

Supporting Information

Photochromic Inorganic-Organic Complex Derived from Low-cost Deep Eutectic Solvents with Tunable Photocurrent responses and Photocatalytic Properties

Junbiao Wu,^{†a} Luqi Lou,^{†a} Huaying Sun,^a Chuanyao Tao,^b Teng Li,^c Zhuopeng Wang,^{*a} Xia Zhang^{*a} and Jiyang Li^{*b}

- a. *Department of Chemistry, College of Sciences, Northeastern University, Shenyang, Liaoning 110819, China. Email: wangzhuopeng@mail.neu.edu.cn; xzhang@mail.neu.edu.cn; Tel.: +86-024-83684533; Fax: +86-024-83684533.*
- b. *State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China. E-mail: lijiyang@jlu.edu.cn; Tel: (+86) 431 8516-8608; Fax: (+86) 431 8516-8608.*
- c. *State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, China.*

† These authors contributed equally.

Table S1. Crystal data and structure refinement for $|C_{10}H_{10}N_2| [GaF(C_2O_4)_2]$.

Empirical formula	$C_{14}H_{10}FGaN_2O_8$
Formula weight	422.96
Temperature	293(2) K
Wavelength(Å)	0.71073
Crystal system, space group	Monoclinic, C2/m
Unit cell dimensions	
a (Å)	18.4449(10)
b (Å)	10.4561(5)
c (Å)	3.8127(2)
α (deg)	90
β (deg)	93.617(2)
γ (deg)	90
Volume(Å ³)	733.86(7)
Z , calculated density(mg m ⁻³)	2,1.914
Absorption coefficient(mm ⁻¹)	1.940
$F(000)$	424
Crystal size(mm ³)	$0.245 \times 0.123 \times 0.104$
θ range(°) for data collection	3.85–27.456
Limiting indices	$-23 \leq h \leq 23, -13 \leq k \leq 13, -4 \leq l \leq 4$
Reflections collected/unique	5805/ 882, [R (int) = 0.0248]
Completeness to θ (%)	25.242, 99.4
Absorption correction	semi-empirical from equivalents
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	882/6/67
Goodness-of-fit on F^2	1.167
Final R indices [$I > 2 \sigma(I)$]	$R_1 = 0.0272, wR_2 = 0.0680$
R indices (all data)	$R_1 = 0.0272, wR_2 = 0.0680$
Largest diff. peak and hole (eÅ ⁻³)	0.534 and -0.496

^a $R_1 = \sum(\Delta F / \sum(F_o))$, $wR_2 = (\sum[w(F_o^2 - F_c^2)]) / \sum[w(F_o^2)^{1/2}]$ and $w = 1 / [\sigma^2(F_o^2) + (0.0595P)^2 + 2.8937P]$ where $P = (F_o^2 + 2F_c^2)/3$

