Supporting Information

Pyridine-amide-based hetero-copper iodide for the photocatalytic degradation of dyes and aerosol discolouration of VOC gases

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Table S1 Crystallographic data for the CPs.

CP	**1**	**2**
CCDC number	2277061	2277062
Formula	$C_7H_7N_2OCuI$	$C_{41}H_{46}Cl_9Cu_4I_4N_9O_4$
Formula wt	325.59	1809.72
Crystal system	Monoclinic	Monoclinic
Space group	$P\ 2_1/c$ (14)	$P\ 2_1/c$ (14)
T (K)	296(2)	293(2)
a (Å)	12.3490(5)	24.0552(16)
b (Å)	4.7530(2)	9.5569(6)
c (Å)	18.9761(6)	25.9626(17)
α (°)	90	90
β (°)	125.299(2)	90.200(2)
γ (°)	90	90
V (Å^3)	909.02(6)	5968.6(7)
Z	4	4
D_{calc} (g cm^{-3})	2.379	2.013
F(000)	612.0	3468
θ_{max} (°)	25.242	25.242
R_{int}	0.0249	0.1718
R_1 [a] $[I > 2\sigma(I)]$	0.0342	0.1354
wR_2 [b] (all data)	0.0984	0.1927
GOF	1.069	1.065

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, [b] $wR_2 = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

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Table S2 Selected bond distances (Å) and angles (°) for CP **1**.

I1–Cu1	2.5577(8)	Cu1–Cu1#2	3.0506(9)
I1–Cu1#1	2.5786(10)	Cu1–N1	2.025(4)
Cu1–Cu1#1	3.0506(9)	Cu1–I1–Cu1	72.87(2)
I1–Cu1–I1	121.64(4)	Cu1–Cu1–Cu1	102.34(4)
I1–Cu1–Cu1	53.88(3)	N1–Cu1–I1	113.69(13)
I1–Cu1–Cu1	53.250(19)	N1–Cu1–I1	112.64(13)
I1–Cu1–Cu1	127.45(5)	N1–Cu1–Cu1	114.90(13)
I1–Cu1–Cu1	69.02(4)	N1–Cu1–Cu1	135.09(14)

Symmetry codes: #1: $1 - x$, $0.5 + y$, $-0.5 - z$; #2: $1 - x$, $-0.5 + y$, $-0.5 - z$.

Table S3 Selected bond distances (Å) and angles (°) for CP **2**.

I1–Cu1	2.7816(16)	Cu4–N6#2	2.048(9)
I1–Cu2	2.6752(15)	I1–Cu1–Cu4	56.94(4)
I1–Cu4	2.6703(15)	N1–Cu1–I1	96.9(3)
Cu1–N1	2.045(8)	N1–Cu1–I2	112.1(2)
Cu1–I2	2.6407(16)	N1–Cu1–Cu2	137.6(3)
Cu1–Cu2	2.6441(19)	N1–Cu1–Cu3	155.0(3)
Cu1–Cu3	2.7151(18)	N1–Cu1–I4	110.0(2)
Cu1–I4	2.6716(15)	N1–Cu1–Cu4	140.5(2)
Cu1–Cu4	2.8199(17)	I2–Cu1–I1	116.82(6)
I3–Cu3	2.7567(16)	I2-Cu1-Cu2	62.01(5)
I3–Cu4	2.6577(16)	I2-Cu-1-Cu3	60.82(5)
Cu3–I4	2.6262(16)	I2-Cu1-I4	112.02(6)
Cu3–Cu4	2.6431(19)	I2-Cu1-Cu4	106.50(6)
I4–Cu4	2.7733(16)	Cu2-Cu1-I1	59.02(4)
Cu2–Cu1–Cu3	63.27(5)	Cu1–Cu3–Cu2	57.13(5)
Cu2–Cu1–I4	110.58(5)	Cu1–Cu3–I3	108.00(5)
Cu2–Cu1–Cu4	57.75(5)	I2–Cu3–Cu1	58.23(4)
Cu3–Cu1–I1	107.65(5)	I2–Cu3–Cu2	59.03(4)
Cu3–Cu1–Cu4	57.01(5)	I2–Cu3–I3	106.68(5)
I4–Cu1–I1	107.90(5)	N2–Cu3–Cu1	152.8(3)
I4–Cu1–Cu3	58.35(4)	N2–Cu3–I2	108.9(3)
I4–Cu1–Cu4	60.59(4)	N2–Cu3–Cu2	140.9(3)
I1–Cu2–I2	117.71(5)	N2–Cu3–I3	98.6(3)
I1–Cu2–Cu3	107.92(5)	N2–Cu3–I4	111.9(2)
Cu1–Cu2–I1	63.05(5)	N2–Cu3–Cu4	139.6(3)
Cu1–Cu2–I2	58.93(5)	I3–Cu3–Cu2	57.28(4)
Cu1–Cu2–I3	112.85(5)	I4–Cu3–Cu1	60.00(4)
Cu1–Cu2–Cu3	59.60(5)	I4–Cu3–I2	111.20(5)
I2–Cu2–Cu3	58.66(4)	I4–Cu3–Cu2	106.91(5)
I3–Cu2–I1	112.65(5)	I4–Cu3–I3	118.50(6)
I3–Cu2–I2	108.91(5)	I4–Cu3–Cu4	63.51(5)
I3–Cu2–Cu3	60.33(4)	Cu4–Cu3–Cu1	63.49(5)

