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Inter-ligands charge-transfer interactions in a photochromic and redox active zinc-organic framework

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Experimental

General infomation

H_2NDI-ATZ (2,7-di(1H-tetrazol-5-yl)benzo[Imn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone) was synthesized according to the procedure of literature.[13] $Zn(NO_3)_2\cdot 6H_2O$ and terephthalic acid were received and used without further purification. FT-IR spectra were recorded on a Shimadzu FTIR-8900 spectrometer using KBr pellets in the range of 400–4000 cm^{-1}. Elemental analyses were carried out on an Elementar Vario EL III analyser. Powder X-ray diffraction (PXRD) measurements were carried out on a Bruker D8 ADVANCE X-ray powder diffractometer using Cu Kα (λ = 1.5418 Å) at 40 KV and 40 mA. Thermogravimetric measurements were performed from room temperature to 800 °C at a heating rate of 10 °C/min under air atmosphere using a SII TG/DTA7300 apparatus. UV-visible (UV-vis) spectra were recorded at room temperature on a PerkinElmer Lambda 900 UV/vis/NIR spectrophotometer equipped with an integrating sphere in the wavelength range of 200-1200 nm. $BaSO_4$ plates were used as reference (100% reflection), on which the finely ground power of the sample was coated. ESR spectra were measured on a Bruker ER-420 spectrometer with a 100 kHz magnetic field in X band at room temperature. Fluorescence spectra were recorded with an FL-F4600 spectrometer.

Synthesis of $\{[Zn_4(NDI\text{-}ATZ)_2(BDC)_2(DMF)_6]\cdot(DMF)\}_n$ (NBU-4)

A mixture of $Zn(NO_3)_2\cdot6H_2O$ (0.0300 g, 0.1 mmol), H_2NDI-ATZ (0.0201 g, 0.05 mmol), and terephthalic acid (0.0042 g, 0.025 mmol) were dissolved in 3 mL DMF. Then, the resulting clear solution was sealed in a Pyrex tube and heated at 80 °C for 24 h. Yellow rod crystals were obtained with 37% yield based on $Zn(NO_3)_2\cdot6H_2O$. Anal. Cal. for $C_{69}H_{65}N_{27}O_{23}Zn_4$ (%): C 43.57, H 3.45, N 19.89; found (%): C 43.52, H 3.46, N 19.88. IR (KBr, cm^{-1}): 3440 (s), 1700 (vs), 1502 (s), 1338 (vs), 1255 (s), 1108 (w), 989 (w), 840 (m), 748 (m).

X-ray Crystallography

Single crystal data of **NBU-4** was collected on a Bruker Apex II CCD area-detector diffractometer using Mo-Kα radiation (λ = 0.71073 Å). The structure was solved with direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package. Absorption correction was applied by using multi-scan program SADABS. All non-hydrogen atoms were refined anistropically. Hydrogen atoms bonded to carbon atoms were placed at calculated positions and refined using a riding model approximation, with C−H = 0.93 (aromatic CH) and with $U_{iso}(H) = 1.2U_{eq}(C)$. The CH_3 hydrogen atoms of DMF molecules (C−H = 0.96 with $U_{iso}(H) = 1.5Ueq(C)$. Crystallographic data and refinement details are shown in Table S1, selected bond distances and bond angles are listed in Tables S2 (ESI†). Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 1846228.

Electrochemical studies

The electrochemical measurements were carried out using a CHI 760E electrochemical analyser with three-electrode system. **NBU-4** was coated at FTO substrate and acted as a working electrode, AgCl/Ag and a platinum wire as auxiliary and counter electrodes, respectively. An amount (5 mg) of **NBU-4** or H_2NDI-AZT ligand was dispersed in 0.5% Nafion / ethanol solution for 10 min. 25μL of the above dispersion solution was dropped onto the pre-cleaned FTO electrode and dried under ambient conditions and used as the working electrode. Electrochemical test was performed in 0.1M TBAP ($[(n\text{-}Bu)_4N]PF_6$) electrolyte.

Computational Details

The B3LYP functional [S1] was employed in the density functional theory (DFT) calculations, which were carried out using the Gaussian 09 software package.[S2] The geometries model used for the optimization were taken from the crystallographic coordinates extracted from the crystal structure. The Stuttgart relativistic small core potential and the valence basis sets for Zn [S3] and the 6-31+G** [S4] basis set for the other elements (C, N, O, H) were used in our DFT calculations. The same functional and RECP basis sets have been chosen for the Time-dependent density functional theory excited-state calculation. Solvent effects (DMF) were included during the optimization and TD-DFT calculations using the polarizable continuum model [S5] (PCM, ε = 37.219) .

