Supporting information

Columnar Self-Assembly of a 3D-Persulfurated Coronene Asterisk. The Dominant Role of Aryl-Sulfur Bonds.†

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Surface morphology of DPTC on HOPG(0001)

Tunneling spectroscopy of DPTC on HOPG(0001)

Figure S1. STM constant current image ($V = 1.1$ V, $I = 0.17$ nA) obtained for the monolayer DPTC covered HOPG(0001) surface at a temperature $T = 77$ K. Molecular motions are reduced in comparison to measurements at room temperature. In the latter case, no structural resolution is obtained. At $T = 77$ K, the STM image shows a monolayer with features of single molecules.

Figure S2. A set of single $I(V)$ traces obtained on the DPTC covered HOPG(0001) surface at $T = 77$ K. Each curve was recorded with the tunneling set point values $V_{SP} = 1.45$ V and $I_{SP} = 0.17$ nA. The curves exemplify that a determination of the onset of the orbital mediated tunneling (OMT) is not possible without ambiguity. The measured HOMO-LUMO gap varies in a range of $\pm 0.2$ eV around the mean value $\Delta E_{STS} \approx 2.3$ eV. These variations are believed to originate from the disordered nature of the DPTC layer as well as from residual molecular motions even at $T = 77$°.

Figure S3. STM constant current topographic image of a DPTC monolayer on Au(111) at room temperature showing an ordered columnar structure.

Figure S4a. STM constant current topographic image of a DPTC monolayer on Au(111) at room temperature. Some bright spots of nearly identical size corresponding to single DPTC molecules adsorbed on the monolayer are observed.
The intensity correlation function was determined by cross correlating the signal originating from the same sample volume but detected in two detectors via a software correlator using a multiple tau algorithm. In this way the artificial contribution to the signal from detector after pulsing can be suppressed. A 1nM Rhodamine 6G (Rh6G, Aldrich) dimethylformamide (DMF) solution was used as reference for which the diffusion coefficient was determined to be $D_{\text{ref}}^\text{Rh6G} = (4.2 \pm 0.2) \times 10^{-10}$ m²/s at T=20°C. $D_{\text{ref}}^\text{Rh6G}$ was derived using the relationship $D_{\text{DMF}}^\text{Rh6G} = \eta_{\text{H}_2\text{O}} \eta_{\text{DMF}}^3/2 \eta_{\text{DMF}}$, where $D_{\text{ref}}^\text{Rh6G} = (3.8 \pm 0.2) \times 10^{-10}$ m²/s denotes the diffusion coefficient of Rh6G in water, $\eta_{\text{H}_2\text{O}} = 1.003$ Pas and $\eta_{\text{DMF}} = 0.9189$ Pas are the viscosities of water and DMF, respectively. The reference measurement yields for the lateral focus dimension $w_\text{ref} = (262 \pm 12)$ nm. The fit is insensitive to the vertical focus dimension and the measured correlation functions $G(t)$ measured for Rh6G as well as for the DPTC solutions are sufficiently described by the approximate relation,

$$
G(t) = \frac{1}{N} \left( 1 + 4 \frac{t}{w_\text{ref}^2} D t \right)^{-1} + 1
$$

where $N$ is the average number of labeled molecules in the focus, $D$ their diffusion coefficient and $t$ the lag time. For more details see Ref. (4) and (5).

The hydrodynamic radius $R_h$ of the DPTC molecule can be derived from the measured diffusion coefficients using the Stokes-Einstein relation,

$$
D_0 = \frac{k_B T}{6 \pi \eta_{\text{DMF}} R_h}
$$

where $D_0$ is the diffusion coefficient in the limit of zero concentration, $T$ is the temperature (here $T=20^\circ\text{C}$), $\eta_{\text{DMF}} = 0.9189$ Pas is the viscosity of DMF, and $k_B$ is the Boltzmann constant. By averaging the diffusion coefficients measured for samples with different DPTC concentrations we obtain $\bar{D}_0 = (3.2 \pm 0.2)$ m²/s, yielding $R_h = (0.72 \pm 0.04)$ nm for the hydrodynamic radius. Note, that the error given for the values of $\bar{D}_0$ and $R_h$ include systematic errors (around 6%) originating from measuring against a standard for the determination of the illumination profile which is assumed to be Gaussian. The standard deviation resulting from fitting the data are significantly smaller, $\Delta R_h = 0.02$ nm and $\Delta \bar{D}_0 = 0.006$ nm, respectively.

**References:**