Supporting Information for

Unprecedented five-fold interpenetrated donor-acceptor hybrid heterostructure induced by anion-π interactions

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1. Experimental Details and Synthesis

1.1. Materials and methods:

Hydroiodic acid (55%, w/w), *N*, *N*-Dimethylformamide and methanol in AR grade were purchased commercially and used without further purification. The starting materials tri(tetraphenyl phosphonium) hexacyanoferrate, $(Ph_4P)_3Fe(CN)_6$ and *N*, *N'*-dipyridyl-naphthalene diimide , DPyNDI, were synthesized according to the same procedures reported in the literatures [S1-S2]. The infrared spectra have been measured in the range of 400-4000 cm^{-1} by use of a Perkin-Elmer FT-IR spectrophotometer. Powder X-ray diffraction (PXRD) intensities were recorded on a Rigaku Mini Flex-II X-Ray diffractometer. The electron spin resonance (ESR) measurements were recorded on a Bruker A300 instrument operating in the X-band at room temperature. The XPS studies were performed with a Thermo Fisher ESCALAB250 X-ray photoelectron spectrometer (powered at 150 W) using Al Kα radiation (λ = 8.357 Å). To compensate for surface charging effects, all XPS spectra were referenced to the C 1s neutral carbon peak at 284.7 eV. UV-Vis diffuse reflectance spectra were recorded at room temperature on a Varian Cary 500 UV-Vis spectrophotometer equipped with an integrating sphere by using $BaSO_4$ as a white standard in the range of 200-800 nm. Luminescent properties were made with an Edinburgh Instrument FLS 980 luminescence spectrometer.

1.2. Synthesis

Synthesis of 1 :   Under room temperature, in a crystallization tube, a $(PPh_4)_3[Fe(CN)_6]\cdot6H_2O$ solution in MeOH (2.5 mL) was carefully added on an around 0.25 mL buffered layer of DMF/MeOH (1 : 1, v/v), which was further layered on a solution of DPyNDI(0.10 mmol, 0.042 g) and 0.2 mL HI (55%, w/w) in DMF (2.5 mL). Dark yellow block crystals of complex **1** were obtained after several days (yield 40% based on DPNDI). IR (KBr, cm-1): 3094 (w), 2462 (w), 2072 (w), 1715 (s), 1678 (s), 1656 (s), 1345 (m), 1248 (m), 1192 (s), 985 (s), 857 (m), 832 (s), 767 (m), 752 (s), 572 (m), 520 (s).

2. Single-crystal X-ray diffraction analysis

The suitable single crystals of hybrid **1** were mounted on glass fiber for X-ray measurements. Diffraction data were collected on a Rigaku-AFC7 equipped with a Rigaku Saturn CCD area-detector system. The measurements were made using graphic monochromatic Mo Kα radiation (λ = 0.71073 Å) at 293 K. The frame data were integrated and absorption correction were calculated the Rigaku CrystalClear program package. All calculations were performed with the SHELXTL-97 program package [S3] and structures were solved by direct methods and refined by full-matrix least-squares against F^2. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms. The crystal data and structure refinements are summarized in Table S1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 1945154 for hybrid **1**, which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Crystal data and structure refinement for hybrid 1

Identification code	**1**
Empirical formula	$C_{33}H_{21}FeN_{11}O_5$
Formula weight	707.46
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	12.8757(7)
b/Å	13.7673(6)
c/Å	13.9810(6)
α/°	112.203(4)
β/°	112.169(5)
γ/°	101.951(4)
Volume/Å^3	1940.19(18)
Z	2
ρ_{calc}g/cm^3	1.211
μ/mm^{-1}	0.439
F(000)	724.0
Crystal size/mm^3	0.21 × 0.15 × 0.08
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.45 to 59.066
Index ranges	-17 ≤ h ≤ 15, -18 ≤ k ≤ 18, -18 ≤ l ≤ 15
Reflections collected	26813
Independent reflections	9042 [R_{int} = 0.0714, R_{sigma} = 0.1203]
Data/restraints/parameters	9042/0/456
Goodness-of-fit on F^2	0.871
Final R indexes [I>=2σ (I)]	R_1 = 0.0625, wR_2 = 0.1440
Final R indexes [all data]	R_1 = 0.1295, wR_2 = 0.1637
Largest diff. peak/hole / e Å^{-3}	0.52/-0.31

