Lone pair- $\boldsymbol{\pi}$ interaction-induced generation of

photochromic coordination networks with

photoswitchable conductance

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1. Materials and Physical Measurements

All chemicals were obtained from commercial sources and used as received without further purification. NMR spectra were recorded with a Bruker Avance III 400MHz NMR spectrometer. Elemental analyses of C, H, N and S were carried out with a Vario EL III elemental analyzer. Powder X-ray diffraction (PXRD) were collected on Rigaku desktop MiniFlex 600 diffractometer with Cu K α radiation (λ =1.5418 Å). IR spectra were recorded in the range 4000–400cm⁻¹ on a Perkin-Elmer FT-IR spectrum 2000 spectrometer with pressed KBr pellets. Optical diffuse reflectance spectra were measured at room temperature on a Perkin Elmer Lambda-950 UV/Vis/NIR spectrophotometer. ESR spectra were recorded on a Bruker BioSpin E500 ESR spectrometer with a 100 KHz magnetic field modulation at room temperature equipped with an UV light source (16 mW). Thermal analyses were performed on a TGA/DSC 1 STAR^e system from room temperature to 1000°C with a heating rate of 10 K/min under nitrogen.

2. Experimental Section

Synthesis of N, N'-di(ethanesulfonic acid)-1,4,5,8-naphthalenediimide (H₂TauNDI). A mixture of 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NDA) (1.41 g, 5.26 mmol) and taurine (1.316 g, 10.52 mmol) in DMF (65 mL) was heated under 423K for about 19 h. When the reaction mixture reached room temperature, a light yellow crystalline solid precipitated out, which was collected by filtration. ¹H NMR (400 MHz, DMSO- d_6) δ 8.66 (s, 4H), 4.43-4.18 (m, 4H), 2.95-2.27 (m, 4H) (Fig. S1). IR(cm⁻¹): 3447(m), 2981(w), 2779(w), 2440(w), 1706(m), 1664(s), 1584(m), 1456(m), 1381(m), 1343(s), 1206(s), 1097(m), 1039(s), 1005(s), 877(w), 802(m), 766(s), 631(m), 535(s).

Synthesis of complex 1. A mixture of H₂TauNDI (0.0480 g, 0.1 mmol), NaNO₃ (0.0085 g, 0.1 mmol), H₂O (2 mL), and EtOH (2 mL) were heated in a 25 mL Teflon-lined autoclave at 120°C for 3 days, followed by programmed cooled for 1 day to room temperature. After suction filtration, the faint yellow crystals were collected. Yield: 81% (based on Na). Anal. Calcd for Na(C₁₈H₁₂N₂O₁₀S₂)_{0.5}(H₂O)₂: C 36.12, H 3.36 N 4.68, S 10.72%. Found: C 36.07, H 3.22, N 4.70, S 10.82%. IR (cm⁻¹): 3486(m), 3067(w), 2960(w), 1713(s), 1660(s), 1583(m), 1460(m), 1423(m), 1344(s), 1215(s), 1157(s), 1046(m),1005(m), 919(w), 866(m), 774(m), 571(m), 501(m).

3. Crystallographic Data Collection and Refinement

Suitable single crystal of complex **1** was mounted on loop for the X-ray measurement. Diffraction data was collected on SuperNova (Dual source) diffractometer equipped with the CrysAlis^{pro} X-ray crystallography data systems. The measurement was made by using graphic monochromatic Cu K α radiation (λ =1.54184 Å) at 100 K under a cold nitrogen stream. Using Olex2^{S1}, the structure was solved with the ShelXT^{S2} structure solution program using Intrinsic Phasing and refined with the ShelXL^{S3} refinement package using Least Squares minimisation. Crystallographic data has been deposited at the Cambridge Crystallographic Data Center with reference number CCDC 1554405. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>http://www.ccdc.cam.ac.uk/data_request/cif</u>.

4. Crystal Data for Complex 1

NaC₉H₁₀O₇NS, Mr=299.23, Light yellow crystal, Orthorhombic, Space group *P*bca (no. 61), a=6.8364(2) Å, b=11.9343(4) Å, c=27.7283(9) Å, V=2262.29(12) Å³, Z=8, ρ_{calcd} = 1.757 g·cm⁻³, μ =3.263 mm⁻¹, λ (CuKα)=1.54184 Å, F(000)=1232, T=100.00(10) K, GooF=1.04, Final R indices: R1 =0.0286, wR2=0.0791 for 1869 reflections [I>2σ(I)]; R1=0.0304, wR2=0.0811 for 2002 independent reflections (all data) and 188 parameters.

5. Related Figures of Complex 1



Figure S2. View of the coordination environment of the Na cations in **1** with the thermal ellipsoids drawn at 30% probability level. All hydrogen atoms are omitted for clarity. Symmetry code: i) 0.5+x, y, 0.5-z; ii) -0.5+x, y, 0.5-z; iii) 0.5-x, 1-y, 0.5+z; iv) 1-x, 1-y, 1-z; v) 1.5-x, 1-y, 0.5+z.



Figure S3. (a) View of one dimensional network with the one-dimentional $[Na-O-Na]_n$ chain in complex **1**, where the Na-O-Na-O chain is highlighted in celeste; (b) adjacent networks are linked by deprotonated TauNDI motifs to form two-dimentional structure (dotted line: C-H... π interactions).



