

## A Hybrid Bonding Strategy for Tetrathiafulvalene-Based Hydrogen-Bonded Organic Frameworks with Electrical- and Photo-Conductivity

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### Experimental Section

**Characterizations.** Data collection for SCXRD were performed using Bruker APEX-II CCD diffractometers and using graphite monochromatic MoK $\alpha$  rays ( $\lambda = 0.71073 \text{ \AA}$ ), data acquisition with CrysAlisPro-Agilent software at room temperature. The crystal structure is solved directly by the ShelXT program and corrected on F<sub>2</sub> using the full matrix least squares method. The PXRD data were collected with a scanning range of 5-60 ° and a scanning speed of 0.1 °·s<sup>-1</sup> on a Bruker D8 Advance diffractometer (40 kV, 40 mA) with Cu radiation ( $\lambda = 1.54056 \text{ \AA}$ ) at room temperature. TGA data were obtained on TG 209F3 thermal analysis system at a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere. We used the 2-probe method to characterize the electrical conductivity of pressed pellets of PTP-HOF3 and PTP-HOF4. Gold wires were attached to the surface using conductive carbon adhesive paste for two-probe resistance measurements from I-V runs at room temperature. The complexes were tested using the CHI-660E electrochemical workstation. At the same time, the photocurrent response of the complex was measured by the CHI-660E electrochemical workstation. The modified ITO conductive glass is used as the working electrode, the platinum electrode as the auxiliary electrode, and the saturated calomel electrode (SCE) as the reference electrode. Adopt 0.1 mol·L<sup>-1</sup> sodium sulfate solution as a supporting electrolyte. The light source is a high-voltage xenon lamp with a power of 150 W, the distance between the light source and the ITO glass is 20 cm, the initial voltage of the test is 0.8 V, and the light switch is controlled using the baffle with a time interval of 20 s.

All reagents and solvents of reagent grade were obtained from commercial channels and used directly without further purification unless otherwise indicated. In addition, the H4TTFTB, Py3-TTF-Py3 and Py4-TTF-Py4 were prepared according to the previous literature <sup>1,2</sup>.

#### The synthesis of **PTP-HOF3**.

Py3-TTF-Py3 (0.021 g, 0.059 mmol) and H4TTFTB (0.020 g, 0.029 mmol) were placed in a flask containing of 30 ml THF. The mixed solution was stirred by ultrasound and refluxed for 12 hours under heating treatment. After the solution was cooled to room temperature, it was filtered and transferred to six clean glass pipes. A layer of ether solution was added to each tube and then sealed the tube with sealing film with five holes. The tube was placed at room temperature, and then the solution in the tube was evaporated. Black massive crystals were gradually observed at the bottom of the tube. The precipitate was washed with hexane, ethanol, and distilled water and dried to obtain 11 mg of the product. The yield was 26.83 %. Anal. Calcd. (%) for C<sub>33</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>S<sub>6</sub>: C, 56.55 %, H, 2.88 %, N, 4.00 %. Found (%): C, 56.59 %, H, 2.92 %, N, 4.02 %.

#### The synthesis of **PTP-HOF4**.

Py4-TTF-Py4 (0.0158 g, 0.044 mmol) and H4TTFTB (0.015 g, 0.022 mol) were put into a 20 ml glass bottle, then 15 ml DMF was added into a single ended flask. After ultrasonic treatment, the reaction mixture was stirred evenly, and then the bottle mouth was sealed with a sealing film. The mixed solution was then stirred at 100 °C for 12 hours. After cooling to room temperature, the solution was filtered, divided into six equal parts, and put into six clean glass bottles. Finally, the glass bottle was placed in room temperature. About a week later, black blocky crystals precipitated in the glass bottle. The solution was filtered and washed with ethanol, and then dried at room temperature to obtain 7.5 mg of product. The yield was 24.35 %. Anal. Calcd. (%) for C<sub>33</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>S<sub>6</sub>: C, 56.55 %, H, 2.88 %, N, 4.00 %. Found (%): C, 56.57 %, H, 2.90 %, N, 4.03 %.

