Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Supramolecular aggregation of redox-active copper-naphthalenediimide network with intrinsic electron conduction

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S1. Materials and methods

All of the materials for syntheses were obtained commercially and used without further purification. Thermogravimetric analyses (TGA) experiments was performed on a Mettler Toledo TGA/DSC 1 STAR system instrument with a heating rate of 5°C/min under nitrogen atmosphere. Powder X-ray diffraction measurements were recorded on a Rigaku Miniflex600 X-ray diffractometer using Cu-Kα radiation. Energy Dispersive Spectrometer (EDS) tests and SEM were measured on field emission scanning electron microscopy (SEM, HITACHI SU1510). Elemental analyses for C, H, and N were obtained on Elementer Vario EL cube. FT-IR spectra were measured using a Thermo Nicolet is50 FT-IR spectrophotometer. UV-Vis absorption and diffuse reflectance spectra were recorded on a Perkin Elmer Lambda-950 UV/Vis/NIR spectrophotometer. For diffuse reflectance, spectra were recorded with an integrating sphere and were converted from reflection to absorbance by the Kubelka–Munk method. The solid-state NMR experiments were performed in a 9.4 T magnetic field with a Bruker Advance III HD spectrometer. The ^{13}C NMR spectra were acquired using a 4 mm probe-head at a spinning frequency of 12 kHz and with cross-polarization magic angle spinning (CP-MAS) method. The chemical shift of ^{13}C was calibrated using TMS (0 ppm).

S2. Synthesis and single crystal structure analysis

The ligand DPNDI and $[Cu(CH_3CN)_4]PF_6$ were prepared according to the reference.[1,2] A solution of DPNDI (45mg) in DMA(8ml) was placed in a test tube (inner diameter 1cm × height 10 cm). 1ml DMAc and 1ml acetonitrile mixed solvent was layered above this solution as buffer layer, and then an acetonitrile solution of fresh prepared $[Cu(CH_3CN)_4]PF_6$ (120mg) was layered carefully on the top of the buffer layer. The resulting solution was sealed and allowed to stand for one week at room temperature without exposing to strong solar light or in the dark. Then red and rod shape crystal formed on the surface of the glass and isolated by filtration to give compound 46mg in 60% yield base on DPNDI. The formula of the crystal was determined to be $Cu(DPNDI)_2PF_6{\cdot}4DMA{\cdot}CH_3CN$ on the basis of the combined results of X-ray single crystal structure analysis, elemental analysis, EDS, solid-state NMR and thermogravimetric analysis. Elemental analysis: Calculated, C: 55.09, H: 4.41, N: 12.65; Found, C: 51.72, H: 4.93, N: 11.38. Infrared (single crystal, cm^{-1}) 3416(w), 2924(w), 1713 (m), 1675(s), 1625(m), 1586(m), 1441(w), 1347(s), 1246(s), 1195(m), 1140(w), 1056(w), 1012(w), 981(m), 837(s), 766(s), 754(s), 709(m), 635(s), 583(m), 554(s).

Crystal Data for Cu^I-NDI: $C_{48}H_{24}CuN_8O_8{\cdot}4C_4H_9NO{\cdot}CH_3CN$ (M =1438.78 g/mol): tetragonal, space group $P4_2/n$ (no. 86), a = 23.6145(7) Å, c = 6.5579(3) Å, V = 3657.0(3) $Å^3$, Z = 2, T = 100.01(10) K, μ(CuKα) = 0.745 mm^{-1}, *Dcalc* = 0.821 g/cm^3, 6850 reflections measured ($7.488° \leq 2\theta \leq 148.664°$), 3597 unique ($R_{int}$ = 0.0285, R_{sigma} = 0.0368) which were used in all calculations. The final R_1 was 0.0475 ($I > 2\sigma(I)$) and wR_2 was 0.1445 (all data). CCDC deposit number 1590515. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

As synthesized crystals of **Cu^I-NDI** was coated with oil and placed on top of a nylon cryoloop and then mounted in the diffractometer. Single-crystal XRD data were collected on an Agilent SuperNova diffractometer equipped with the CrysAlis^{pro} X-ray crystallography data systems. The data collected by using mirror-monochromatic Cu Kα radiation (λ=1.54184 Å) at 100 K under a cold nitrogen stream with an Oxford-Diffraction Cryojet system. The structure was solved by direct methods and was refined by the least-squares method with *SHELXL-2014* program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms of the ligands were located by geometrical calculations, and their positions and thermal parameters were fixed during structural refinement. Residual electron densities in the solvent-accessible void due to disordered solvent molecules were treated with the PLATON SQUEEZE program.

