Electronic Supplementary Information for:

A solvent-controlled photoresponsive ionic hydrogen-bonded organic framework for encryption applications

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Experimental section

Materials and reagents.

All reagents and solvents, including Tetraphenylethylene (TPE), terephthalimidine dihydrochloride (PAM·2HCl), [1,1'-biphenyl]-4,4'-bis(carboximidamide) dihydrochloride (BPAM·2HCl), polyvinyl alcohol (PVA), concentrated sulfuric acid, ethyl acetate and N, N-dimethylacetamide (DMA) were obtained from the commercial companies and used without further purification. Deionized water was used throughout all experiments wherever is needed.

Characterization.

Thermogravimetric analysis (TGA) measurements were performed on a TGA-55 instrument from 25 ºC to 800 ºC at a heating rate of 10 ºC/min under N2 atmosphere. Powder X-ray diffraction (PXRD) measurements were carried out in Bruker D8 Advance with a Cu X-ray source over a range of 2θ = 3.0~50.0º. The solid-state UV-vis spectra were obtained from a Cary 5000 spectrophotometer. Fluorescence spectra were recorded on an Edinburgh FlS-1000 fluorescence spectrometer. The solid-state EPR spectra were recorded at ambient temperature with a Bruker A300 Electron Spin Resonance Spectrometer. X-ray photoelectron spectroscopy (XPS) was obtained by ESCALAB 250 X-ray photoelectron spectrometer and the C 1s peak at 284.8 eV as internal standard.

Single-Crystal X-ray Diffraction.

Single-crystal X-ray diffraction data for compounds **iHOF-17** and **iHOF-18** were collected on a Bruker SMART APEX CCD diffractometer equipped with a graphite-monochromated Cu Kα radiation (λ = 1.54184 Å) using the ω-scan technique. Using Olex2,[1] the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimization. The diffused electron densities resulting from these solvent molecules were removed using the SQUEEZE[4] routine of PLATON; structures were then refined

again using the data generated. The contents of the solvent region are not represented in the unit cell contents in the crystal data. All nonhydrogen atoms were refined with anisotropic displacement parameters. Crystal data collection and structure refinement details are summarized in Table S1. More details on the crystallographic studies as well as atomic displacement parameters are given in Supporting Crystallographic Data as CIF files.

Synthesis of ligand (H_4TPE).

Tetrakis(4-sulfophenyl)ethylene (H_4TPE) was synthesized using reported literature procedure. To concentrated H_2SO_4 (10 mL) heated at 115 ºC was added tetraphenylethylene (0.51 g, 1.5 mmol) and the solution was stirred for 4 h at 115 ºC. To ethyl acetate at 0 ºC was very slowly added dropwise the reaction mixture. The resulting precipitate was filtered and dried at 80ºC to give H_4TPE (0.89 g, yield 90 %) as a gray solid.[5]

Preparation of iHOF-17.

Water (3 mL) was added to completely dissolve H_4TPE (13.06 mg, 0.02 mmol), and PAM·2HCl (9.4 mg, 0.04 mmol) was dissolved in water (2 mL) to obtain a clarified solution. Then, the two clarified solutions were mixed and placed in a hydrothermal reactor. After sealing, the hydrothermal reactor was placed in an oven at 70 ℃ for 2 days, and colorless flaky crystals were obtained after natural cooling of the solution. The yield was 63%.

Preparation of iHOF-18.

DMA (2 mL) was added to completely dissolve H_4TPE (13.06 mg, 0.02 mmol), and BPAM·2HCl (12.44 mg, 0.04 mmol) was dissolved with DMA (2 mL) and water (1 mL) to obtain a clarified solution. Then, the two clarified solutions were mixed and placed in a hydrothermal reactor. After sealing, the hydrothermal reactor was placed in an oven at 100 ℃ for 3 days, and the reaction solution was filtered after natural cooling. The filtrate was placed in an oven at 55 ℃ and colorless flaky crystals were obtained after 4 days. The yield was 58 %.

Preparation of 10%-iHOF-18-PVA Composite Membrane.

The **iHOF-18** (20 mg) was ground and added to 2 mL of water. The mixture was stirred for 6 h to obtain a well-dispersed suspension. Next, a dispersion of 10 wt % PVA (0.2 g) in 4 mL of water was added to the suspension and stirred continuously for 6 h at room temperature to obtain a homogeneous solution. The resulting mixed solution was poured onto a glass mold and dried at room temperature for 48 h to remove the solvent, resulting in a **10%-iHOF-18-PVA** composite membrane.