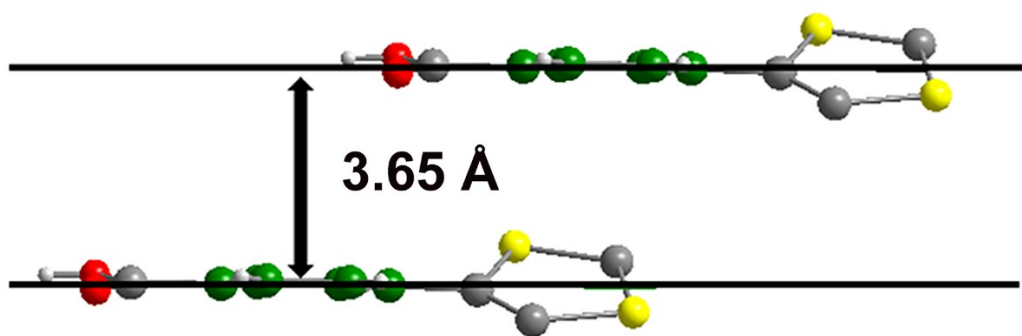
Synthesis of **PTP-HOF3@I<sub>2</sub>** and **PTP-HOF4@I<sub>2</sub>**.

Immerse **PTP-HOF3** and **PTP-HOF4** in a cyclohexane solution (0.1 M) of I<sub>2</sub> guest. After two days it is filtered and used Cyclohexane rinses to remove excess iodine from the surface.

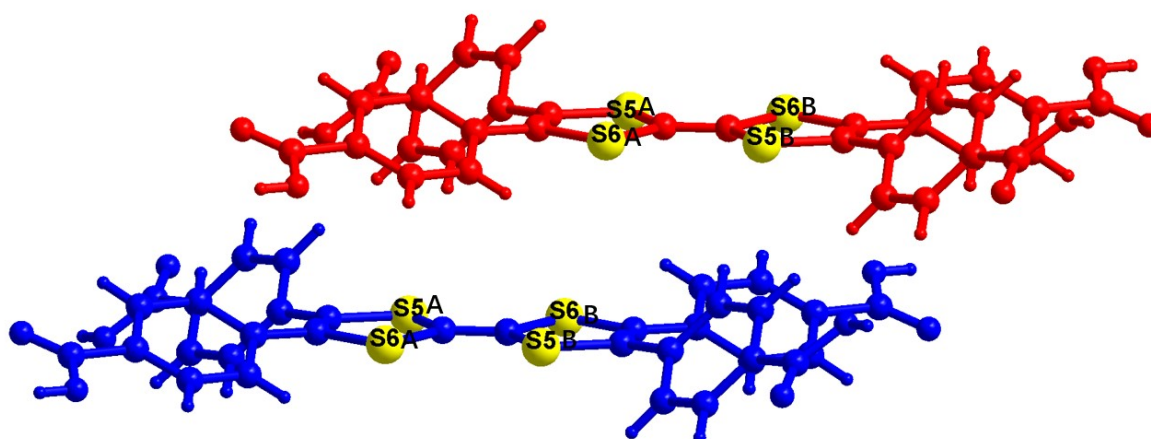
**Table S1.** Crystal data and structure refinement for **PTP-HOF3** and **PTP-HOF4**

