6. MS (MALDI): m/z calcd for C₁₁₂H₁₈₂N₄O₄S₆: 1839.249 [M]⁺; found: 1839.529.

Synthesis of DPP3: Compound **3** was prepared in 43% yields from the corresponding parent precursor (7) following the procedure as described for the synthesis of 1. ¹H NMR (400 MHz, CDCl3, Me4Si) δ : 8.93 (2H, d, J = 4.0 Hz),8.86 (2H, d, J = 4.0 Hz), 7.41 (2H, d, J = 4.0 Hz), 7.17 (2H, d, J = 4.0 Hz), 4.04 (4H, d, J = 7.6 Hz), 3.99 (4H, d, J = 7.6 Hz), 2.99 (4H, q, J = 7.6 Hz),1.94 (4H, br s), 1.39-1.22 (134H, m), 0.88-0.82 (24H, m); 13C NMR (100 MHz, CDCl3, Me4Si) δ : 161.6, 161.5, 143.7, 141.0, 140.0, 139.0, 136.4, 132.0, 131.1, 130.0, 126.2, 109.3, 108.3, 46.8, 38.4, 32.6, 32.4, 31.7, 30.5, 30.1, 30.0, 29.8, 26.8, 23.1, 15.1, 14.6. MS (MALDI): m/z calcd for C₁₆₆H₂₆₈N₆O₆S₈: 2697.862 [M]⁺; found: 2697.922.

Synthesis of DPP4: Compound 4 was prepared in 41% yields from the corresponding parent precursor (8) following the procedure as described for the synthesis of 1. ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ : 8.93 (2H, d, J = 4.0 Hz), 8.86 (2H, d, J = 4.0 Hz), 7.41 (2H, d, J = 4.0 Hz), 7.17 (2H, d, J = 4.0 Hz), 4.04 (4H, d, J = 7.6 Hz), 3.99 (4H, d, J = 7.6 Hz), 2.99 (4H, q, J = 7.6 Hz), 1.94 (4H, br s), 1.39-1.22 (134H, m), 0.88-0.82 (24H, m); ¹³C NMR (100 MHz, CDCl3, Me4Si) δ : 161.6, 161.5, 143.7, 141.0, 140.0, 139.0, 136.4, 132.0, 131.1, 130.0, 126.2, 109.3, 108.3, 46.8, 38.4, 32.6, 32.4, 31.7, 30.5, 30.1, 30.0, 29.8, 26.8, 23.1, 15.1, 14.6. MS (MALDI): m/z calcd for C₂₂₀H₃₅₄N₈O₈S₁₀: 3556.475 [M]⁺; found: 3556.721.

3. Additional Experimental Data and Ana	lysis
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Electrochemical properties ^a				Optical Properties ^b	
Molecules	E _{HOMO} (V)	$E_{LUMO}\left(V\right)$	$\Delta E_{g}^{EC}\left(eV\right)$	$\Delta E_{g}^{opt}\left(eV\right)$	λ_{max}
DPP1	5.15	3.47	1.68	1.98	546, 584
DPP2	4.97	3.50	1.47	1.61	650, 680
DPP3	4.94	3.59	1.35	1.48	702, 739
DPP4	4.87	3.52	1.35	1.44	725, 766

Table S1. E_{HOMO} , E_{LUMO} and ΔE_g^{EC} determined from CV data, ΔE_g^{opt} determined from solution phase UV-vis data.



Figure S1. 2D conductance-displacement histograms for (a) DPP1, (b) DPP2 and (c) DPP3 taken at a low tip bias of 90 mV, and (d) DPP1, (e) DPP2, (f) DPP3 and (g) DPP4 taken at a high applied bias of > 650 mV. All histograms use 100 bins/decade along the conductance axis and 450 bins/nm along the displacement axis.



Figure S2. Conductance determined from Gaussian fits to histogram peaks of DPP1 (red), DPP2 (green) and DPP3 (blue) as a function of the molecular length and bias.



