Supporting Information

UV and X-ray dual-induced photochromism in a benzophenone-based metal-organic framework for inkless erasable printing

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Table S1. Crystallographic data and structure refinement for **1** before and after UV irradiation.

Compound	**1**	**1-after**
Chemical formula	$Zn_4C_{37}H_{19}O_{21}N$	$Zn_4C_{37}H_{19}O_{21}N$
Formula weight	1075.01	1075.01
Temperature/(K)	293(2)	293(2)
Wavelength/(Å)	1.54184	1.54184
Crystal system	Triclinic	Triclinic
Space group	*P 1*	*P 1*
a/(Å)	9.8670(5)	9.8663(3)
b/(Å)	12.0062(7)	11.9838(6)
c/(Å)	13.1276(6)	13.1236(5)
α/(°)	115. 459(5)	115.559(4)
β/(°)	93.033(4)	93.042(3)
γ/(°)	91.808(4)	91.661(3)
Volume/(Å^3)	1399.63(14)	1395.54(11)
Z	1	1
*D*c/(g cm^{-1})	1.275	1.279
Absorption coefficient	2.505	2.512
F(000)	536	536
Reflections collected	28574	29070
Index ranges	-12 ⩽ h ⩽ 12 -15 ⩽ k ⩽ 15 -16 ⩽ l ⩽ 16	-12 ⩽ h ⩽ 12 -15 ⩽ k ⩽ 15 -16 ⩽ l ⩽ 16
Data/Restraints/parameters	10641/21/571	10652/22/571
GOF on F^2	1.063	1.039
[a] R_1/wR_2 [$I>2\sigma(I)$]	0.0378/0.1062	0.0323/0.0934
[a] R_1/wR_2 [(all data)]	0.0398/0.1086	0.0346/0.0970
Largest diff. peak/hole / e Å^{-3}	2.67/-1.02	2.8/-0.8
Flack parameter	0.36(3)	0.39(2)

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

Table S2. Selected bond lengths for **1**.

Bond lengths (Å)			
O(1)[10]-Zn(1)	1.963(4)	O(11)-Zn(3)[5]	1.975(3)
O(2)[13]-Zn(4)	2.052(4)	O(11)-Zn(4)[6]	2.131(3)
O(3)[7]-Zn(2)	1.972(4)	O(12)-Zn(2)	1.984(4)
O(4)[14]-Zn(4)	2.138(4)	O(14)-Zn(3)[7]	2.003(4)
O(7)-Zn(3)	1.890(4)	O(15)-Zn(1)[8]	1.981(4)
O(9)-Zn(2)	1.966(4)	O(17)-Zn(4)	2.014(3)
O(10)-Zn(1)	1.882(4)	O(19)-Zn(4)[9]	2.262(4)
O(10)-Zn(2)	1.944(4)	O(20)-Zn(3)	1.978(4)
O(11)-Zn(1)	1.963(3)	O(21)-Zn(4)	2.076(4)

Table S3. Selected bond angles for **1**.