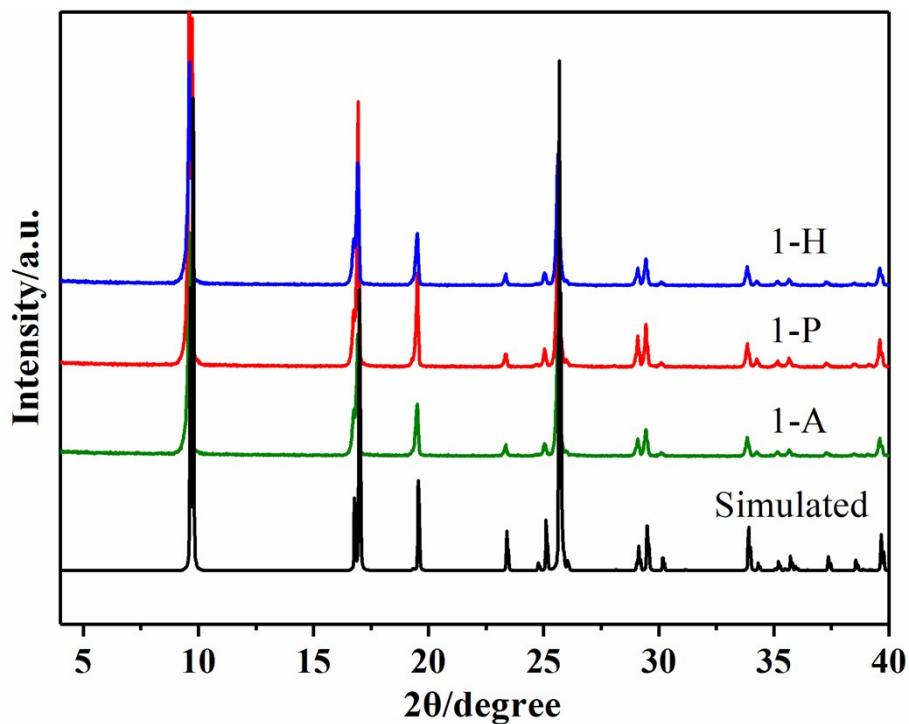


Figure S1. PXRD pattern of $|\text{C}_{10}\text{H}_{10}\text{N}_2|[\text{GaF}(\text{C}_2\text{O}_4)_2]$.

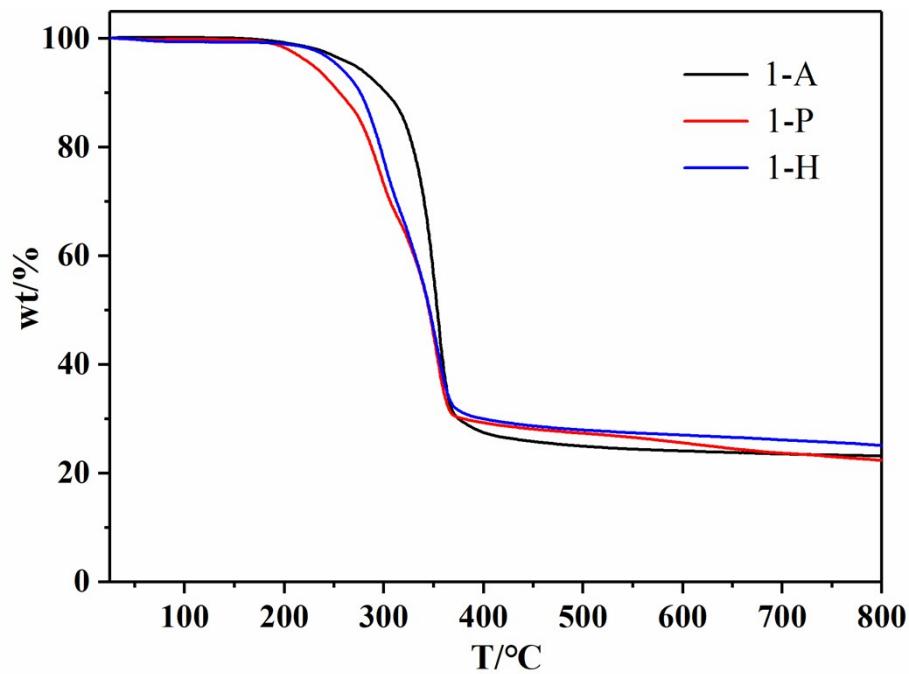


Figure S2. TG curve of $|\text{C}_{10}\text{H}_{10}\text{N}_2|[\text{GaF}(\text{C}_2\text{O}_4)_2]$.