Figure S3. 2D conductance-displacement histograms for DPP1 taken at an applied bias of 750 mV (with a 100 k Ω resistor in series with the junction). (a) Histogram compiled from 1374 traces (selected from 10000) which show a molecular conductance in the range 0.03 G₀ to 0.5 G₀. (b) Histogram compiled from 5707 traces (selected from 10000) which show a molecular conductance in the range 10⁻⁴ G₀ - 0.03 G₀. These results imply we form and measure two types of molecular junctions which show distinct conductance plateaus. Because the exact alignment of molecular resonance relative to Fermi level can vary from junction to junction, we attribute the higher conductance seen in ~20% of traces that form a junction to off-resonant transport mechanism.

4. Theoretical Calculations

We utilize DFT and determine the energy dependent transmission functions using the nonequilibrium Green's function (NEGF) formalism. We model these oligomers by simplifying their structure replacing all alkyl chains with ethyl groups due to computational constraints. We use the projector augmented wave method implemented in GPAW with the Atomic Simulation Perdew-Burke-Ernzerhof exchange-correlation Environment (ASE). The (PBE-XC) functional 28 and the double- ζ plus polarization basis set was used for the calculations. In order to simulate the metal-molecule-metal system, we first optimize the gas phase molecular structures. We then attach gold electrodes to form junctions. The electrodes consist of 4×6 fcc Au (111) surfaces with three under-coordinated Au atoms forming a trimer on each surface. The molecule, trimers and top layer of the Au are further relaxed to a maximum atomic force of 0.05 eV Å⁻¹ while keeping the remaining Au-atoms fixed. We then calculate the Landauer transmission across these junctions.

Sensitivity to the choice of functional for DFT calculations: The large size of the DPP molecules, in particular DPP4 means that we do not go beyond DFT for our description of the electronic structure. In order to have some sense of the potential errors introduced by using PBE, we performed model transport calculations for the isolated molecules. In these model calculations, the binding groups were replaced by hydrogen atoms. The geometry of the H atoms was then relaxed, using the same settings as for the full junction except only the Γ -point was probed, while all other atoms where held fixed. We then used a range of functionals and the 6-31G basis set in the Gaussian09 software package to calculate the electronic structure from which we calculated the transport properties.

As the molecules used in these model calculations are not bound between gold electrodes, we do not have an explicit coupling to the electrodes within the calculations and this needs to be set. We can perform a basis transformation to Natural Atomic Orbitals (NAO) for both the model calculations and the full junctions and then set the coupling elements to the same value as was obtained in the PBE full junction calculations. We set $\Gamma_{ii}^{L}(E) = \Gamma_{kk}^{R}(E) = 0.6$ eV where i and k are the NAOs corresponding to the p_z orbital on the carbon atoms bound to the electrodes (i.e. the carbon atom where the hydrogen was added after the binding group was removed) and all other elements set to zero. We evaluated the Green's function elements as $G_{ik}^{r}r(E) =$ $[EI - H - \Sigma^{L} - \Sigma^{R}]^{-1}_{ik}$ where H is the Fock matrix of the relaxed gas phase molecules rotated to the orthogonal NAO basis. In the case where all elements in Γ^L and Γ^R are zero except Γ^L_{ii} and Γ^R_{kk} the transmission can be written as:

$$T(E) = \Gamma_{ii}^{L}(E) |G_{ik}^{r}(E)|^{2} \Gamma_{kk}^{R}(E)$$

We set the Fermi energy in the model calculations to match the offset from the center of the HOMO-LUMO gap obtained from the full junction calculation (including Au) using PBE. We calculated the conductance by numerical integration of the transmission in accordance with the Landauer formula assuming no voltage dependence of the transmission and an electrode temperature of 300K. Our code for calculating the Natural Atomic orbitals is available on GitHub (https://github.com/andersborges/natural-orbitals) including examples for calculating transport properties using both GPAW and Gaussian09 for generic molecules.

