## Electronic Supplementary Material (ESI) for RSC Advances. This journal is © The Royal Society of Chemistry 2021

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.

Top View	XX		×		Top View	XX		×	
Side View	केल् केल् केल् केल्या-सारकारकेल्या केल्	la serie de la			Side View	24 84 84 84 84 84 84 84 84 84 84 84 84 84	Januar di se		and the second
Orbital	TFPP	Diradical TFPP	Dianionic TFPP	Au-TFPP	Orbital	TFPP	Diradical TFPP	Dianionic TFPP	Au-TFPP
LUMO+4	-1.665 eV	-1.704 eV	2.644 eV	-1.031 eV	НОМО	-6.387 eV	-6.284 eV	0.169 eV	-4.606 eV
LUMO+3	-1.696 eV	-2.282 eV	2.623 eV	-1.051 eV	HOMO-1	-6.428 eV	-7.224 eV	-0.166 eV	-5.977 eV
LUMO+2	-1.905 eV	-3.457 eV	2.606 eV	-1.555 eV	HOMO-2	-7.439 eV	-7.533 eV	-0.527 eV	-5.978 eV
LUMO+1	-3.481 eV	-3.457 eV	2.606 eV	-3.007 eV	HOMO-3	-7.569 eV	-7.533 eV	-1.288 eV	-7.027 eV
LUMO	-3.510 eV	-6.052 eV	2.590 eV	-3.012 eV	HOMO-4	-7.850 eV	-7.533 eV	-1.288 eV	-7.034 eV

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.



LUMO thru LUMO+4 of Au-TFPP HOMO thru HOMO-4 of Au-TFPP 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  $0.64 \pm 0.04$  molecules/nm<sup>2</sup>. Annealing the sample to 200°C resulted in a packing density of  $0.38 \pm 0.03$  molecules/nm<sup>2</sup>, 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<sup>2</sup>, 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.