3. Infrared spectral analysis
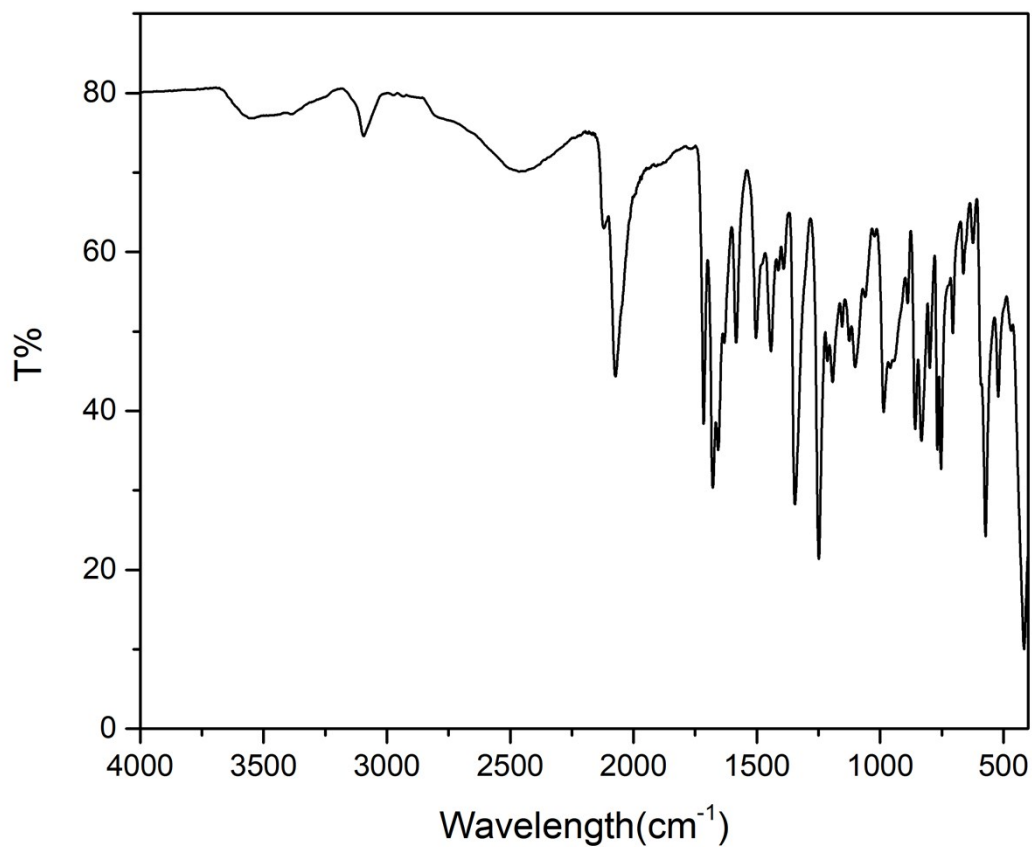

Figure S1. Infrared spectrum of hybrid **1**
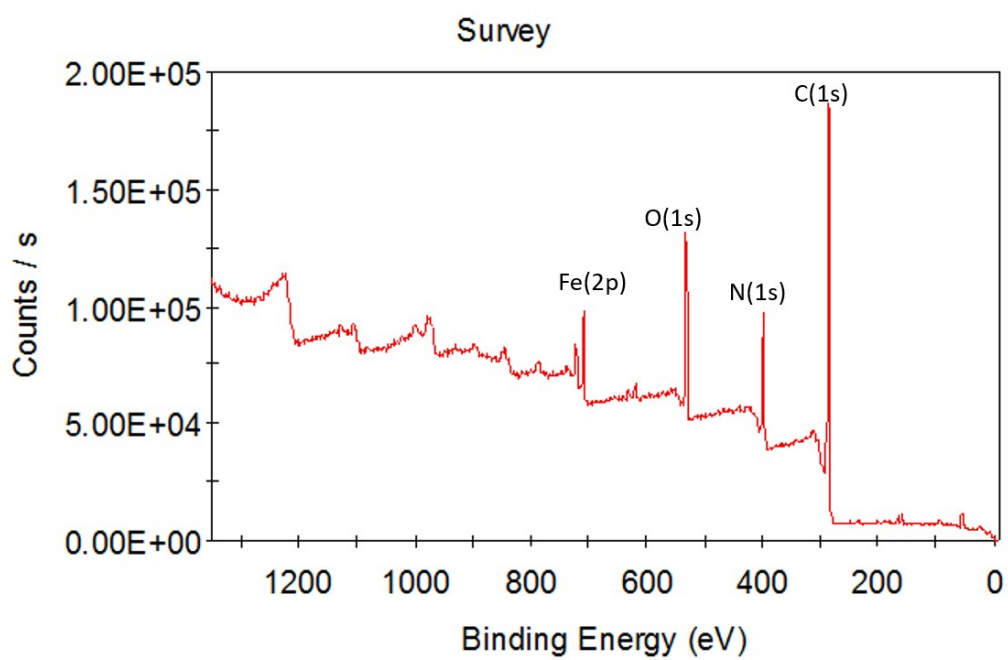
4. XPS survey spectra analysis

Figure S2. XPS survey spectra for **1**

5.   Molecular orbital calculations

The simulated models were constructed from their cif files and electronic structure calculations were conducted without further optimization. The calculation was based on density function theory (DFT) [S4], in which wave functions were explained in a plane wave basis set and the spin polarized version of the GGA/PBE was employed for the exchange-correlation functional in the CASTEP code [S5]. In this case, a 3×2×2 Monkhorst-Pack grid with a total number of 6 k points in the irreducible Brillouin zone was adopted. The number of plane waves included in the basis was determined by a cutoff energy Ec of 381 eV.