Figure S4 shows the transmission through DPP1 for a variety of functionals. HF is known to overestimate the band gap while PBE is known to underestimate it. Our calculations reflect this and also demonstrate that while magnitude of the transmission at low bias for DPP1 clearly depends on the band gap/method all methods produce the same qualitative trends for transport.



Figure S4. Transmissions of DPP1 calculated from the gas phase molecule using a variety of functionals from Gaussian. Fermi level alignment was determined from a full junction calculation.

Difference between model and full junction DFT calculations

To verify the validity of the model approach (above) we can compare a model calculation for DPP1 using PBE with the full junction calculation shown in Figure S5. The black line shows the full transmission evaluated at the Gamma point and the orange one shows the contribution from $\Gamma_{ii}^{L}(E)|G_{ik}^{r}(E)|^{2}\Gamma_{kk}^{R}(E)$. We see that the approximation is quite good throughout the band-gap.



Figure S5. The full transmission calculated at the Gamma point as well as the contribution $\Gamma_{ii}^{L}(E)|G_{ik}^{r}(E)|^{2}\Gamma_{kk}^{R}(E)$ where *i* and *k* are the indices of the p_{z} -orbitals calculated as the natural atomic orbitals of the equivalent gas phase molecule with binding groups substituted for H's.

Length and Bias dependence with HSE06: We can calculate the length and bias dependence of the transmission and conductance from the model calculations with HSE06 to provide a comparison with the PBE results we have for the full junctions. The transmission for DPP1-DPP4 is shown in Figure S6 using HSE06/6-31G. From these transmissions we calculated the current by numerical integration of the transmission. The resulting conductance for three different biases of 0.1, 1.3 and 1.8 V is shown in Figure S7, displaying the same trends as seen for PBE with the full junction calculations.



Figure S6. Calculated transmission of DPP1-DPP4 using Gaussian09 and HSE06/6-31G.



Figure S7. Conductance calculated from numerical integration of the transmission in Figure S6 at a bias of 0.1 V (off-resonant transport for DPP1-DPP4), 1.3 V (resonant transport for DPP2-DPP4) and 1.8 V (resonant transport for DPP1-DPP4).

Conductance and differential conductance calculations from Landauer formula.

We start from the Landauer formula for an arbitrary transmission function and consider the differential conductance first:

$$I(V) = \frac{2e}{h} \int_{-\infty}^{\infty} dE T(E) \cdot \left[f\left(E - \frac{eV}{2}\right) - f\left(E + \frac{eV}{2}\right) \right]$$
$$\frac{dI}{dV}(V) = \frac{2e}{h} \int_{-\infty}^{\infty} dE T(E) \cdot \frac{d}{dV} \left[f\left(E - \frac{eV}{2}\right) - f\left(E + \frac{eV}{2}\right) \right]$$
$$\frac{df(E)}{dE} = -\frac{1}{4k_BT} \operatorname{sech}^2 \left(\frac{E}{2k_BT}\right)$$
$$\frac{dI}{dV}(V) = \frac{e^2}{4hk_BT} \int_{-\infty}^{\infty} dE T(E) \cdot \left[\operatorname{sech}^2 \left(\frac{E - \frac{eV}{2}}{2k_BT}\right) + \operatorname{sech}^2 \left(\frac{E + \frac{eV}{2}}{2k_BT}\right) \right]$$

In the limit of low temperature:

$$\lim_{T \to 0} \frac{df}{dE} = -\delta(E)$$
$$\lim_{T \to 0} \frac{dI}{dV}(V) = \frac{e^2}{h} \int_{-\infty}^{\infty} dE \ T(E) \cdot \left[\delta\left(E - \frac{eV}{2}\right) + \delta\left(E + \frac{eV}{2}\right)\right] = \frac{G_0}{2} \left[T\left(\frac{eV}{2}\right) + T\left(-\frac{eV}{2}\right)\right]$$