Cu4–Cu2–I1	60.28(5)	Cu4–Cu3–I2	109.63(5)
Cu4–Cu2–Cu1	64.47(5)	Cu4–Cu3–Cu2	57.87(5)
Cu4–Cu2–I2	109.32(5)	Cu4–Cu3–I3	58.92(5)
Cu4–Cu2–I3	60.04(4)	I1–Cu4–Cu1	60.81(4)
Cu4–Cu2–Cu3	57.87(5)	I1–Cu4–I4	108.18(5)
N5–Cu2–I1	106.9(2)	Cu2–Cu4–I1	60.46(4)
N5–Cu2–Cu1	138.1(2)	Cu2–Cu4–Cu1	57.79(5)
N5–Cu2–I2	101.2(3)	Cu2–Cu4–I3	60.47(4)
N5–Cu2–I3	108.5(2)	Cu2–Cu4–Cu3	64.26(5)
N5–Cu2–Cu3	145.0(2)	Cu2–Cu4–I4	107.55(5)
N5–Cu2–Cu4	149.4(3)	I3–Cu4–I1	113.18(5)
I3–Cu4–Cu1	107.80(6)	N6–Cu4–I1	109.7(3)
I3–Cu4–I4	116.82(5)	N6–Cu4–Cu1	142.9(3)
Cu3–Cu4–I1	113.25(5)	N6–Cu4–Cu2	153.1(3)
Cu3–Cu4–Cu1	59.50(5)	N6–Cu4–I3	108.6(2)
Cu3–Cu4–I3	62.67(5)	N6–Cu4–Cu3	135.8(3)
Cu3–Cu4–I4	57.95(4)	N6–Cu4–I4	99.3(3)
I4–Cu4–Cu1	57.06(4)		

Symmetry codes: $^{\#1}$: $-x$, $0.5 + y$, $1.5 - z$; $^{\#2}$: $-x$, $-0.5 + y$, $1.5 - z$; $^{\#3}$: $1 - x$, $0.5 + y$, $1.5 - z$; $^{\#4}$: $1 - x$, $-0.5 + y$, $1.5 - z$.

Table S4 Cartesian coordinates of the geometrically optimized CP **1**.

Atom	*x*	*y*	*z*
N	6.40562948	0.61699204	0.32280202
H	5.90618342	1.34216809	0.81652906
C	5.71186943	–0.47192903	–0.11449401
O	6.24425344	–1.50088611	–0.51446604
C	4.20874730	–0.34418003	–0.09318801
C	3.45965325	–1.52404211	–0.07711401
C	3.52234125	0.87360306	–0.12431001
C	2.07419715	–1.44618710	–0.06149700
H	3.97018328	–2.47983518	–0.08245201
H	4.04464929	1.82229613	–0.18898401
C	2.13193915	0.86850706	–0.11521301
N	1.41620110	–0.26955302	–0.07577401
H	1.45539810	–2.33715717	–0.03811200
H	1.55840411	1.78949513	–0.14304601
Cu	–0.58039704	–0.20303301	–0.03064800
I	–2.43021417	–2.19389416	0.06316300
I	–1.64157512	2.44681418	–0.03415800
Cu	–3.01674322	0.30189502	0.04101800
C	7.85734455	0.60635105	0.40709103
H	8.24816058	1.60096412	0.17523701
H	8.20496558	0.30604702	1.40339810
H	8.23056760	–0.11348301	–0.32168602

Table S5 Cartesian coordinates of the geometrically optimized solvent-free CP **2**.

Atom	*x*	*y*	*z*
C	–3.90859707	–3.66839352	2.54996911
C	–5.11678112	–4.30705665	1.92774407
O	–5.12045910	–4.64262167	0.74270998
N	–6.18057018	–4.49846373	2.75215913
H	–6.20317923	–4.01190270	3.63681519
C	–3.58607605	–3.74489151	3.90847721
C	–3.03389205	–2.98322442	1.70332805
H	–4.21554006	–4.29663859	4.59992926
C	–2.42021400	–3.13137939	4.36398824
N	–1.91963801	–2.38435730	2.14207908
H	–3.24124607	–2.91522943	0.64140597
H	–2.13234398	–3.17925837	5.40834129
C	–1.61676298	–2.45768829	3.45079618
Cu	–0.79082801	–1.20196514	0.88579399
H	–0.69952595	–1.96351019	3.75384320
I	1.83863320	–1.44768300	1.73193105
Cu	0.83112796	1.06577412	0.87033399
Cu	1.15432612	–0.90119000	–0.92342714
I	–1.32467300	–1.96834923	–1.71280219
Cu	–1.09916916	0.72558497	–0.92155714
I	–1.84968225	1.35005297	1.64571404
I	1.43214196	1.76349721	–1.72256120
N	2.55172028	–1.93216198	–2.03917722
N	–2.35133130	1.67366796	–2.25354823
N	1.84873996	2.32149128	2.15084808
C	–2.15022728	1.50571996	–3.57344033
C	–3.35852543	2.45640795	–1.84816221
C	2.34313227	–1.97679800	–3.32335831
C	3.64727540	–2.53957295	–1.53456318
C	1.56564294	2.29233626	3.46594118
C	2.83663997	3.11621040	1.72114105
C	–2.95223837	2.11587195	–4.53105340
H	–1.32500518	0.85809797	–3.84960635
C	–4.20496453	3.12252595	–2.73823827
H	–3.49797345	2.55961295	–0.77793813
C	3.14746937	–2.60363899	–4.26049038
C	4.53236151	–3.22259095	–2.36662824
H	3.80314941	–2.47704394	–0.46438511
H	0.75853992	1.63123316	3.76319520
C	2.26286394	3.05667136	4.39446325