Bond angles (º)			
O(1)[10]-Zn(1)-O(15)[11]	101.26(18)	O(2)[13]-Zn(4)-O(19)[16]	87.28(16)
O(10)-Zn(1)-O(1)[10]	112.6(2)	O(2)[13]-Zn(4)-O(21)	84.57(17)
O(10)-Zn(1)-O(11)	117.17(17)	O(4)[14]-Zn(4)-O(19)[16]	172.02(15)
O(10)-Zn(1)-O(15)[11]	102.68(18)	O(11)15-Zn(4)-O(4)[14]	87.70(14)
O(11)-Zn(1)-O(1)[10]	115.08(16)	O(11)15-Zn(4)-O(19)[16]	85.46(14)
O(11)-Zn(1)-O(15)[11]	105.53(15)	O(17)-Zn(4)-O(2)[13]	172.40(16)
O(3)[7]-Zn(2)-O(12)	101.87(19)	O(17)-Zn(4)-O(4)[14]	95.97(15)
O(9)-Zn(2)-O(3)[7]	105.25(17)	O(17)-Zn(4)-O(11)[15]	91.11(14)
O(9)-Zn(2)-O(12)	111.20(19)	O(17)-Zn(4)-O(19)[16]	88.28(16)
O(10)-Zn(2)-O(3)[7]	113.3(2)	O(17)-Zn(4)-O(21)	89.23(17)
O(10)-Zn(2)-O(9)	103.28(19)	O(21)-Zn(4)-O(4)[14]	97.21(19)
O(10)-Zn(2)-O(12)	121.1(2)	O(21)-Zn(4)-O(11)[15]	175.01(19)
O(7)-Zn(3)-O(11)[12]	129.62(18)	O(21)-Zn(4)-O(19)[16]	89.58(19)
O(7)-Zn(3)-O(14)[3]	110.37(18)	O(5)-C(9)-C(4)	120.7(4)
O(7)-Zn(3)-O(20)	107.70(19)	O(5)-C(9)-C(10)	120.4(5)
O(11)[12]-Zn(3)-O(14)[3]	103.74(15)	O(16)-C(26)-C(24)	120.7(5)
O(11)12-Zn(3)-O(20)	99.17(16)	O(16)-C(26)-C(27)	120.8(5)
O(20)-Zn(3)-O(14)[3]	102.98(17)	O(2)[13]-Zn(4)-O(11)[15]	94.68(14)
O(2)[13]-Zn(4)-O(4)[14]	89.19(16)		

Symmetry transformations used to generate equivalent atoms: [1] 1+X,+Y,-1+Z; [2] 2+X,1+Y,+Z; [3] +X,+Y,-1+Z; [4] 1+X,1+Y,+Z; [5] +X,1+Y,1+Z; [6] 1+X,1+Y,1+Z; [7] +X,+Y,1+Z; [8] +X,-1+Y,+Z; [9] 1+X,+Y,+Z; [10] -1+X,+Y, 1+Z; [11] +X,1+Y,+Z; [12] +X,-1+Y,-1+Z; [13] -2+X,-1+Y,+Z; [14] -1+X,-1+Y,+Z; [15] -1+X,-1+Y,-1+Z; [16] -1+X,+Y,+Z.

Table S4. Selected bond lengths for **1** after UV irradiation.

Bond lengths (Å)			
O(2)-Zn(3)[1]	1.963(3)	O(11)-Zn(2)	1.902(4)
O(3)-Zn(1)	1.894(4)	O(11)-Zn(3)	1.949(4)
O(6)-Zn(4)[2]	2.141(4)	O(12)-Zn(3)	1.975(4)
O(7)-Zn(3)[3]	1.969(3)	O(14)-Zn(1)[6]	2.002(3)
O(8)-Zn(4)[4]	2.051(3)	O(15)-Zn(2)[7]	1.993(3)
O(9)-Zn(2)	1.967(3)	O(17)-Zn(4)[6]	2.267(4)
O(10)-Zn(1)[5]	1.975(3)	O(18)-Zn(1)[8]	1.983(3)
O(10)-Zn(2)	1.956(3)	O(20)-Zn(4)	2.015(3)
O(10)-Zn(4)[4]	2.132(3)	O(21)-Zn(4)	2.077(4)

Table S5. Selected bond angles for **1** after UV irradiation.