Supporting Figures

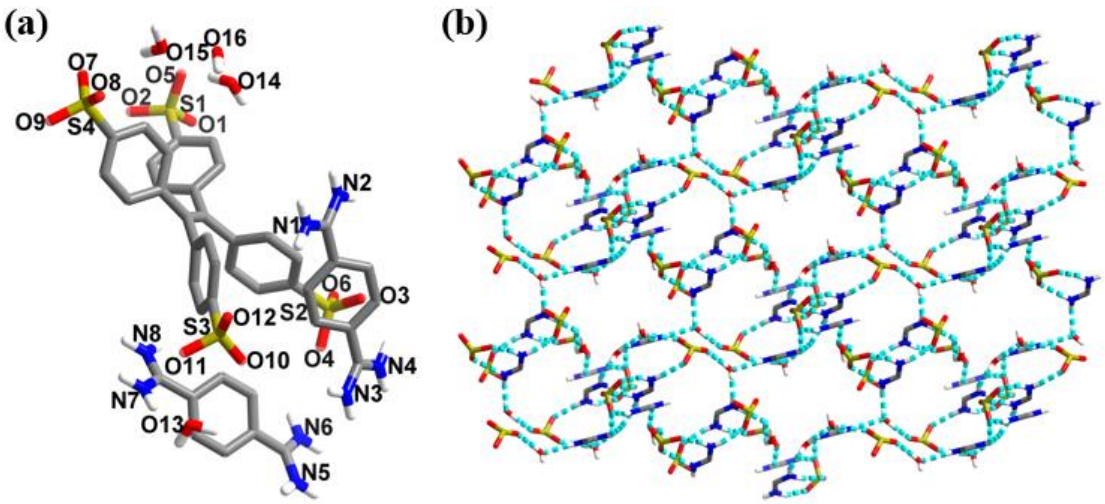


Fig. S1. (a) The asymmetric unit of **iHOF-17**. (b) The 2D hydrogen bond network diagram of **iHOF-17**.

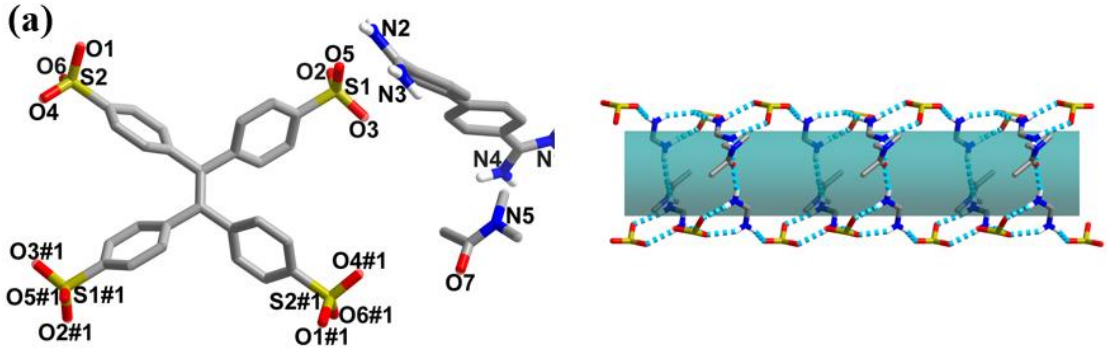


Fig. S2. (a) The asymmetric unit of **iHOF-18**. Symmetry codes: #: -1-x, y, 1/2-z. (b)The 1D hydrogen bond network of **iHOF-18**.