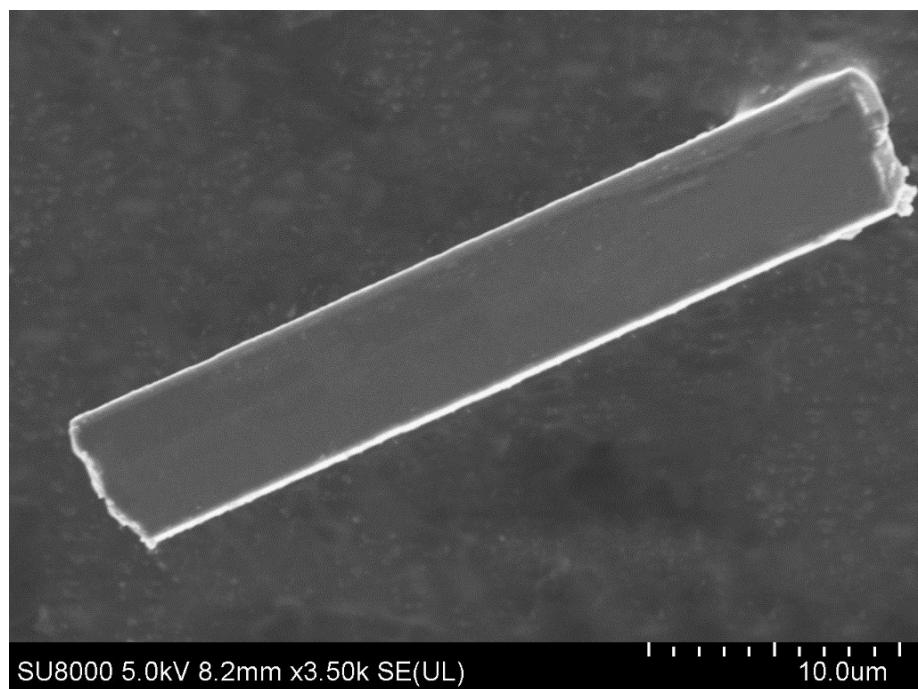


Figure S3. SEM image of $|\text{C}_{10}\text{H}_{10}\text{N}_2|[\text{GaF}(\text{C}_2\text{O}_4)_2]$.

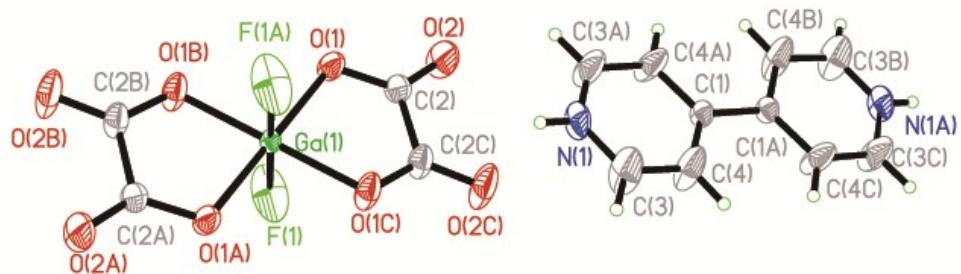


Figure S4. Thermal ellipsoids of $|\text{C}_{10}\text{H}_{10}\text{N}_2|[\text{GaF}(\text{C}_2\text{O}_4)_2]$ given at 50% probability, showing the atomic labelling scheme.

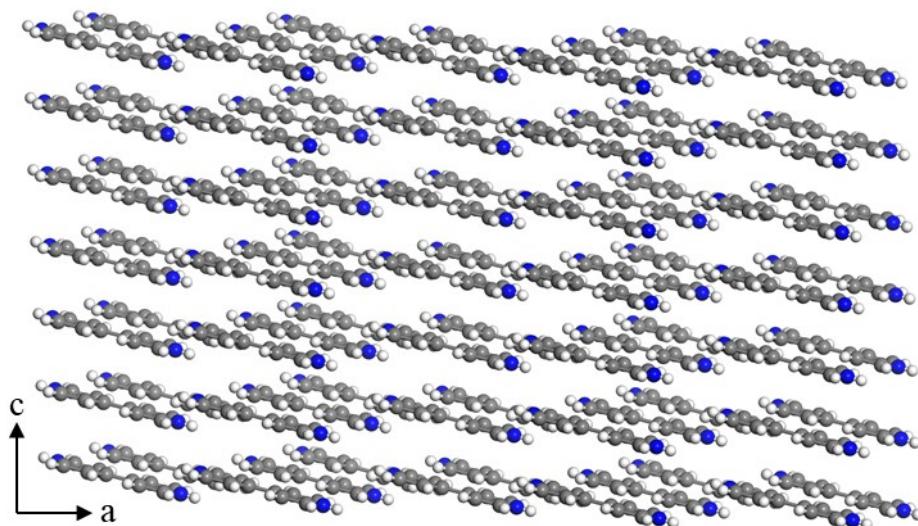


Figure S5. Dense packing mode of $\text{H}_2\text{bpy}^{2+}$ cations along the [010] direction displaying the $\pi - \pi$ stacking interactions between the adjacent pyridinium rings of the $\text{H}_2\text{Bpy}^{2+}$ dications.