Bond angles (º)			
O(3)-Zn(1)-O(10)[9]	129.77(17)	O(8)[12]-Zn(4)-O(10)[12]	94.22(13)
O(3)-Zn(1)-O(14)[3]	110.14(16)	O(8)[12]-Zn(4)-O(17)[3]	87.41(15)
O(3)-Zn(1)-O(18)[1]	107.91(17)	O(8)[12]-Zn(4)-O(21)	85.02(16)
O(10)[9]-Zn(1)-O(14)[3]	103.52(14)	O(10)[12]-Zn(4)-O(6)[11]	87.34(13)
O(10)[9]-Zn(1)-O(18)[1]	99.11(14)	O(10)[12]-Zn(4)-O(17)[3]	85.64(13)
O(18)[1]-Zn(1)-O(14)[3]	103.21(15)	O(20)-Zn(4)-O(6)[11]	96.45(14)
O(9)-Zn(2)-O(15)[10]	101.20(16)	O(20)-Zn(4)-O(8)[12]	172.38(15)
O(10)-Zn(2)-O(9)	115.37(15)	O(20)-Zn(4)-O(10)[12]	91.36(13)
O(10)-Zn(2)-O(15)[10]	105.84(14)	O(20)-Zn(4)-O(17)[3]	87.85(14)
O(11)-Zn(2)-O(9)	112.24(19)	O(20)-Zn(4)-O(21)	88.95(15)
O(11)-Zn(2)-O(10)	117.41(16)	O(21)-Zn(4)-O(6)[11]	97.80(17)
O(11)-Zn(2)-O(15)	102.12(16)	O(21)-Zn(4)-O(10)[12]	174.78(17)
O(2)[8]-Zn(3)-O(7)[6]	104.99(16)	O(21)-Zn(4)-O(17)[3]	89.17(17)
O(2)[8]-Zn(3)-O(12)	111.26(17)	O(5)-C(9)-C(7)	120.5(4)
O(7)[6]-Zn(3)-O(12)	101.76(17)	O(5)-C(9)-C(10)	120.2(4)
O(11)-Zn(3)-O(2)[8]	102.33(17)	O(16)-C(26)-C(24)	120.7(4)
O(11)-Zn(3)-O(7)[6]	114.22(18)	O(16)-C(26)-C(27)	121.1(4)
O(11)-Zn(3)-O(12)	121.44(19)	O(8)12-Zn(4)-O(6)[11]	89.00(15)
O(6)[11]-Zn(4)-O(17)[3]	171.85(14)		

Symmetry transformations used to generate equivalent atoms: [1] -1+X,+Y,1+Z; [2] +X,1+Y,1+Z; [3] -1+X,+Y,+Z; [4] 1+X,1+Y,1+Z; [5] 1+X,1+Y,+Z; [6] 1+X,+Y,+Z; [7] +X,-1+Y,+Z; [8] 1+X,+Y,-1+Z; [9] -1+X,-1+Y,+Z; [10] +X,1+Y,+Z; [11] +X,-1+Y,-1+Z; [12] -1+X,-1+Y,-1+Z.

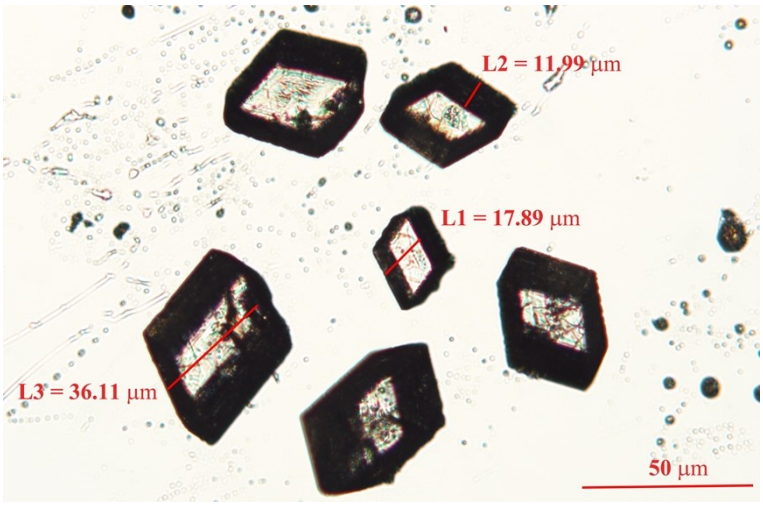

Figure S1. Optical image of as-synthesized **1** single crystals.

