#### Supporting Information

# Sunlight-driven photocatalytic degradation of organic dyes using Cu(I) coordination polymers: an efficient and recyclable solution for wastewater remediation

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#### 1. Materials and instrumentations

All the chemicals were used as received if not mentioned somewhere. All the chemicals used were purchased from Avra Chemicals and Dichloroethane (DCE), Acetonitrile (ACN), etc. were procured from Spectrochem and were directly used for synthesis. Photophysical studies were performed with HPLC-grade chemicals. All the reactions were performed under the nitrogen environment because of moisture or oxygen sensitivity. In contrast, others were performed under air and checked by TLC using a Merck 60 F254 pre-coated silica gel plate (0.25 mm thickness). Mass spectra were obtained through the Bruker Daltonik High-Performance LCMS spectrometer. All the <sup>1</sup>H & <sup>13</sup>C {<sup>1</sup>H} NMR spectra were obtained on Bruker 500 MHz spectrometer in CDCl<sub>3</sub>. Chemical shifts are mentioned in delta ( $\delta$ ) units, shown in ppm downfield from tetramethyl silane (TMS) for <sup>1</sup>H NMR. CDCl<sub>3</sub> is used as an internal standard, which shows a peak at 7.26 ppm. The <sup>1</sup>H NMR splitting patterns have been mentioned as singlet(s), double(d), triplet(t) & multiplet(m). NMR data was processed by Mestre Nova. A Fluoromax-4p spectrofluorometer from Horiba JobinYvon was used to record the luminescence spectra at 365 nm excitation of all the compounds (model: FM-100). OriginPro 8.1 was used to evaluate the luminescence emission spectrum.

#### 2. Synthesis of ligand (3-(1,3-dithian-2-yl)pyridine)

In a clean and dry two-necked round bottom flask, freshly distilled 3-pyridine carboxaldehyde (1 mL, 10.51 mmol, 1 equiv.) and 1,3-propane dithiol (1.16 mL, 11.56 mmol, 1.1 equiv.) were dissolved in 1,2-dichloroethane (DCE) (20 mL). Subsequently, *p*-toluene sulphonic acid (200 mg, 1.05 mmol, 0.1 equiv.) was added to the mixture and the solution refluxed for 24 h. The reaction was cooled to room temperature and quenched with a 10% aqueous NaOH solution (10 mL). The layers were separated, and the organic phase was collected and washed with water (10 mL) and brine solution (10 mL). The organic solvent was dried over anhydrous MgSO<sub>4</sub> and filtered. The solvent was evaporated, and the product was isolated by column chromatography (Hex: AcOEt, 90:10) to give **DTP** as a white solid; yield 85%; HRMS m/z calculated for  $C_8H_{10}NS_2$  [M+H]<sup>+</sup> 198.0406, found 198.0401.

<sup>1</sup>**H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  8.68 (d, J = 2.6 Hz, 1H), 8.56 – 8.51 (m, 1H), 7.81 (dt, J = 7.9, 2.1 Hz, 1H), 7.27 (dd, J = 8.1, 4.6 Hz, 1H), 5.17 (s, 1H), 3.06 (t, J = 14.7, 12.3, 2.5 Hz, 4H), 2.01 – 1.87 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} **NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  149.72, 149.17, 135.45, 135.10, 123.64, 48.42, 31.90, 24.89.



## Scheme S1. Synthesis of DTP

#### 3. HRMS of ligand



Figure S1. HRMS of DTP.

# 4. <sup>1</sup>H NMR of ligand



**Figure S2.** <sup>1</sup>H NMR of Ligand **DTP**.

# 5. <sup>13</sup>C{<sup>1</sup>H} NMR of ligand



S5

#### 6. Synthesis of CP1

In a 50 ml Schlenk tube, under N<sub>2</sub> atmosphere, **DTP** (0.333 g, 1.80 mmol) and CuI (1.71 g, 9.04 mmol) was separately dissolved in acetonitrile. Subsequently, CuI solution was added to the ligand solution and the reaction mixture was stirred for 2 hours at room temperature. A pale-yellow colour precipitate was observed for **CP1**, Furthermore, the precipitate was washed with dichloromethane (2-3 times) to remove the unreacted ligand. The yield of the final compound is 87 %. **CP1** Anal. Calc. for C<sub>9</sub>H<sub>11</sub>CuINS<sub>2</sub> (387.75): C, 27.88; H, 2.86; N 3.61; S 16.54 Found: C, 27.90; H, 2.87; N, 3.65; 16.58 %.

