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Electronic Supplementary Information

Synthesis and characterization of a single-layer conjugated metal-organic structure featuring a non-trivial topological gap

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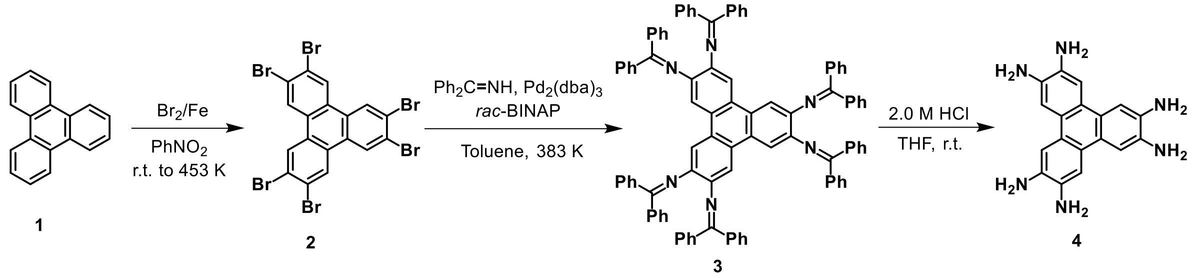
Methods

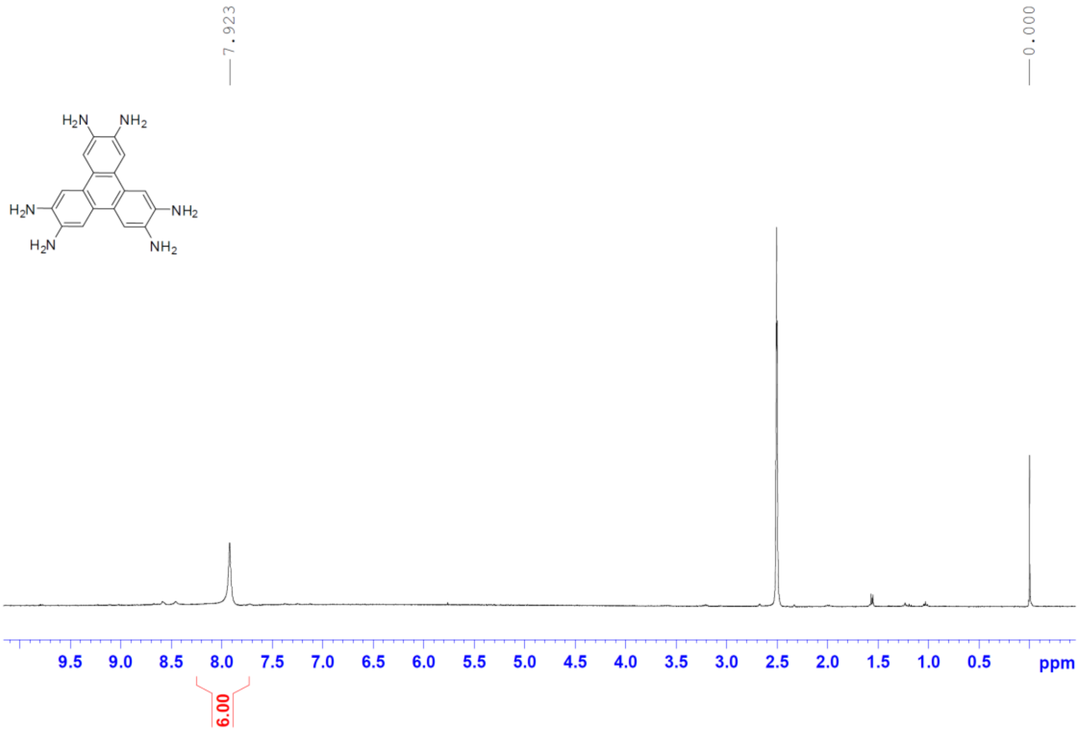
Synthesis of 2,3,6,7,10,11-hexaaminotriphenylene (HATP) 4[1]



2: 2,3,6,7,10,11-hexabromo-triphenylene **2** was synthesized according to the previous report.[2]

A toluene solution (50 mL) of *rac*-BINAP (0.607 g, 0.98 mmol) and tris(dibenzylideneacetone)dipalladium(0) (0.448 g, 0.49 mmol) was thoroughly degassed by four freeze-pump-thaw cycles, purged with Ar, and stirred at 110 °C for 30 min. After cooling to r.t., the mixture was added with benzophenone imine (2.65 mL, 15.77 mmol), 2,3,6,7,10,11-hexabromo-triphenylene **2** (1.419 g, 2.02 mmol), and sodium tert-butoxide (1.516 g, 15.77 mmol), and the mixture was stirred at 110 °C for 12 hours. The mixture was cooled to room temperature and diluted with CH_2Cl_2, then filtered through a pad of Celite, and evaporated to dryness. The residue was subjected to column chromatography on silica gel with AcOEt/hexane (1:4) as eluent to give **3** (1.55 g, 1.19 mmol) as yellow solid, which was then added to a mixture of THF (70 mL) and 2.0 M aqueous HCl solution (3.5 mL, 7.0 mmol). After stirring for 30 min at room temperature, the precipitate was isolated by centrifugation, washed with hexane and then suspended in EtOH (30 mL). Et$_3$N (1.09 g, 1.08 mmol) was added to the mixture and stirred at room temperature for 30 min. Then the solvent was evaporated and residue was dissolved in CH$_2$Cl$_2$ and water. CH$_2$Cl$_2$ was separated and dried over MgSO$_4$. Then the solvent was evaporated and the residue was passed over the flash chromatography on silica gel to afford **4** (0.32 g, 1.0 mmol) as light yellow solid in 50% yield. ^{1}H NMR (DMSO-*d*$_6$, 400 MHz) δ 7.92 (6H, s). HRMS (EI, TOF) calcd for C$_{18}$H$_{18}$N$_6^+$ [M]$^+$: 318.1593, found: 318.1597.