C	–3.99578050	2.93792094	–4.10844036
H	–2.76623835	1.94261995	–5.58512645
C	–5.30372565	3.96190694	–2.15279023
H	2.92488635	–2.59132301	–5.32064848
C	4.27703749	–3.24637897	–3.74759734
C	5.72925962	–3.86189892	–1.72053019
C	3.57870098	3.93253651	2.57872012
H	3.04658299	3.10590341	0.65749997
H	–4.65041658	3.40236794	–4.83945242
O	–5.74745469	3.73594089	–1.02608315
N	–5.77492778	4.96284598	–2.94244528
H	4.96687057	–3.73708495	–4.42855439
O	6.17989363	–3.43836086	–0.65596212
N	6.27601773	–4.91284896	–2.38667324
C	3.28543996	3.89070749	3.94516121
C	4.66603000	4.77052463	1.96991707
H	2.01330693	2.99249634	5.44773134
H	–5.23943574	5.23647403	–3.75359734
H	5.74422375	–5.35305100	–3.12354930
H	3.86022996	4.47592756	4.65625226
O	5.19838906	4.44951565	0.90674599
N	5.02431895	5.88112973	2.66724212
H	4.41937589	6.20992571	3.40592418
C	7.40527287	–5.64337092	–1.83233520
H	7.86434795	–6.23872893	–2.62393026
H	8.13480287	–4.93050784	–1.44403918
H	7.10009090	–6.30560498	–1.01291314
C	6.03312997	6.79512886	2.15524109
H	6.39141996	7.42237493	2.97394614
H	6.86473604	6.21613089	1.74999106
H	5.63717188	7.43494887	1.35692803
C	–7.42573621	–5.05935285	2.25154309
H	–7.19673317	–5.89216387	1.58447404
H	–8.01722524	–5.42070092	3.09521515
H	–8.01070134	–4.31944383	1.69145405
C	–6.80311690	5.87422995	–2.46545825
H	–6.39822793	6.61661404	–1.76663720
H	–7.24412194	6.38958699	–3.32101731
H	–7.57529493	5.30182188	–1.94839621

Table S6 The UV photocatalytic degradation rates of two photocatalysts against five organic dyes (After 4 hours of irradiation using a UV lamp with a wavelength of 254 nm and a power of 20 W).

Dye	MB	MO	CR	GV	RhB
CP **1**	83.76%	40.06%	97.98%	93.20%	51.90%
Solvent-free CP **2**	12.79%	44.02%	99.19%	75.70%	8.86%

Table S7 Emission lifetimes of CP **1** and solvent-free CP **2** in different concentrations of CR solution.

CR (mg/L) (298.15 K)	0	10	20	30
CP **1** (μs)	1.82	1.80	1.79	1.65
$\chi^2_{\text{CP } \mathbf{1}}$	1.11	1.16	1.10	1.07
Solvent-free CP **2** (μs)	2.46	2.38	2.37	2.26
$\chi^2_{\text{Solvent-free CP } \mathbf{2}}$	1.48	1.21	1.12	1.05

Table S8 Emission lifetimes of solvent-free CP **2** and solvent-free CP **2**@PAN after the addition of different volumes of toluene

Toluene (μL) (298.15 K)	0	5.0	6.0	7.0	8.0	9.0	10.0
Solvent-free CP **2** (μs)	4.13	4.45	4.65	4.68	4.48	4.45	4.41
$\chi^2_{\text{solvent-free CP } \mathbf{2}}$	1.02	1.06	1.09	1.03	1.04	1.13	1.04
Solvent-free CP **2**@PAN (μs)	3.02	4.15	5.51	5.58	5.65	5.91	6.01
$\chi^2_{\text{CP } \mathbf{2}\text{@PAN}}$	1.22	1.05	1.05	1.05	1.04	1.04	1.01

Supporting Information

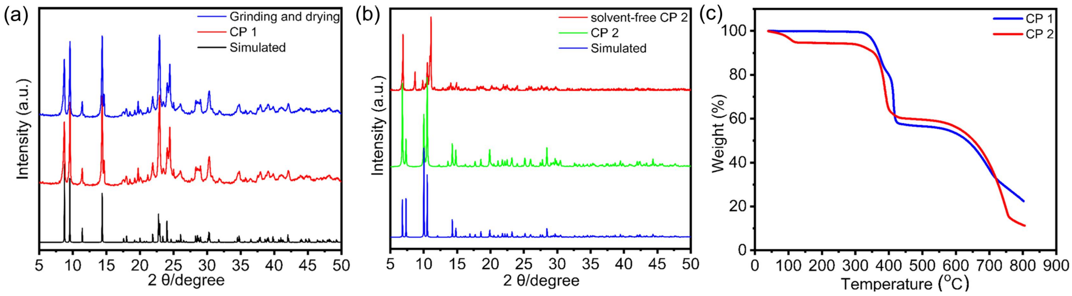

Fig. S1 (a) The black line is the PXRD simulated by Mercury, the red line is the PXRD of CP **1**, and the blue line is the PXRD of the sample after grinding vacuum treatment; (b) The blue line is the PXRD simulated by Mercury, the green line is the PXRD of CP **2** and the red line is the PXRD of the sample after grinding vacuum treatment; (c) Thermogravimetric curves of CP **1** and CP **2**.