Therefore, $\frac{dI}{dV} = G_0$ if and only if $T\left(\frac{eV}{2}\right) = T\left(-\frac{eV}{2}\right) = 1$, even at 0 Kelvin. In most situations, one frontier orbital lies closer to Fermi than the other. Therefore, either $T\left(\frac{eV}{2}\right) = 1$ or $T\left(-\frac{eV}{2}\right) = 1$, but not both. For example, for a LUMO conducting molecule, $T\left(\frac{eV}{2}\right) = 1$ and $T\left(-\frac{eV}{2}\right) \ll 1$. Therefore, max $\left[\frac{dI}{dV}\right] \sim \frac{G_0}{2}$ in most situations.

Now consider the conductance:

$$G(V) = \frac{I(V)}{V}$$
$$0 = \frac{d}{dV} \left(\frac{I(V)}{V} \right) \Big|_{V=V_{max}} = \frac{1}{V^2} \left[I(V) - V \frac{dI}{dV} \right] \Big|_{V=V_{max}}$$

1 (17)

Where V_{max} is defined such that $max[G(V)] = G(V_{max})$

$$I(V_{max}) = V_{max} \frac{dI}{dV}\Big|_{V=V_{max}}$$
$$\max[G(V)] = \frac{I(V_{max})}{V_{max}} = \frac{dI}{dV}\Big|_{V=V_{max}}$$
$$\frac{dI}{dV}\Big|_{V=V_{max}} \le \max\left[\frac{dI}{dV}\right]$$

But we have shown that under most circumstances, the maximum differential conductance is close to $G_0/2$. Therefore,

$$\max[G(V)] \le \max\left[\frac{dI}{dV}\right] \le \frac{G_0}{2}$$

This is confirmed with numerical calculations, where the conductance (G) and differential conductance (dI/dV) are calculated numerically from the current. For the purposes of this demonstration, we use a single Lorentzian transmission function. We set $\varepsilon = 0.5 \ eV$ and $\Gamma = 1 \ meV$.

$$T(E) = \frac{\Gamma^2}{(E-\varepsilon)^2 + \Gamma^2}$$

The conductance (red) and differential conductance (blue) for T=300 K and T= 0 K are shown in Figures S8a and S8b, respectively. At room temperature, both the peak conductance and peak differential conductance are much smaller than G_0 , on the order of 10^{-3} - 10^{-2} G_0 . At 0 K, the peak

differential conductance reaches $\frac{1}{2}G_0$, as shown above. However, the conductance is still on the order of 10^{-3} G₀. Note that in both cases, the maximum value of conductance occurs at the intersection between the conductance and differential conductance.



Figure S8. Numerically calculated conductance (G, red) and differential conductance (dI/dV, blue) from a single Lorentzian transmission at (a) T=300 K and (b) T=0 K

5. NMR Data

¹H NMR spectrum of **DPP1**



¹³C NMR spectrum of **DPP1**



¹H NMR spectrum of **DPP2**



¹³C NMR spectrum of **DPP2**



¹H NMR spectrum of **DPP3**



¹³C NMR spectrum of **DPP3**



¹H NMR spectrum of **DPP4**



¹³C NMR spectrum of **DPP4**



6. X-Ray single crystal structure of the DPP1-Hex

For unambiguous structure determination we have performed X-Ray single crystal structure analysis of **DPP1-Hex** where the N-alkyl group is hexyl. Since we could not afford a single crystal for the molecule with 2-octyl-1-dodecyl group (N.B. the molecules which are originally used for the present study contain 2-octyl-1-dodecyl group), we therefore synthesized the hexyl analogue. The single crystal structure depicted below shows the distance between two end-capping sulphur atom to be 1.45 nm.



Figure S9. X-Ray single crystal structure of DPP1-Hex showing the distance between two end capping sulfur atoms.

7. MALDI-MS spectra





MALDI-MS spectrum of **DPP2**



MALDI-MS spectrum of **DPP3**



MALDI-MS spectrum of **DPP4**

