

Supporting information for

**Hydrogen-Bonding Self-Assembly of Two  
Dimensional (2D) Layer Structures  
Generating Metal-Organic Nanotubes**

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# Supporting Information

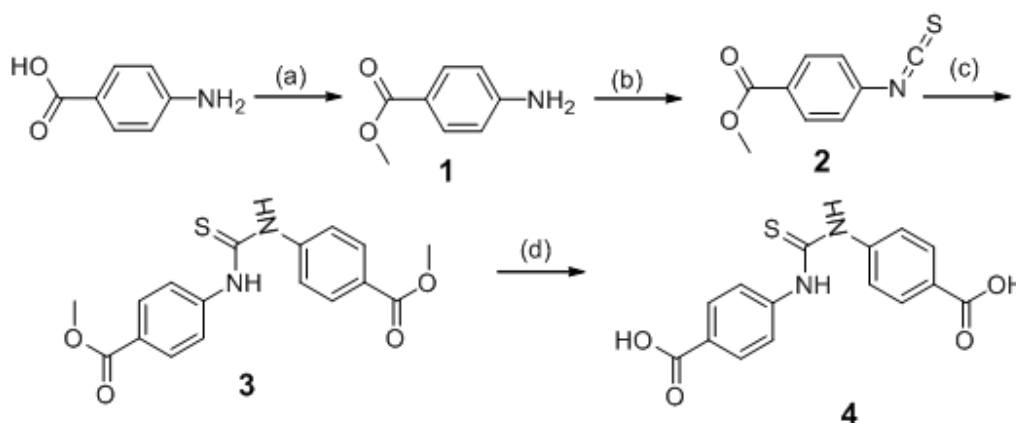
## Contents:

<b>1. General methods</b> .....	<b>3</b>
<b>2. Synthesis of ligand (bfpt)</b> .....	<b>3</b>
<b>3. The x-ray crystallography</b> .....	<b>4</b>
<b>4. The UV-vis spectra of bfpt, complex 1 and complex 2</b> .....	<b>6</b>

## 1. General methods

Reactions were carried out under an atmosphere of dry nitrogen. Reagents and solvents were commercially available and used as received unless otherwise noted. THF was distilled over Na under nitrogen atmosphere.  $^1\text{H}$  NMR spectra were recorded on a 300 MHz spectrometer, with  $\text{CDCl}_3$  or  $\text{DMSO}-d_6$  as solvent using TMS as an internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, br = broad). The elemental analysis was carried out with a Perkin-Elmer 240C elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range of  $4000\text{--}400\text{ cm}^{-1}$  on a VECTOR 22 spectrometer. XRD measurements were performed on a Bruker D8 Advance X-ray diffractometer using  $\text{Cu K}\alpha$  radiation (0.15418 nm), in which the X-ray tube was operated at 35 kV and 20 mA.

## 2. Synthesis of ligand (bfpt)



**Scheme S1** The synthesis of  $N,N'$ -bis(*p*-formylphenyl)thiourea (bfpt)

Reagents and conditions: (a)  $\text{CH}_3\text{OH}$ , conc.  $\text{H}_2\text{SO}_4$ , refluxed, 85% yield; (b) THF,  $\text{Et}_3\text{N}$ ,  $\text{CS}_2$ ,  $\text{TsCl}$ , refluxed, 73% yield; (c) **1**, acetone, reflux 90% yield; (d) Saturated  $\text{NaOH}/\text{H}_2\text{O}$  solution, rt, 95% yield.

**The synthesis of 4-amino benzoic acid methyl ester (1):** 4-amino benzoic acid methyl ester (**1**) was synthesized according to ref. 1.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.87 (s, 3H), 4.08 (s, 2H), 6.64-6.67 (m, 2H), 7.85-7.88 (m, 2H) ppm.

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**The synthesis of 4-isothiocyanato-benzoic acid methyl ester (2):**

4-isothiocyanato-benzoic acid methyl ester (**2**) was synthesized according to ref. 2. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.94 (s, 3H), 7.27-7.30 (m, 2H), 8.03-8.06 (m, 2H) ppm.

**The synthesis of N, N'-bis(p-methylformatephenyl)thiourea (3):** A mixture of 4-isothiocyanato-benzoic acid methyl ester (**2**) (0.68 g, 3.5 mmol) and 4-amino benzoic acid methyl ester (0.55 g, 4 mmol) in 15 mL of actone was refluxed overnight. After the reaction mixture was cooled to room temperature, the resultant mixture was concentrated in vacuo to obtain a white solid, which was washed by acetic ester (3×10 mL) and petroleum ether (3×10 mL). The product obtained as a white solid (yield 90%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ 3.70 (s, 6H), 6.68-6.73 (br, 2H), 6.99 (d, 4H *J* = 8.4 HZ), 7.82 (d, 4H *J* = 8.7 Hz) ppm.

**The synthesis of N, N'-bis(p-formylphenyl)thiourea(4): 3** (1.38 g, 4 mmol) was suspended in 15 mL of saturated NaOH/H<sub>2</sub>O solution. The reaction mixture was stirred overnight at room temperature. Concentrated HCl was added dropwise to the solution until the PH is 4-5. The resultant mixture was filtered, and the filtrate was washed by H<sub>2</sub>O (3×20 mL), acetic ester (3×10 mL) and petroleum ether (3×10 mL). The product obtained as a white solid (yield 95%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ 7.64-7.69 (m, 4H), 7.89-7.92 (m, 4H), 10.31 (s, 2H) ppm. Elemental analysis (%) calcd: C 56.95, H 3.82, N 8.86, S 10.14; found: C 56.95, H 3.76, N 8.89, S 10.10.

