

## Electronic Supplementary Information

### One-step solution synthesis of two dimensional semiconducting covalent organometallic nanosheet *via* condensation of boronic acid

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**Materials and Methods.....S2-S5**

**Supplementary Figures and Tables.....S6-S15**

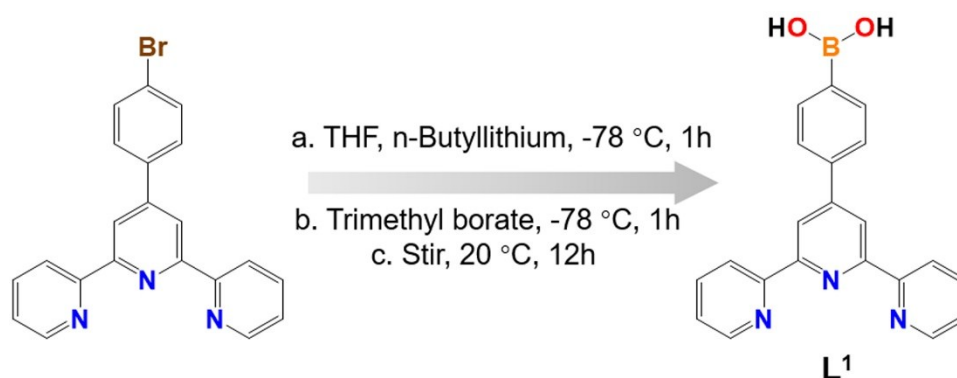
## Materials and Methods

### Materials

n-Butyllithium and trimethyl borate were purchased from Sigma-Aldrich. 4'-(4-bromophenyl)-2,2':6',2''-terpyridine (97%, J&K Scientific Ltd.), tetrahydrofuran (THF, 99.9%, SuperDry), cobalt dichloride (CoCl<sub>2</sub>, 99%, J&K Scientific Ltd.), N, N-dimethylformamide (DMF, J&K Scientific Ltd.), trimethylbenzene (J&K Scientific Ltd.), dioxane (J&K Scientific Ltd.), acetone (Sinopharam Chemical), potassium hydroxide (KOH, Sinopharam Chemical), HCl (Sinopharam Chemical) were all of analytical grade. The acetone, trimethylbenzene, dioxane and N, N-dimethylformamide were treated by molecular sieve to remove the H<sub>2</sub>O. The deionized water utilized in all experiments were obtained from Milli-Q, ultrapure purification.

### Methods

#### Synthesis of Ligand L<sup>1</sup>



#### Scheme 1. Synthesis route of ligand L<sup>1</sup>.

4'-(4-bromophenyl)-2,2':6',2''-terpyridine (500 mg) dissolved in THF (60 mL) was added to a 250 mL Schlenk reaction tube and stir for 30 mins at -78 °C (under Ar atmosphere). Under same reaction conditions, n-butyllithium (0.71 mL) was added very slowly into the above reaction tube and stir continuously for 1h. It is then followed by further addition of trimethyl borate (0.17 mL) and then proceed to stir for another 1h. The reaction flask was moved to room temperature and allowed to stir for 12 h. After completion, the aqua solution of 1M HCl was slowly added to precipitate cream yellow solid from the solution, and it results into turbid solution after addition of 1M KOH aqua solution. The solvent was evaporated from the reaction to obtain ligand L<sup>1</sup> as a primrose yellow, crystal-containing powder. Elemental analyses calculated for L<sup>1</sup>: C, 71.42; H, 4.57; N, 11.90; Found: C, 71.31; H, 4.49;

N, 11.85. High resolution mass spectrometry (HR MS), APCI-MS (CH<sub>3</sub>OH), m/z for [tpy-B(OMe)<sub>2</sub>]<sup>+</sup> found: 381.

#### **Synthesis of two dimensional covalent organometallic nanosheet (2D COMS-Co).**

2D COMS-Co was prepared *via* one-step condensation of boronic acid. Typically, the ligand L<sup>1</sup> (0.68 mmol) was dispersed in 16 mL mesitylene/dioxane (1:1 in volume) to form a yellow solution and move into a Schlenk tube with a PTFE stirring bar (Note: this step should performed in glove box, all solvents must be treated without H<sub>2</sub>O). Subsequently, the amount of CoCl<sub>2</sub> (0.34 mmol) was added to the bottom of tube. The Schlenk tube was flash frozen at liquid N<sub>2</sub> bath for 90 s, evacuated to an internal pressure of 142-150 mtorr. The mixture was heated to 120 °C and stir very slowly (about 2 cycles per second) for 72 h. The products were thoroughly washed with 23 mL mesitylene/dioxane/acetone (1:1:0.3 in volume) to remove the unreacted L<sup>1</sup> and CoCl<sub>2</sub> and then dried under vacuum (60-80 °C). 2D COMS-Co was obtained as brown, crystal-containing powder with yield of 73.1%. High resolution mass spectrometry (HR MS), ESI-MS, m/z calculated for [two B<sub>3</sub>O<sub>3</sub> link with TMT]<sup>+</sup>: 836, found, 836, while the TMT is consist of terpyridine and Co(II) metal center. These results can directly demonstrate the successful synthesis of 2D COMS-Co.