#### 7. Synthesis of CP2

In a 50 ml Schlenk tube, under N<sub>2</sub> atmosphere, **DTP** (1.80 mmol) and CuBr (9.04 mmol) were separately dissolved in acetonitrile. To avoid the oxidation of copper, 2 ml methanol was added to the CuBr solution. Subsequently, CuBr solution was added to the ligand solution and the reaction mixture was stirred for 2 hours at room temperature. A yellowish-green colour precipitate was observed. Furthermore, the yellow product was washed with dichloromethane (2-3 times) to remove the unreacted ligand and acetonitrile to remove. The yield of the final compounds is 80%. **CP2** Anal. Calc. for C<sub>9</sub>H<sub>11</sub>BrCuNS<sub>2</sub> (340.76): C, 31.72; H, 3.25; N, 4.11; S, 18.82, Found: C, 31.75; H, 3.27; N, 4.14; S 18.86 %.

# 8. Crystallographic details of CP1 and CP2:

 Table S1. Crystallographic details of CP1 and CP2

Compound	CP1	CP2		
CCDC No.	2415699	2415702		
Formula	C <sub>9</sub> H <sub>11</sub> CuINS <sub>2</sub>	$C_9H_{11}BrCuNS_2$		
Formula Weight	387.75	340.76		
Wavelength	0.71073	0.71073		
Crystal System	orthorhombic	orthorhombic		
Space group	Pbcn	Pbcn		
a/Å	19.1339(7)	18.7689(4)		
b/ Å	8.8168(3)	8.6676(3)		
c/ Å	14.5828(5)	14.2353(4)		
<b>V</b> / Å <sup>3</sup>	2460.12(15)	2315.82(11)		
Z	8	8		
p <sub>calcd</sub> (g/cm <sup>3</sup> )	2.094	1.955		
Temperature/K	293(2)	298		
GOF	1.106	1.064		
2θ range for data collection	5.804 to 57.586	5.916 to 58.034		
Reflections collected	9780	29540		
Independent	$2895 [R_{int} = 0.0345,$	2951 [R <sub>int</sub> = 0.0709, R <sub>sigma</sub>		
reflections	$R_{sigma} = 0.0291$ ]	= 0.0328]		
Completeness to 0=25.242	100	100		
Final R indices	R1 = 0.0306, wR2	R1 = 0.0342, wR2 =		
[I>2σ(I)]	= 0.0743	0.0769		
Final R indices	R1 = 0.0343, wR2	R1 = 0.0568, wR2 =		
[all data]	= 0.0766	0.0879		
Largest diff. peak/hole/ e Å <sup>-3</sup>	0.61/-1.06	0.66/-0.58		

# 9. Thermogravimetric analysis (TGA)



Figure S4. TGA graph of CP1 and CP2.



# **10. Conductivity:**

Figure S5. Electrical conductivity of CP1 and CP2

#### 11. Solid state Uv-spectra of polymers:



Figure S6. UV-Vis DRS spectra of (a) CP1 and (b) CP2.

#### 12. Photocatalytic procedure

To quantify the intensity, concentration, and % degradation of degraded dye using **CP1** and **CP2** as photocatalysts, we prepared six standard solutions (10 ppm) of both dye MB and RHB. The photocatalytic degradation of the dye MB by visible light was studied using **CP1** and **CP2** as a photocatalyst through UV-vis spectra. By adding 5 mg of each **CP1** and **CP2** in the standard solution of both dyes (100 ml of 10 ppm), degrading the MB in 80 min and RHB in 90 min using **CP1** and MB in 110 min, RHB in 130 min using **CP2** as shown in Figure S5 (a-d). When  $H_2O_2$  (200 µL) as a radical initiator and CPs (2mg) are simultaneously added to the standard solution of MB and RHB, the degradation rate increases significantly. For **CP1**, MB and RHB are degraded in 15 and 25 min, respectively. For **CP2**, MB and RHB are almost completely degraded after 18 and 30 min as shown in Figure 3.



