Supplemental Information

Density Functional Theory (DFT) calculations were performed on 2HTFPP with intact pyrrolic hydrogens, dehydrogenated TFPP, and deprotonated (dianionic) TFPP. The only molecular orbitals that display the double-dot feature in the theoretical STM image are HOMO-2, HOMO-3, and HOMO-4, Figure 1. The HOMO-3 and HOMO-4 of the diradical TFPP exhibit a similar double-dot feature, but are perpendicular and appear as four dots when combined. The HOMO-3 and HOMO-4 of dianionic TFPP and Au-TFPP are also perpendicular double-dot features that create squares when combined. As the magnitude of the bias voltage is increased, more states are included in the STM image. The double-dot features remained in the experimental images, even when more electronic states were included, indicating that the adsorbed molecules are 2HTFPP.

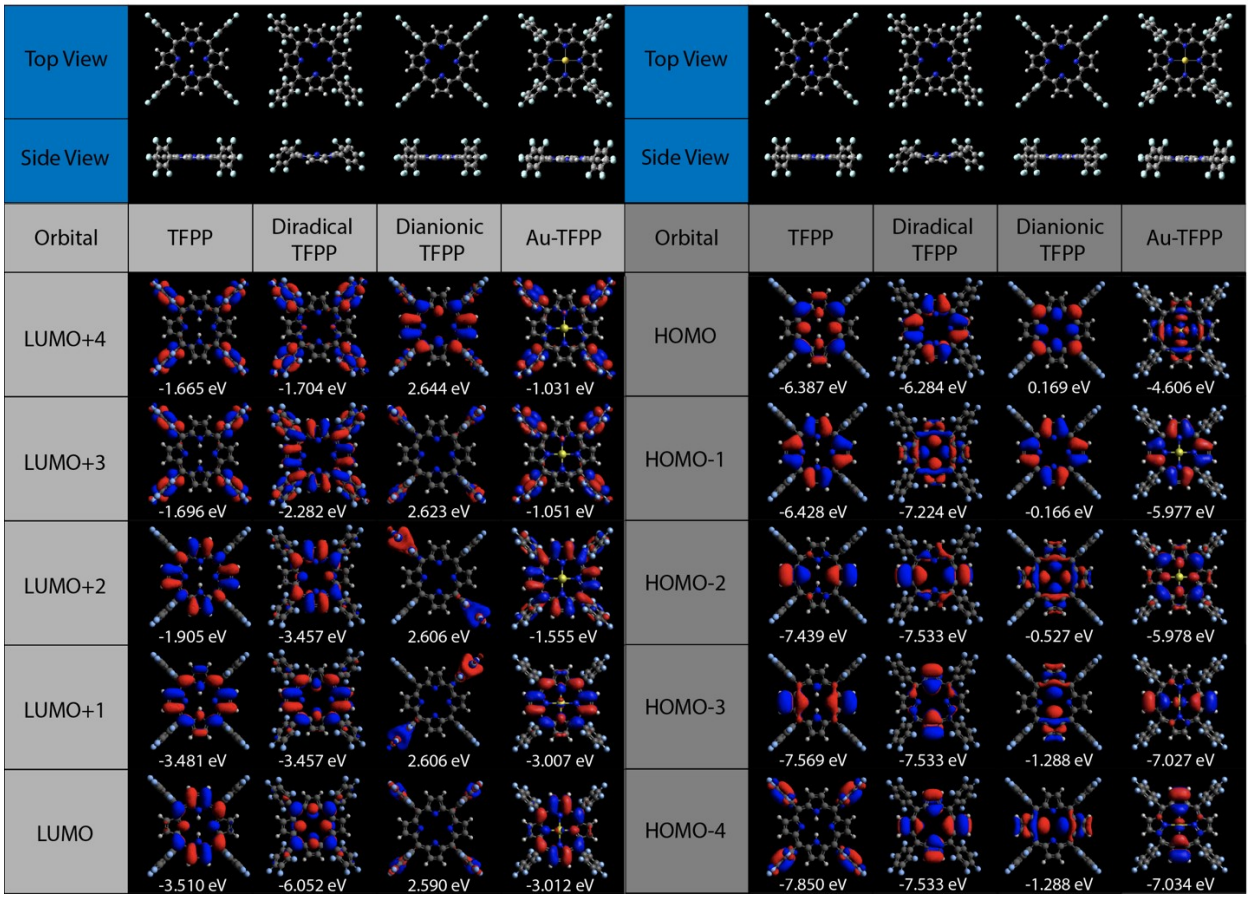

Figure 1: DFT models and calculations of charge density for 2HTFPP, neutral TFPP, dianionic TFPP, and Au-TFPP.