#### **Fabrication of sample for scanning tunneling microscopy (STM).**

The substrate Si/SiO<sub>2</sub> (1 × 1 cm<sup>2</sup>) was cleaned by ultrasonication in 5 mL deionized water, 5 mL acetone and 5 mL ethanol in turn for 10 mins each and then treated with O<sub>2</sub> plasma, these steps can remove the impurities on the surface of substrate Si/SiO<sub>2</sub>. After cleaning the Si/SiO<sub>2</sub> substrate, mechanically exfoliated graphite flakes were used as back contact on the Si wafer with 300 nm thick SiO<sub>2</sub> layer on top, to provide stable tunnel junction. Then the 2D COMS-Co (Solvent: DMF) was deposited on graphite flakes by drop coating method (Note: The concentration of DMF solution of 2D COMS-Co should be 30% ~ 45%, which can ensure the 2D COMS-Co deposited onto the graphite flakes).

#### **Preparation of COMS-based Field-effect transistor (FET) devices.**

The DMF solution of 2D COMS-Co was dropping coating onto the cleaned Si/SiO<sub>2</sub> substrate with melt heat in vacuum (60 °C for 5 mins). Then the gold stripes were transferred very carefully on the

semiconducting 2D COMS-Co sample as the source and drain electrodes to form the field-effect transistor devices.

#### **Characterization techniques.**

The morphology and structure of the products were characterized by **scanning electron microscope (SEM, VEGA 3 SBH)** and **transmission electron microscope (TEM, Tecnai G<sup>2</sup> 20, FEI)**. SEM samples were prepared by drop-casting the DMF solution of 2D COMS-Co onto a cleaned SiO<sub>2</sub> substrate with melt heat in vacuum (60 °C for 5 mins), then the SiO<sub>2</sub> substrate was transferred into the SEM sample chamber without metal spraying (Note: metal spraying can destroy the surface morphology of 2D COMS-Co). TEM samples were prepared by dropping the DMF solution of 2D COMS-Co onto carbon-coated copper grids with melt heat in vacuum (60 °C for 5 mins). **Atomic force microscope (AFM)** measurements were performed using a scanning probe microscope (SPM9700, Shimadzu) operated in tapping mode. The 2D COMS sample for AFM was prepared *via* drop coating method using cleaned SiO<sub>2</sub> substrate followed by melting heat in vacuum (60 °C for 5 mins, solvent: DMF). **Optical microscopy (OM)** observations carried out with an ultra-depth microscope (DSX 510) from Olympus, Japan. **Scanning tunneling microscopy (STM)** was performed on an upgraded instrument mentioned in the literature,<sup>S1</sup> and the temperature of the substrate was setting at room temperature. The FET devices were characterized by a Keithley 4200-SCS system and the V<sub>DS</sub> is constant at -40 V and the V<sub>G</sub> is from 10 to -80 V. **Fourier transform infrared spectroscopy (FT-IR)** was performed on a VERTEX 70 (Bruker) using KBr pellets. **X-ray photoelectron spectroscopy (XPS)** measurements were performed on AXIS-ULTRA DLD-600W spectrometer. **UV-vis measurements** were performed on a Lambda 35 spectrophotometer (PerkinElmer, U.S.A). The **specific surface area** was measured with a Micromeritics (ASAP 2420, USA). Nitrogen adsorption/desorption isotherms were obtained at 77 K on an accelerated surface area and porosimetry system. The surface area and porosity analysis were calculated using the Brunauer-Emmett-Teller (BET) equation. **Powder X-ray diffraction (PXRD)** measurements were performed on x'pert3 powder (PANalytical B.V.). All the samples were recorded in the range of 5-45 degrees with a scan rate of 1 degree per second. The **thermal properties** of L<sup>1</sup> and 2D COMS-Co were evaluated by using thermogravimetric analysis (TGA) instrument (Pyris 1) over the temperature range of 25-800 °C under nitrogen atmosphere with a heating rate of 10 °C/min. **Room temperature Raman spectroscopy (Raman)** measurement was performed on inVia-ReflexinVia-Reflex (Renishaw).

### **Theoretical simulation**

The geometry and electronic structure of fragment of 2D COMS-Co was obtained at B3LYP/6-31G(d) level with Grimme's D3BJ empirical<sup>S2</sup> dispersion correction, using Gaussian09 program<sup>S3</sup>. The 2D periodic structure of 2D COMS-Co was optimized at PBEsol<sup>S4</sup>/DNP level with DFT semi-core pseudopotentials<sup>S5</sup> for heavy atoms, using DMol3 program in Materials Studio of Accelrys Inc.<sup>S6</sup> The 2D COMS-Co remains planar and the dihedral angle between B<sub>3</sub>O<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>)<sub>3</sub> and the terpyridine unit was around 40 degree in this condition. The diameter (metal to metal distance) of the circle that composed by 6 fragments is 42.5 angstrom for 2D COMS-Co.