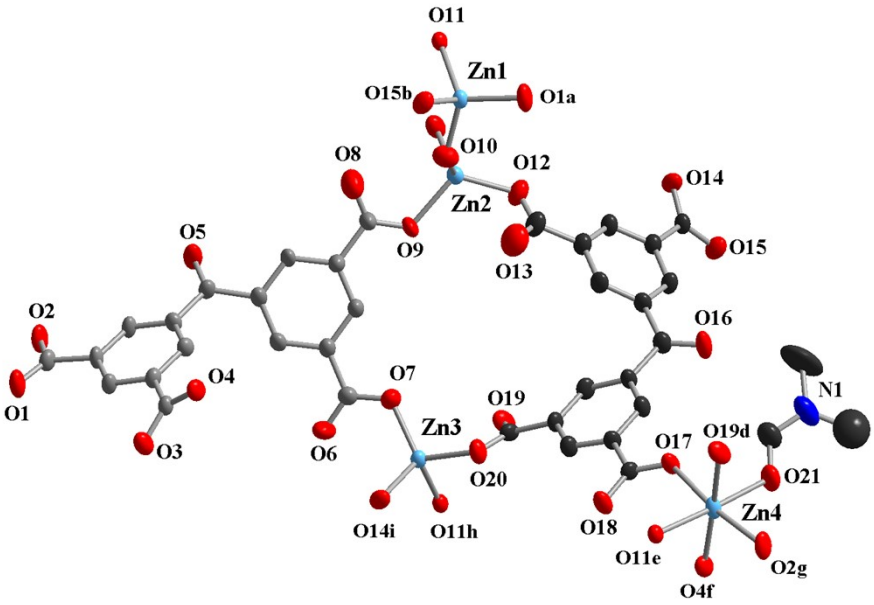

Figure S2. The coordination environments of Zn^{2+} cations and $cdip^{4-}$ ligands in **1**. H atoms are omitted for clarity (similarly hereafter). Colour code: Zn in cyan, O in red, N in blue, and C in grey and black.

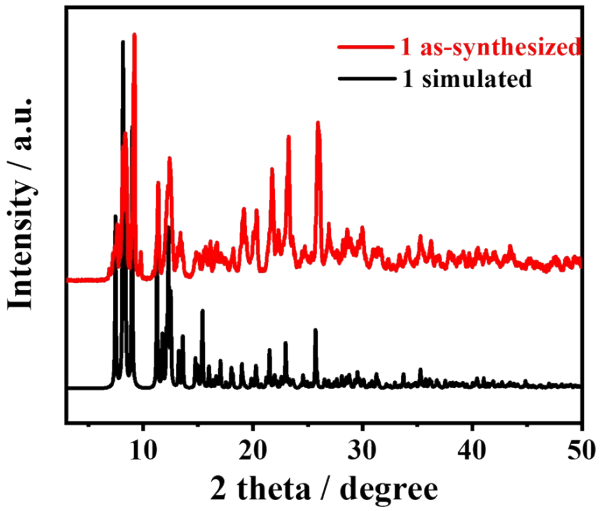

Figure S3. The PXRD patterns for the as-synthesized **1**, compared with the simulated pattern of **1**.