A level-A alert are suggested for the X-ray data of the Cu^I-NDI by PLATON/CIF check program: PLAT602_ALERT_2_A VERY LARGE Solvent Accessible VOID(S) in Structure.
This type of error is very common for the MOFs materials structure because the disorder solvent molecules was squeezed by the PLATON program.

A level-B alert are suggested that the Calculated Density Less Than 1.0 gcm^{-3}. For the unit cell, there are a lot of lightweight C, N and O element and just a few Cu atoms, in addition, the presence of large voids in the porous framework is another factor for the density less than 1.0g cm^{-3}.

Table : Crystal data and structure refinement

Identification code	Cu^{I}-NDI	
Empirical formula	$C_{48}H_{24}CuN_8O_8PF_6$	
Formula weight	1049.25	
Temperature	100.01(10)K	
Wavelength	1.54184 Å	
Crystal system	Tetragonal	
Space group	$P4_2/n$	
Unit cell dimensions	a = 23.6145(7) Å	α= 90°.
	b = 23.6145(7) Å	β= 90°.
	c = 6.5579(3) Å	γ = 90°.
Volume	3657.0(3) $Å^3$	
Z	2	
ρ_{calc}	0.821 g cm^{-3}	
Absorption coefficient	0.745 mm^{-1}	
F(000)	922	
Crystal size	0.300 × 0.200 × 0.150 mm^3	
Theta range for data collection	3.744 to 74.332°.	
Index ranges	-28<=h<=29, -29<=k<=9, -7<=l<=4	
Reflections collected	6850	
Independent reflections	3597 [R(int) = 0.0285]	
Completeness to theta = 67.684°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3597 / 0 / 148	
Goodness-of-fit on F^2	1.004	
Final R indices [I>2sigma(I)]	R1 = 0.0475, wR2 = 0.1373	
R indices (all data)	R1 = 0.0593, wR2 = 0.1445	
Extinction coefficient	0.00069(17)	
Largest diff. peak and hole	0.264 and -0.447 e.$Å^{-3}$	

S3: Crystal index and electronic conductivity measurement

(i) Crystal index:

Suitable single crystals of **Cu^{I}-NDI** were selected coated with oil and placed on top of a nylon cryoloop and then mounted in the diffractometer. Diffraction data (φ- and ω-scans) were collected on an Agilent SuperNova diffractometer by using mirror-monochromatic Cu Kα radiation (λ=1.54184 Å) at 100 K under a cold nitrogen stream. Crystal indexing was performed with CrysAlis^{pro} X-ray crystallography data systems.

Fig. S1: Three crystals were selected as candidates for crystal index. **a)** the monography of crystal 1;**b)** the monography of crystal 2; **c)** the monography of crystal 3;