	PTP-HOF3	PTP-HOF4
Formula	C <sub>41</sub> H <sub>36</sub> N <sub>2</sub> O <sub>6</sub> S <sub>6</sub>	C <sub>33</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> S <sub>6</sub>
FW	845.08	700.93
T (K)	273(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> -1
<i>a</i> (Å)	6.261(3)	6.965(4)
<i>b</i> (Å)	19.641 (9)	13.923(9)
<i>c</i> (Å)	32.842(15)	21.536 (14)
<i>α</i> (deg)	90	106.716(2)
<i>β</i> (deg)	94.938(10)	91.562(2)
<i>γ</i> (deg)	90	103.885(2)
<i>V</i> (Å <sup>3</sup> )	4023.7(3)	1931.2(2)
<i>Z</i>	4	2
$\rho_{\text{calcd}}$ (mg/cm <sup>3</sup> )	1.395	1.205
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.390	0.389
<i>F</i> (000)	1760.0	721.8
Reflns collected	79963	48135
Unique	9236	6797
Data/restraints/params	9236/122/519	6797/0/406
GOF on <i>F</i> <sup>2</sup>	1.04	1.05
<i>R</i> <sub>1</sub> <sup><i>a</i></sup> , <i>wR</i> <sub>2</sub> <sup><i>b</i></sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.067, 0.196	0.074, 0.270
<i>R</i> <sub>1</sub> <sup><i>a</i></sup> , <i>wR</i> <sub>2</sub> <sup><i>b</i></sup> (all data)	0.102, 0.226	0.093, 0.290
CCDC NO	2069241	2069238

$$R_1^a = \frac{\sum ||F_o| - |F_c||}{\sum F_o}, \quad wR_2^b = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)} \right]^{1/2}$$



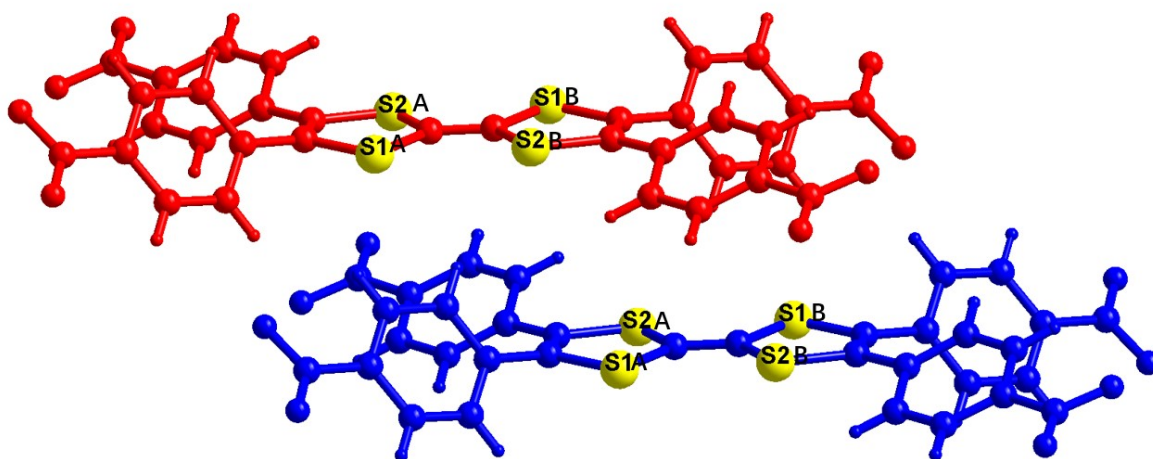
**Figure S1.**  $\pi$ - $\pi$  stacking distance between benzene planes from PTP-HOF3.



**Figure S2.** Representation of neighboring layers in PTP-HOF3 with the sulphur labelling (S $\cdots$ S distances summarized in Table S2).

**Table S2.** Distances (in Å) between sulphur atoms (S $\cdots$ S) from closest neighboring layers in PTP-HOF3.

S5A $\cdots$ S5A	6.26	S5B $\cdots$ S5A	8.35	S6A $\cdots$ S5A	5.65	S6B $\cdots$ S5A	8.77
S5A $\cdots$ S5B	6.85	S5B $\cdots$ S5A	6.26	S6A $\cdots$ S5B	4.73	S6B $\cdots$ S5B	7.98
S5A $\cdots$ S6A	7.98	S5B $\cdots$ S5A	8.77	S6A $\cdots$ S6A	6.26	S6B $\cdots$ S6A	10.07
S5A $\cdots$ S6B	4.73	S5B $\cdots$ S5A	5.65	S6A $\cdots$ S6B	3.89	S6B $\cdots$ S6A	6.26