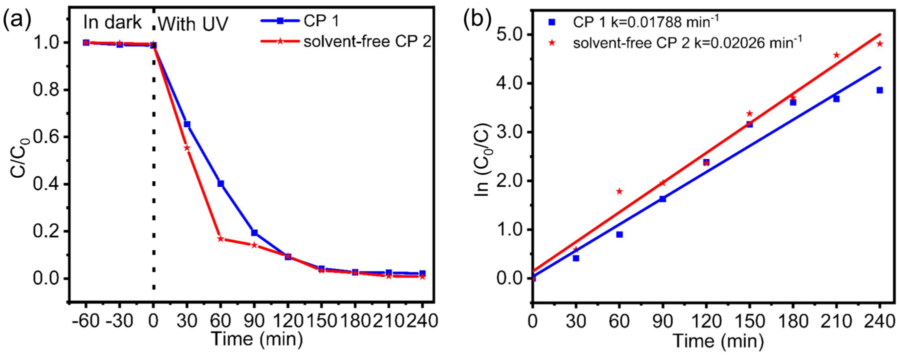

Fig. S2 (a) Comparison of the degradation of CR by CP **1** and solvent-free CP **2**; (b) The linear relationship of ln(C_0/C) versus the reaction time in CP **1** and solvent-free CP **2** for CR degradation experiments.

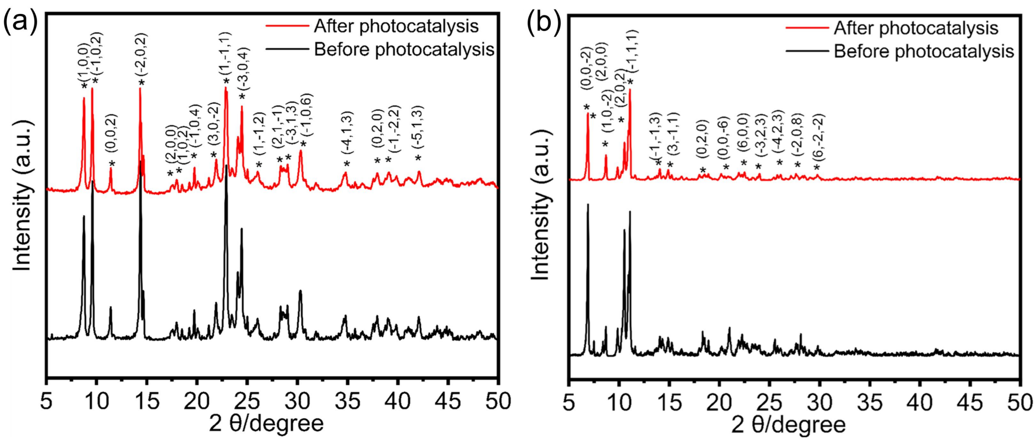

Fig. S3 (a) The PXRD patterns of CP **1** under different conditions; (b) The PXRD patterns of solvent-free CP **2** under different conditions.

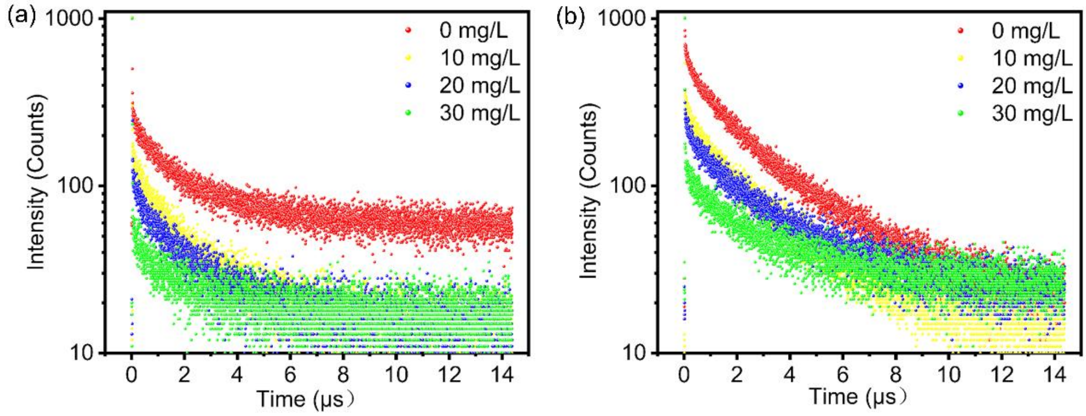

Fig. S4 (a) Emission lifetimes of CP **1** in different concentrations of Congo red solution; (b) Emission lifetimes of solvent-free CP **2** in different concentrations of CR solution.