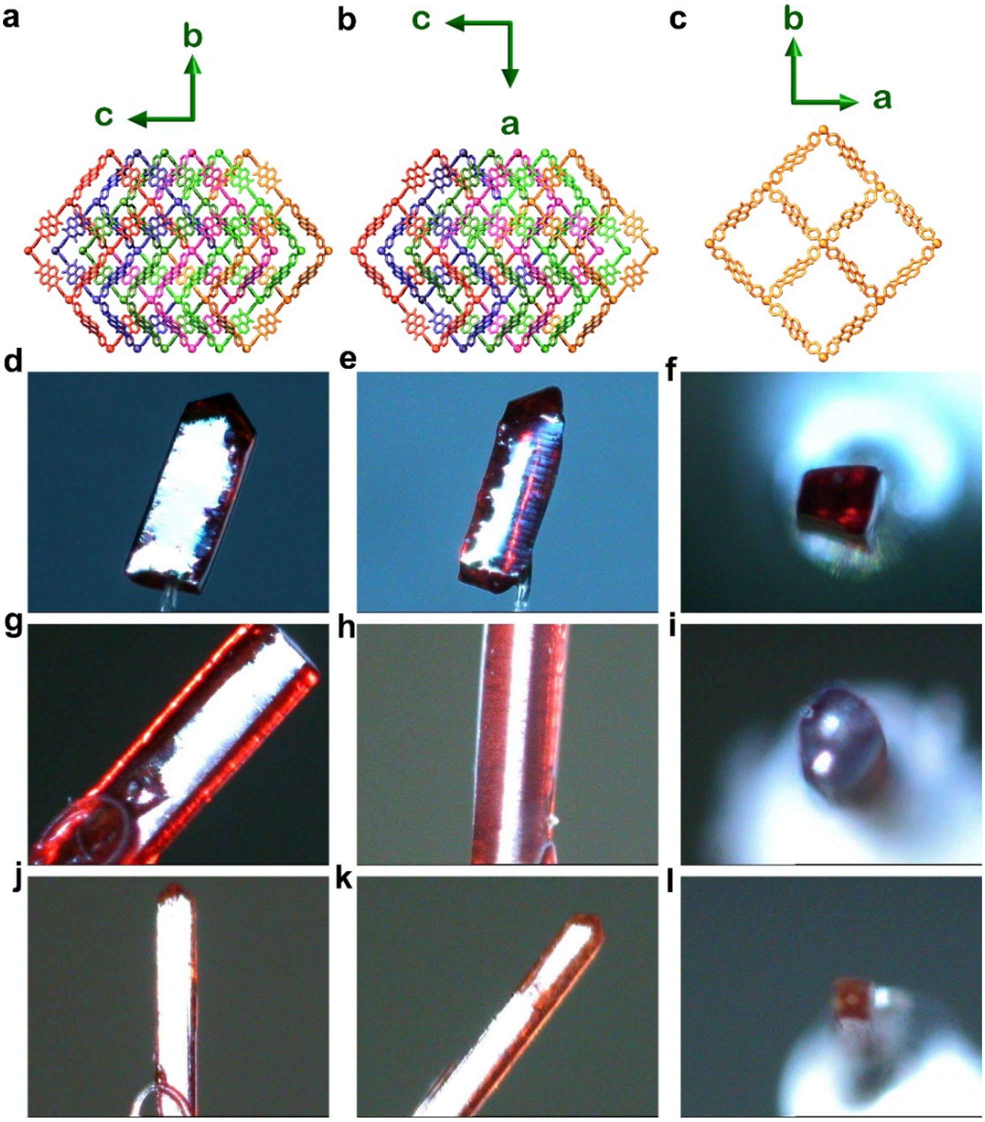

Fig. S2: single crystal structure of **a)** *a*-axis (*bc*-plane); **b)** *b*-axis (*ac*-plane); **c)** *c*-axis(*ab*-plane); **d)**, **e)**, **f)** are the *a*-axis, *b*-axis, *c*-axis of **crystal 1**; **g**), **h)**, **i)** are the *a*-axis, *b*-axis, *c*-axis of **crystal 2**; **j)**, **k)**, **l)** are the *a*-axis, *b*-axis, *c*-axis of **crystal 3**.

(ii) Single crystal electronic conductivity measurement

Single crystal electronic conductivity measurement was conducted by two-probe contact method. The electronic conduction electrodes were fabricated by attaching two gold wire (ф 0.05mm) at the both end of the crystal with the long c axis with silver paste on the glass substrates. The electronic conductivity measurement was performed on the semiconductor analyzer Keithley 4200A under ambient condition. Linear *I-V* curve was obtained by sweeping the voltage from -2V to 2V. The crystal dimension was determined by using SEM.