**Figure S7.** Time-dependent UV/vis spectra of MB solution during photocatalytic degradation using (a) catalyst **CP1** (b) catalyst **CP2**. The UV–vis spectra of RHB solution during photocatalytic degradation using (c) catalyst **CP1**, and (d) catalyst **CP2**.



**Figure S8.** Time-dependent UV/vis spectra of MO solution during photocatalytic degradation using (a) catalyst **CP1**, (b) catalyst **CP1** and H<sub>2</sub>O<sub>2</sub>. The UV–vis spectra of Rh-6G solution during photocatalytic degradation using (c) catalyst **CP1**, and (d) catalyst **CP1** and H<sub>2</sub>O<sub>2</sub>.

#### 13. Degradation efficiency comparison

Table S2. Dye degradation efficiency of CP1 and CP2 (with and without H<sub>2</sub>O<sub>2</sub>)

Dve		MB			RHB			
Catalyst	CP1	CP1/ H <sub>2</sub> O <sub>2</sub>	CP2	CP2/ H <sub>2</sub> O <sub>2</sub>	CP1	CP1/ H <sub>2</sub> O <sub>2</sub>	CP2	CP2/ H <sub>2</sub> O <sub>2</sub>
% of degradation	92%	96%	95%	96%	94%	97%	95%	97%
Time (min)	80	15	110	25	90	18	130	30

# 14. Kinetic study:



Figure S9. The kinetic regression curve of  $-\ln(C_0/C_t)$  versus time (min) of degradation for (a) CP1 MB and CP1 RHB, (b) CP2 MB and CP2 RHB.

# **15.** Comparison Table

Table S3. Comparison of % efficiency and rate of degradation for photocatalytic degradation

of MB/RHB by various related catalyst

Entry	CPs/MOFs	Degradation efficiency (%)	Dye degradation Time(min)	Reference
1.	Cu(I)-CPs	99.1	90	1
2.	Cu(I)-CPs	98	40	2
3.	Cu(I)-CPs	-CPs 84 120		3
4.	Cu(I)-CPs	99	50	4
5.	Cu(I)-CPs	91.8	1920	5
6.	Cu(I)-CPs	96.75	21	6
7.	<sup>7</sup> . Zn (II)-CPs 78.3 45		7	

8.	Cu (II)-MOFs	63.0	150	8
9.	Cu (II)-MOFs	98.2	120	9
10.	NDCQs/Znf-8	93.5	240	10
11.	Zn (II)-MOFs	67.31	40	11
12.	Co3O4-CQD	90.00	60	12
13.	Co (II)-CPs	90.88	160	13
14.	Ag(I)-CPs	100	50	14
15.	Cu(I)-CPs	98	24	15
16.	Zn (II)-CPs	70	180	16
17.	Zn (II)-MOFs	99	45	17
18.	Co (II)-CPs	97.3	120	18
19.	Cu (II)-CPs	99	120	19
20.	g-C <sub>3</sub> N <sub>4</sub> -TiO <sub>2</sub>	60	150	20
21.	TiO <sub>2</sub> nanoparticle	96	110	21
22.	Cu(I)-CPs	96	15	This work

# 16. Cycle test:



**Figure S10.** Cycle test for MB using (a) **CP1** and (b) **CP2.** (c) The photocatalytic efficiency of CPs with MB and RHB using various scavengers.

## 17. Powder X-ray diffraction patterns:



**Figure S11.** PXRD pattern of (a) **CP1** and (b) **CP2** before and after the first seven cycles for **MB** dye degradation.

# 18. Energy dispersive spectroscopy spectra:



**Figure S12.** EDS of **CP1** and **CP2**, before (a) and (c) and after (b) and (d) the first seven cycles for **MB** dye degradation.