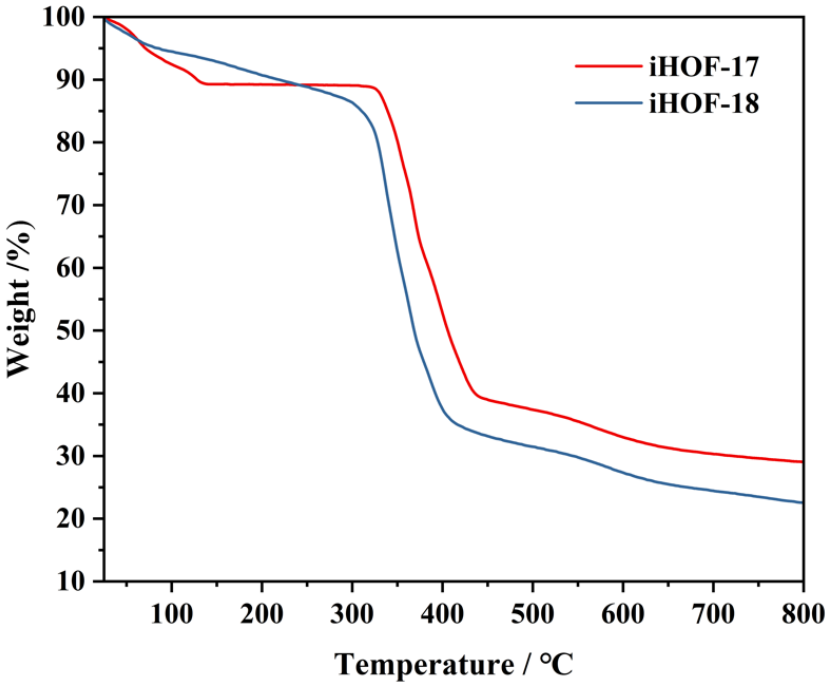


Fig. S3. TGA plot of **iHOF-17** and **iHOF-18**.

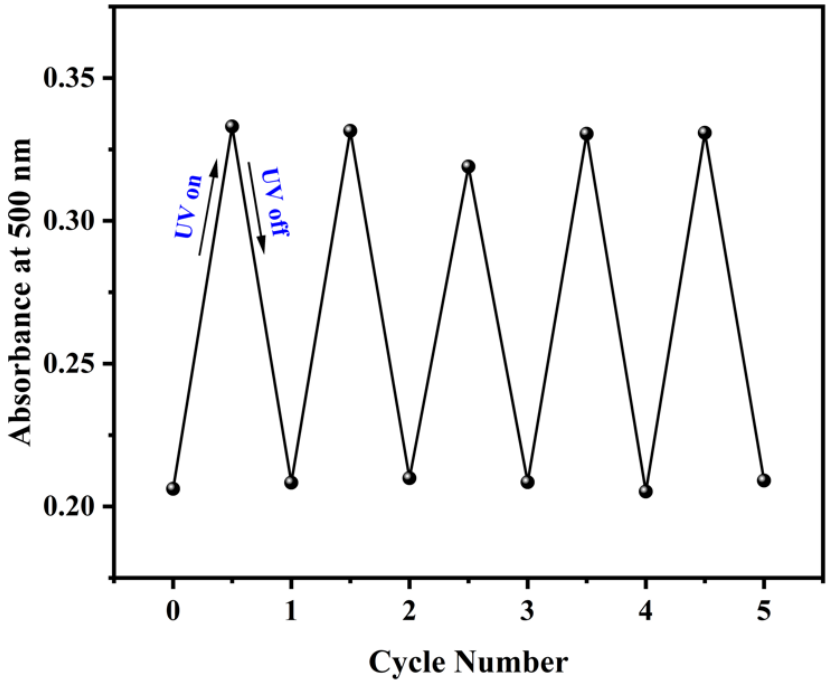


Fig. S4. Fatigue resistance of original powder of **iHOF-18** upon irradiation with 365 nm UV light (5 s) and standing under room light (2 min).

