Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Two new photochromic supramolecular compositions based on viologen: photocontrolled fluorescence, aniline detection and inkless erasable printing performance

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Synthesis of 3-BCBPY·2Cl and 4-BCBPY·2Cl.

3-BCBPY·2Cl: Dissolve 4,4'-bipyridine (10 mmol, 1.56 g) and 3-cyanobenzyl chloride (20 mmol, 3.92 g) in 25mL of N, N'-dimethylformamide (DMF), and stir at 110°C for 6h. Filtration yielded a light yellow product. The obtained product was washed 3 times with hot DMF and recrystallized with methanol to finally obtain a pale yellow solid. The yield was 90%.

4-BCBPY·2Cl: The synthesis process is similar to 3-BCBPY·2Cl except that 4-cyanobenzyl chloride (20 mmol, 3.92 g) is used instead of 4-cyanobenzyl chloride (20 mmol, 3.92 g). A yellow solid is obtained. The yield was 90%.

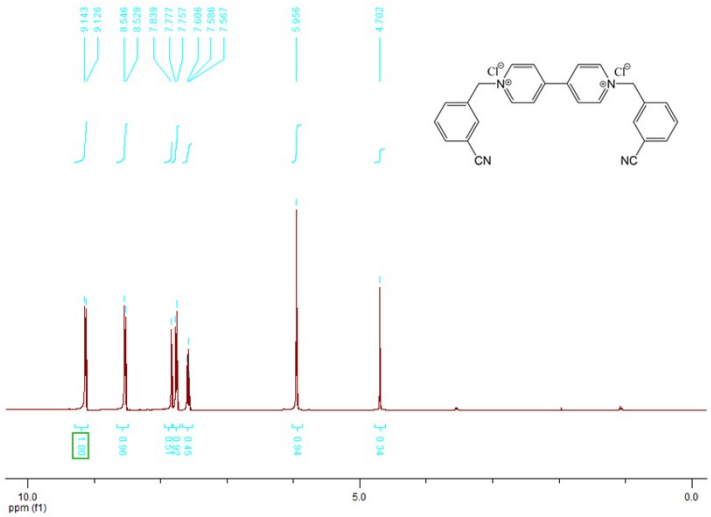


Figure S1. The ^{1}H NMR spectrum of 3-BCBPY·2Cl in D_2O (600 MHz).

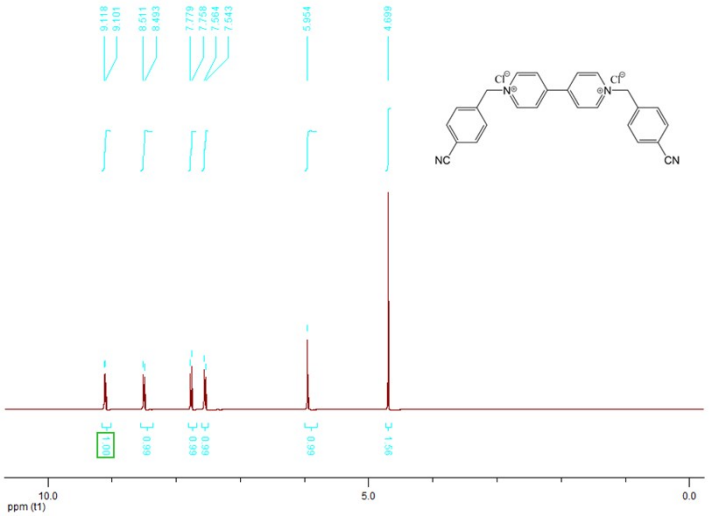


Figure S2. The ^{1}H NMR spectrum of 4-BCBPY·2Cl in D_2O (600 MHz).