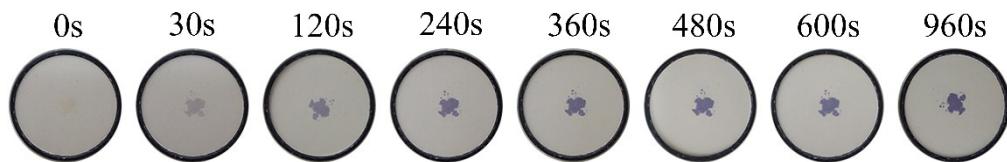


Figure S6. Colourless to purple upon light irradiation (48W UV light)

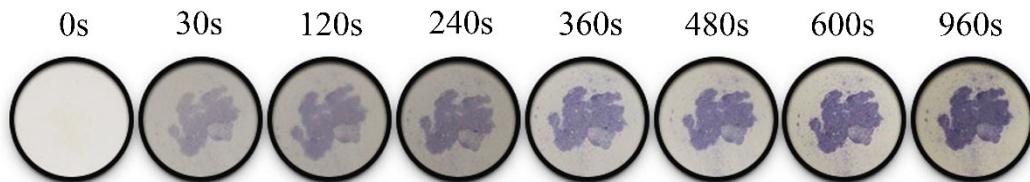


Figure S7. Colourless to purple upon light irradiation (300W visible light)

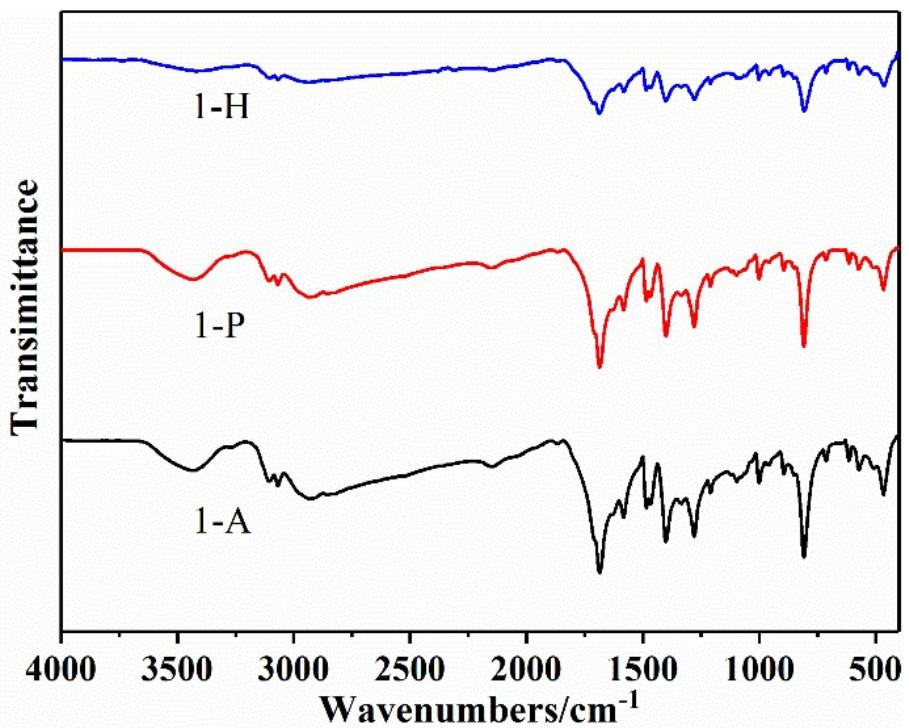


Figure S8. IR curves of $|C_{10}H_{10}N_2| [GaF(C_2O_4)_2]$.

