

*Supporting Information for*

**Biomimetic Control of Charge Transfer in MOFs by Solvent Coordination  
for Boosting Photocatalysis**

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## 1. Experimental Section

### 1.1 Materials:

All chemicals were used without further purification. Perylene-3,4,9,10-tetracarboxylic dianhydride (98%, Shanghai Aladdin Biochemical Technology Co., Ltd), Nickel(II) acetate tetrahydrate (AR, Sinopharm Chemical Reagent Co., Ltd), Sodium hydroxide (AR, Sinopharm Chemical Reagent Co., Ltd). Acetonitrile, Methanol, N,N-Dimethylformamide, Dimethyl sulfoxide, Ethanol (AR, all solvents are from Sinopharm Chemical Reagent Co., Ltd).

### 1.2 Preparation of Na-PTCA

First, PTCDA needs to be deprotonated by NaOH. PTCDA (1.256 g) and NaOH (0.512 g) are dispersed in deionized water (200 mL). After it is completely hydrolyzed to form a transparent solution (stirring at 70°C, at least 3h), fluorescent-green Na-PTCA aqueous solution is obtained<sup>1</sup>.

### 1.3 Synthesis of [Ni(PTCA)·sol]-MOF

Nickel acetate (0.199 g) is dissolved in deionized water (25 mL). The obtained nickel acetate solution and Na-PTCA aqueous solution (25 mL) are fully mixed under vigorous stirring. Then, the mixed solution is transferred to a polytetrafluoroethylene lined reactor. The reactor is reacted at 120 °C for 24 h. After natural cooling to room temperature and washing with deionized water and ethanol, the final product (Actual yield= 96.8%) is dried in a vacuum oven at 70 °C for 10 h. [Ni(PTCA)·sol]-MOFs are synthesized by changing the dissolved solvent of Ni(CH<sub>3</sub>COO)<sub>2</sub>.

## 2. Characterization

### 2.1 Instrument parameters

**XRD:** Powder X-ray diffraction (PXRD) measurement was tested by Bruker D8 ADVANCE with an operating voltage 40 kV and operating current of 40 mA (Cu K $\alpha$  radiation,  $\lambda=1.54056$  Å).

**FT-IR:** Fourier transform infrared (FT-IR) spectra was measured by Nicolet NEXUS870 spectrometer using KBr pellets supporter at room temperature.

**PL:** Photoluminescence emission spectra was obtained on Shimadzu RF-5301PC fluorometer spectrometer in the aqueous solution and the excitation wavelength was 380 nm.

**XPS:** X-ray photoelectron spectroscopy (XPS) measurement was performed on PHI 5000 Versa Probe X-ray photoelectron spectrometer (a monochromatic Al K $\alpha$  X-ray radiation).

**LRS:** Raman spectra was taken on Renishanplc H33148 Laser Confocal Raman spectrometer.

**BET:** The Brunauer-Emmett-Teller (BET) surface area experiment was measured on Micromeritics ASAP-2020 adsorption analyzer under N<sub>2</sub>-physisorption at 77 K. In order to study the effect of solvent, the pretreatment temperature is kept at 90 °C.

**ICP-OES:** Inductively coupled plasma-optical emission spectrometry (ICP-OES) measurement was carried out on Avio500 spectrometer.

**TGA:** Thermogravimetric analysis (TGA) experiment was measured by NETZSCH STA 449C under N<sub>2</sub> atmosphere with heating rate of 20 °C/min .

**EPR:** Electron paramagnetic resonance (EPR) measurement was carried out on Bruker BioSpin EMX PLUS (PPMS). In-situ EPR test is realized by taking a small amount of photocatalytic system solution and testing under light conditions.

**UV-Vis:** UV-vis spectra was collected by Shimadzu UV-3600 spectrometer.

**UV-vis DRS :**UV-vis diffused reflectance spectroscopy (DRS) was acquired through Shimadzu UV-3600 spectrometer with BaSO<sub>4</sub> as reflectance.

**TRF:** Time-resolved fluorescence (TRF) decay spectra was obtained by Edinburgh FLS920.

**SEM:** Scanning electron microscope (SEM) was measured by Hitachi S-4800 FESEM system.

## ***2.2 Electrochemical measurements***

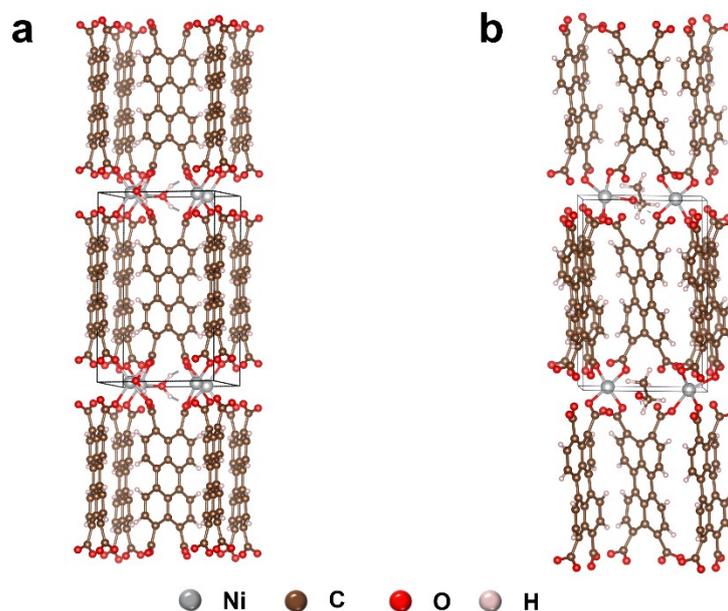
The photo-electrochemical measurement was tested with a standard three-electrode system by using Chenhua CHI 660D electrochemical analyzer<sup>2</sup>. It consisted of ITO glass coated by samples as working electrode, the saturated calomel reference electrode (SCE) (saturated KCl) and Pt counter electrode. The 300 W xenon lamp was used as light source and 0.2 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution as electrolyte. To prepare the working electrode, 5 mg sample and 10 μL 0.25% Nafion were dispersed in 1 ml isopropanol. At last, the obtained dispersion solution was coated on FTO glass surface and dried under infrared lamp. The electrochemical impedance spectra (EIS) were measured at the open circuit voltage in 0.1 M ascorbic acid aqueous solution.