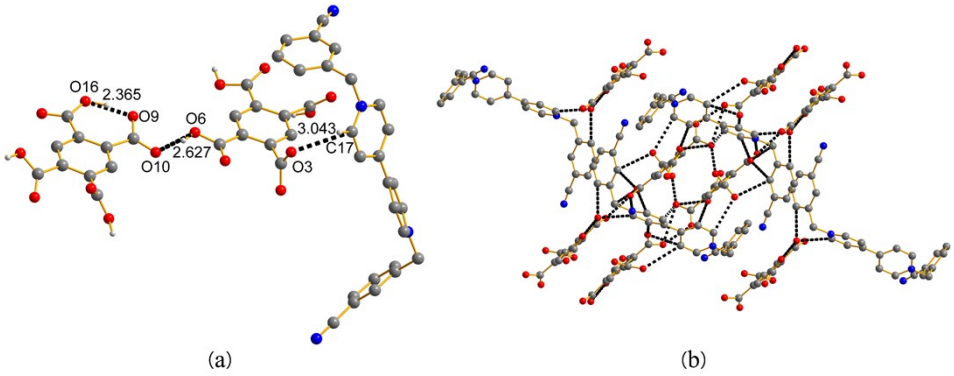


Figure S3. (a) Schematic diagram of partial hydrogen bond of Compound **1**; (b) The hydrogen bond network of Compound **1**.

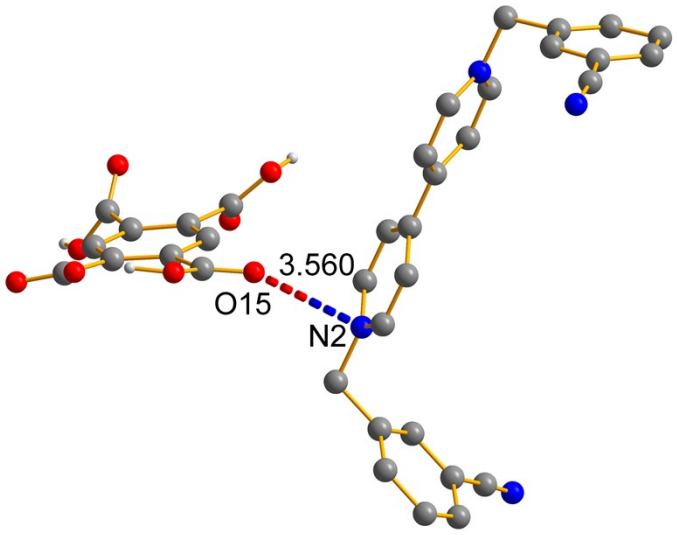


Figure S4. ET distances for Compound **1**.

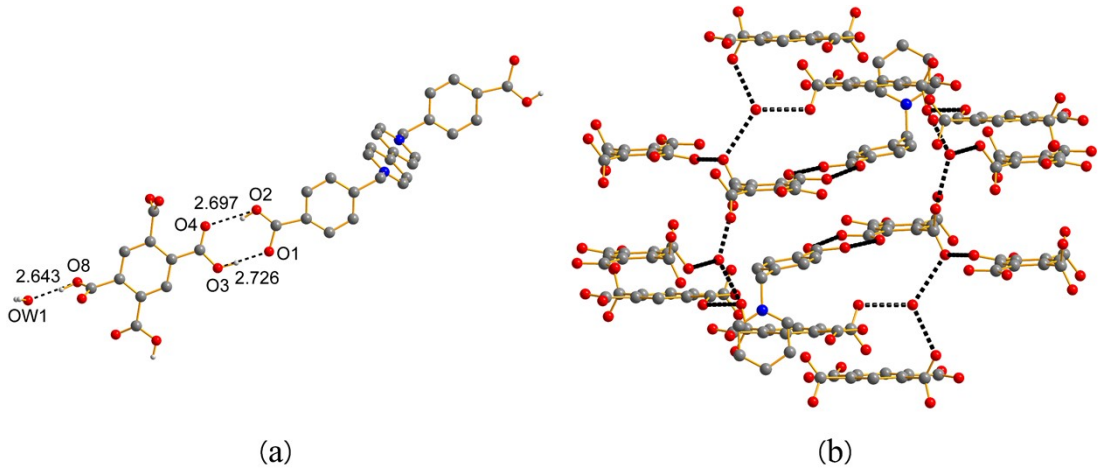


Figure S5. (a) Schematic diagram of partial hydrogen bond of Compound **2**; (b) The hydrogen bond network of Compound **2**.