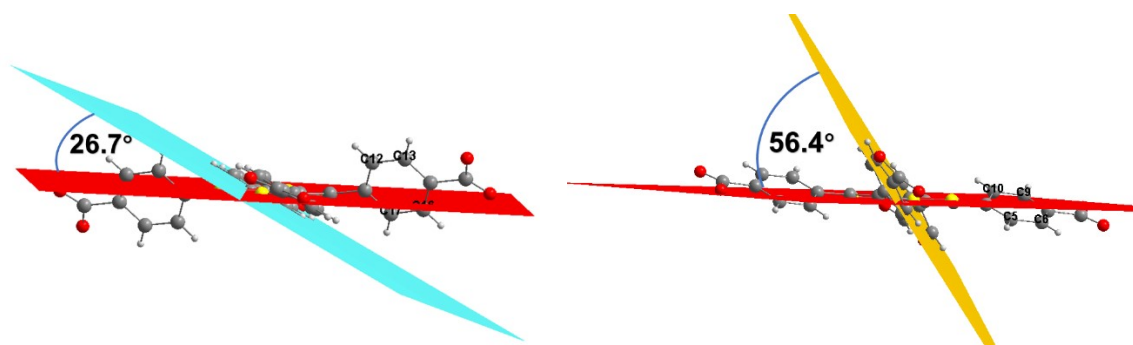
**Figure S3.** Representation of neighboring layers in PTP-HOF4 with the sulphur labelling (S $\cdots$ S distances summarized in Table S3).

**Table S3.** Distances (in Å) between sulphur atoms (S $\cdots$ S) from closest neighboring layers in PTP-HOF4.

S1A $\cdots$ S1A	6.70	S1B $\cdots$ S1A	7.04	S2A $\cdots$ S1A	8.48	S2B $\cdots$ S1A	5.12
S1A $\cdots$ S1B	9.26	S1B $\cdots$ S1B	6.97	S2A $\cdots$ S1B	9.58	S2B $\cdots$ S1B	6.51
S1A $\cdots$ S2A	6.51	S1B $\cdots$ S2A	5.12	S2A $\cdots$ S2A	6.97	S2B $\cdots$ S2A	4.48
S1A $\cdots$ S2B	9.58	S1B $\cdots$ S2B	8.48	S2A $\cdots$ S2B	10.73	S2B $\cdots$ S2B	6.97

**Table S4.** Distances (in Å) and angle between hydrogen bond in HOFs

PTP-HOF3	distances	angle(°)	PTP-HOF4	distances	angle(°)
O2-H $\cdots$ N2	1.81	171	O2 $\cdots$ H-N1	1.76	175
O3-H $\cdots$ N1	1.85	169	O3 $\cdots$ H-N2	1.76	172



**Figure S4.** Angles formed by the plane 1 between plane 2 and 3 computed for benzene groups and the TTF moiety in PTP-HOF4.