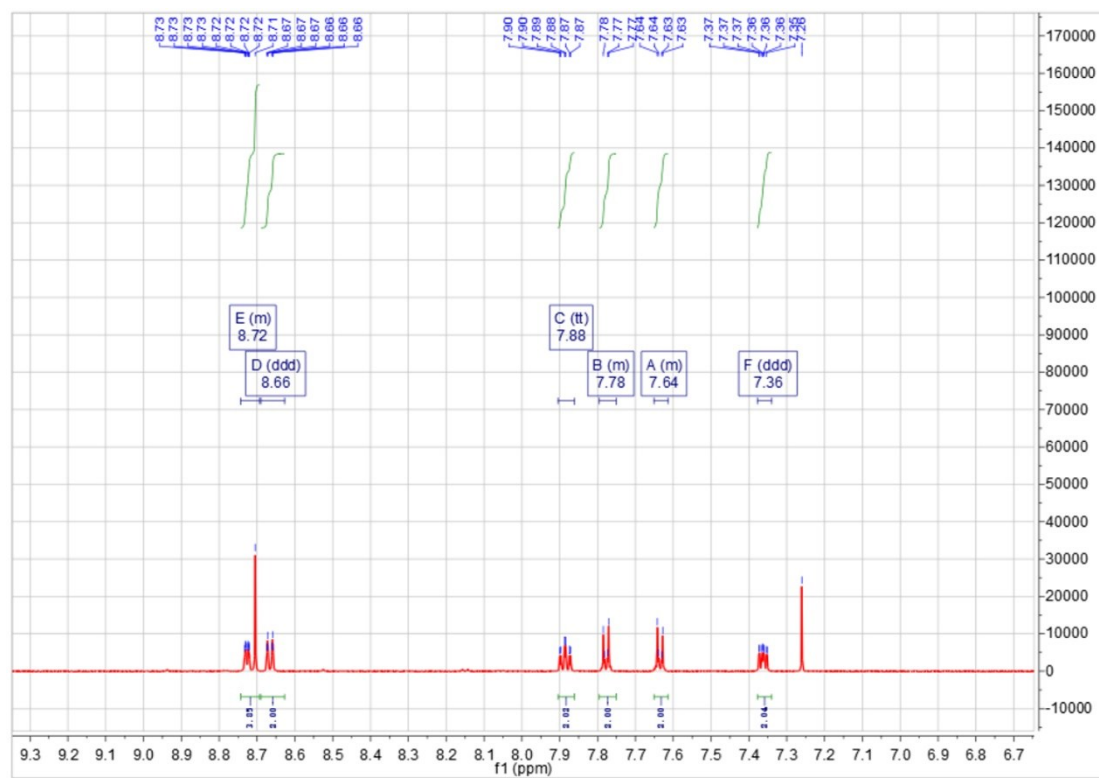
### **Mobility calculation**

The mobility was calculated from the saturated region characteristics by the following equation:

$$I_{DS} = (W/2L)C_i\mu(V_G - V_T)^2,$$

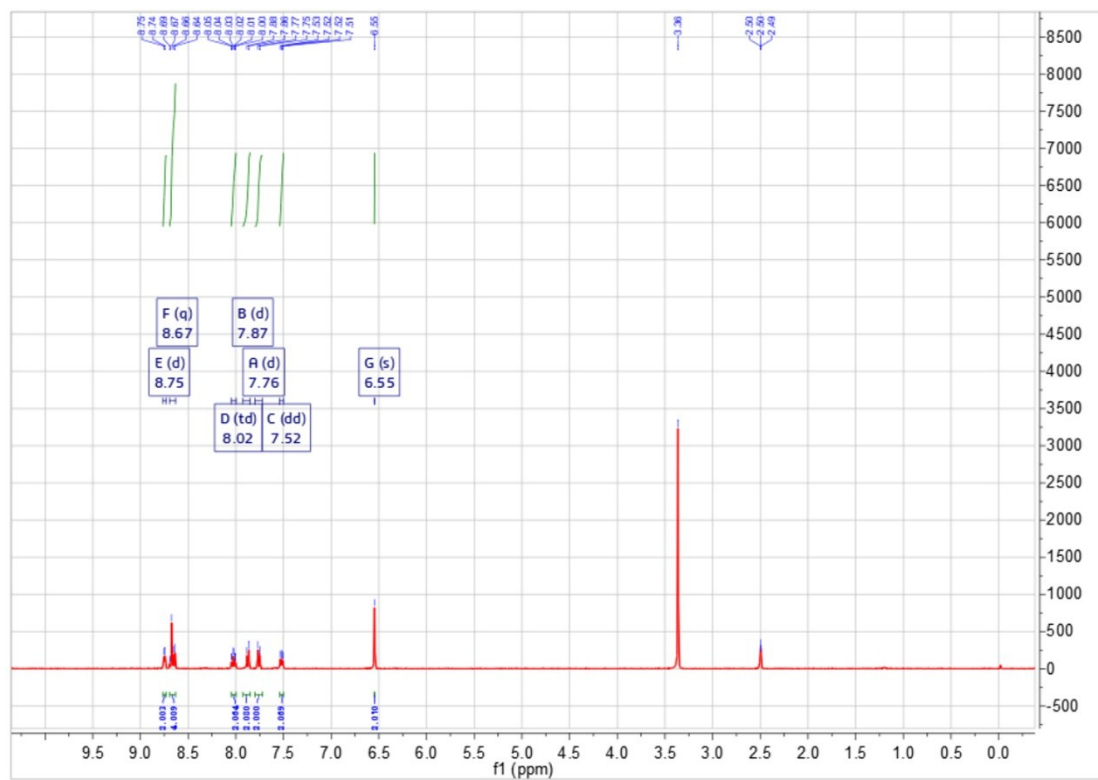
Where W and L are the width and length of the channel, C<sub>i</sub> is the gate dielectric capacitance, V<sub>G</sub> and V<sub>T</sub> are the gate voltage and threshold voltage, I<sub>DS</sub> is the source-drain current.