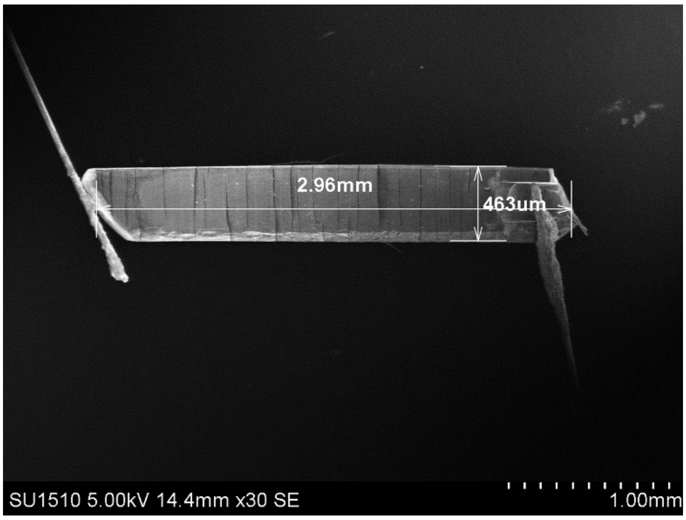

Fig. S3: the crystal dimension determined by the SEM

The electronic conductor σ could be calculated by the express $\sigma = \frac{I}{V}\frac{L}{S}$, where the *L* is the length of the crystal, *S* represent the cross-sectional area of the crystal. The value of *I* and *V* could obtained by the *I-V* curve.

S4: The FT-IR spectrum

The peaks at 554cm^{-1} and 837cm^{-1}, corresponding to PF_6^- stretches, indicates that the existent of the PF_6^- in the void of the metal-organic network.[3]