## ***2.3 Photocatalytic water oxidation reaction***

The photocatalytic reactions were carried out in a quartz reactor (300 mL) and tested in Automatic on-line Photocatalytic analysis system (300 W, xenon lamp, Simulated sunlight). The specific steps were taken as follows: photocatalyst (30 mg) with 100 uL H<sub>2</sub>PtCl<sub>6</sub> solution (1mg/100 mL) was added into 100 mL ascorbic acid aqueous solution (0.1 mol/L). Before the visible light irradiation, the system was bubbled with argon and evacuation several times. The amount of H<sub>2</sub> evolved was analyzed by gas chromatography (GC-14C, Shimadzu, TCD, Ar as the carrier).

### 3 Methods and Models

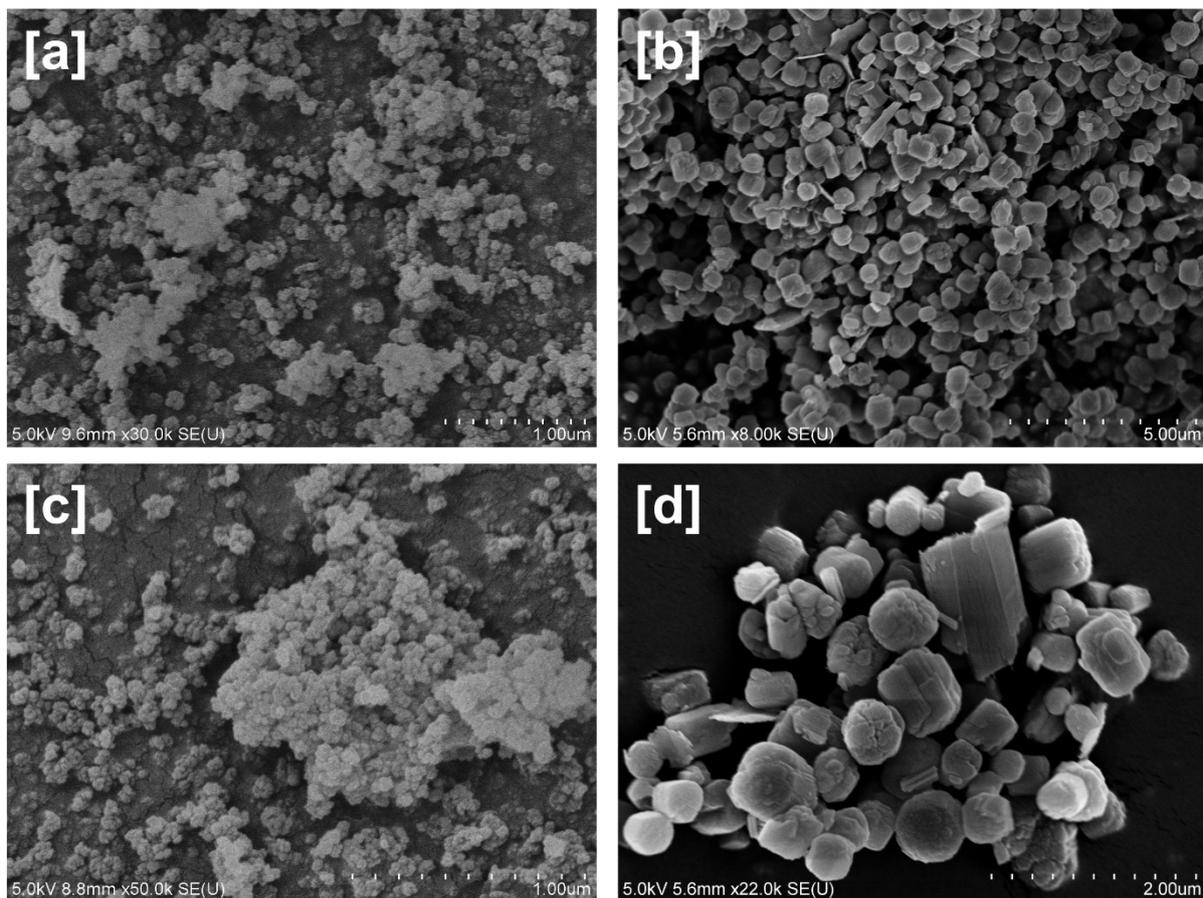
The first principle simulations were performed using the Vienna ab initio simulation package (VASP)<sup>3</sup>. The generalized gradient approximation (GGA) was chosen to describe the exchange–correlation interaction with the revised Perdew–Burke–Ernzerhof (PBE) functional<sup>4</sup>. The energy cutoff was set to 400 eV.  $2 \times 2 \times 2$  was chosen to be the gamma k-point mesh. The slab for DFT simulation contains 4 Ni atoms, 16 O atoms, 18 H atoms, and 48 C atoms, namely [Ni(PTCA)·sol]-MOF. As for the geometry optimization, the corresponding threshold was set to  $2 \times 10^{-2}$  eV/Å. And for the self-consistent field (SCF) energy convergence, it was  $10^{-4}$  eV. As the descriptor of HER activity,  $\Delta G_{\text{H}}^*$  was defined as  $\Delta G_{\text{H}}^* = \Delta E_{\text{H}}^* + \Delta E_{\text{ZPE}} - T\Delta S_{\text{H}}$ .  $\Delta E_{\text{H}}^*$  is the hydrogen chemisorption energy expressed by the following equation:  $\Delta E_{\text{H}}^* = E_{(\text{Slab-H}^*)} - E_{(\text{Slab})} - \frac{1}{2}E_{\text{H}_2}$  [30].  $E_{(\text{Slab-H}^*)}$  and  $E_{(\text{Slab})}$  are the computed energies of the active sites with and without adsorbed  $\text{H}^*$ , respectively.  $\Delta E_{\text{ZPE}}$  is the zero-point energy difference between the adsorbed and gas phases.  $\Delta S_{\text{H}}$  is the entropy change between the adsorbed H and gas-phase  $\text{H}_2$  at 1 atm and T is 298.15 K. The thermal correction to Gibbs free energy is the sum of them and could be obtained via vibrational frequency calculations. VASPKIT was used [31] to directly read this value from OUTCAR file. As for computing the density of states, the SCF energy convergence is changed to  $10^{-5}$  eV along with the previously optimized geometric structure.