Figure S4. Hydrogen bonds in this three-dimensional supermolecular structure.



Figure S5. The intramolecular lone pair- π and intermolecular C-H... π interactions in complex **1**.

| D—H····A [#] | [Symmetry code] | d(D—H) | $d(H \cdots A)$ | $d(D \cdots A)$ | ∠DHA |
|--------------------------------|---------------------|--------|-----------------|-----------------|------|
| O6—H6A…O7 ⁱ | [-x, -1/2+y, 1/2-z] | 0.82 | 2.09 | 2.9022 | 170 |
| O6—H6B…O3 ⁱⁱ | [-1/2+x, y, 1/2-z] | 0.87 | 2.08 | 2.9379 | 169 |
| O7—H7F⋯O3 ⁱⁱⁱ | [-x, 1/2+y, 1/2-z] | 0.78 | 2.18 | 2.9485 | 171 |
| O7— $H7W$ ···O16 ^{iv} | [1/2-x, 1/2+y, z] | 0.86 | 2.01 | 2.8686 | 173 |
| C1—H1A…O4 | - | 0.99 | 2.49 | 3.0499 | 116 |
| C2—H2B…O5 | - | 0.99 | 2.31 | 2.7365 | 105 |

Table S1 Hydrogen-bond Geometry (Å, °) for Complex 1

 $^{\#}$ D = Donor, A = Acceptor.

6. X-ray Powder Diffraction

The phase purity of the complex is convincingly established by comparison of the powder Xray diffraction patterns of the as-synthesized products with the simulated ones from the singlecrystal date. The PXRD patterns for complex **1** before irradiation and that after irradiation by LED light with power of 3 W (460-465 nm) are in accordance with the simulated PXRD pattern based on the single crystal **1**, indicating that the crystal structure of **1** were left unchanged.



Figure S6. (a)The simulated PXRD pattern based on the single crystal **1**; (b) PXRD pattern of the assynthesized coordination complex **1**; (c) for **1** after irradiated by LED light with the power of 3 W (460-465 nm).

7. In-situ Ultraviolet-visible Absorption Spectra of Complex 1

Optical diffuse reflectance spectra were measured at room temperature on a Perkin Elmer Lambda-950 UV/Vis/NIR spectrophotometer. The sample was irradiated by LED light with power of 3 W (460-465 nm) for different illumination time.



Figure S7. The estimated energy band gap by the UV/Vis diffuse reflectance spectroscopy based on the Kubelka-Munk Function.

8. Computational Studies

All calculations were performed with the *Vienna ab initio simulation package* (VASP)^{S4,S5} and Perdew-Burke-Ernzerhof (PBE)^{S6} type generalized gradient approximation (GGA) to describe the exchange-correlation energy. We have used a projector-augmented-wave (PAW) method^{S7} for the ionic pseudo-potentials. Monkhorst-Pack meshes^{S8} of ($4 \times 2 \times 1$) was used to sample the reciprocal space. The energy cutoff and convergence criteria for energy and force were set to be 500 eV, 1 $\times 10^{-7}$ eV, and 0.01 eV/Å, respectively.



Figure S8. The electronic band structure of 1 (Fermi level located at 0 eV).

9. Conductivity Measurement

Conductivity measurement was conducted using Keithley 2400 SourceMeter, equipped with 2-terminal probe station at 30°C under 50% relative humidity, which was measured in Labonce-60CH stability chambers. The fresh sample (yellow) was ground and pressed into 6-mm-diameter pellets using a manual tablet press at the pressure of 10.0 MPa. The thickness of the pellet was measured by micrometer (L=0.553 mm). Silver paste was used to connect the pellet samples to the electode probes. The sample was irradiated by simulated sunlight (300 W Xenon lamp, 320-780 nm; PLS-SXE300C, Beijing Perfectlight, Co. Ltd.) for 20 minutes. It will transform to yellow after dark treatment.



Figure S9. The photo images of 1 showing the photochromism.

10. Thermogravimetric Analyses

TGA of an air-dried sample of complex **1** was conduced on a TGA/DSC 1 STAR^e system with a heating rate of 10 K/min under an N₂-atmosphere. Thermogravimetric analyses revealed that **1** exhibits relatively excellent thermal stability.



Figure S10. TGA/DSC curve of complex 1.

11. UV-Vis Spectra of H₂TauNDI powder





Slight color change of the H₂TauNDI powder was observed after irradiated by blue light for 4 min (3 W, 460-465 nm), as shown in figure S11. With the prolonged irradiation time, the color of the sample no longer deepens. The darkened sample has no obvious change by dark treatment overnight. From the UV-Vis spectra of the H₂TauNDI (Figure S11), we can see that the major effect of the irradiation by blue light is forming obviously absorption band at about 450 to 600 nm, which is quite different from complex **1**. The specific reason is hard to determine due to the lack of the single crystal structure. Presumably there are charge transfer interactions between the central rings and the oxygen atoms from the carbonyl or sulfonic acid of H₂TauNDI molecules in the powder under light irradiation, which is the main reason for this photochromic behavior. But the molecules are not packed into well-ordered crystalline state, thus display different phenomenon. These results further demonstrate that the unique lone pair- π interactions in complex **1** have important effects on the long-lived charge-separated state.

12. Reference

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