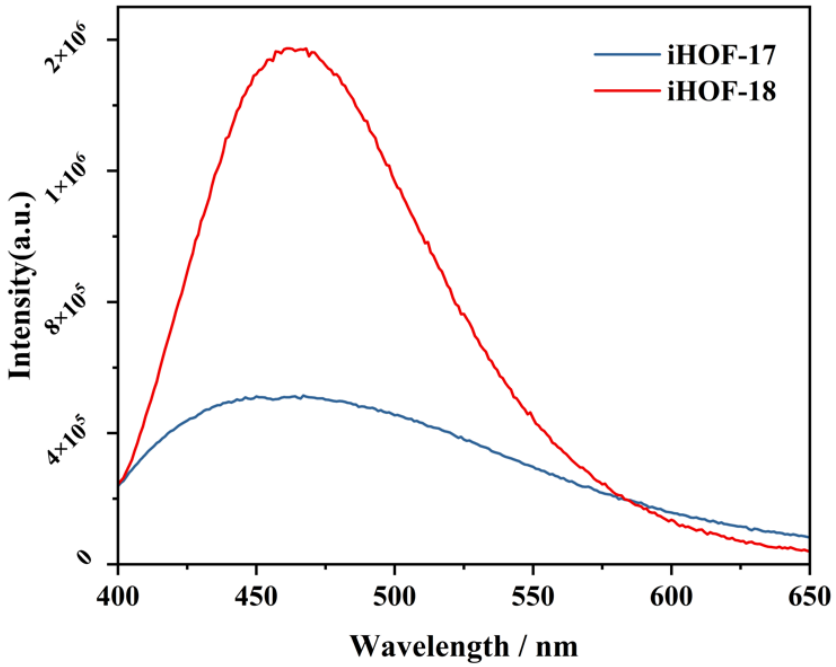


Fig. S5. Fluorescence emission spectra of **iHOF-17** and **iHOF-18.**

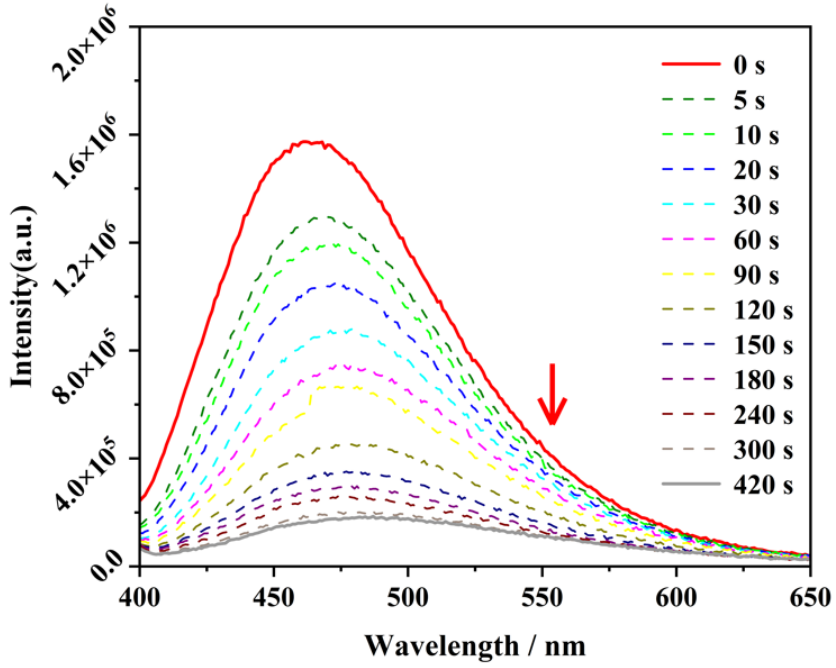


Fig. S6. Time-dependent photoluminescence spectra of **iHOF-18** before and after irradiation.

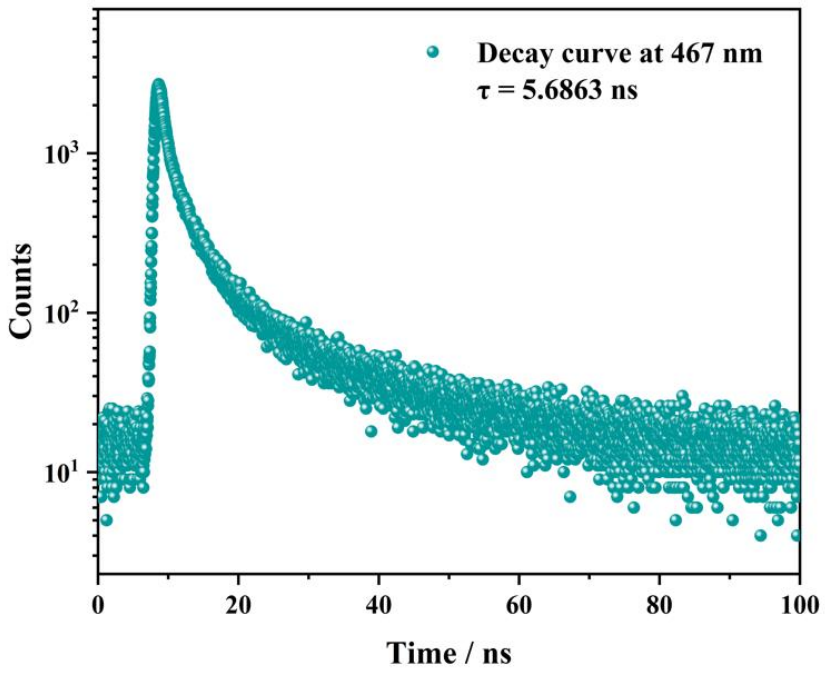


Fig. S7. FL lifetime decay curve of **iHOF-17** at 467 nm.