For the calculated band structure and density of state (DOS), they have been carefully discussed in the main manuscript. For frontier molecular orbital calculations, as shown in Fig. S2, the calculated energy gaps between HOMO and LUMO levels for **1** is ca. 1.455 eV, also well consistent with the experimental result. In addition, the LUMO orbits are mainly originated from the π bonding orbitals of DPyNDI cores, while the contributions of HOMO orbits is Fe-3d, which also confirmed that upon irradiation, an electron in $Fe(CN)_6^{4-}$ anions is anticipated to transfer to DPyNDI tectons to form radical anionic species.
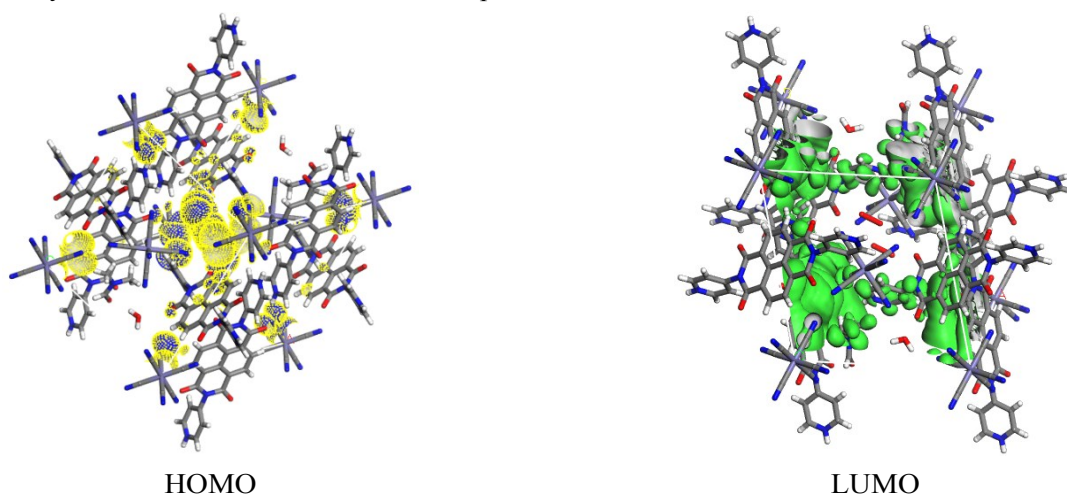