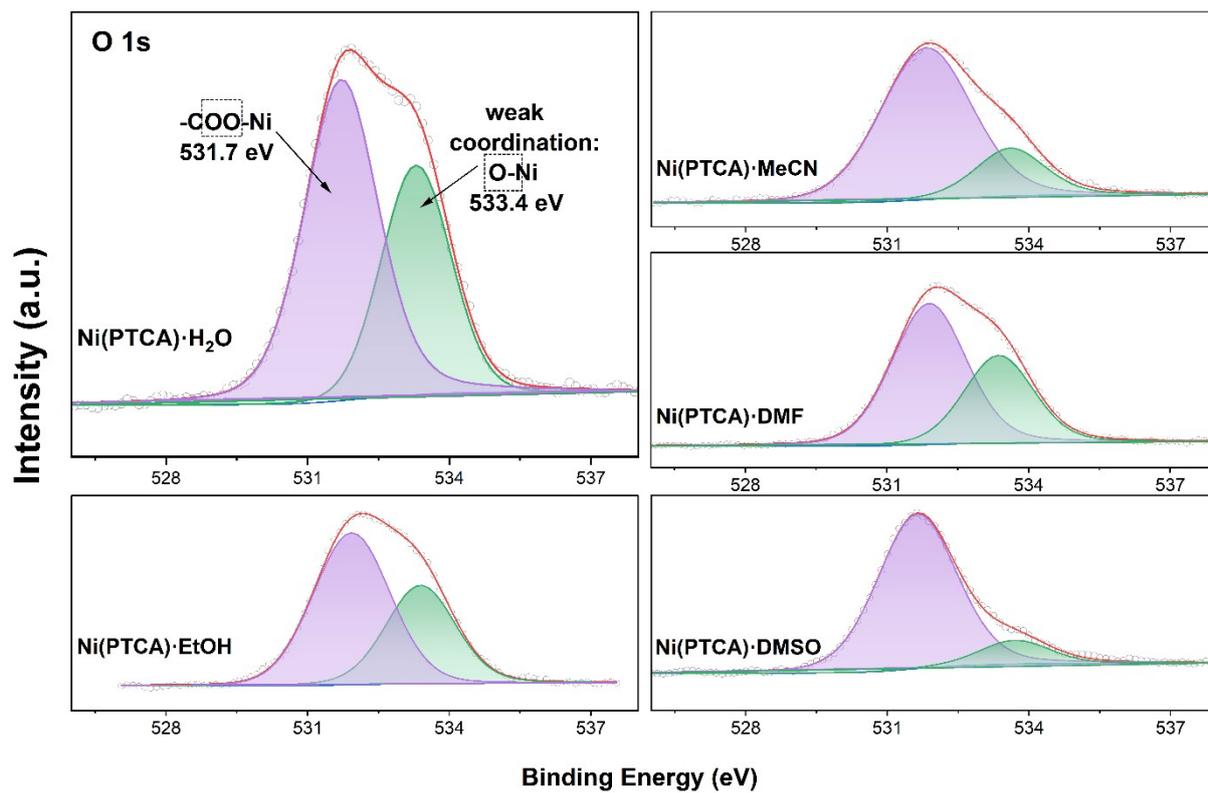
**Scheme 1.** Optimized structures of (a) [Ni(PTCA)·H<sub>2</sub>O]-MOF and (b) [Ni(PTCA)·EtOH]-MOF.

**Table S1.** Structural parameters. Atomic coordinates for [Ni(PTCA)·H<sub>2</sub>O]-MOF in the Pbam space group. ( $R_{wp}$  = 9.97 %,  $R_p$  = 11.0%)

<b>Atom</b>	<b>Wyckoff</b>	<b>x/a</b>	<b>y/b</b>	<b>z/c</b>	<b>Occupancy</b>
<b>Ni1</b>	4g	0.25648	0.11097	0.00000	0.500
<b>O1</b>	8i	0.39603	0.19559	0.09193	1.000
<b>O2</b>	8i	0.35013	0.51250	0.12019	1.000
<b>O3</b>	4g	0.13947	0.35570	0.00000	0.500
<b>C1</b>	8i	0.37729	0.33492	0.11859	1.000
<b>C2</b>	8i	0.42185	0.34699	0.24089	1.000
<b>C3</b>	8i	0.36581	0.19952	0.30222	1.000
<b>C4</b>	8i	0.36470	0.20504	0.40380	1.000
<b>C5</b>	8i	0.43949	0.32450	0.43887	1.000
<b>C6</b>	4e	0.50000	0.50000	0.40642	0.500
<b>C7</b>	4e	0.50000	0.50000	0.29310	0.500



**Fig S1.** Comparison of [Ni(PTCA)·sol]-MOF: SEM of [Ni(PTCA)·EtOH]-MOF (a), [Ni(PTCA)·MeCN]-MOF (b), [Ni(PTCA)·DMF]-MOF (c) and [Ni(PTCA)·DMSO]-MOF (d).