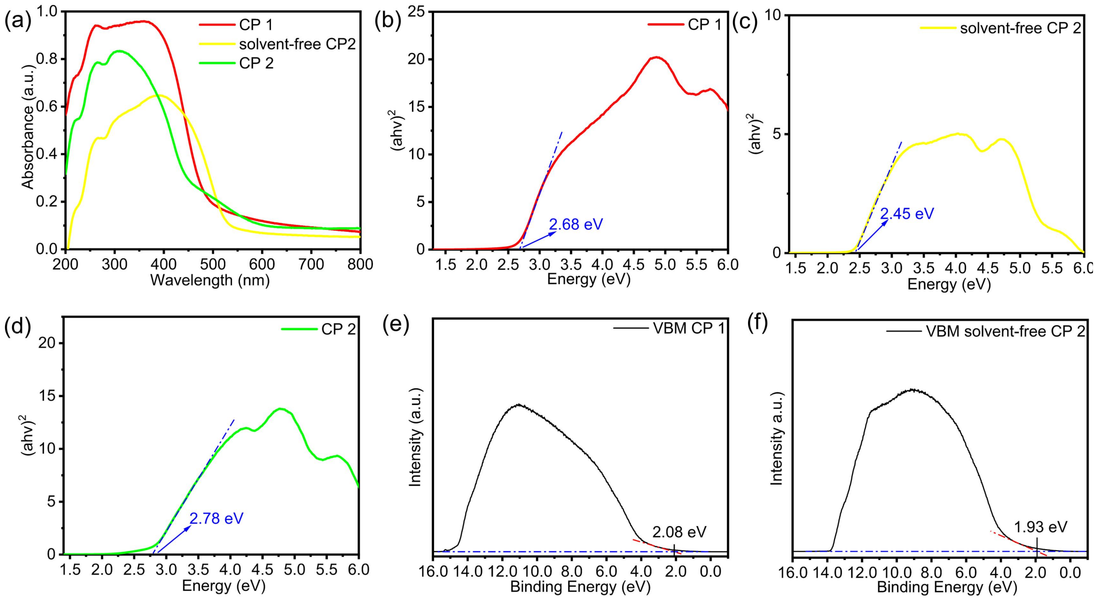

Fig. S5 (a) UV-Vis diffuse reflectance absorption spectrum; (b–d) Tauc curves of cuprous iodide polymers with the red line representing CP **1**, the yellow line representing solvent-free CP **2**, the green line representing CP **2**; (e) Ultraviolet photoelectron spectra (UPS) of CP **1**; (f) Ultraviolet photoelectron spectra (UPS) of solvent-free CP **2**.

Supporting Information

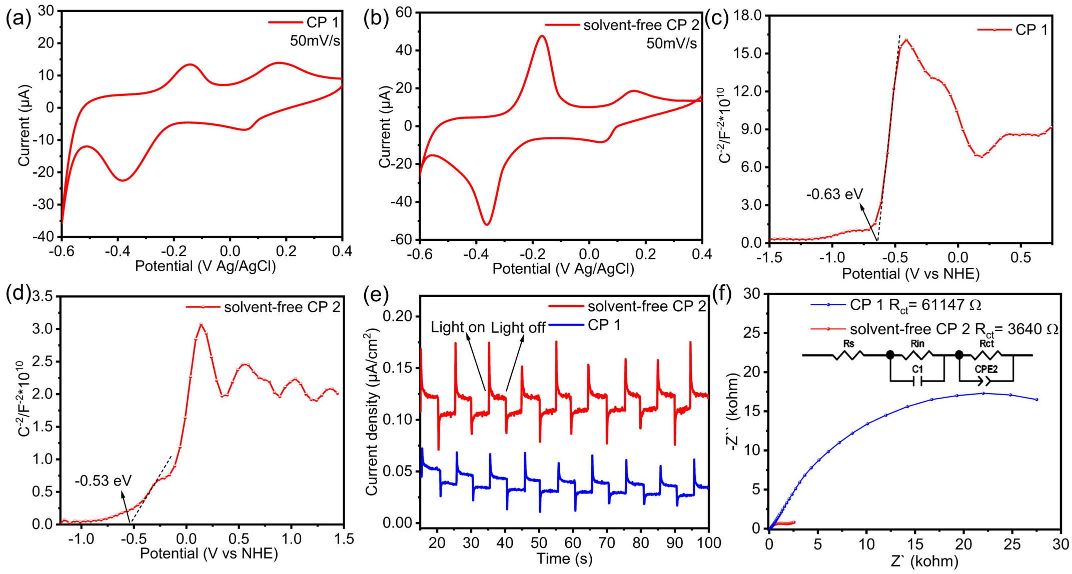

Fig. S6 (a) The CV curve of CP **1**; (b) The CV curve of solvent-free CP **2**; (c) M-S curve of CP **1**; (d) The M-S curve of solvent-free CP **2**; (e) Transient photocurrent responses of CP **1** and solvent-free CP **2** under visible light irradiation; (f) Electrochemical impedance spectra (EIS) of CP **1** and solvent-free CP **2**.

The working electrode utilizes a glassy carbon electrode (GCE). The fabrication process involves polishing the GCE into a mirror-like surface on deer skin in an "8"-shaped trajectory using various sizes of alumina powder. Subsequently, the polished electrode is ultrasonicated sequentially in anhydrous ethanol and ultrapure water for 15 minutes, followed by air-drying at room temperature for later use. The GCE is activated in 20.0 mL of 0.1 mol/L H_2SO_4 using cyclic voltammetry (CV). The voltages of the oxidation and reduction peaks are observed, and their difference should be less than 80 mV.

For sample preparation, 10.0 mg of the sample is ground with 40.0 mg of acetylene black in a quartz mortar for 20 minutes until homogeneous. 5.0 mg mixture is added to a 1.0 mL sample vial along with 100 μL anhydrous ethanol, 100.0 μL ultrapure water, and 40.0 μL Nafion^{TM}. After ultrasonication for 40 minutes at room temperature, 5.0 μL of the resulting mixture is pipetted onto the dry, smooth spots of the GCE. The electrode is air-dried at room temperature afterward.