HOMO   LUMO

Fig. S3: The calculated frontier molecular orbits for hybrid **1**.
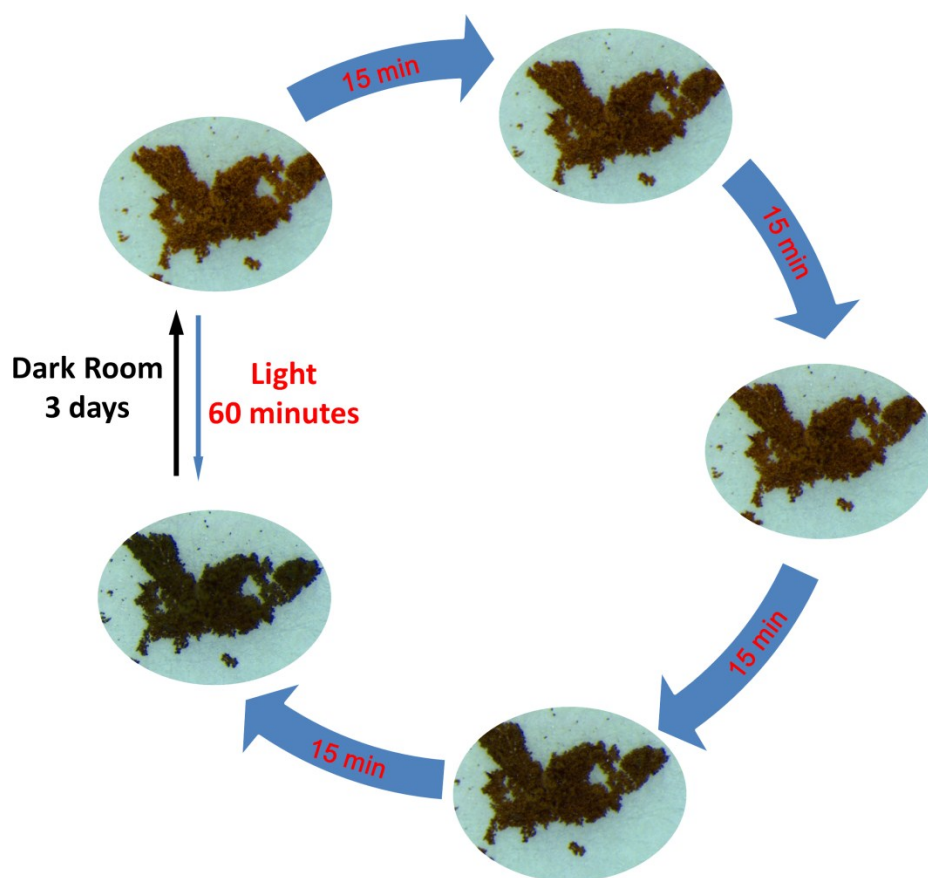
6. Light-induced color changes

Fig. S4 The appearance color changes of hybrid **1** before (left) and after (right) the irradiation by Xenon lamp.