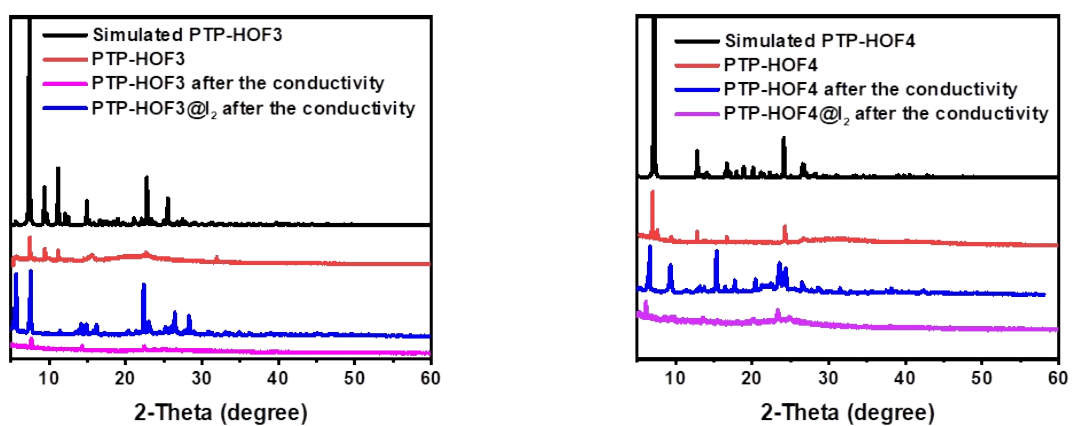


Figure S5. Simulated, synthetic, iodine doped and conductive PXRD patterns of two HOFs.

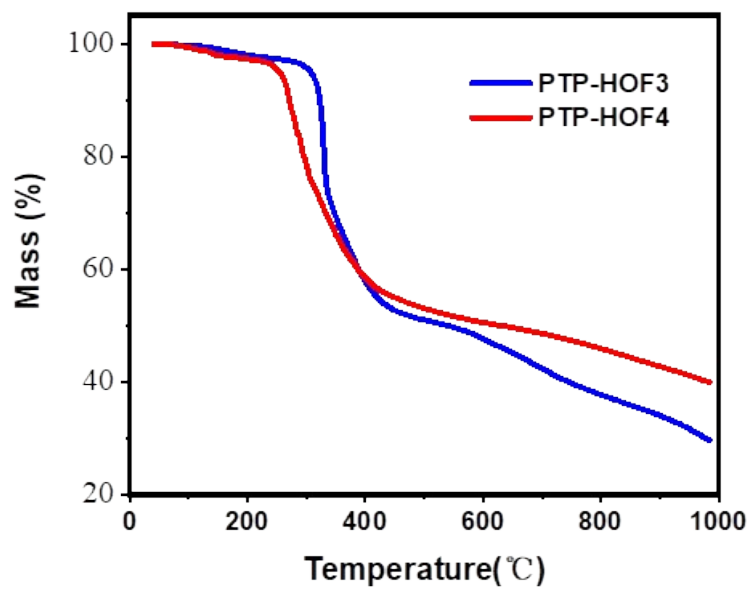


Figure S6. TGA spectra of PTP-HOF3 and PTP-HOF4.