**Fig S2.** XPS O 1s of [Ni(PTCA)-sol]-MOF.

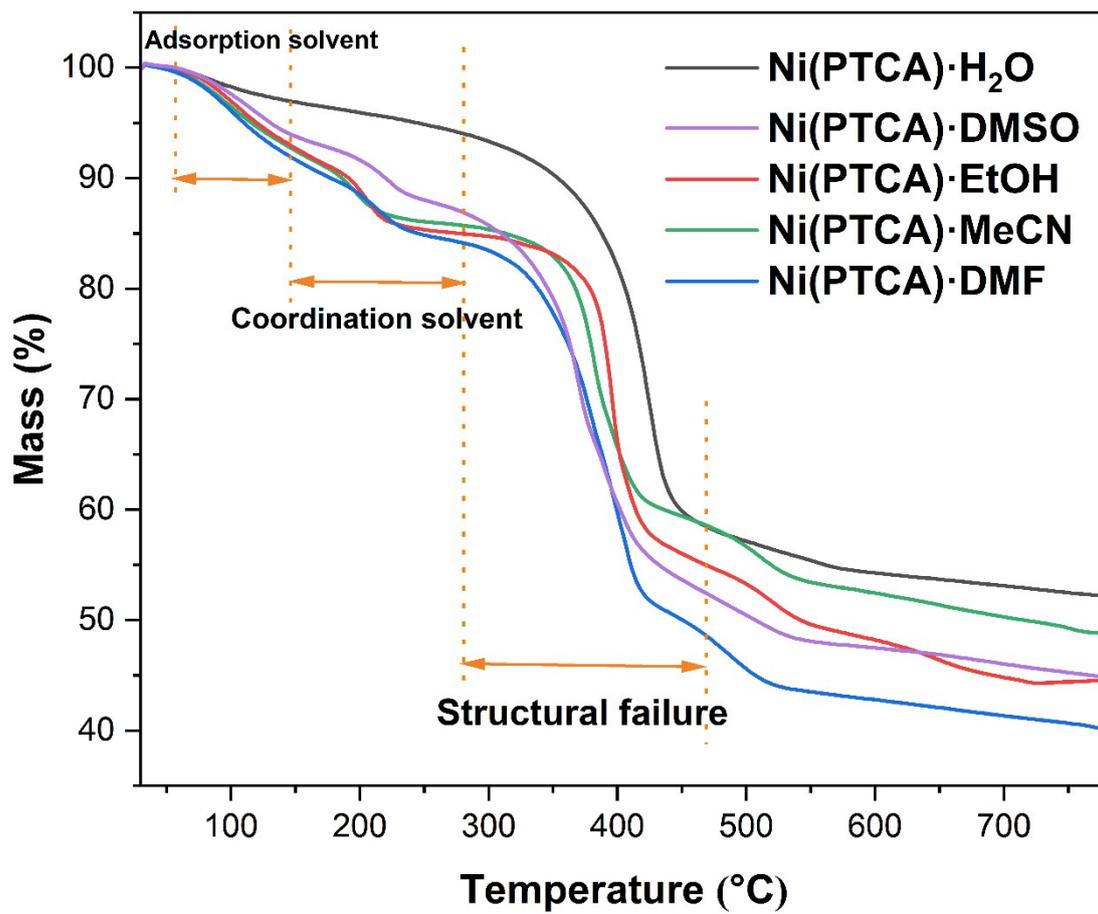
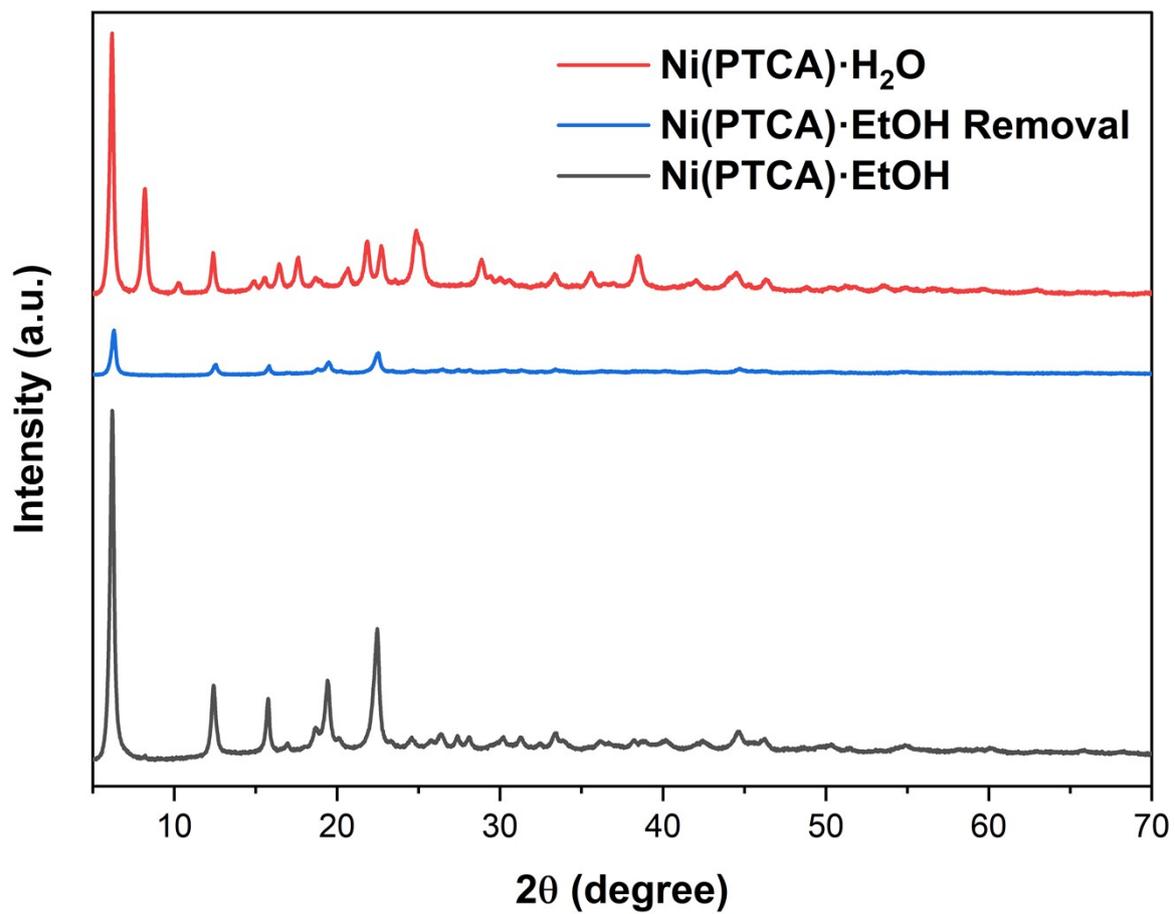


Fig S3. TGA curves of [Ni(PTCA)·sol]-MOF.