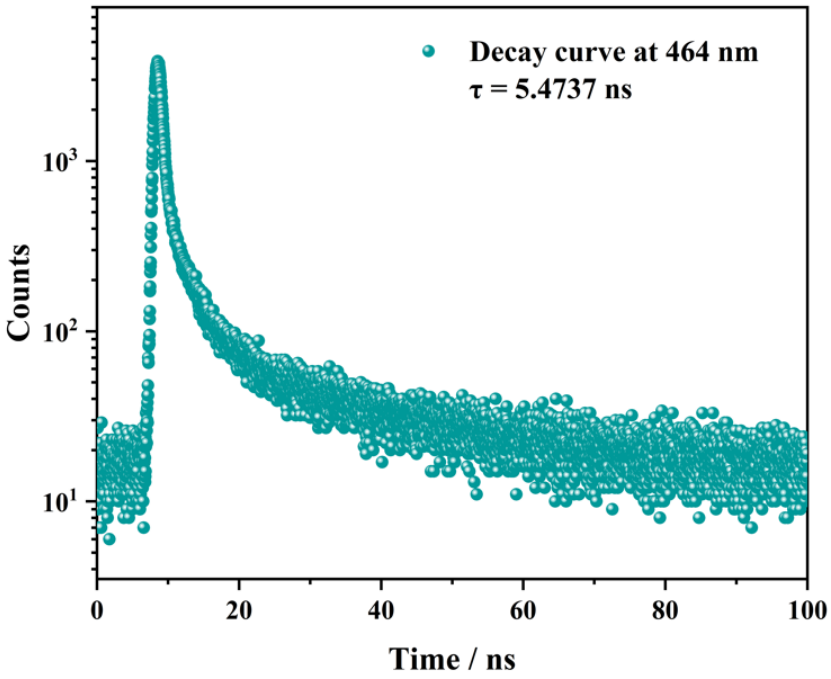


Fig. S8. FL lifetime decay curve of **iHOF-18** at 464 nm.

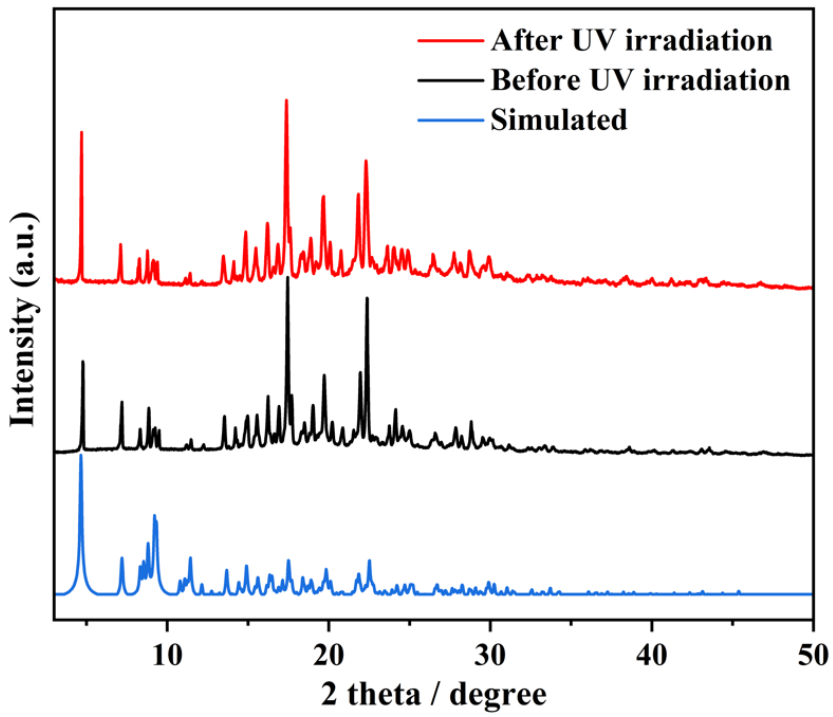


Fig. S9. PXRD patterns of **iHOF-18** before and after UV irradiation.