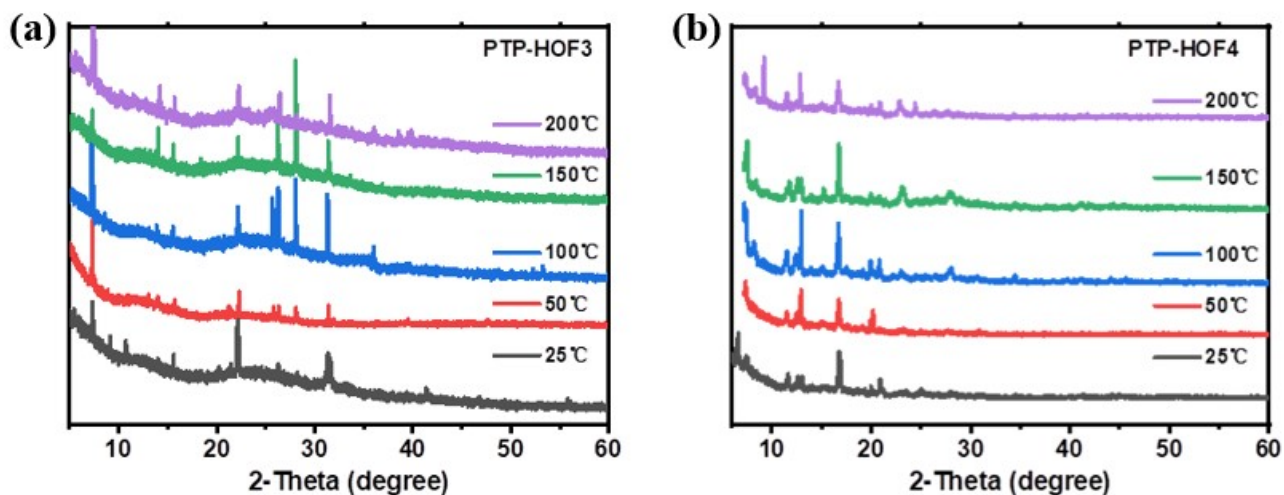


Figure S7. XRD patterns obtained for samples at different temperatures.

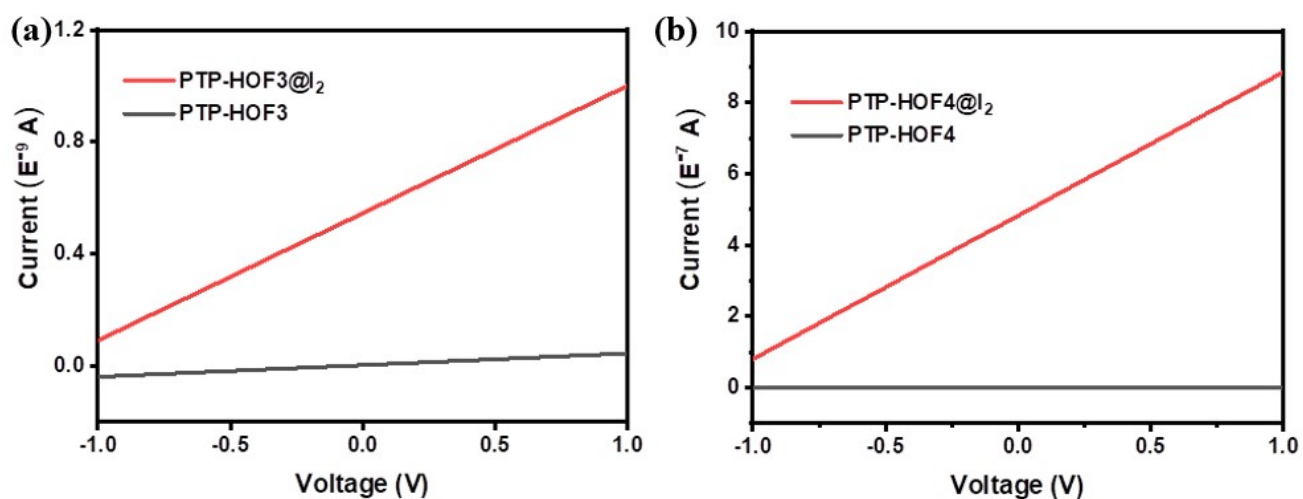
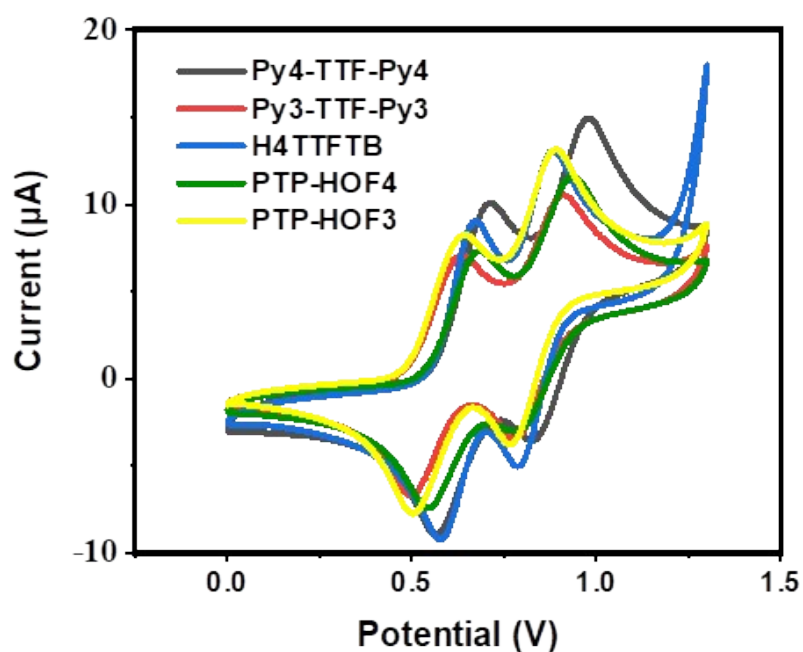