#### 19. BET isotherm



Figure S13. BET isotherm of (a) CP1 (b) CP2. Inset Images: Porosity distribution by BJH method



Figure S14. Complete XPS survey scan of CP1 (a) before and (b) after 7<sup>th</sup> cycle of dye degradation.

#### References

- P. Tang, X.-X. Xie, Z.-Y. Huang, Z.-Y. Kuang, S.-L. Cai, W.-G. Zhang and S.-R. Zheng, CrystEngComm, 2023, 25, 417–424.
- M. Murillo, A. García-Hernan, J. López, J. Perles, I. Brito and P. Amo-Ochoa, *Catalysis Today*, 2023, 418, 114072.
- 3. J.-W. Cui, W.-J. An, K. V. Hecke and G.-H. Cui, *Dalton Trans.*, 2016, 45, 17474–17484.
- M. Murillo, R. Wannemacher, J. Cabanillas-González, U. R. Rodríguez-Mendoza, J. Gonzalez-Platas, A. Liang, R. Turnbull, D. Errandonea, G. Lifante-Pedrola, A. García-Hernán, J. I. Martínez and P. Amo-Ochoa, *Inorg. Chem.*, 2023, 62, 10928–10939.
- 5. X.-Y. Xu, Q.-C. Chen, Y.-D. Yu and X.-C. Huang, *Inorg. Chem.*, 2016, 55, 75–82.
- 6. M. Singh and S. Neogi, *Inorg. Chem.*, 2022, **61**, 10731–10742.
- Y. Pan, Q. Ding, H. Xu, C. Shi, A. Singh, A. Kumar and J. Liu, *CrystEngComm*, 2019, 21, 4578–4585.

- V. Kim, D. W. Lee, H. R. Noh, J. Lee, T.-H. Kim, J. Park, J.-Y. Kim and S. H. Lim, *Inorg. Chem.*, 2024, 63, 8832–8845.
- Y. Chen, A. Liu, P. Liu, Z. Zhang, F. Yu, W. Qi and B. Li, *Inorg. Chem.*, 2022, 61, 16009– 16019.
- A. A. Abd El Khalk, M. A. Betiha, A. S. Mansour, M. G. Abd El Wahed and A. M. Al-Sabagh, ACS Omega, 2021, 6, 26210–26220.
- 11. W. Hu, C. Rao, C. Chen, Z. Liao, D. Srivastava and A. Kumar, *Inorganic Chemistry Communications*, 2021, **130**, 108685.
- E. Shanmugasundaram, K. Vellaisamy, V. Ganesan, V. Narayanan, N. Saleh and S. Thambusamy, ACS Omega, 2024, 9, 14101–14117.
- 13. W. Zuo, Y. Fan, L. Yang and L. Cui, J Inorg Organomet Polym, 2020, 30, 2105-2113.
- F. Wang, F.-L. Li, M.-M. Xu, H. Yu, J.-G. Zhang, H.-T. Xia and J.-P. Lang, *Journal of Materials Chemistry A*, 2015, 3, 5908–5916.
- 15. T. Wen, D.-X. Zhang and J. Zhang, Inorg. Chem., 2013, 52, 12–14.
- 16. F.-K. Wang, S.-Y. Yang and H.-Z. Dong, Journal of Molecular Structure, 2021, 1227, 129540.
- A. Karmakar, A. Paul, I. R. M. Santos, P. M. R. Santos, E. P. Sabatini, A. V. Gurbanov, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Crystal Growth & Design*, 2022, 22, 2248–2265.
- 18. L. Fan, W. Fan, B. Li, X. Zhao and X. Zhang, CrystEngComm, 2015, 17, 9413–9422.
- 19. N. Hussain and V. K. Bhardwaj, Dalton Transactions, 2016, 45, 7697–7707.
- 20. M. Nemiwal, T. C. Zhang and D. Kumar, Science of The Total Environment, 2021, 767, 144896.
- S. D. Gallegos-Cerda, J. D. Hernández-Varela, J. J. Chanona Pérez, C. A. Huerta-Aguilar, L. González Victoriano, B. Arredondo-Tamayo and O. Reséndiz Hernández, *Carbohydrate Polymers*, 2024, **324**, 121476.