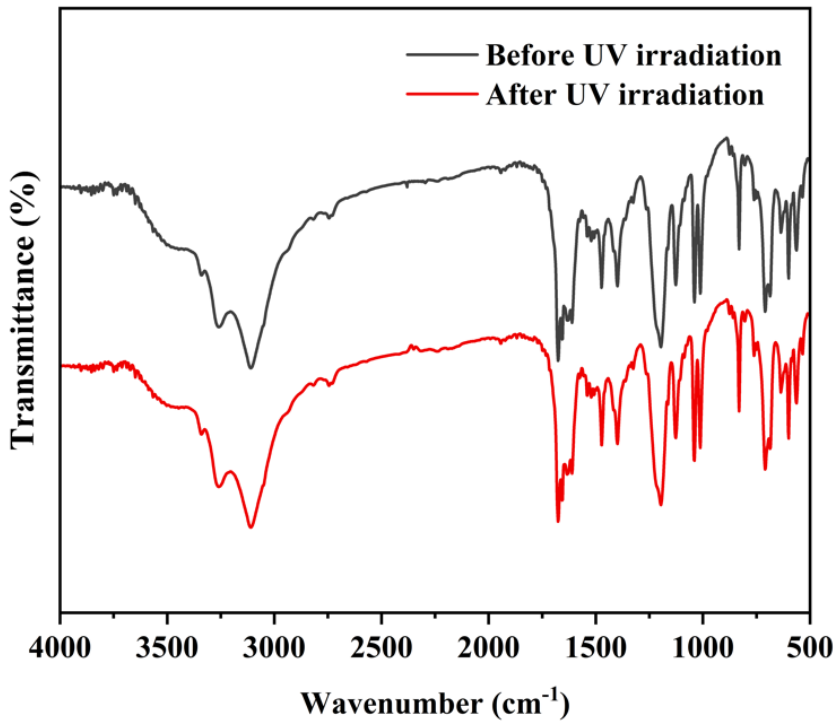


Fig. S10. IR spectra of **iHOF-18** before and after UV irradiation.

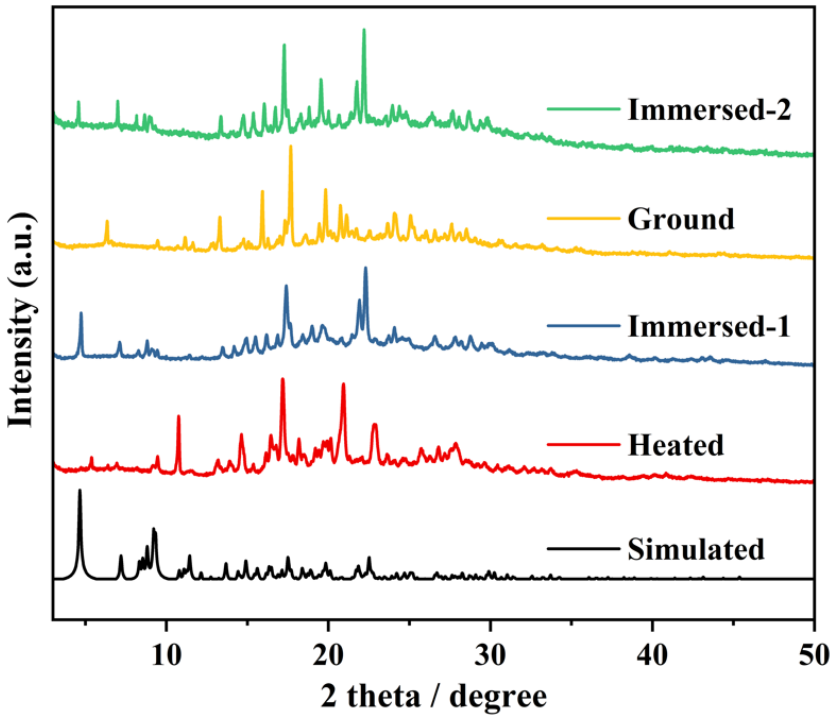


Fig. S11. PXRD patterns of **iHOF-18** in different aggregation states. Immersed-1: Heated and then immersed, Immersed-2: Ground and then immersed.