## Supplementary Figures and Tables



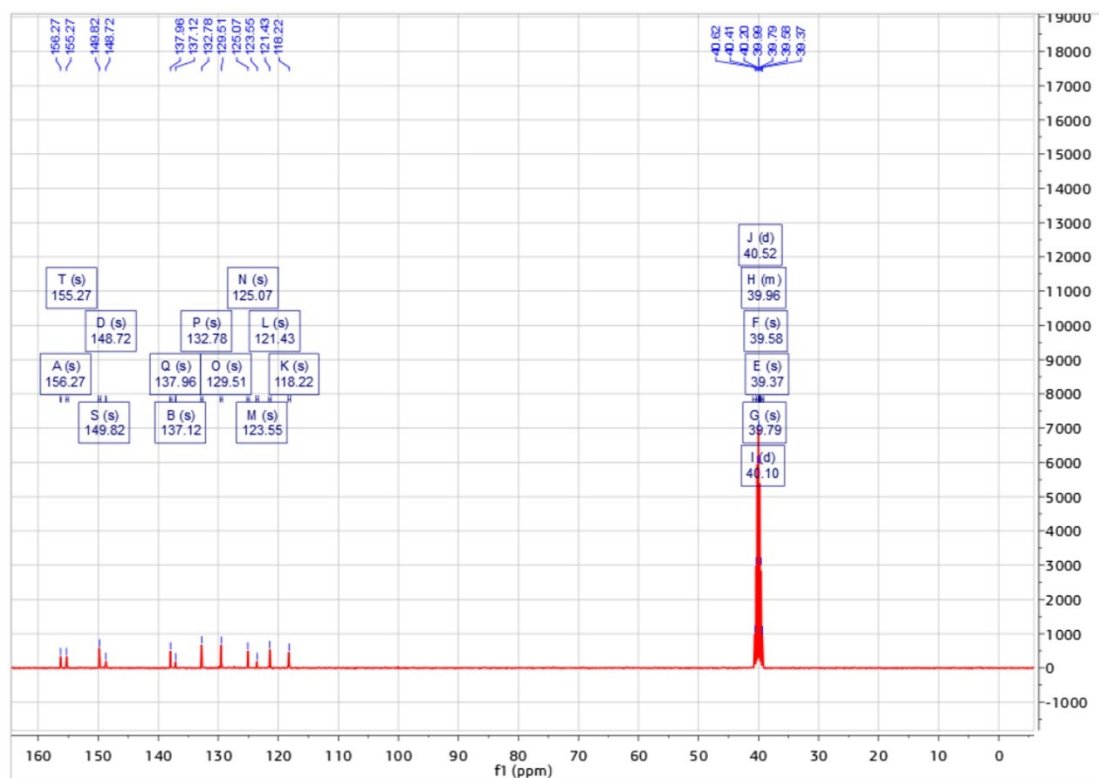
**Fig. S1**  $^1\text{H}$  NMR of 4'-(4-bromophenyl)-2,2':6',2''-terpyridine in chloroform- $d_1$ .

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ - $d_1$ )  $\delta$  8.74-8.69 (m, 4H), 8.66 (ddd,  $J = 8.9, 3.2, 2.3$  Hz, 2H), 7.88 (tt,  $J = 5.6, 2.8$  Hz, 2H), 7.80-7.75 (m, 2H), 7.65-7.61 (m, 2H), 7.36 (ddd,  $J = 7.4, 4.8, 1.2$  Hz, 2H).



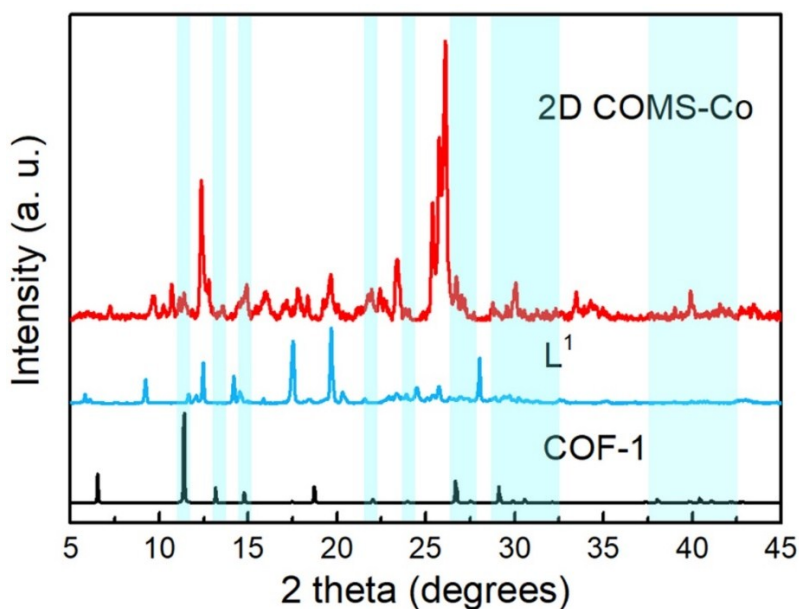
**Fig. S2** <sup>1</sup>H NMR of the as synthesized ligand L<sup>1</sup> in DMSO-*d*<sub>6</sub>.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.75 (d,  $J$  = 4.0 Hz, 2H), 8.67 (q,  $J$  = 8.1 Hz, 4H), 8.02 (td,  $J$  = 7.8, 1.7 Hz, 2H), 7.87 (d,  $J$  = 8.5 Hz, 2H), 7.76 (d,  $J$  = 8.5 Hz, 2H), 7.52 (dd,  $J$  = 6.7, 4.8 Hz, 2H), 6.55 (s, 2H).