Supporting Information

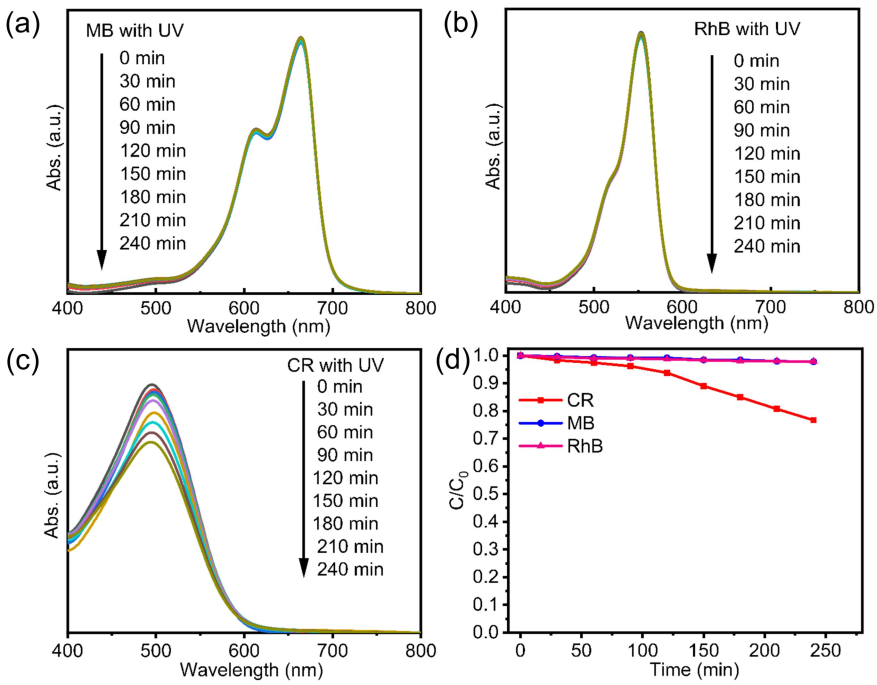

Fig. S7 (a) UV-vis absorption spectra of MB without CPs (50 ml of dye solution, 20 mg/L) irradiated under 254 nm UV light; (b) UV-vis absorption spectra of RhB without CPs (50 ml of dye solution, 20 mg/L) irradiated under 254 nm UV light; (c) UV-vis absorption spectra of MB without CPs (50 ml of dye solution, 20 mg/L) irradiated under 254 nm UV light. (d) Self-degradation trend of three dyes (CR, MB and RhB) after irradiation under 254 nm UV light.

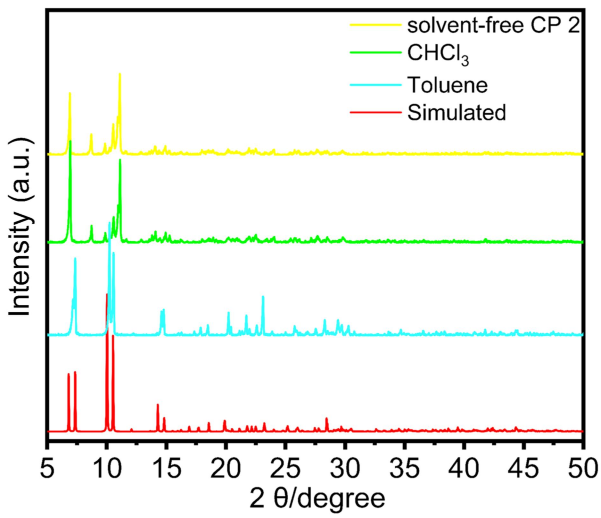

Fig. S8 PXRD of solvent-free CP **2** in different polar VOC gas atmospheres, the green line represents the moderately polar $CHCl_3$ and the blue line represents the weakly polar Toluene.

Supporting Information

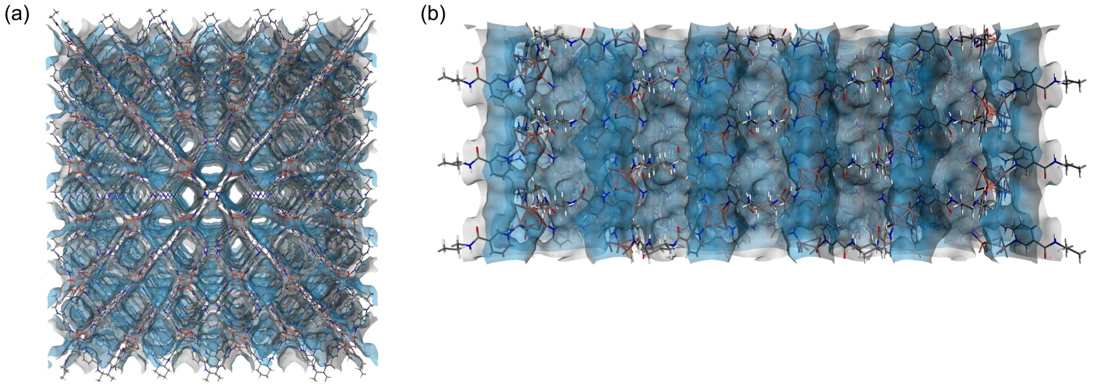

Fig. S9 Simulated solvent-free CP **2** pore diagram from Materials Studio 2020.[S1-S4] Materials Studio 2020 simulated solvent-free CP **2** pore diagram, blank and grey represent pores.