It is unlikely that the shifted electronic energies of 2HTFPP is due to coordinating with underlying gold atoms. Theoretical STM images of Au-TFPP do not exhibit double-dot characteristics, Figure 2.

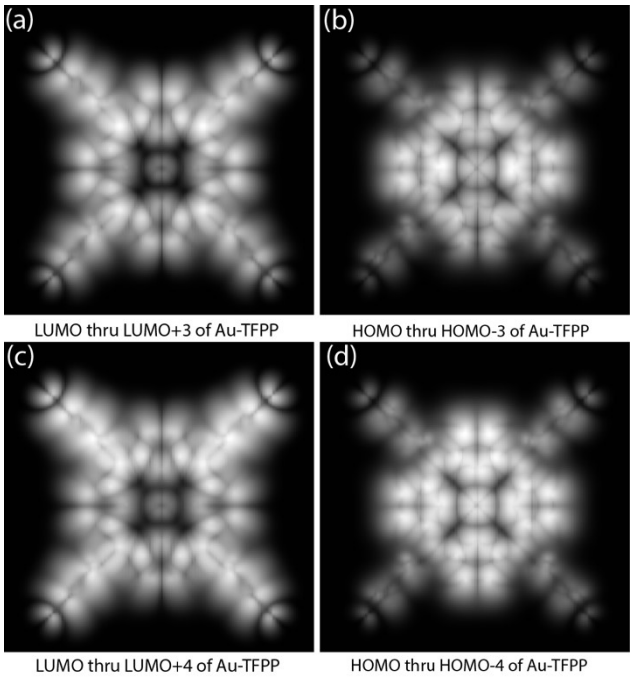

Figure 2: Theoretical STM images of Au-TFPP. No double-dot features are present.

Deposition via a pulsed solenoid valve can stabilize meta-stable molecular motifs through rapid solvent evaporation in vacuum. Room-temperature deposition resulted in a close-packed island, Figure 2a, with a density of 0.64 ± 0.04 molecules/nm^2. Annealing the sample to 200°C resulted in a packing density of 0.38 ± 0.03 molecules/nm^2, Figure 2b. Drop-casting followed by annealing at 200°C resulted in similar packing observed after annealing the pulse-deposited sample, but we did observe one area with a 4-molecule unit cell and a packing density of 0.21 molecules/nm^2, Figure 2c.

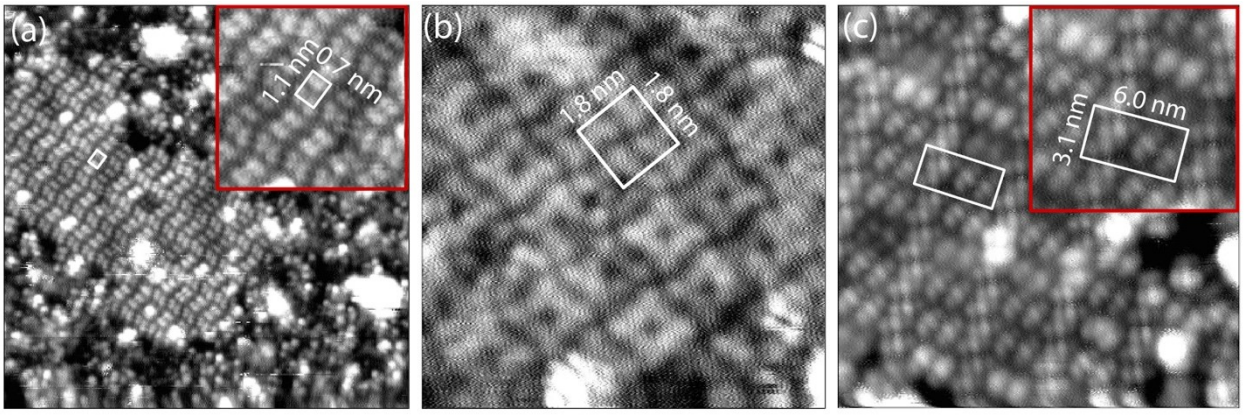

Figure 3: (a) -1.5 V and 5 pA. Unit cell of 2HTFPP pulse-deposited at room temperature. (b) -0.5 V and 5 pA. Pulse-deposited 2HTFPP annealed to 200°C. (c) 2.0 V and 5 pA. 2HTFPP that was drop-cast and annealed to 200°C.