**Fig. S3**  $^{13}\text{C}$  NMR of the as synthesized ligand  $\text{L}^1$  in  $\text{DMSO-}d_6$ .

$^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  156.27 (s), 155.27 (s), 149.82 (s), 148.72 (s), 137.96 (s), 137.12 (s), 132.78 (s), 129.51 (s), 125.07 (s), 123.55 (s), 121.43 (s), 118.22 (s).

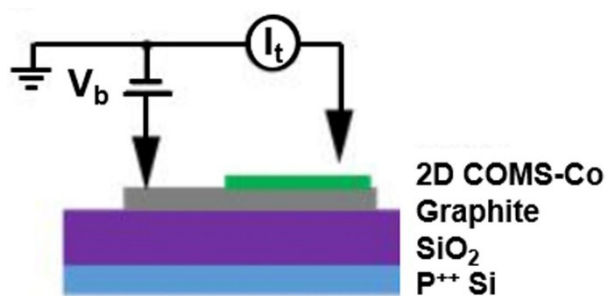


**Fig. S4** The powder X-ray analysis of ligand  $\text{L}^1$  (blue), 2D COMS-Co (red) and COF-1 (black), respectively.



**Note.**

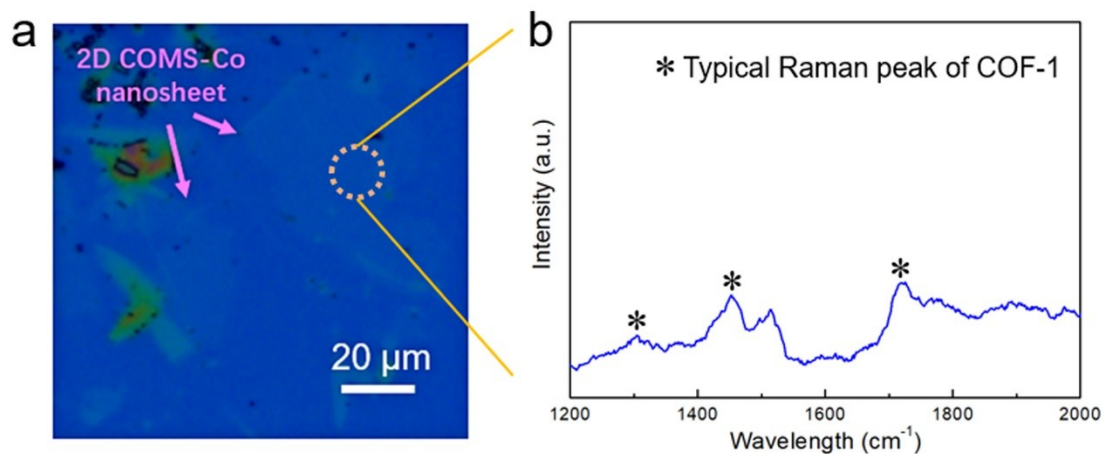
The X-ray diffraction (XRD) analysis was performed to estimate the purity and structure of the synthesized 2D COMS-Co. Compared to ligand L<sup>1</sup> and COF-1, the appearance of strong diffraction peaks in 2D COMS-Co reveals the high crystallinity. In addition, most of the diffraction peak values are located similar to the ligand L<sup>1</sup>, which reveals that 2D COMS-Co retained the structure of L<sup>1</sup>. Furthermore, the majority of the diffraction peak values of 2D COMS-Co are also located similar to typical COF-1 (cyan part), which provides a strong evidence that 2D COMS-Co owing the original structure of COF-1. This phenomenon can further demonstrate that 2D COMS-Co was successfully synthesized which are composed of linking terpyridine motif and B<sub>3</sub>O<sub>3</sub> covalent unit.



**Fig. S5** Schematic of the measurement set-up showing the STM tip to measure the sample and the bias tip to supply voltage.

**Note.**

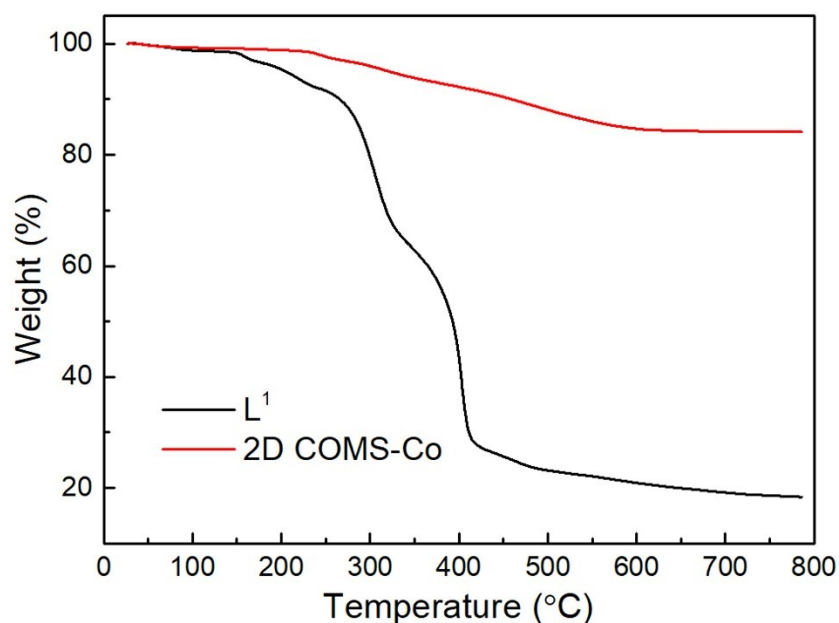
The experimental setup is shown in Fig. S5 (ESI<sup>†</sup>), where the tunnel junction is formed by applying bias voltage on graphite flakes and the STM tip is grounded.