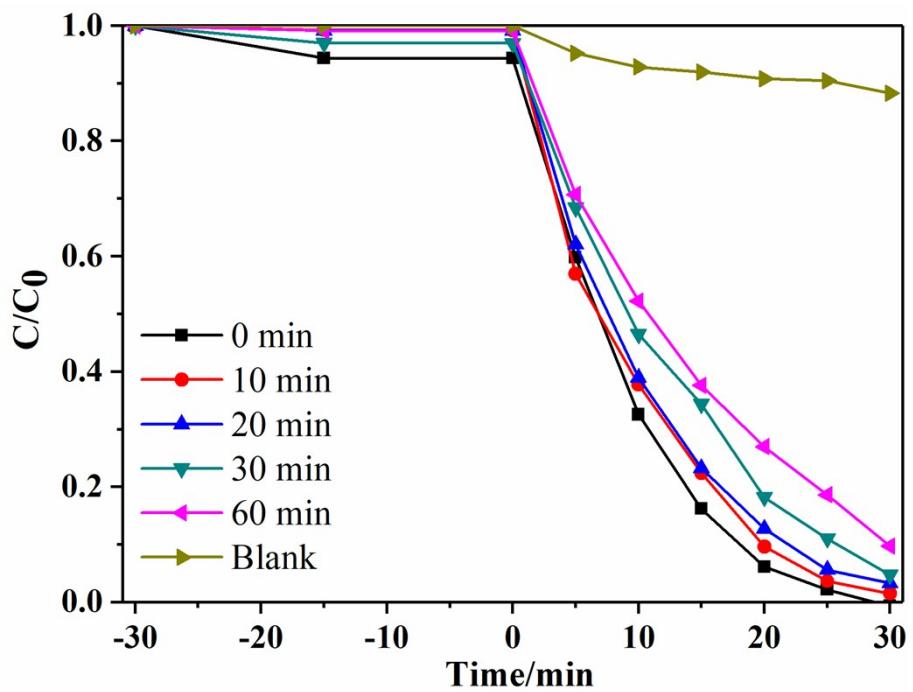


Figure S9. Photocatalytic degradation curves (under UV light)

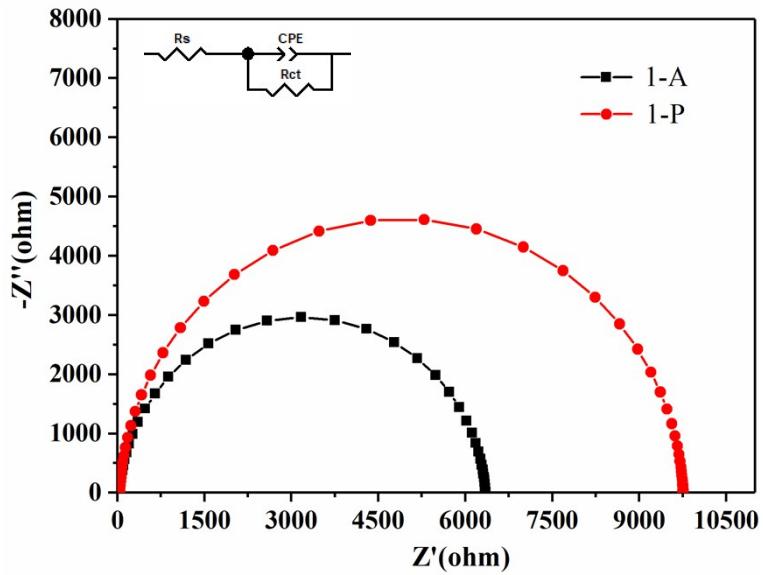


Figure S10. Nyquist impedance plots the corresponding equivalent circuit of **1-A** and **1-P**.