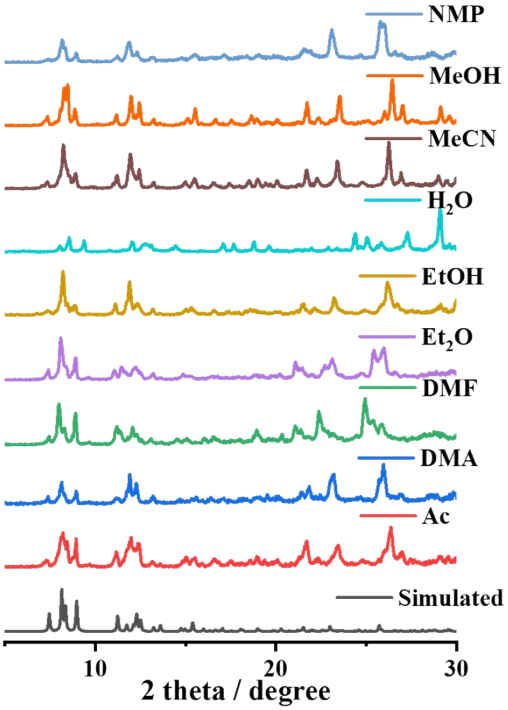

Figure S4. The PXRD patterns of **1** soaked in different solvents for 72 h.

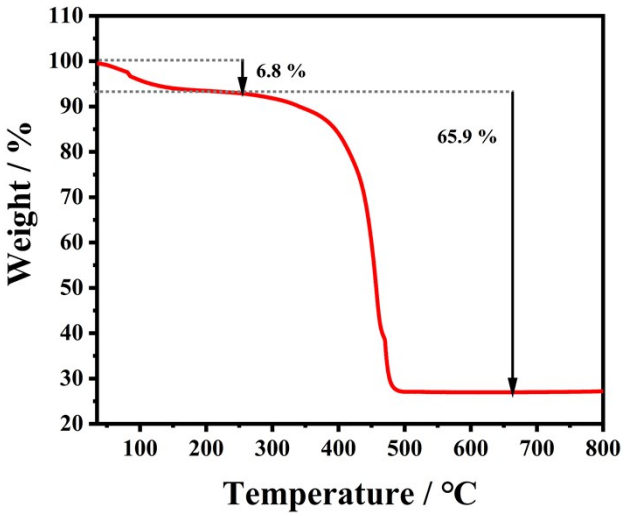

Figure S5. Thermogravimetric analysis (TGA) curve of activated **1**.

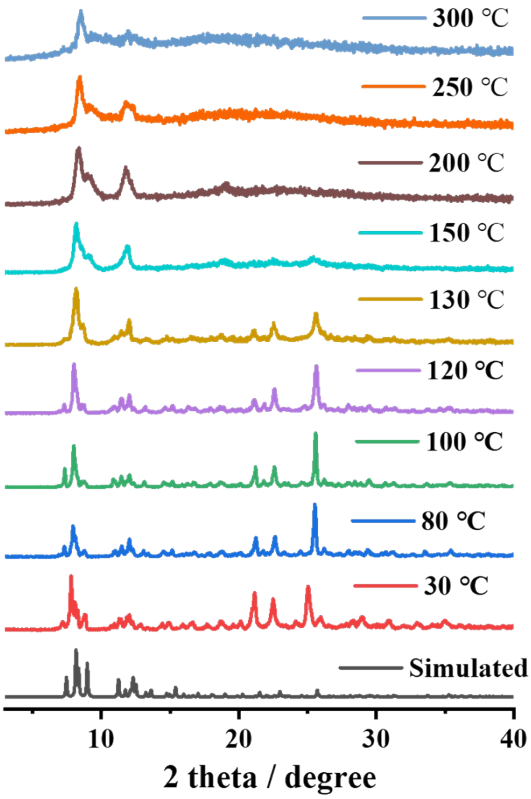

Figure S6. Variable temperature PXRD patterns of **1**.