**Fig. S6** (a) The ultra-depth microscope image of 2D COMS-Co. (b) Room temperature Raman spectra on the selected area (cream yellow circle).

**Note.**

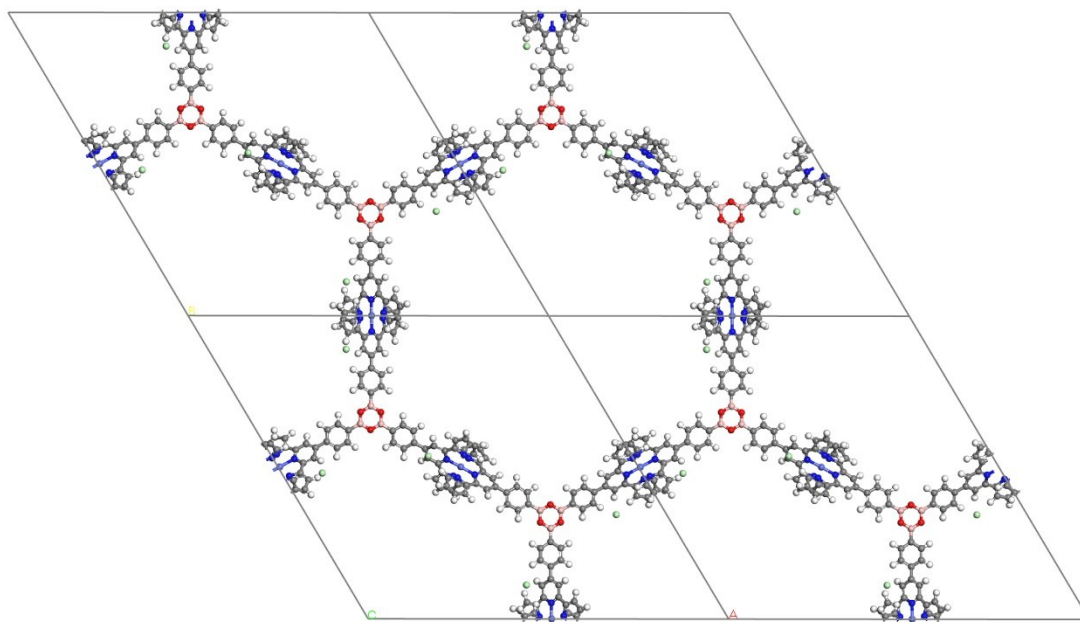
The morphology of the synthesized COMS-Co was visualized using ultra-depth microscope. Fig. S6a shows that 2D COMS-Co consists of sheet-like morphology, and the size are calculated to be few nanometers. Furthermore, room temperature Raman spectroscopic measurements was performed to identify the structure composition of 2D COMS-Co (Fig. S6b). The Raman spectra on the selected area in Fig. S6a shows the typical observation of Raman peaks corresponds to COF-1,<sup>S7</sup> which indicates that the original motifs of COF-1 were among the structure of 2D COMS-Co.



**Fig. S7** Thermogravimetric analysis curves of ligand  $L^1$  and 2D COMS-Co, respectively.

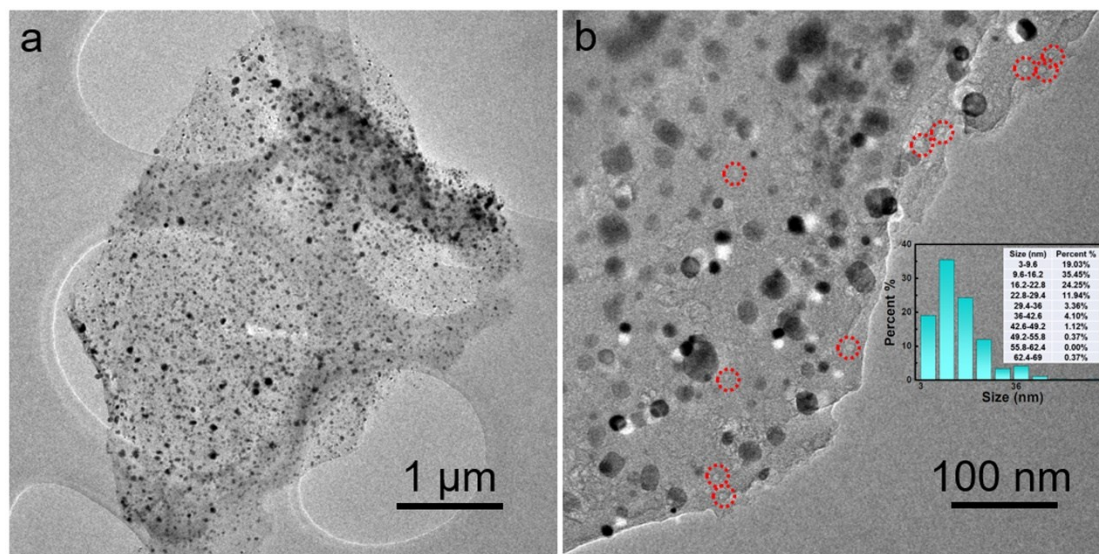
**Note.**

In order to determine the thermal stability, the thermogravimetric analysis (TGA) was performed on the as prepared ligand L<sup>1</sup> and 2D COMS-Co. On the basis of TGA curves (Fig. S7), the weight loss was observed in ligand L<sup>1</sup> and it starts to thermally decompose slowly from 150 °C, which can be assigned to the decomposition of -B(OH)<sub>2</sub>, and also experiences huge ligand loss up to 450 °C. Whereas, the 2D COMS-Co is thermally stable and without any significant weight loss which evidences few -B(OH)<sub>2</sub> groups at the surface of 2D COMS-Co, which is in agreement with the FT-IR results. Hence these results strongly demonstrates the successful synthesis of 2D COMS-Co.