Figure S8. The room-temperature conductivity data for compacted particles for PTP-HOF3 and PTP-HOF4.



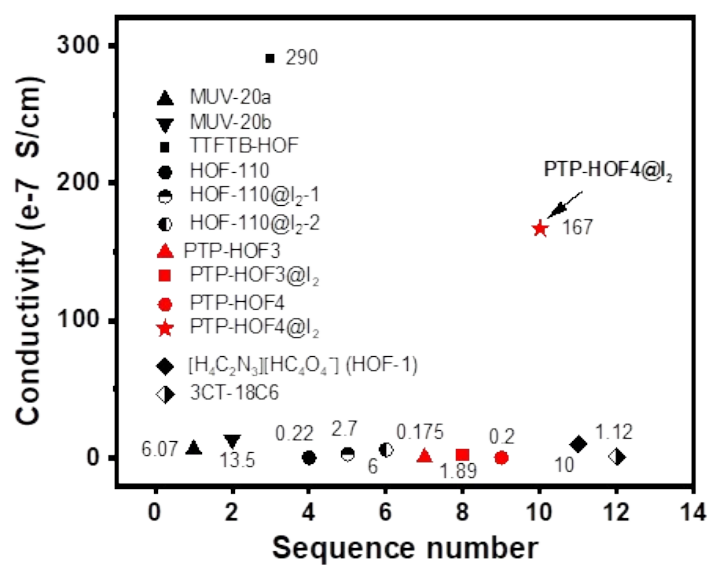
**Figure S9.** Cyclic voltammograms of **HOFs** with ligands. (Table S4)

**Table S5.** Oxidation potential of ligands and HOFs

	$E^1_{1/2}$ (V)	$E^2_{1/2}$ (V)
Py4-TTF-Py4	0.713	0.978
Py3-TTF-Py3	0.634	0.911
H4TTFTB	0.672	0.883
PTP-HOF3	0.643	0.890
PTP-HOF4	0.684	0.936

**Table S6.** The shape parameters of **PTP-HOF3**, **PTP-HOF3@I<sub>2</sub>**, **PTP-HOF4**, and **PTP-HOF4@I<sub>2</sub>** used for the calculation of electrical conductivity.

	Length (cm)	Width (cm)	Thickness (cm)	Cross-sectional area (cm <sup>2</sup> )	Electrical Conductance (S)	Electrical Conductance (S/m)
PTP-HOF3	0.302	0.400	0.0182	7.28e-3	4.22e-10	1.75e-8
PTP-HOF3@I <sub>2</sub>	0.302	0.400	0.0182	7.28e-3	4.53e-9	1.89e-7
PTP-HOF4	0.302	0.400	0.0182	7.28e-3	5.01e-10	2.07e-8
PTP-HOF4@I <sub>2</sub>	0.302	0.400	0.0182	7.28e-3	4.02e-7	1.67e-5



**Figure S10.** Conductivity summary of the representative HOFs vs this work.

**Reference:**

- 1 W. Pana, X. Xiao, Z. Wang, L. Shenb, J. F. b, H. Gao and X. Li, *Synthetic Metals*. 2014, **194**, 132-136.
- 2 T. C. Narayan, T. Miyakai, S. Seki and M. Dinca, *J. Am. Chem. Soc.* 2012, **134**, 12932-12935.