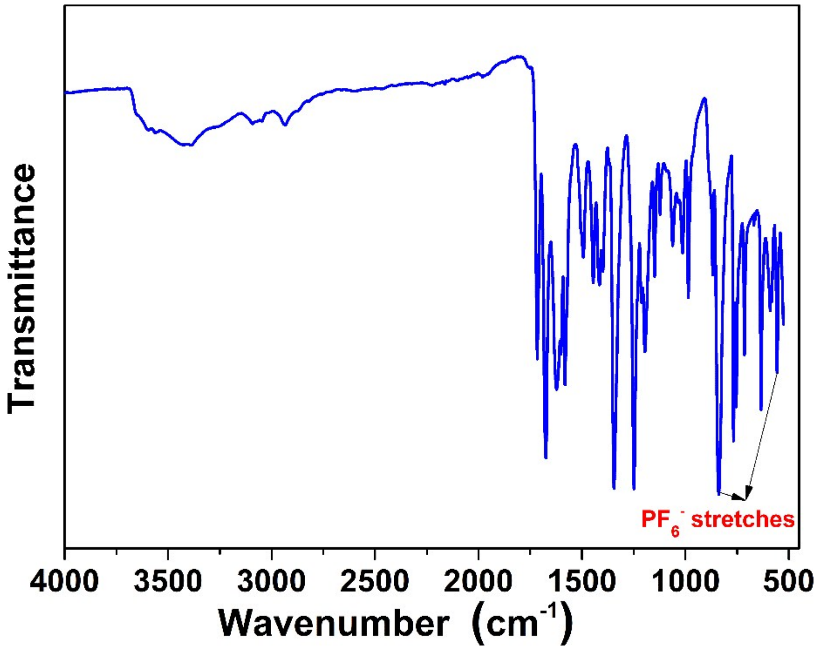

Fig. S4: the FT-IR spectrum of Cu^I-NDI

S5: Solid-State NMR

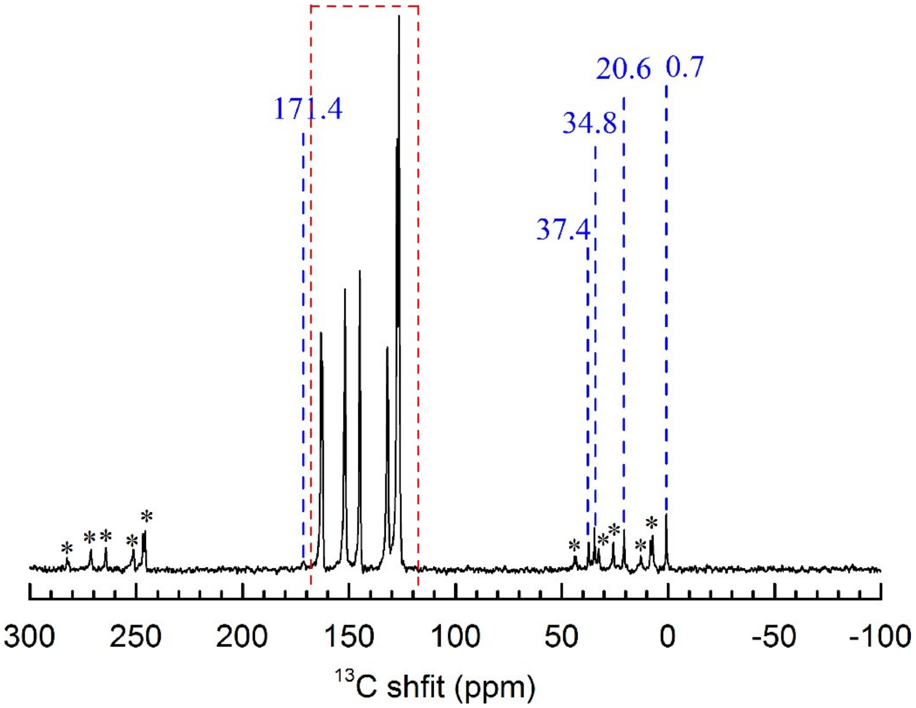

Fig. S5: the ^{13}C chemical shift of the solid-state Cu^I-NDI. The red zone are the ^{13}C chemical shift of the DPNDI ligand. The blue dash line represent the ^{13}C chemical shift of DMA and CH_3CN, the * represent spinning sidebands.

S6: TGA

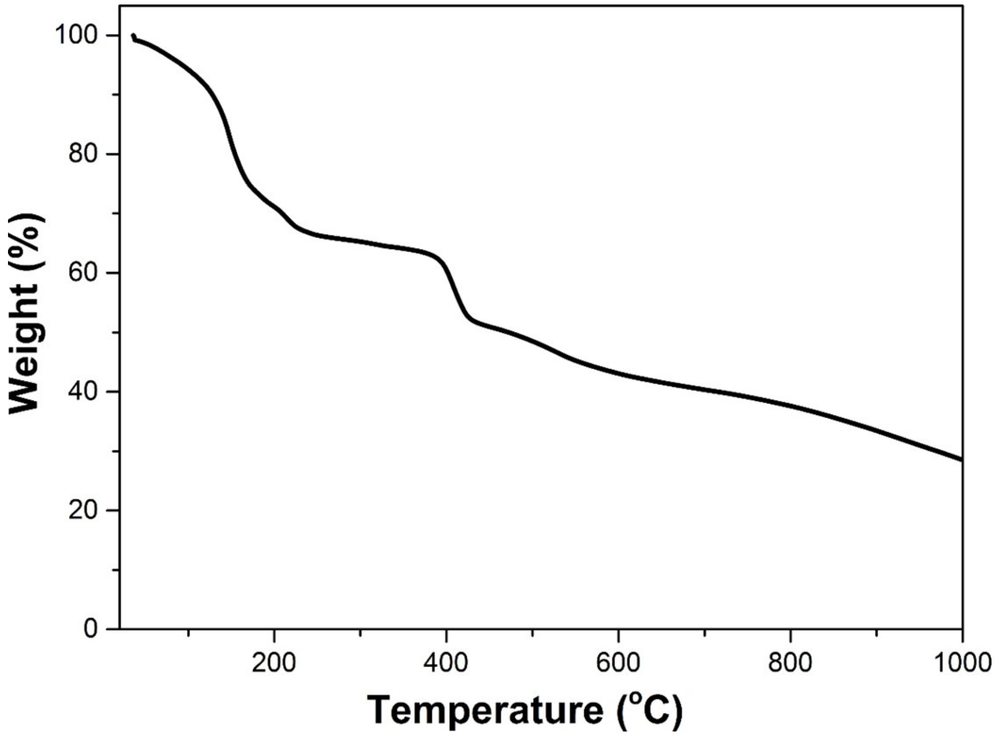

Fig. S6: the thermogravimetric analyses curve of the Cu^{I}-NDI with a heating rate of 5°C/min under nitrogen atmosphere.