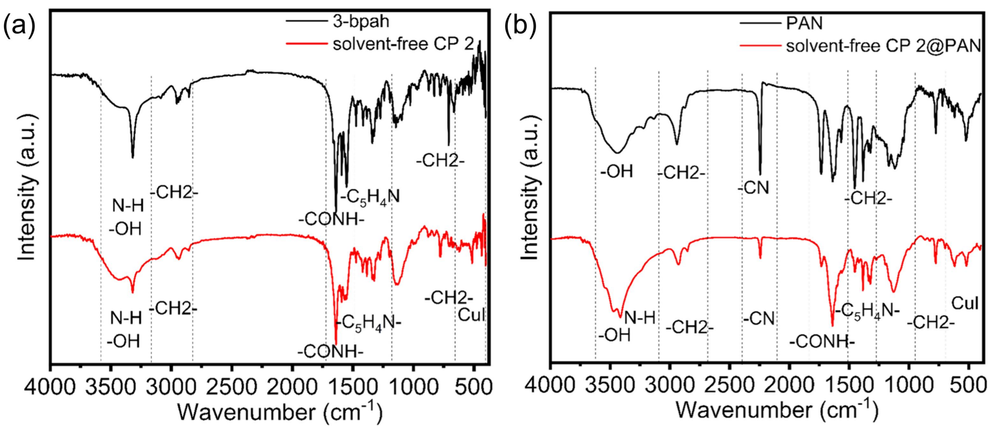

Fig. S10 (a) IR spectra of 3-bpah (black line) and solvent-free CP **2** (red line); (b) IR spectra of PAN (black line) and solvent-free CP **2**@PAN (red line).

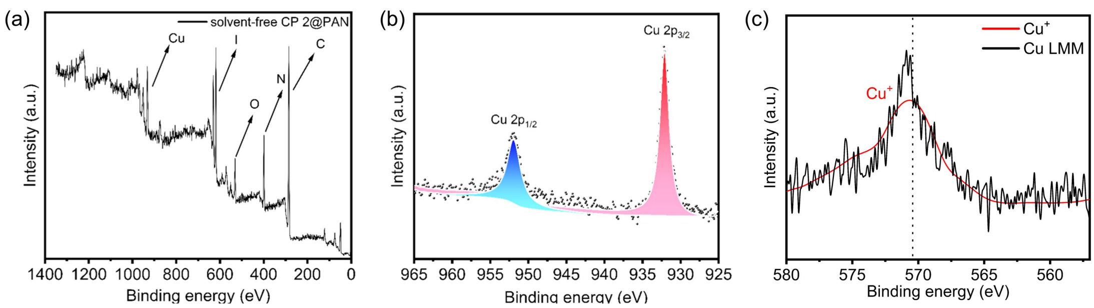

Fig. S11 (a) Full XPS spectra of solvent-free CP **2**@PAN with all characteristic peaks identified; (b) XPS spectra of Cu 2p of solvent-free CP **2**@PAN; (c) Cu LMM Auger spectra of solvent-free CP **2**@PAN.

Supporting Information

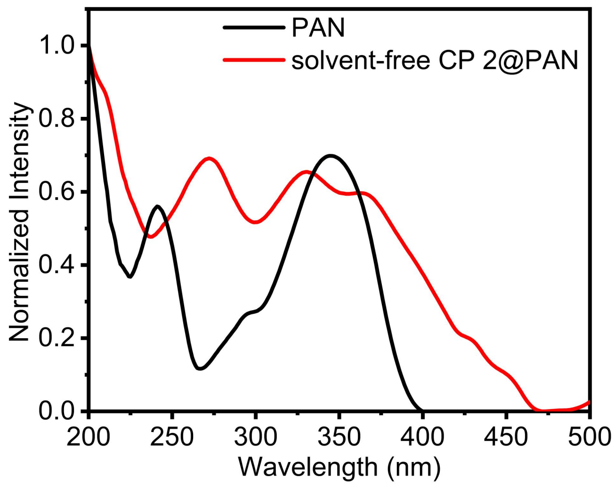

Fig. S12 Normalized excitation spectrum of solvent-free CP **2**@PAN and PAN.