**Fig. S8** Geometry optimized, hypothetical space-filling model of 2D COMS-Co (hole size, 4.25 nm).

Cell parameters:  $a = 85.078 \text{ \AA}$ ,  $b = 83.171 \text{ \AA}$ ,  $c = 35.000 \text{ \AA}$ ,  $\alpha = 90.000^\circ$ ,  $\beta = 90.000^\circ$ ,  $\gamma = 120.761^\circ$ . Legend: H, white; C, gray; N, blue; O, red; Boron, pink; Cl<sup>-</sup>, green; Co, violet.



**Fig. S9** (a) TEM image of 2D COMS-Co after annealed to 800 °C. (b) magnified pattern. (visible holes, red circle. size, 5.0 nm).

**Note.**

In order to exploit the insight structure properties of 2D COMS, the powder of 2D COMS-Co was sealed in a pipe furnace under argon and annealed from room temperature to 800 °C with a heat rate of 2 °C/min. Considering the presence of nitrogen and boron heteroatoms in 2D COMS-Co, the as prepared 2D COMS-Co-800 can be described to nanoparticles loaded, heteroatoms doped carbon materials. Fig. S9a shows the typical 2D nanosheet morphology of the COMS-Co-800 with homogeneous distribution of nanoparticles. Most interestingly, we found that many visible holes with sized of 5.0 nm were distributed in 2D COMS-Co-800, this phenomenon not only demonstrates the porous structure of the original 2D COMS-Co, but can also illustrates its structural stability (form carbon framework). These results may helpful for further design of homogeneous single atom catalysts by controlling the temperature or atmosphere conditions.

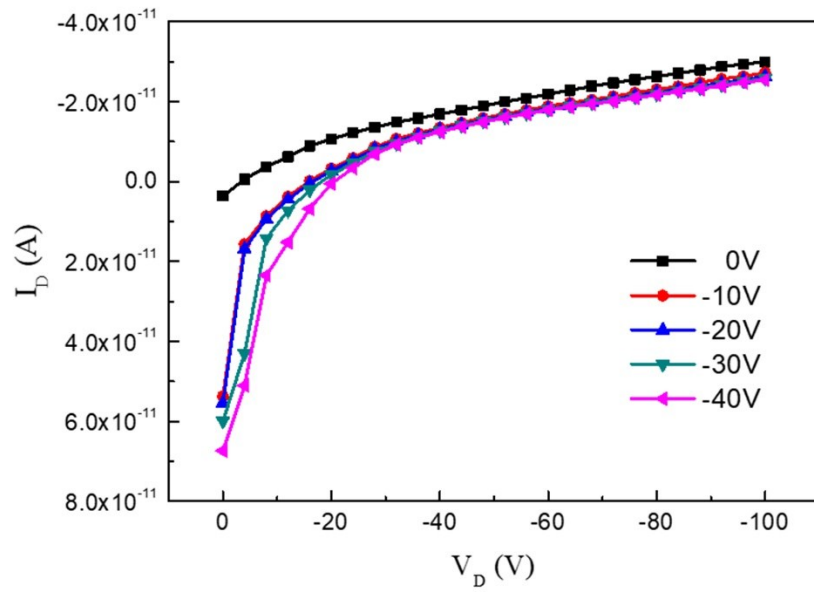


Fig. S10 Output plot of a typical 2D COMS-Co transistor.