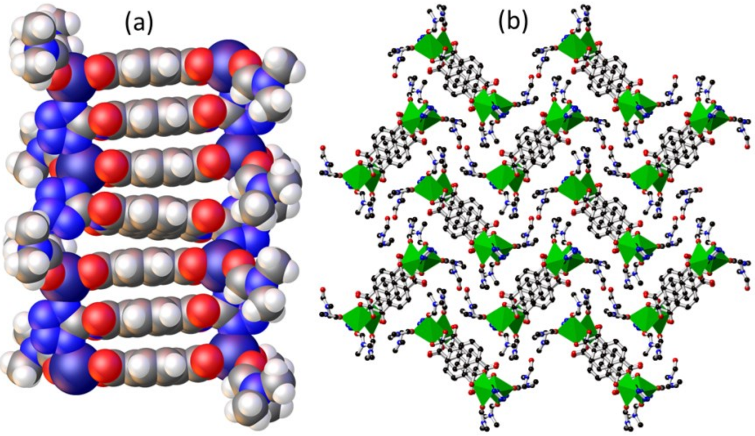

Fig. S1 (a). Space filling structure of **NBU-4**; (b). Packing structure of **NBU-4** showing the neighboring 1D stair-like chains perpendicular to each other.

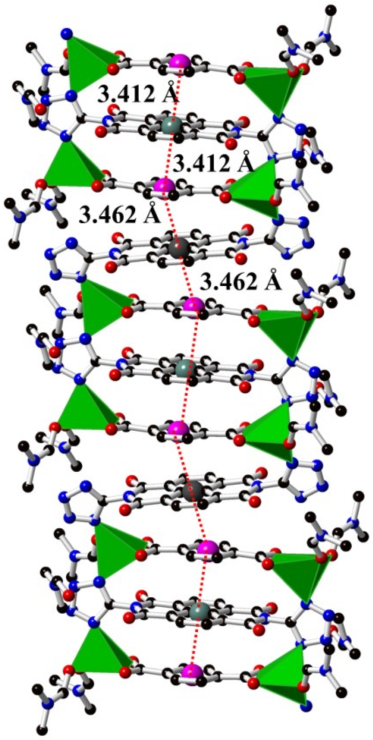

Fig. S2. Strong π-π stacking interactions in **NBU-4**.

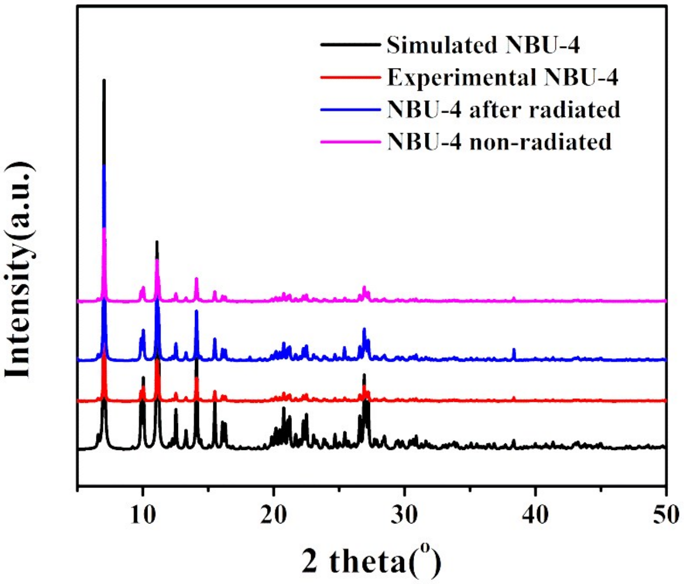

Fig. S3. PXRD patterns of **NBU-4**, its radiated and non-radiated samples (the radiated sample was treated in the dark for overnight.).

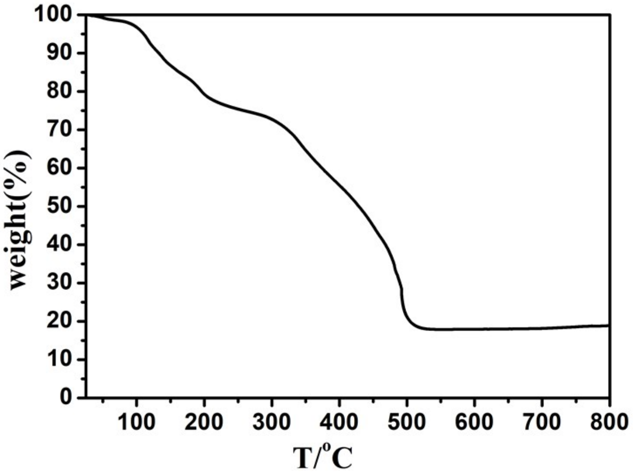

Fig. S4. TGA result of **NBU-4**.

