

ELECTRONIC SUPPLEMENTARY INFORMATION

Self-assembly of metal-organic coordination networks using on-surface synthesized ligands

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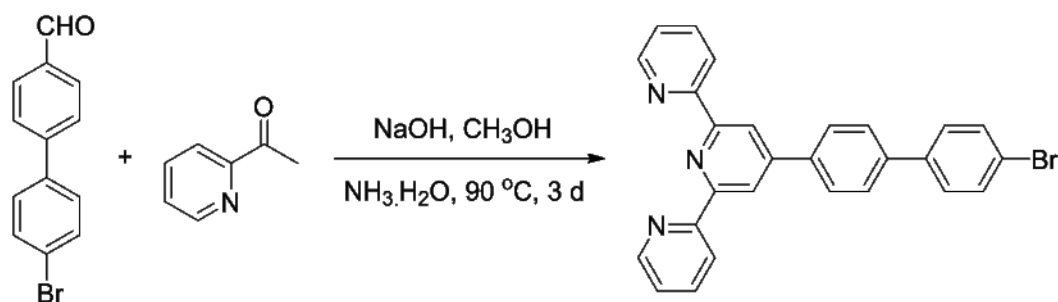
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1. Synthesis of ligand 1



To a mixture of NaOH (0.30 g, 7.50 mmol), methanol (120 mL) and 4'-bromo-[1,1'-biphenyl]-4-carbaldehyde (0.90 g, 3.57 mmol), aqueous ammonium (30 mL) and 2-acetyl-pyridine (0.90 g, 7.44 mmol) were added. The resulting solution was stirred at 90 °C for 3 days. The reaction mixture was cooled and filtrated to afford white solid, which was washed by water. Then the solid was subjected to flash column chromatography on silica gel to afford ligand **1** (0.5 g) in 32% yield. Mp: 212~216 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.80 (s, 2H), 8.76 (d, 2H, J = 4.8 Hz), 8.70 (d, 2H, J = 8.00 Hz), 8.01 (d, 2H, J = 8.00 Hz), 7.89-7.93 (m, 2H), 7.71 (d, 2H, J = 8.4 Hz), 7.61 (d, 2H, J = 8.8 Hz), 7.54 (d, 2H, J = 8.8 Hz), 7.38 (dd, 2H, J₁ = 5.2 Hz, J₂ = 7.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 118.7, 121.4, 121.9, 123.9, 127.4, 127.9, 128.7, 132.0, 136.9, 137.7, 139.3, 140.6, 149.2, 149.6, 156.0, 156.2. HRMS calcd for C₂₇H₁₉BrN₃⁺ (M+H⁺): 464.0757, found 464.0760.

2. Experimental method

Experiments were performed in an ultrahigh-vacuum system (Omicron Nanotechnology) with base pressure below 5×10^{-10} mbar. A single-crystalline Au(111) substrate was cleaned by Argon-ion sputtering and annealing to ~ 630 °C. The molecules were thermally evaporated by an organic molecular beam evaporator and deposited onto the Au(111) substrate which was held at room temperature. The evaporation temperature for **1** and **2** (Sigma Aldrich) is 200°C and 350°C, respectively. Fe was evaporated using an electron beam evaporator. The STM measurements were conducted at 78K. The data analysis used WSxM software.^{S1}

3. Supporting figure

Mixing of molecules of **3** and Fe atoms on the surface at 150°C formed chain structures, as shown in the up panel in Fig. S1. The periodic length of the chains is 3.30 ± 0.04 nm. The chains consist of head-to-head aligned molecules of **3**. We propose that the chains are stabilized by metal-organic coordination bond between Fe atoms and terpyridyl groups. However, due to the weak electronic signature of the metal atoms, we did not resolve Fe atoms.^{S3} Assuming only one Fe atom sits halfway between the two terpyridyl groups, the nearest bonding length of Fe-N is about 0.40 nm, which is much larger than the typical value of coordination bond length. Similar structures were observed in Cu-coordinated bis-terpyridyl systems.^{S2} A tentative model of terpyridyl-(Cu)₃-terpyridyl was proposed and supported by DFT calculation.^{S2} Here we propose a similar model as shown in the bottom panel in Fig. S1. We propose that three Fe atoms are involved in this coordination motif. In this configuration, the Fe-N distance is about 0.20 nm, which falls in the range of typical coordination bond length.

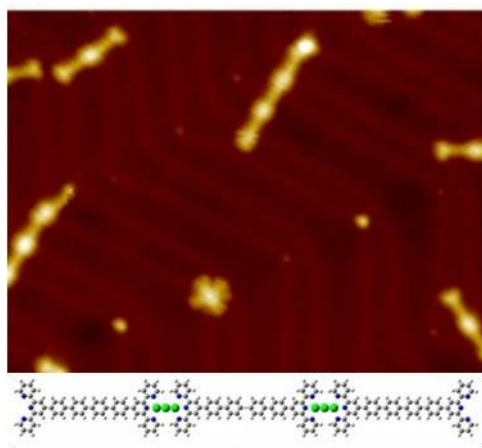


Fig. s1 Up: STM image (42×33 nm²) showing the coordination chains formed by **3** and Fe. Bottom: A tentative model of the chain structure. The green balls represent Fe atoms

4. References

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