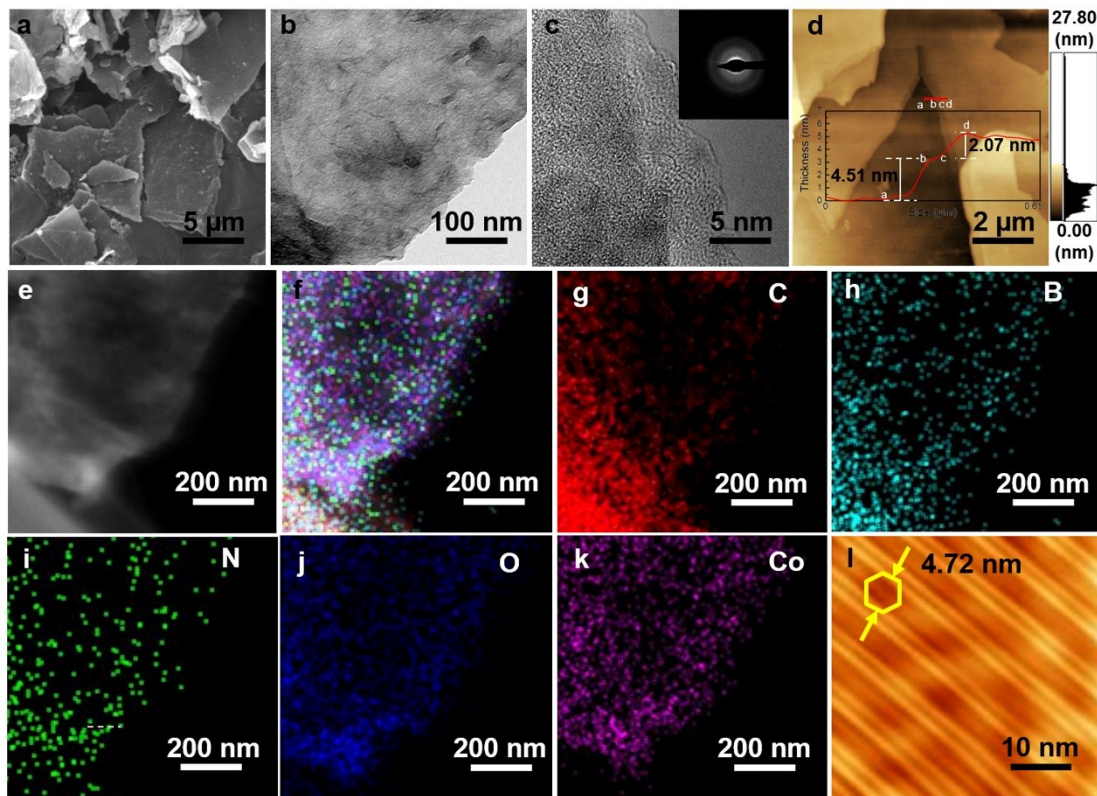


Fig. S11 Enlarged pattern of Fig. 2.



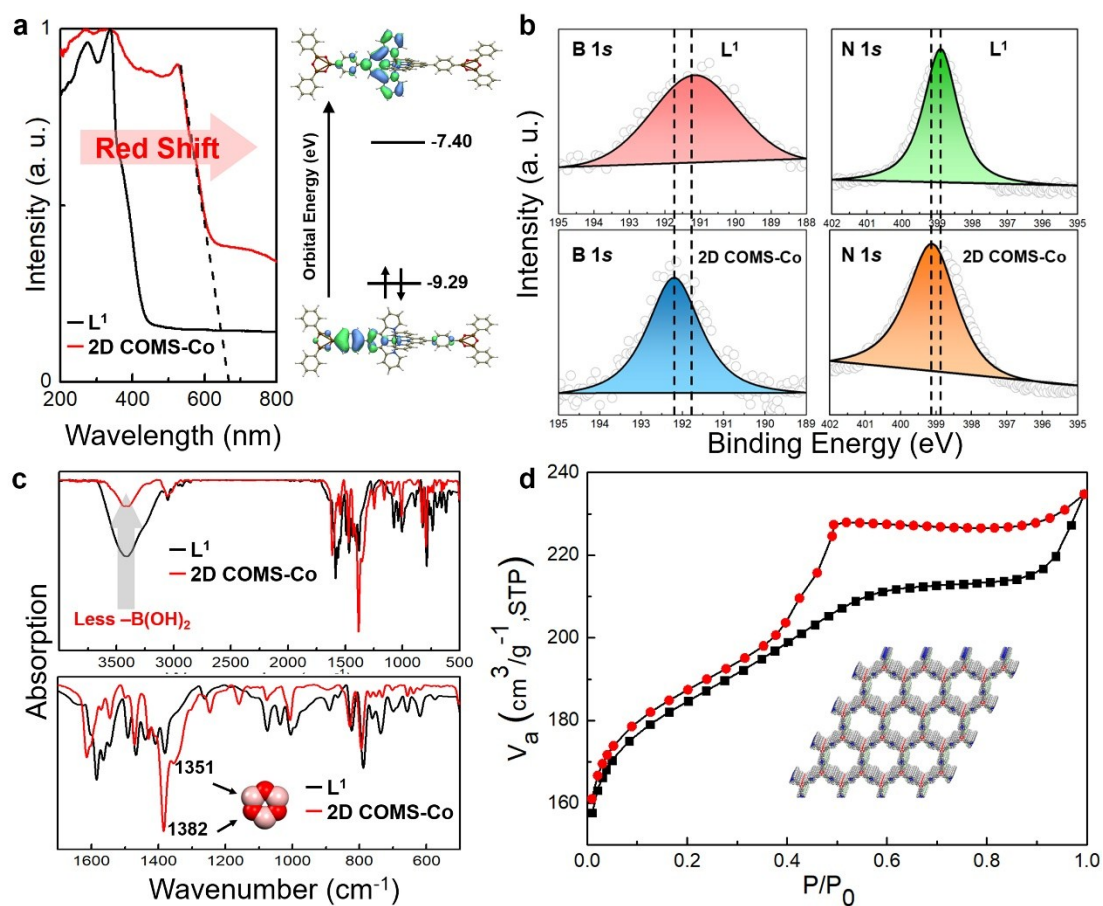


Fig. S12 Enlarged pattern of Fig.3.

Table S1. Comparison of the electronic properties of recently reported 2D materials

Materials	Mobility (cm <sup>2</sup> V <sup>-1</sup> S <sup>-1</sup> )	On/off ratio	Structure	History
2D COMS-Co	5.70×10 <sup>-5</sup>	2.21×10 <sup>2</sup>	Covalent linkages, Complex motif	This work
Monolayer 2DP	1.30×10 <sup>-6</sup>	1.00×10 <sup>2</sup>	Complex motif	2016 <sup>[8]</sup>
PolyTB	3.00×10 <sup>-6</sup>	8.50×10 <sup>2</sup>	Covalent linkages	2015 <sup>[9]</sup>

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