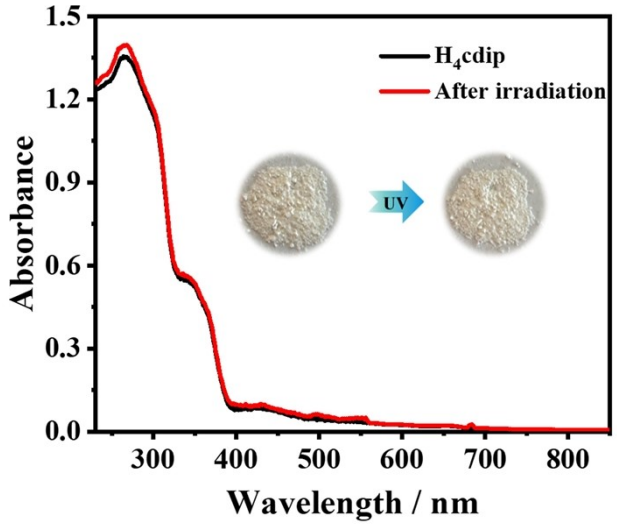

Figure S7. UV-vis absorption spectra of H_4cdip before and after UV irradiation.

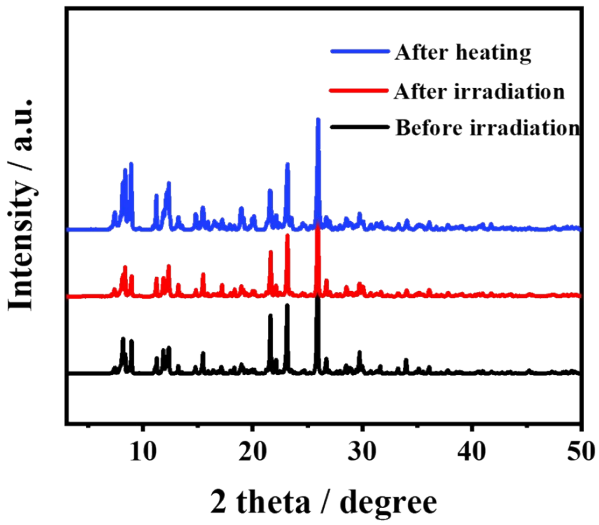

Figure S8. The PXRD patterns of **1** before and after UV irradiation and after heating at 100 ℃.

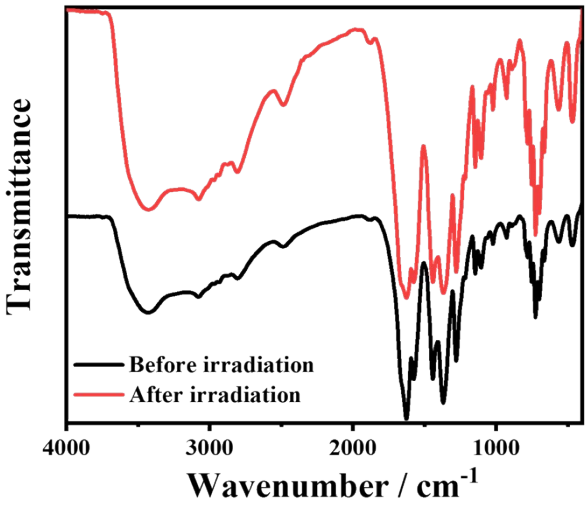

Figure S9. The FT-IR patterns of **1** before and after UV irradiation.