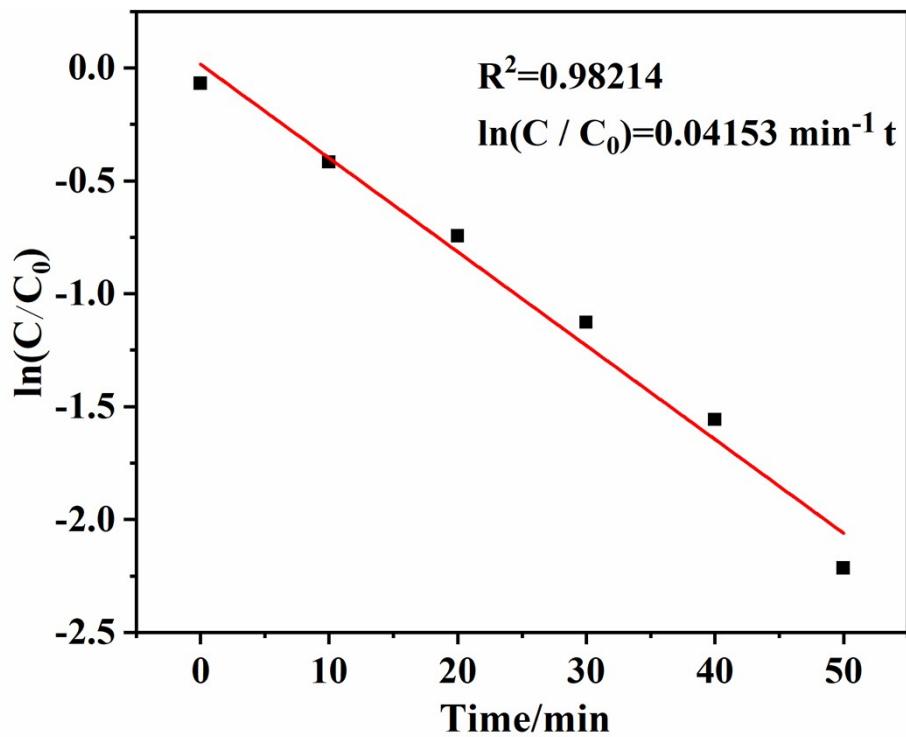


Figure S11. Linear relationship between $\ln(C_0/C)$ and irradiation time for photodegradation of RhB over **1-A**.

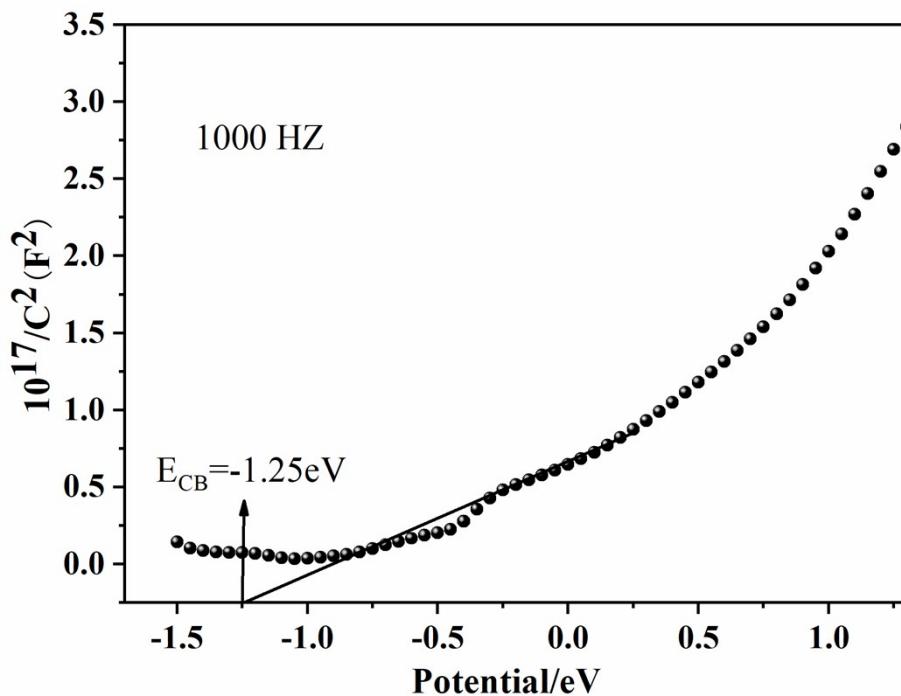


Figure S12. Mott-Schottky plot of **1-A**.