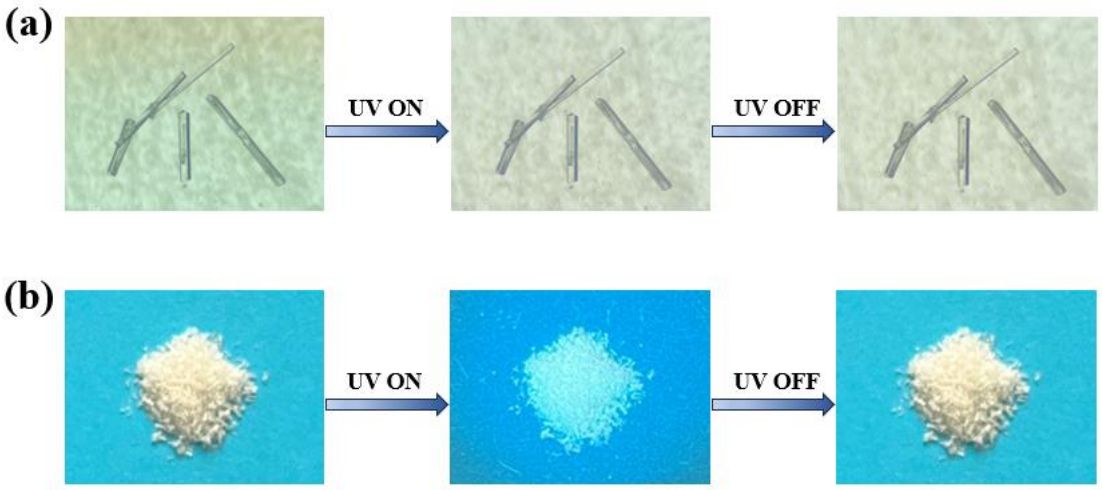


Fig. S12. Images of (a) single crystal and (b) powder of **iHOF-17** without discoloration before and after UV irradiation.

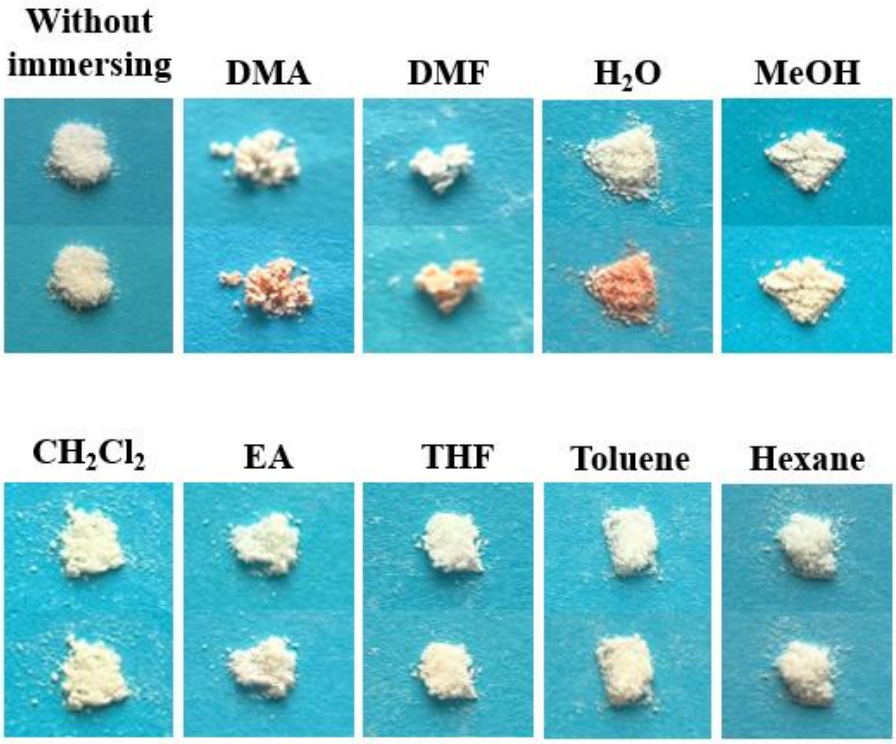
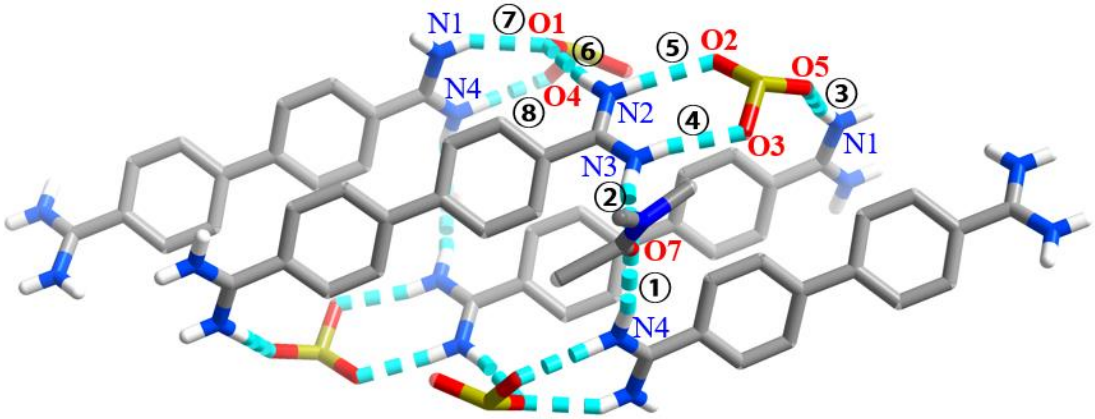


Fig. S13. Solvent-selectivity of **iHOF-18**.