**Fig S4** XRD pattern of [Ni(PTCA)·EtOH]-MOFs after removal solvent at 180°C.

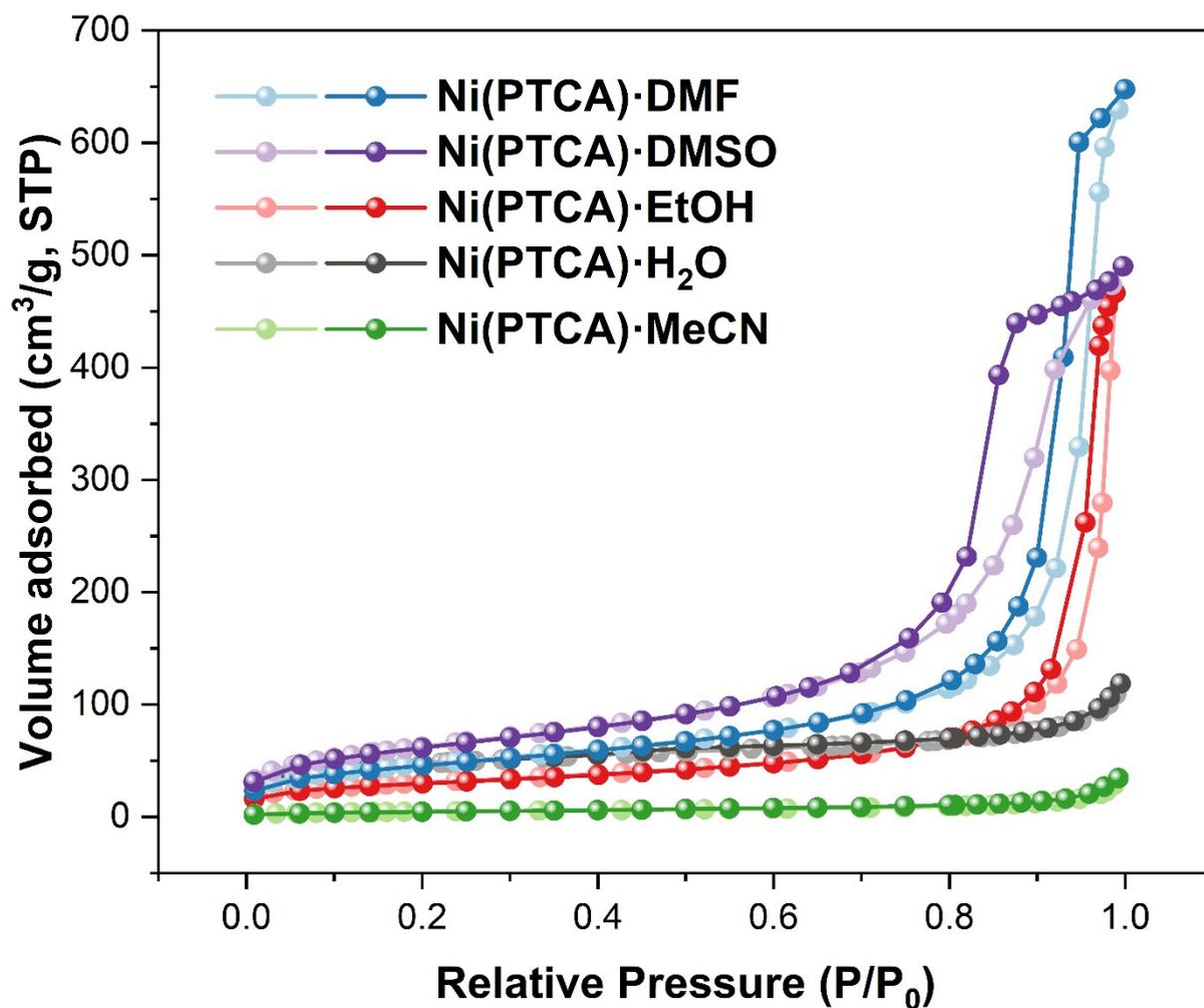


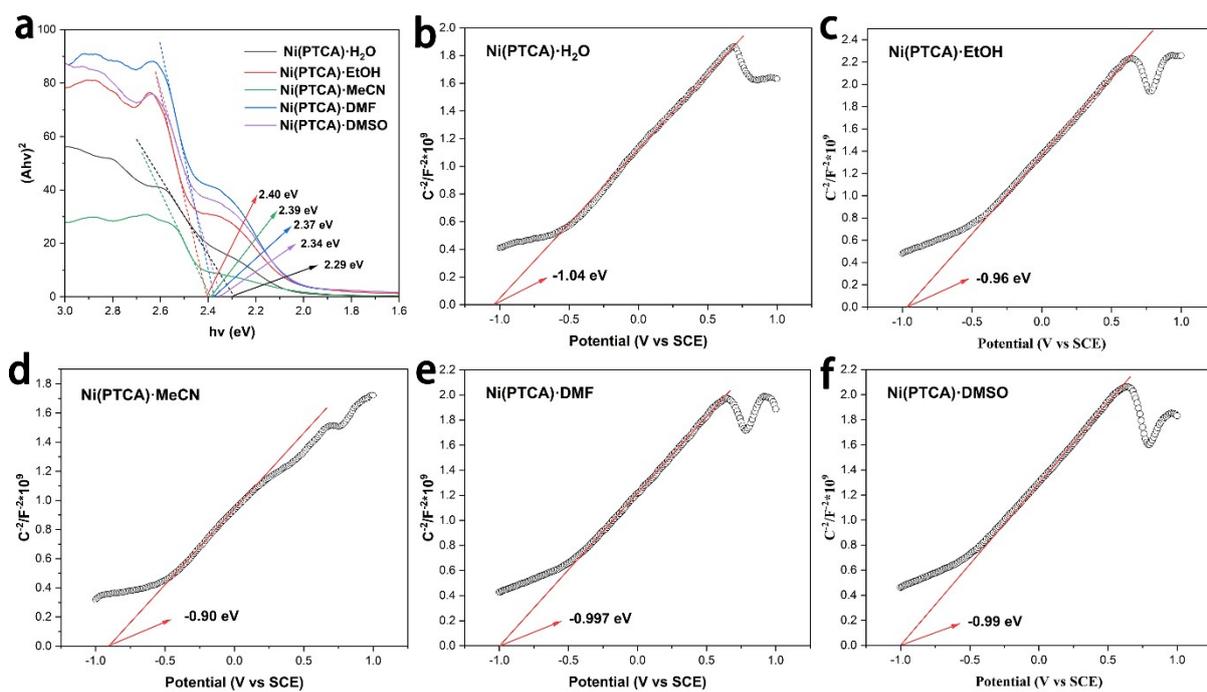
Fig S5. Nitrogen adsorption-desorption isotherm of [Ni(PTCA)·sol]-MOFs.