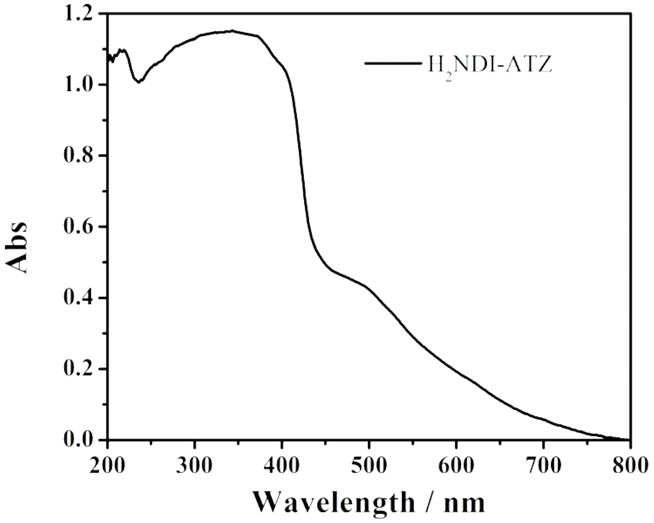

Fig. S5. The UV-Vis spectra of H_2NDI-ATZ.

Table S1. Crystallographic data and refinement details for **NBU-4**

	NBU-4
CCDC Number	1846228
Empirical formula	$\{[Zn_4(NDI\text{-}ATZ)_2(BDC)_2(DMF)_6]\cdot(DMF)\}_n$
Color & habit	Yellow, Rod
Crystal size (mm^3)	0.26 x 021 x 0.17
Temperature (K)	293K
Crystal system	Monoclinic
Space group	$P2_1/c$
a(Å)	13.506(5)
b(Å)	17.590(4)
c(Å)	18.041(6)
α(°)	90
β(°)	97.01(2)
γ(°)	90
V($Å^3$), Z	4254(2) , 2
D_{cal} (Mg/m^3)	1.485
Abs. coeff.(mm^{-1})	1.201
F(000)	1944.0
2θ range for data collection (°)	4.64 to 50
Reflections collected	21398
Indep. Reflection, R(int)	7453, 0.1101
Completeness of data	99.5 %
Data/ restraints / parameters	7453/1/583
Goodness-of-fit on F^2	1.023
R1 [I>2sigma(I)], wR2	0.0682, 0.1240
R1 (all data), wR2	0.1743, 0.1460
Largest diff. peak and hole ($e\cdot Å^{-3}$)	0.49, -0.40

Table S2. Selected bond lengths (Å) and bond angles (°) for **NBU-4**

Zn1 - O1	2.272(5)	Zn1-O2	2.032(5)
Zn1 - O5	1.992(5)	Zn1-O6	1.965(5)
Zn1 - N3	2.000(5)	Zn2-O3[1]	2.450(5)
Zn2 - O4[1]	1.968(4)	Zn2-O9	1.999(5)
Zn2 - N6	2.021(5)	Zn2-N9	1.978(5)
O2 -Zn1-O1	60.04(19)	N3 -Zn1-O1	98.7(2)
O5 -Zn1-O1	153.8(2)	O6 -Zn1-O1	89.0(2)
N3 -Zn1-O2	108.5(2)	O5 -Zn1-O2	98.1(2)
O6 -Zn1-O2	133.5(2)	O5 -Zn1-N3	102.3(2)
O6 -Zn1-O5	98.3(2)	O6 -Zn1-N3	110.0(2)
O4[1] -Zn2-N9	116.3(2)	O4[1] -Zn2-O9	103.5(2)
N9 -Zn2-O9	99.9(2)	O9 -Zn2-N6	95.1(2)
O4[1] -Zn2-N6	114.7(2)	N9 -Zn2-N6	121.0(2)
O4[1] -Zn2-O3[1]	57.87(17)	N9 -Zn2-O3[1]	93.28(19)
O9 -Zn2-O3[1]	160.9(2)	N6 -Zn2-O3[1]	89.79(19)

[1] 1-X,1-Y,-Z.

Table S3. The excited states, transition wavelengths (λ), oscillator strengths (f) and MO transitions with absolute contribution [33] of TD-DFT calculations of **NBU-4** fragment.

Excited States	λ (nm)	*f* (oscillator strength)	Frontier molecular orbitals	Percent (%)
1	418.0	0.0001	222 (HOMO-1) → 224 (LUMO)	55.2
			223 (HOMO) → 224 (LUMO)	29.4
			221 (HOMO-2) → 224 (LUMO)	13.2
2	415.9	0.0035	223 (HOMO) → 224 (LUMO)	49.4
			221 (HOMO-2) → 224 (LUMO)	42.6
3	396.2	0.0052	220 (HOMO-3) → 224 (LUMO)	89.4
4	388.1	0.3963	221 (HOMO-2) → 224 (LUMO)	39.0
			222 (HOMO-1) → 224 (LUMO)	34.4
			223 (HOMO) → 224 (LUMO)	19.8

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