Fig. S14. Printing different patterns on **10%-iHOF-18-PVA** composite membrane.



① = 2.8057Å ② = 2.8491Å ③ = 2.8265Å ④ = 2.8331Å
⑤ = 2.8521Å ⑥ = 2.9364Å ⑦ = 2.8534Å ⑧ = 2.8164Å

Fig. S15. Possible electron transfer pathways by hydrogen bonding of **iHOF-18**.

Supporting Tables

Table S1. Crystal structure data and refinement details of **iHOF-17** and **iHOF-18**.

Compounds	**iHOF-17**	**iHOF-18**
Empirical formula	$C_{42}H_{48}N_8O_{16}S_4$	$C_{26}H_{66}N_{10}O_{14}S_4$
Formula weight	1049.12	1303.49
Temperature / K	150.0	213.15
Wavelength / Å	1.54184	1.54184
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
a/Å	12.9205(2)	37.9540(19)
b/Å	27.6064(4)	10.7480(8)
c/Å	15.3072(2)	24.5839(8)
α/°	90.00	90.00
β/°	113.7185(7)	93.542(4)
γ/°	90.00	90.00
Volume/Å^3	4998.72(13)	10009.4(9)
Z	4	4
ρ_{calc}g / cm^3	1.394	0.865
μ / mm^{-1}	2.395	1.258
F(000)	2192.0	2736.0
Reflections collected	51845	31509
Independent reflections	8696	8619
Data/restraints/parameters	8696/24/643	8619/6/409
Goodness-of-fit on F^2	1.081	1.031
[a]R_1, [b]wR_2 [I> 2σ(I)]	0.0895/0.2377	0.0751/0.2137
[a]R_1, [b]wR_2 (all data)	0.0933/0.2409	0.1026/0.2297
Largest diff. peak/hole / e.Å^{-3}	2.23/-1.31	0.47/-0.36

[a]$R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b]$wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

Table S2. Detailed data of **iHOF-17** hydrogen bond long bond angle.

X-H···Y	X···Y / Å	H···Y / Å	∠XHY / °
N1-H1A···O3	2.8314	1.965	167.411
N2-H2A···O2	2.9279	2.188	141.302
N3-H3A···O14	2.9444	2.082	166.501
N3-H3B···O13	2.8925	2.039	163.700
N4-H4A···O16	2.8790	2.012	168.248
N4-H4B···O3	2.9553	2.273	134.422
N5-H5A···O6	2.8662	2.041	155.824
N5-H5B···O12	2.9383	2.062	174.435
N6-H6A···O4	2.8853	2.019	167.348
N6-H6B···O16	2.9620	2.259	136.855
N7-H7A···O5	2.9399	2.065	174.024
N7-H7B···O13	2.9008	2.103	150.586
N8-H8A···O1	2.8680	2.014	163.222
N8-H8B···O8	2.8768	2.008	169.289
O13-H13B···O10	2.7619	1.971	150.679
O14-H14B···O11	2.6600	2.078	123.523
O15-H15A···O5	2.7872	2.238	120.967
O16-H16A···O14	2.6918	1.825	173.601

Table S3. Detailed data of **iHOF-18** hydrogen bond long bond angle.

X-H···Y	X···Y / Å	H···Y / Å	∠XHY / °	Potential electron acceptor
N1-H1B···O5	2.8265	2.017	154.499	$N1^+$
N1-H1A···O1	2.8534	2.048	153.448	
N2-H2A···O2	2.8521	1.984	174.890	$N2^+$
N2-H2B···O1	2.9364	2.097	162.088	
N3-H3B···O7	2.8491	2.005	163.105	$N3^+$
N3-H3A···O3	2.8331	1.974	169.404	
N4-H4B···O7	2.8057	1.959	164.003	$N4^+$
N4-H4A···O4	2.8164	1.964	166.087	

Table S4. List of representative HOF-based photochromic crystal materials.

Crystalline materials	Photoresponsive time	mechanism of photochromism	References
iHOF-18	**1 s**	**free radical**	**This work**
$[H_2(bpyb)](H_2PO_4)_2 \cdot 2H_2O$	1 s	free radical	6
PFC-26	2 s	free radical	7
$(H_2CV)(H_2BTEC)$	3 s	free radical	8
$[(H_2L)\ (2,7\text{-NDS}) \cdot 5H_2O]$	30 s	free radical	9
SP2 ⊂ HOF2	60 s	isomerization	10
ECUT-HOF-30	180 s	free radical	11
HOF A	300 s	free radical	12

Supplementary Reference.

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