Table S2. Nitrogen adsorption-desorption isotherm results

Sample	Surface Area (m <sup>2</sup> /g) <sup>a</sup>	Pore Volume (m <sup>3</sup> /g) <sup>b</sup>	Pore Size (Å) <sup>b</sup>
Ni(PTCA)·H <sub>2</sub> O	166.6995	0.183627	44.0619
Ni(PTCA)·EtOH	109.4062	0.721355	263.7345
Ni(PTCA)·DMF	170.8292	1.001524	234.5088
Ni(PTCA)·DMSO	228.5810	0.758011	132.6463
Ni(PTCA)·MeCN	17.2377	0.053474	124.0868

<sup>a</sup> Obtained from BET method.

<sup>b</sup> Total pore volume taken from the N<sub>2</sub> adsorption volume at a relative pressure (P/P<sub>0</sub>) of 0.99



**Fig S6.** Bandgap and Mott Schottky plots of [Ni(PTCA)·sol]-MOFs.

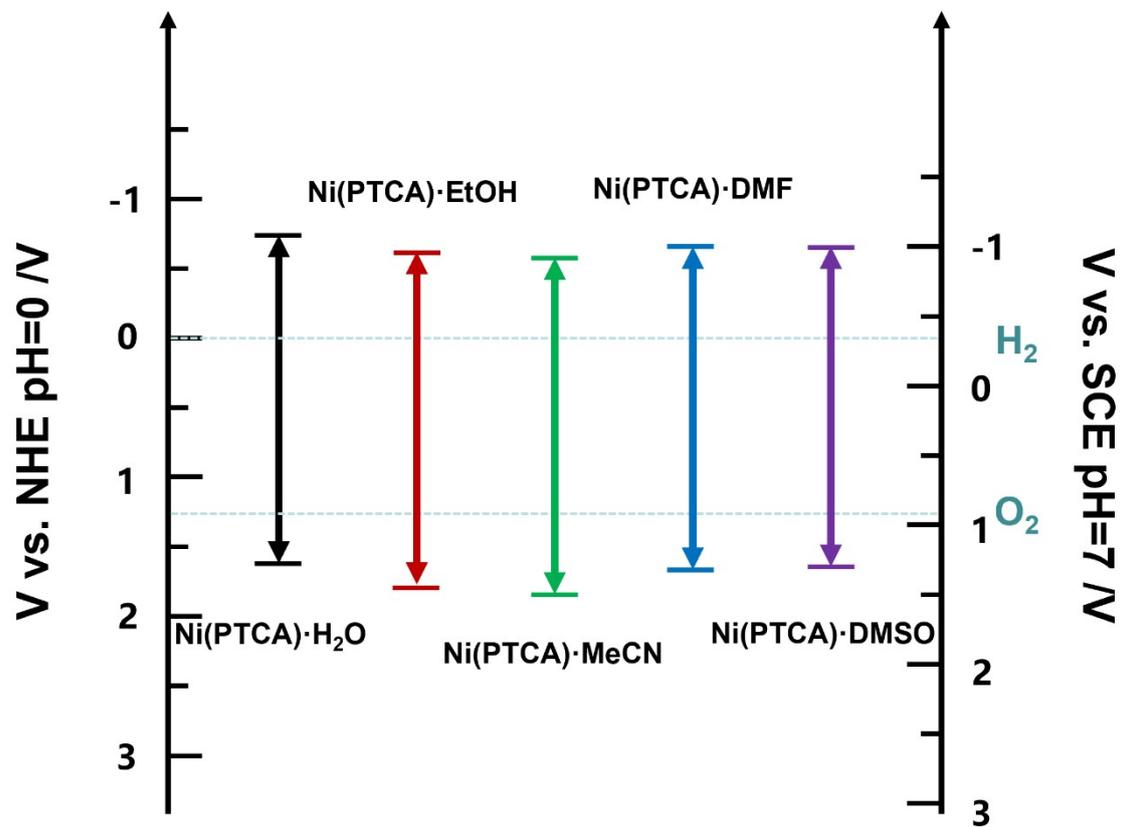
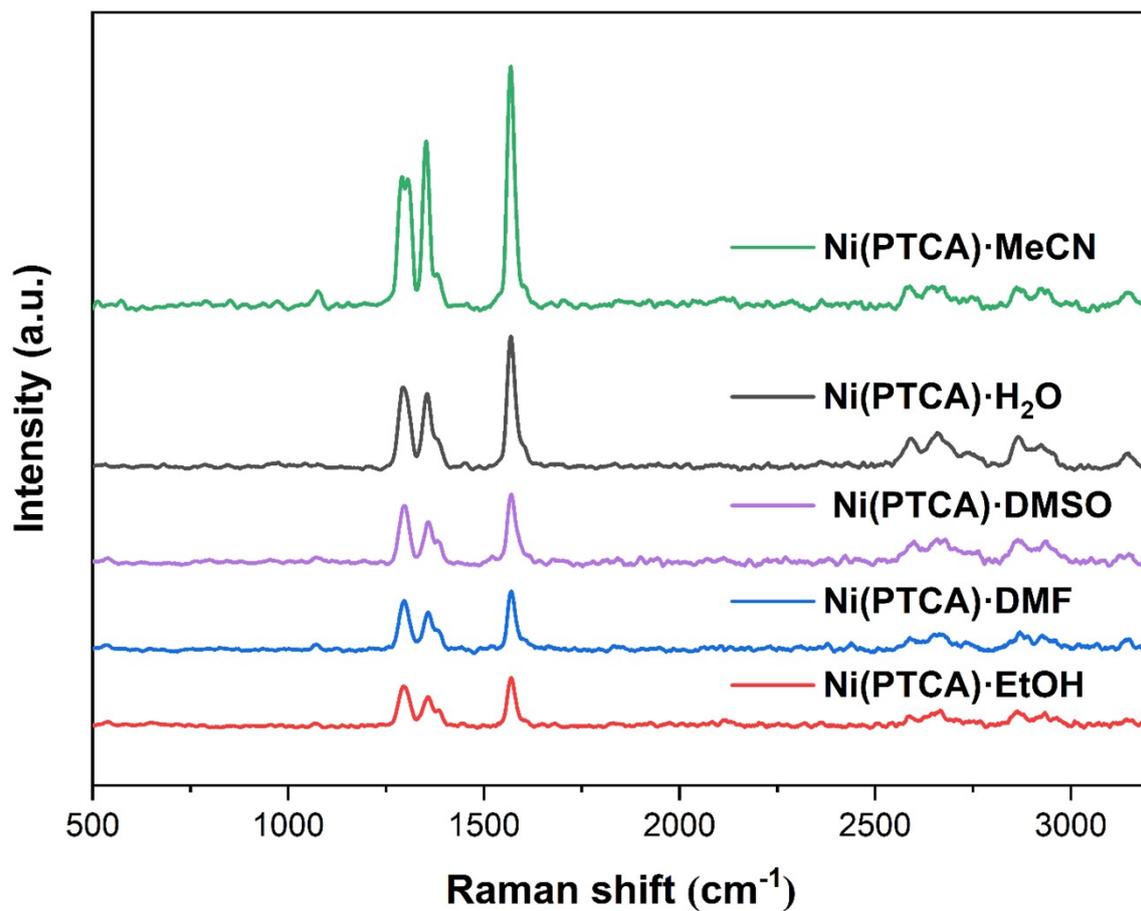