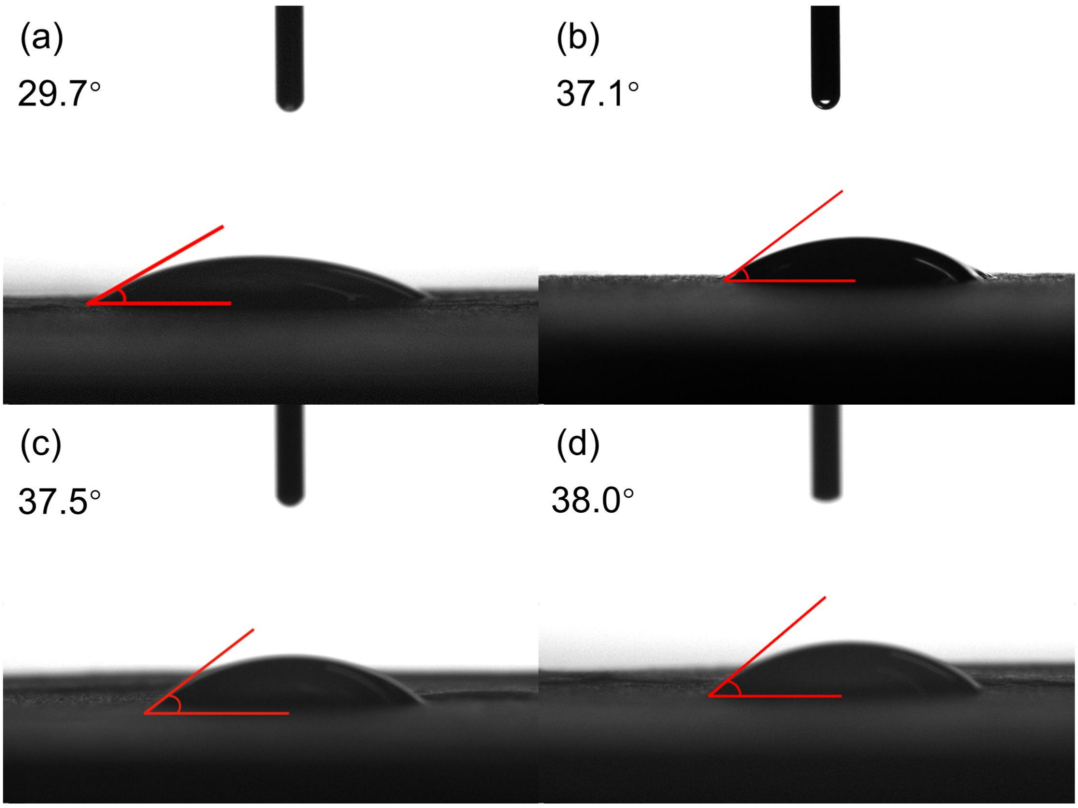

Fig. S13 Film surface wettability. (a) Instantaneous wetting of polyacrylonitrile films by water; (b) Instantaneous wetting effect of water on doped polyacrylonitrile films; (c) Instantaneous wetting effect of water on doped films after primary water rinse drying; (d) Instantaneous wetting effect of water on doped films after second water rinse drying.

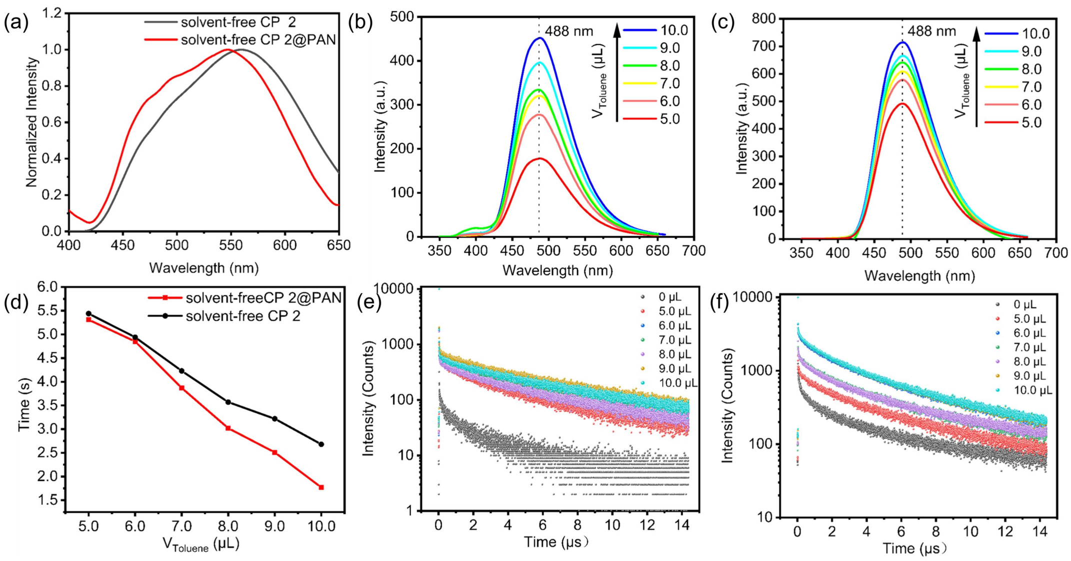

Fig. S14 (a) Normalized emission spectra of solvent-free CP **2** and solvent-free CP **2**@PAN; (b) Change of photoluminescence spectrum of solvent-free CP **2**@PAN after addition of different volumes of toluene; (c) Change of photoluminescence spectrum of solvent-free CP **2** after addition of different volumes of toluene; (d) Comparison of the time required for complete discoloration of solvent-free CP **2** and solvent-free CP **2**@PAN after addition of different volumes of toluene; (e) Emission lifetimes of solvent-free CP **2**@PAN after addition of different volumes of toluene; (f) Emission lifetimes of solvent-free CP **2** after addition of different volumes of toluene.

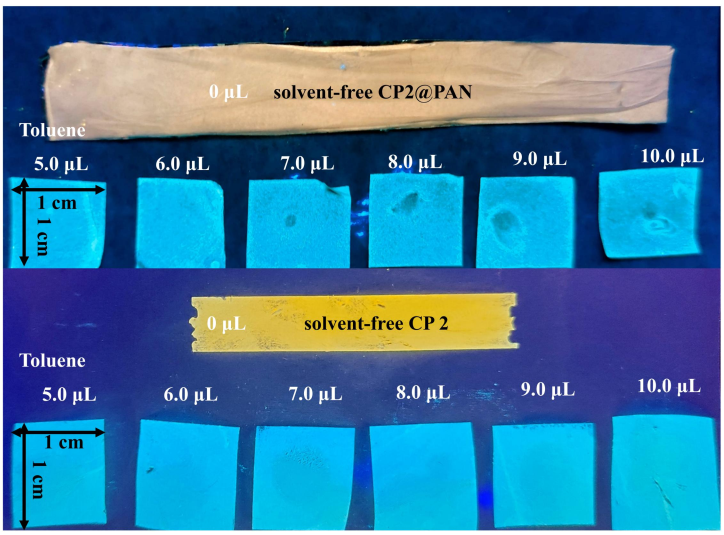

Fig. S15 The picture of complete discoloration of solvent-free CP **2** and solvent-free CP **2**@PAN after addition of different volumes of toluene.

Supporting Information

References

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