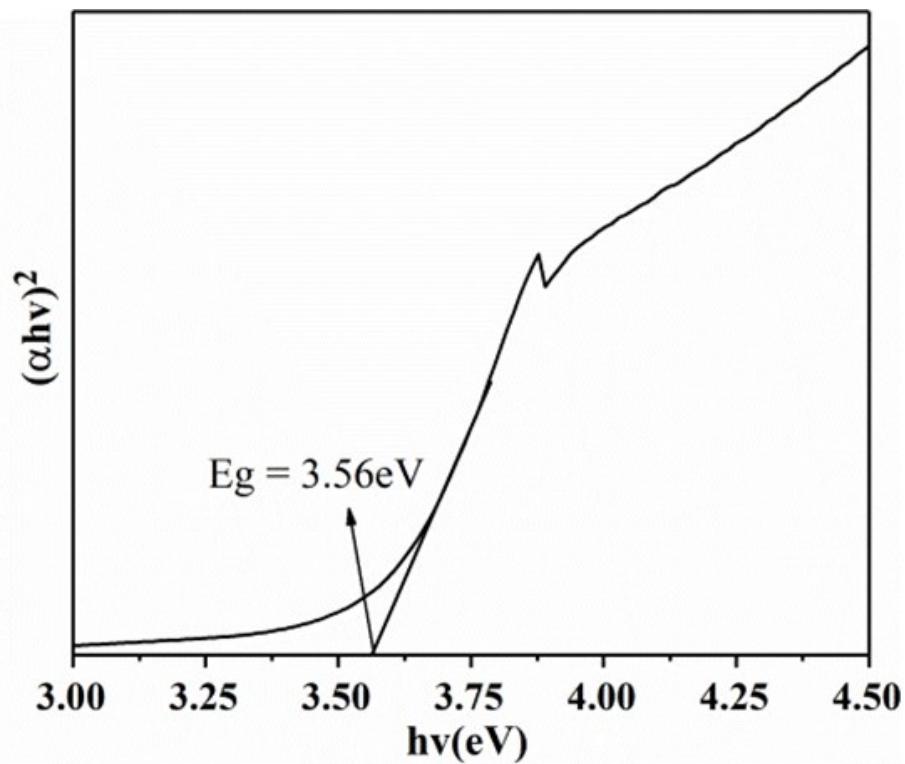


Figure S13. Plot of $(\alpha h\nu)^2$ as a function of $h\nu$ for the bandgap energy of **1-A**, exhibiting its bandgap energy estimated to be 3.56 eV.

Table S2 Summary of photochromic performances in this work compared with literatures

Entr y	sample name	Light sources	Irradiation intensity	Response time	Color transformation	Bleach condition	Ref
1	[C12H14N2][Zn6(P O4)4(HPO4)(H2O)2]	UV light	-	several hours	colorless to blue	230°C for 1 h in air.	1
2	[Cd(CEbpy)(m- BDC)(DMF)]·2H2O	UV light	175W	2min	yellow to darker blue	140°C for 4 ~ 6 h .	2
3	[Zn(HPO3)(4,4'- bipy)0.5]	Xe lamp	300W	>3min	colorless to pink	145°C for 2 hours in air.	3
4	[Zn(bcbpy)0.5(pma 0.5(H2O)]·3H2O	UV light	300W	5s	colorless to blue	50°C for 20 min in air.	4
5	(MV)Bi2Cl8	UV light	-	-	Yellow to black	130°C in air	5
6	[Zn2(Bpy)(CTA)4]	Xe lamp	300W	-	colorless to purple	130°C for 2h in air.	6
7	[Cd1.5(H2L)0.5(Cl) 3(CH3OH)]n	Xe lamp	300W	a few minutes	pale yellow to blue	120°C for 20 min in air.	7
8	[Mg2(1,4- NDC)2(H2O)2](bpy)·(H2O)4	Xe lamp	500W	10min	colourless to blue	60°C for 20 min.	8
9	[Zn(HCOO)2(4,4'- bipy)]	Xe lamp	300 W	-	pale yellow to olive green	120°C for 2h.	9
10	Eu2(m-BDC)4(MV)	Xe lamp or sunlight	-	-	brown to green	-	10
11	[H2CPBPY]·[H2BT EC]	Xe lamp	150 W	-	pale yellow to green	130°C in air.	11
12	TbMOF	Xe lamp	300 W	-	bright yellow to dark green	120°C for 1h in air.	12
13	[Cd(CPBPY)(m- BDC) ·H2O	Xe lamp	-	-	yellow to blue	120°C	13
14	(hMV)[Bi(hMV)Cl5]	Hg UV lamp	150 W	a few minutes	white to blue	120°C for few minutes.	14
15	[Cd(CPBPY)(o- BDC)(H2O)]·H2O	UV light	-	-	yellow to gray	exposed to pure O2 or air, return	15