Fig S7. Energy band structure diagrammatic sketch of [Ni(PTCA)·sol]-MOFs.



**Fig S8.** Raman spectrum of [Ni(PTCA)·sol]-MOFs

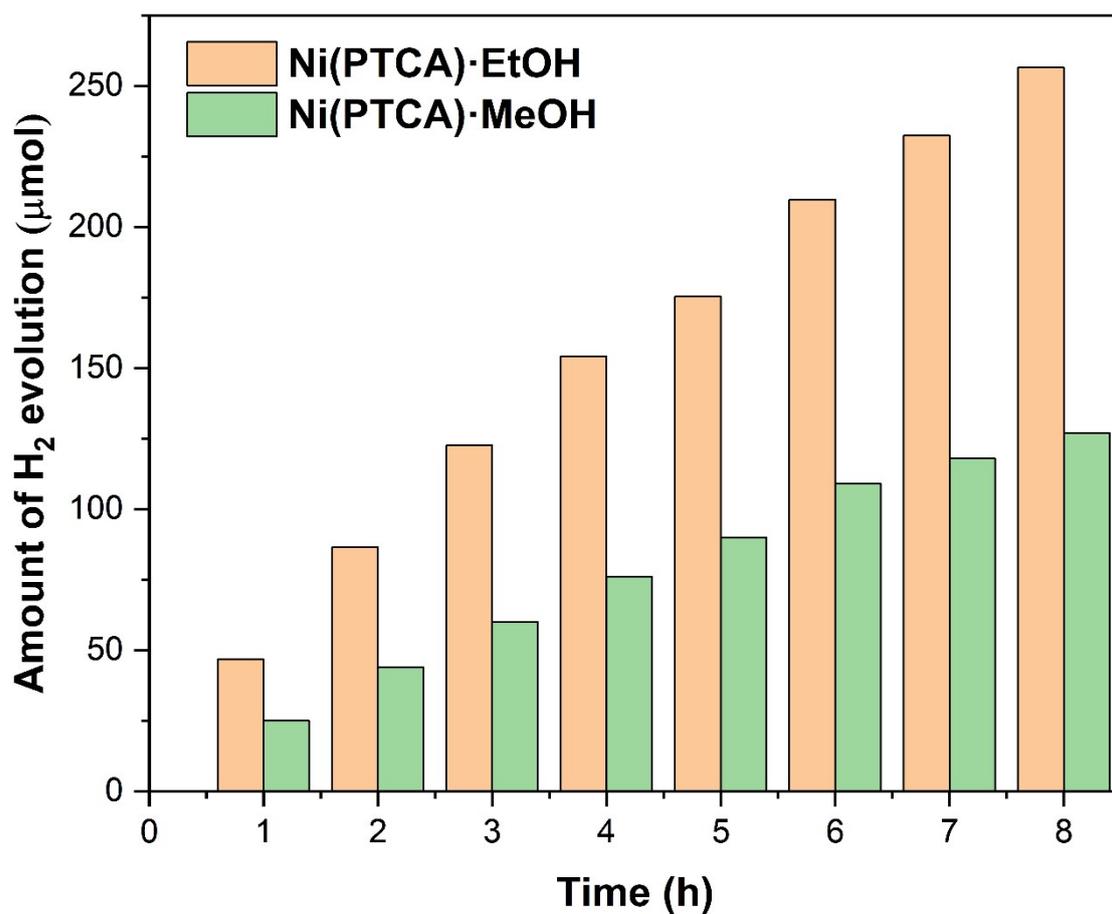
**Table S3.** Kinetic analysis of emission decay

Sample	$\tau_1$ (ns)	Rel.%	$\tau_2$ (ns)	Rel.%	$\chi^2$	$\langle\tau\rangle$ (ns)
Ni(PTCA)·H <sub>2</sub> O	0.33	12.94	4.66	87.06	1.21	3.088
Ni(PTCA)·EtOH	1.62	1.86	4.81	98.14	1.070	9.175
Ni(PTCA)·MeCN	1.31	0.90	4.73	99.10	1.074	9.067
Ni(PTCA)·DMF	4.18	69.54	5.88	30.46	1.014	7.379
Ni(PTCA)·DMSO	2.12	8.44	4.82	91.56	1.131	7.535