**Synthesis of complex 1:** a mixture of bfpt (0.016 g, 0.05 mmol), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.029 g, 0.1 mmol), bpy (0.008 g, 0.05 mmol), NaOH (0.002 g, 0.05 mmol) and H<sub>2</sub>O (8 mL) was stirred for 15 min in air (*Caution: stir is necessary, otherwise, the system easily turns black after solvothermal reaction*). Then the mixture was transferred and sealed in a 20 mL Teflon-lined reactor, which was heated in an oven to 105 °C for 48 h. The oven was cooled to room temperature at a rate of 5 °C h<sup>-1</sup>. The resulting red block crystals were filtered, washed, and dried in air (yield 67% based on bfpt). Elemental analysis (%) calcd: C 54.80, H 3.65, N 10.23; Found: C 54.75, H 3.61, N 10.28.

**Synthesis of complex 2:** a mixture of bfpt (0.016 g, 0.05 mmol),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.116 g, 0.4 mmol), bpe (0.036 g, 0.05 mmol) and  $\text{H}_2\text{O}$  (8 mL) was stirred for 15 min in air (*Caution: stir is necessary, otherwise, the system easily turns black after solvothermal reaction*). Then the mixture was transferred and sealed in a 20 mL Teflon-lined reactor, which was heated in an oven to 80 °C for 48 h. The oven was cooled to room temperature at a rate of 5 °C h<sup>-1</sup>. The resulting red block crystals were filtered, washed, and dried in air (yield 70% based on bfpt). Elemental analysis (%) calcd: C 54.78, H 4.06, N 9.47; Found: C 54.83, H 4.00, N 9.43.

### 3. The x-ray crystallography

Data were measured on a Bruker Smart Apex II CCD diffractometer at 291 K using graphite monochromated Mo/K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), respectively. Data reduction was made with the Bruker Saint program. The structures were solved by direct methods and refined with full-matrix least squares technique using the SHELXTL package. The coordinates of the non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were put in calculated positions or located from the fourier maps and refined isotropically with the isotropic vibration parameters related to the non-hydrogen atom to which they are bonded. CCDC 771360 and 764062 for complexes **1** and **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Basic information pertaining to crystal parameters and structure refinement is summarized in **Table S1**.

**Table S1** The crystal data and structure refinement information for complexes **1** and **2**

Complex	<b>1</b>	<b>2</b>
Empirical formula	$\text{C}_{25}\text{H}_{20}\text{CoN}_4\text{O}_5\text{S}$	$\text{C}_{27}\text{H}_{24}\text{CoN}_4\text{O}_6\text{S}$
Formula weight	547.44	591.49
Space group	C2/c	C2/c
$a$ [Å]	31.561(3)	30.6320(13)

$b$ [Å]	11.4596(10)	13.6735(15)
$c$ [Å]	14.6190(13)	14.9266(16)
$\alpha$ [°]	90.00	90.00
$\beta$ [°]	96.1150(10)	95.758(2)
$\gamma$ [°]	90.00	90.00
$V$ [Å <sup>3</sup> ]	5257.3(8)	6220.4(10)
$Z$	8	8
$D_{\text{calcd.}}$ [g cm <sup>-3</sup> ]	1.383	1.263
$\mu$ [mm <sup>-1</sup> ]	0.773	0.661
$\theta$ range	1.89 -26.00	2.09-26.00
R1, wR2a [ $I > 2\sigma(I)$ ]	0.0496, 0.0930	0.0536, 0.1096
GOF	0.988	0.999

#### 4. The UV-vis spectra of bfpt, complex 1 and complex 2

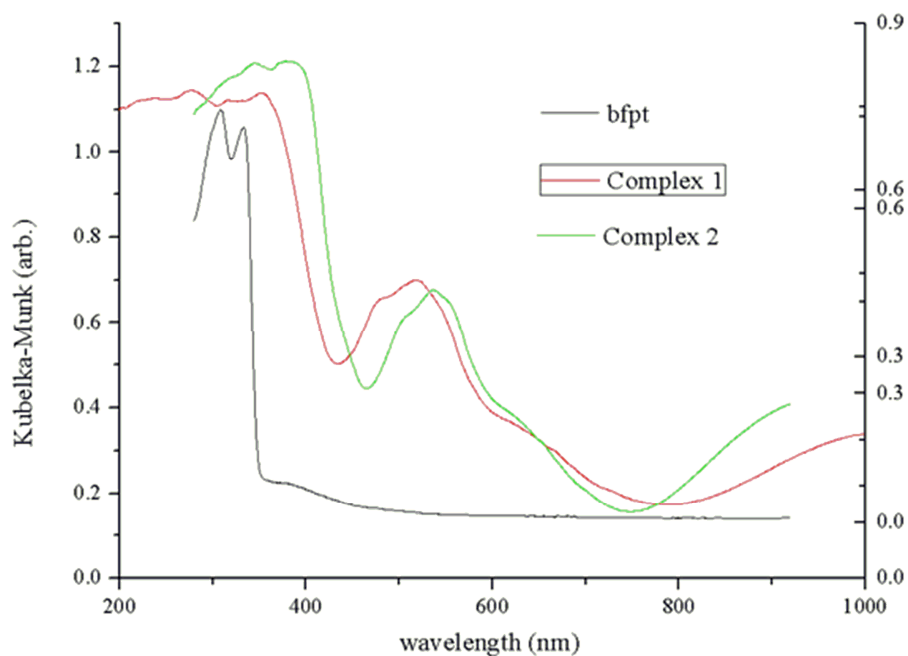


Fig. S1 The diffuse reflectance UV-vis spectra of bfpt ligand and complexes 1 and 2 in

BaSO<sub>4</sub>.

## Reference

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