^{1}H NMR of 2,3,6,7,10,11-hexaaminotriphenylene **4**



Sample preparation and STM experiments

Sample preparation and scanning tunneling microscopy (STM) characterization were conducted in a ultra-high vacuum scanning tunneling microscope system (Omicron Nanotechnology). A single-crystal Au(111) was cleaned by cycles of Ar$^+$ ion sputtering, and annealing to 800 K. HITP molecules were deposited on clean Au(111) surface, which was held at room temperature, using an organic molecular beam deposition source heated to 310°C. Fe atoms were deposited using an e-beam evaporator. The sample was annealed to 250°C to form Ni$_3$(HITP)$_2$ network. Differential tunneling spectra (dI/dV) were recorded at the cryogenic temperature (4.9 K) using Lock-in technique with a modulation of 10 mV (rms) and a frequency of 1.5 kHz.

Density-functional theory calculations

The first-principles calculations were performed using the density functional theory (DFT) using generalized gradient approximation of the Perdew-Burke-Ernzerhof (PBE) and projector-augmented-wave (PAW) potentials,[3-5] as implemented in the Vienna *ab-initio* simulation package (VASP).[6,7] The kinetic energy cutoff was set at 500 eV. The simulated system consists of three Au(111) layers and a $Ni_3(HITP)_2$ adlayer in a unit cell with a vacuum space of ~20 Å. Except the Au bottom layer, the rest atoms were relaxed using conjugate gradient method until the residual forces on each atom were smaller than 0.01 eV/Å. Additionally, the criteria for convergence for self-consistent electronic structure set at 10^{-5} eV. The surface Brillouin-zones (SBZ) were sampled using Γ-centered $3 \times 3 \times 1$ Monkhorst-Pack grid.[8]

The effective mass at K point of the band structure was obtained as the following. A second order polynomial was first used to fit the black circles near K point (Fig. 3d). The effective mass m^* was calculated according to the formula, $m^*/m_0 = \hbar^2/\left[\left(\frac{\partial^2 E(k)}{\partial^2 k}\right) \cdot m_0\right]$, where m_0, $\hbar$, $E(k)$, and k are the effective mass, rest mass of an electron, and the reduced Planck constant, energy and wave vector, respectively.

The charge transfer was quantified using Bader charge analysis.[9, 10] The Bader charges of three systems, free-standing layer $Ni_3(HITP)_2$, bare Au substrate and single-layer of $Ni_3(HITP)_2$ adsorbed on the Au substrate were calculated and listed in Table S1. The charge difference of the adsorbed and free-standing $Ni_3(HITP)_2$ layer is -0.82 e. The negative value means that the charge in $Ni_3(HITP)_2$ layer is depleted. The charge difference of Au(111) after placing $Ni_3(HITP)_2$ on top is 0.82 e. The positive value means charge in Au surface is accumulated.

Table S1: Bader charges of $Ni_3(HITP)_2$ adsorbed on Au(111), free-standing and the Au(111) substrate.

System	Adsorbed layer on Au		Free-standing layer	Bare Au substrate
	$\rho_{\mathrm{Ni3(HITP)2}}$	ρ_{Au}	$\rho_{\mathrm{Ni3(HITP)2}}$	ρ_{Au}
Bader charge (e)	257.18	1881.82	258.00	1881.00

Supplementary figure

The STM data show some less-ordered structures, as highlighted in Fig. S1. These structures consist of motifs that three diimine ligands are joined at a central dot in three-fold symmetry. We speculate that this is a six -fold coordination of imine with Ni. Co-existence of this bonding motif and the four-fold motif results various less ordered structures.

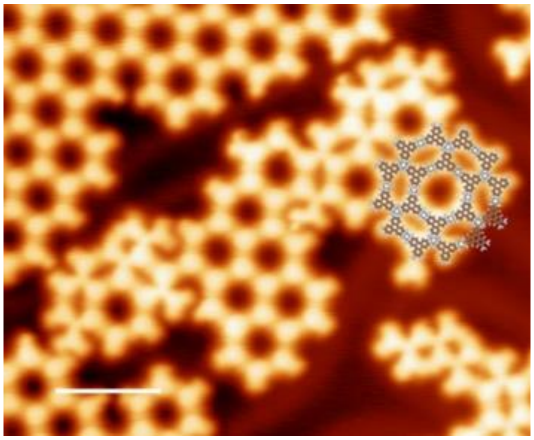


Fig. S1. An STM image showing the less-ordered structures with a molecular model overlaid. Scale bar: 4 nm.

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