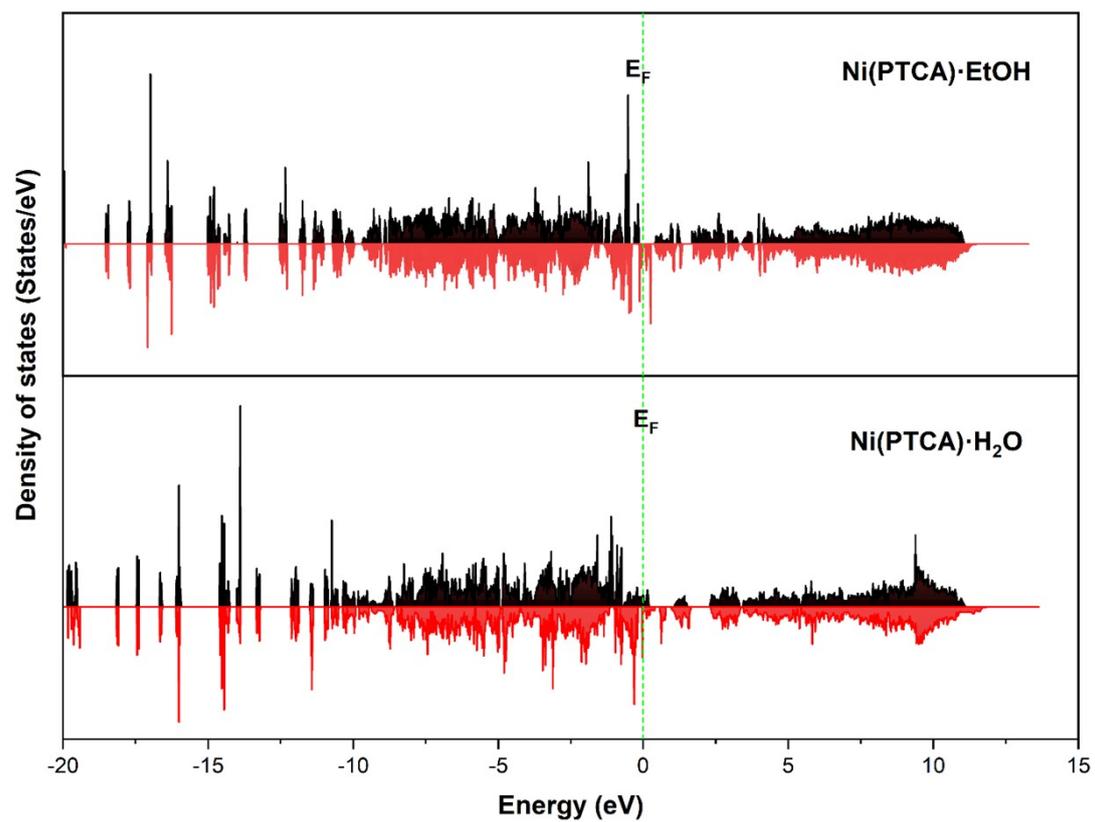
**Table S4.** The physicochemical property of solvents used in this work<sup>a</sup>

Solvent	EtOH	MeCN	DMF	MeOH	DMSO	H <sub>2</sub> O
Polarity	4.3	6.2	6.6	6.6	7.2	10.2
Dielectric Constant ( $\epsilon$ )	24.3	36.6	38.3	33	47.2	80
Dipole Moment (D)	1.69	3.92	3.82	1.70	3.96	1.85

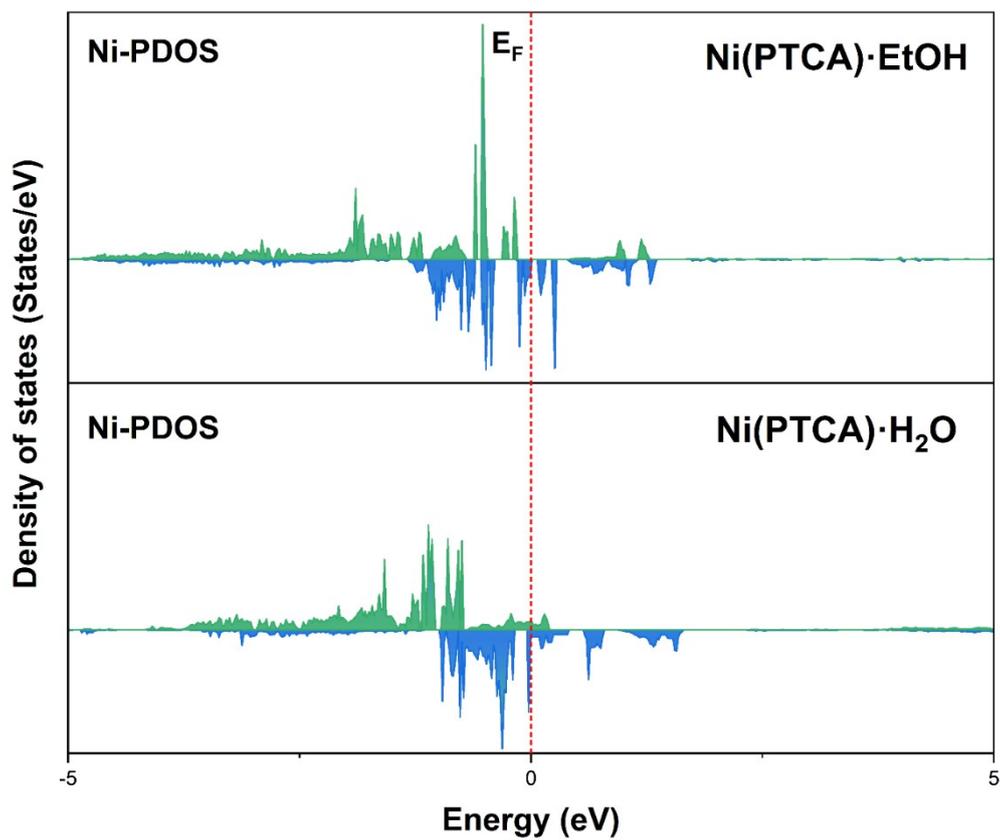
<sup>a</sup> John A. Dean. Lange's handbook of chemistry. 13th ed. BEIJING WORLD PUBLISHING CORPORATION Publishing. 1985, 10-98.



**Fig S9.** Comparison of photocatalytic activities of [Ni(PTCA)·EtOH]-MOF and [Ni(PTCA)·MeOH]-MOF.



**Fig S10.** TDOS spectrum of  $[\text{Ni(PTCA)·EtOH}]$ -MOF and  $[\text{Ni(PTCA)·H}_2\text{O}]$ -MOF.



**Fig S11.** Ni-PDOS spectrum of  $[\text{Ni(PTCA)·EtOH}]$ -MOF and  $[\text{Ni(PTCA)·H}_2\text{O}]$ -MOF.

### Supplementary Reference

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