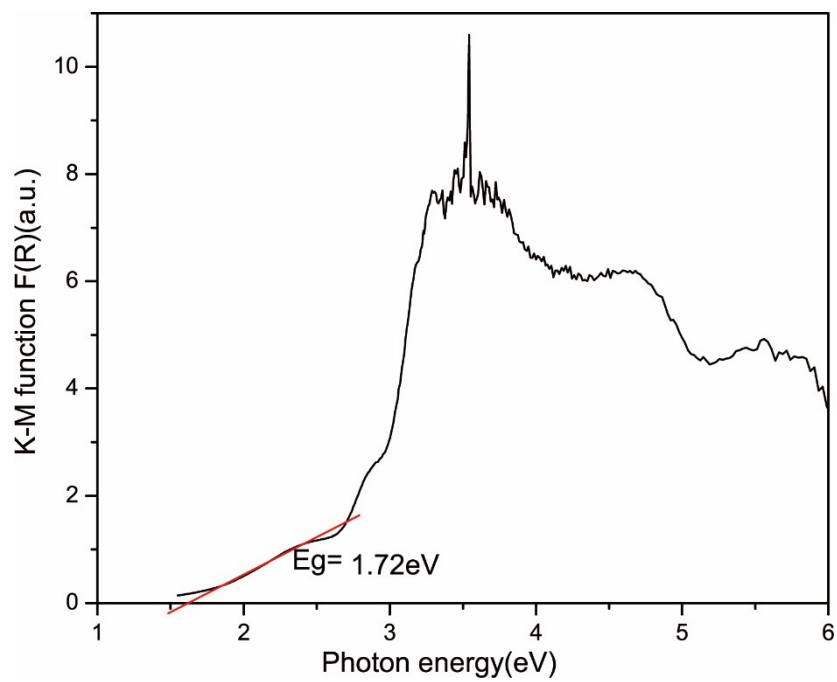## 7. Solid-state diffuse reflectance spectral analysis

Fig. S5 The optical absorption spectra of hybrid **1**.
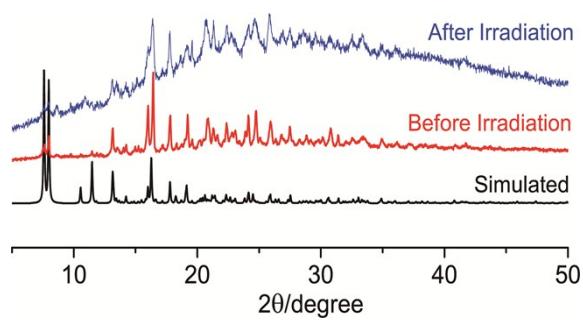
8. Powder X-ray diffraction analysis

Fig. S6 The PXRD pattern of hybrid **1** before and after 15 minutes irradiation by Xenon lamp (300W, 420-780 nm).
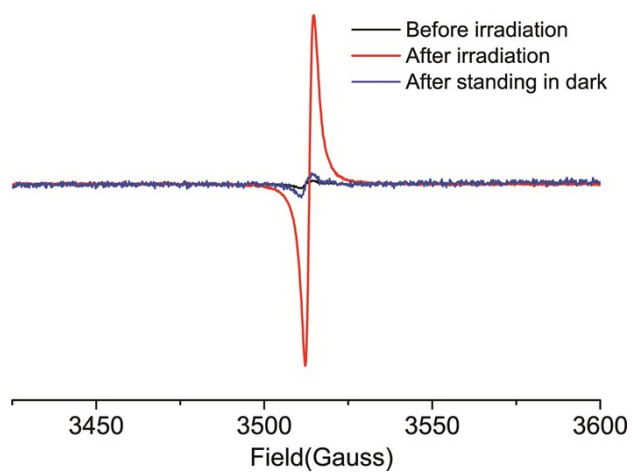
9. Electron paramagnetic resonance (EPR) spectra

Figure S7. EPR spectra of hybrid **1** before, after irradiation by Xenon Lamp for 15 minutes and after standing in dark for 3 days

References

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