							slowly.
16	[Zn(L1)(L3)0.5]·H ₂ O	Xe lamp	250 W	20s	pale yellow to pale green	130 °C for 5 min.	16
17	{[Zn ₃ (Cebpy) ₂ (Hbt _c (H ₂ btc) ₂ (OH) ₂) ₄ ·H ₂ O} _n	Xe lamp	-	10min saturated	pale yellow to dark blue	80 °C for 2 hours.	17
18	NTHU-9	X-rays	-	-	orange to slate gray	200°C for 12h in air.	18
19	[H ₂ (Bpy)][H ₃ (Pma)J ₂	Xe lamp	300 W	-	yellow to grayish purple	80 °C for 3 min.	19
20	[Cd ₂ (ic)(mc)(4,4'-bipy) ₃]n·4nH ₂ O	light with λ<460 nm	-	-	yellow to blue	80°C for several hours.	20
21	C ₁₀ H ₁₀ N ₂ [GaF(C ₂ O ₄) ₂]	UV light	48W	10s	colorless to purple	110°C for 30 min.	This work

- 1 J. B. Wu, Y. Yan, J. Y. Li and J. H. Yu, *Chem. Commun.*, 2013, **49**, 4995.
- 2 J. J. Liu, J. Li and W. B. Lu, *RSC. Adv.*, 2019, **9**, 33155.
- 3 B. D. Ge, Y. Han, S. D. Han and G.M. Wang, *Inorg. Chem. Front.*, 2019, **6**, 2435.
- 4 L. Li, Z. M. Tu, Y. Hua and H. Zhang, *Inorg. Chem. Front.*, 2019, **6**, 3077.
- 5 G. Xu, G. C. Guo, M. S. Wang and J. S. Huang, *Angew. Chem.*, 2007, **119**, 3313.
- 6 J. Liu, P. X. Li, H. Y. Zeng and G. C. Guo, *RSC Adv.*, 2017, **7**, 34901.
- 7 L. K. Li, H. Y. Li, T. Li, F. A. Li and S.Q. Zang, *CrystEngComm.*, 2018, **20**, 6412.
- 8 Z. F. Wu, B. Tan, Z. L. Xie and X. Y. Huang, *J. Mater. Chem. C.*, 2016, **4**, 2438.
- 9 C. J. Zhang, Z. Wei. Chen, M. S.Wang and G. C. Guo, *Inorg. Chem.*,2014, **53**, 847.
- 10 H. J. Chen, G. M. Zheng, M. Li and Z. Y. Fu, *Chem. Commun.*, 2014, **50**, 13544.
- 11 H. J. Chen, M.Li, G. M. Zheng, Z. Y. Fu and J. C. Dai, *RSC Adv.*, 2014, **4**, 42983.
- 12 H. Y. Li, Y.L.Wei, S.Q. Zang and Thomas C. W. Mak, *Chem. Mater.*, 2015, **27**, 1327.
- 13 Y. Tan, Z. Y. Fu, Y. Zeng, J. Zhang and J. C. Dai, *J. Mater. Chem.*, 2012, **22**, 17452.
- 14 Oksana Toma, Nicolas Mercier, and Chiara Botta, *Eur. J. Inorg. Chem.*,2013, **7**, 1113.
- 15 S. L. Li, M. Han, B. Wu, and X. M. Zha, *Cryst. Growth Des.*, 2018, **18**, 3883.
- 16 W. Q. Kan, S. Z.Wen, Y. C. He and C. Y. Xu, *Inorg. Chem.*, 2017, **56**, 14926.
- 17 Q. Shi, S. Yu Wu, X. T. Qiu, Y. Q. Sun and S. T. Zheng, *Dalton Trans.*, 2019,**48**, 954.
- 18 P.-C. Jhang, N.-T. Chuang and S.-L. Wang, *Angew. Chem. Int. Ed.*, 2010, **122**, 4296.
- 19 Z.-W. Chen, G. Lu, P.-X. Li, R.-G. Lin, L.-Z. Cai, M.-S. Wang and G.-C. Guo, *Cryst. Growth Des.*, 2014, **14**, 2527.
- 20 M. S.Wang, G. C. Guo, G. Xu and J. S. Huang, *Angew. Chem.*, 2008, **120**, 3621.