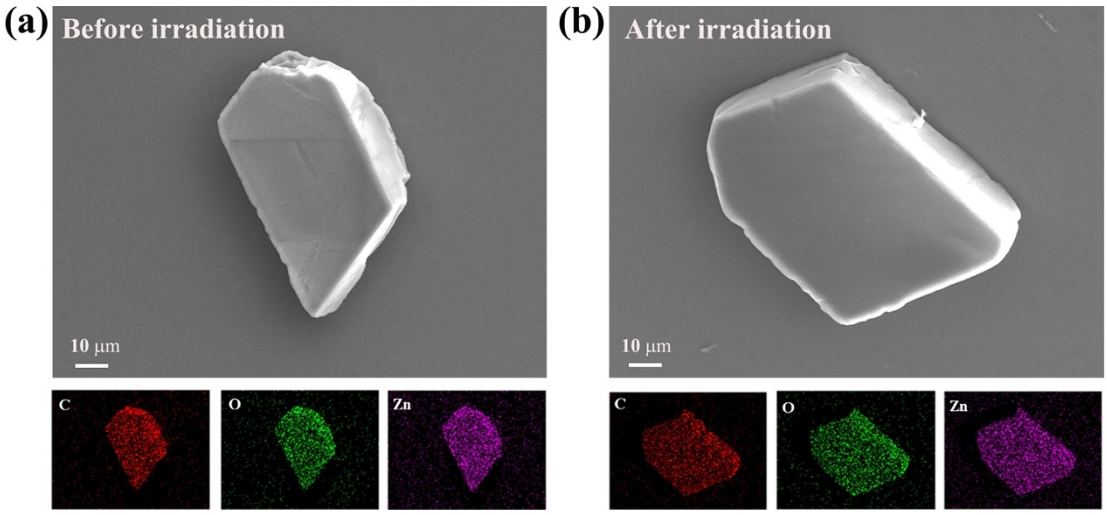

Figure S10. SEM images of **1** before and after UV irradiation.

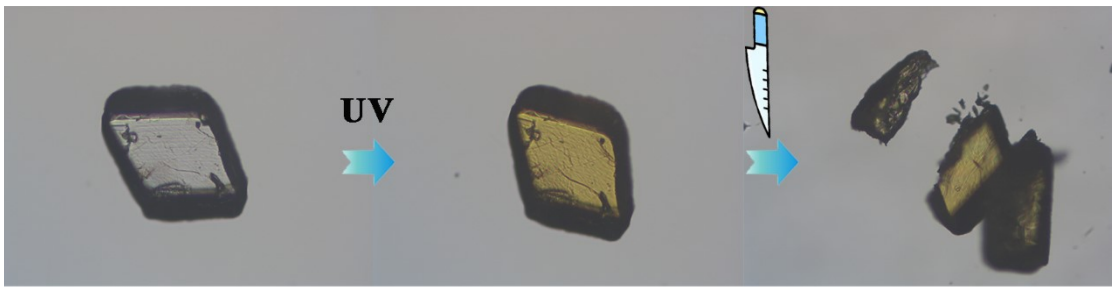

Figure S11. Interiorr and exterior color transition of the single crystal of **1** under UV irradiation.

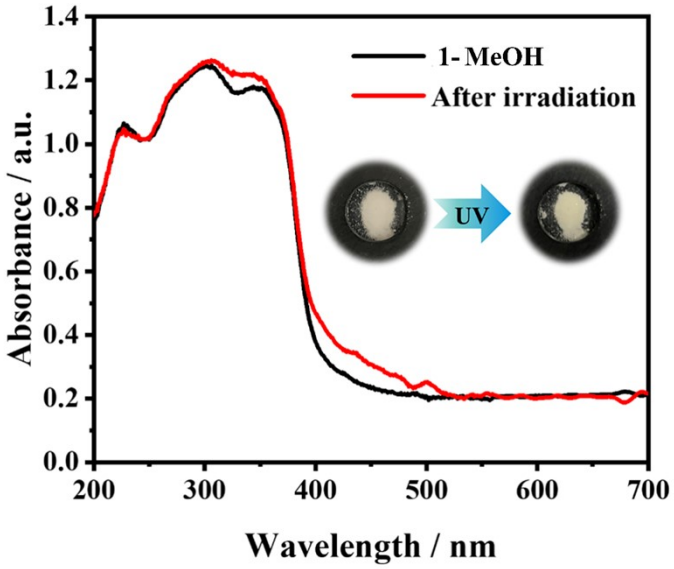

Figure S12. UV-vis absorption spectra of **1-MeOH** before and after UV irradiation for 20 min.

Figure S13. The printing effect of prepared printing paper at different irradiation time.