S7: PXRD

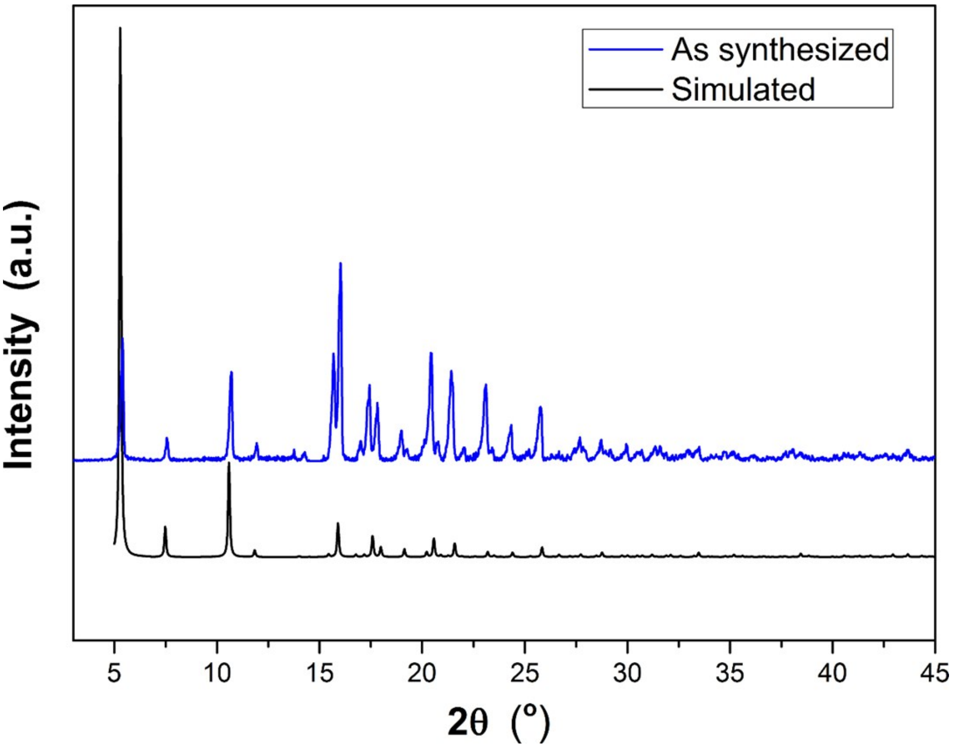

Fig. S7: the powder X-ray diffraction of Cu^{I}-NDI

S8: UV-Vis spectrum

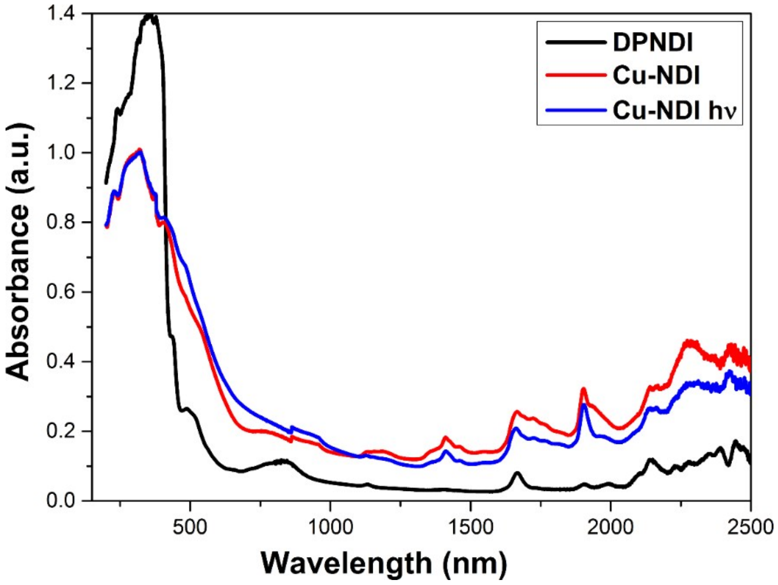

Fig. S8: the solid-state absorption spectra of the DPNDI ligand, Cu^{I}-NDI, and Cu^{I}-NDI after light irradiation for about 30min in the air.

S9: Solid-State cyclic voltammogram

The reduction potentials of the **Cu^{I}-NDI** were measured using a conventional three-electrode cell at room temperature. The **Cu^{I}-NDI**-coated glassy carbon electrode acts as working electrode, Pt wire as the counter electrode, and Ag wire as the quasi- reference electrode, respectively. A known amount (10mg) of Cu-NDI powder was dispersed in 2ml of methol and 20μl of 10% Nafion solution for 5min. A 20μl aliquot of the above dispersion was drop-cast onto the precleaned glassy carbon electrode and dried under ambient conditions for the fabrication of the working electrode. Electrochemical measurements of the sample were carried out using 0.1M TBAP $[(n\text{Bu})_4\text{N}]\text{PF}_6$ solution in acetonitrile under N_2 atmosphere. The reduction potentials of the Cu^{I}-NDI were obtained from the cyclic voltammogram and corrected with respect to the Fc/Fc^{+} internal standard.

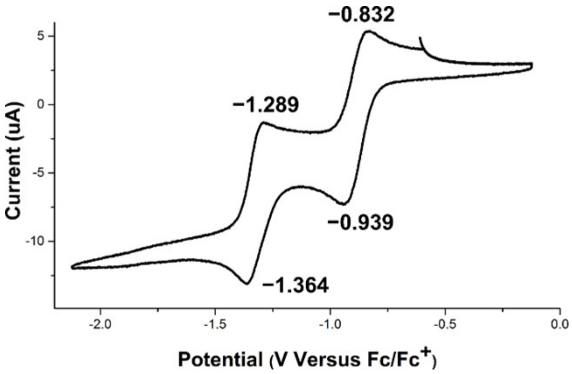

Fig. S9: Solid-state CV of Cu^{I}-NDI at 100 mVS^{-1} in a 0.1 M n-Bu_4NPF_6/CH_3CN electrolyte

S10: SEM and EDS

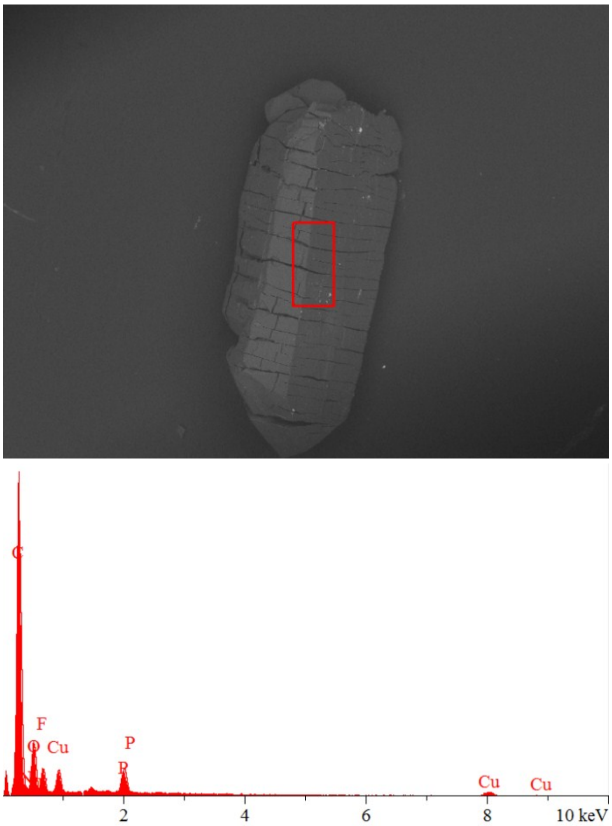

Fig. S10: the SEM surface analysis of Cu^{I}-NDI and the EDX analysis of the elemental distribution.

S12. Computational Details

The electronic band structure of the Cu^{I}-NDI was calculated within density functional theory (DFT), as implemented in the Vienna Ab initio Simulation Package (VASP).[4-6]. We have used the Perdew-Burke-Ernzerhof (PBE) type generalized gradient approximation (GGA) to describe the exchange-correlation energy and a projector-augmented-wave (PAW) method for the ionic pseudo-potentials. Monkhorst-Pack meshes of $(2 \times 2 \times 7)$ was used to sample the reciprocal space. The energy cutoff and convergence criteria for energy and force were set to be 500 eV, 1×10^{-7} eV, and 0.01 eV/A, respectively.

Reference

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