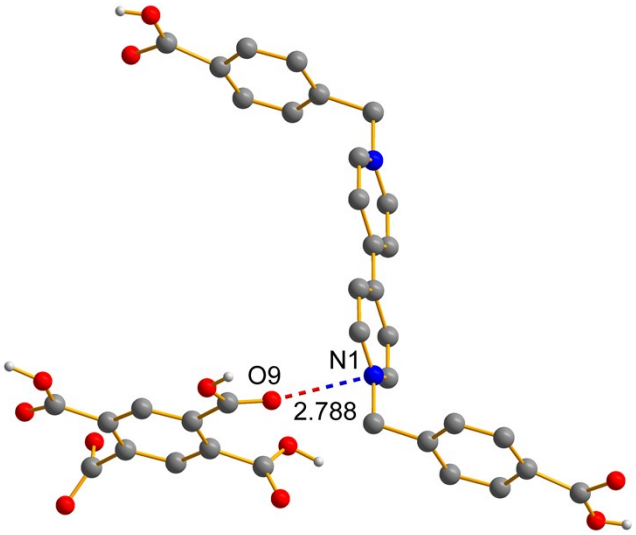


Figure S6. ET distances for Compound **2**.

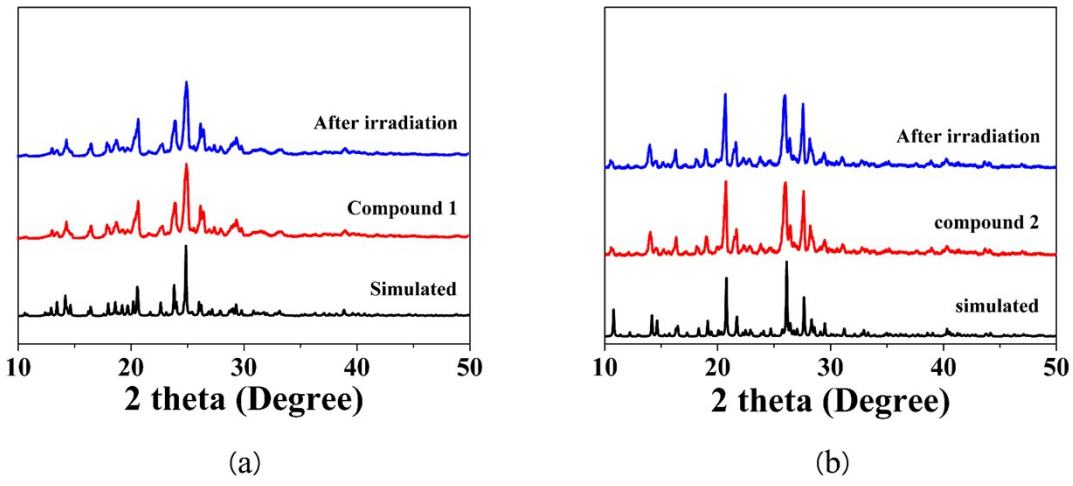


Figure S7. The PXRD spectra before and after irradiation for **1**(a) and **2**(b).

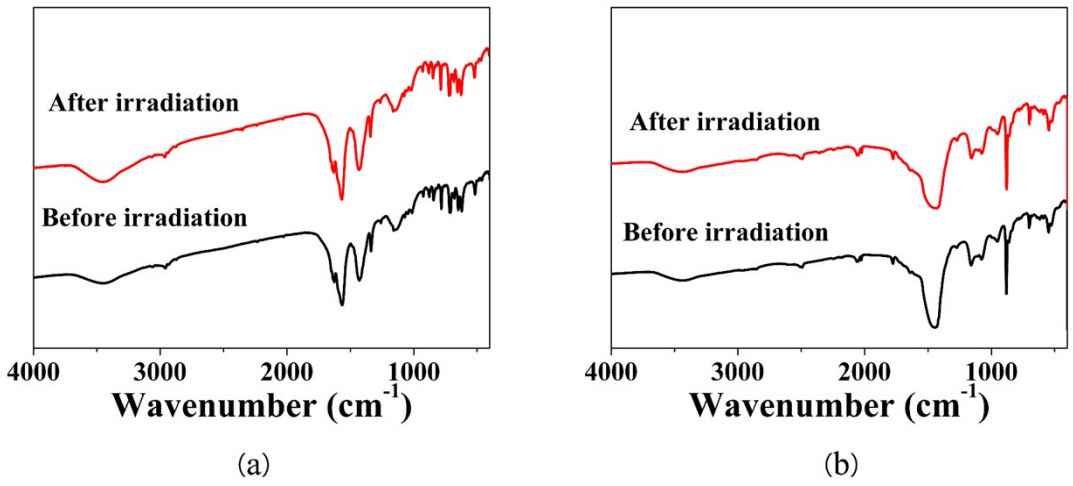


Figure S8. FT-IR spectra of Compounds **1**(a) and **2**(b).

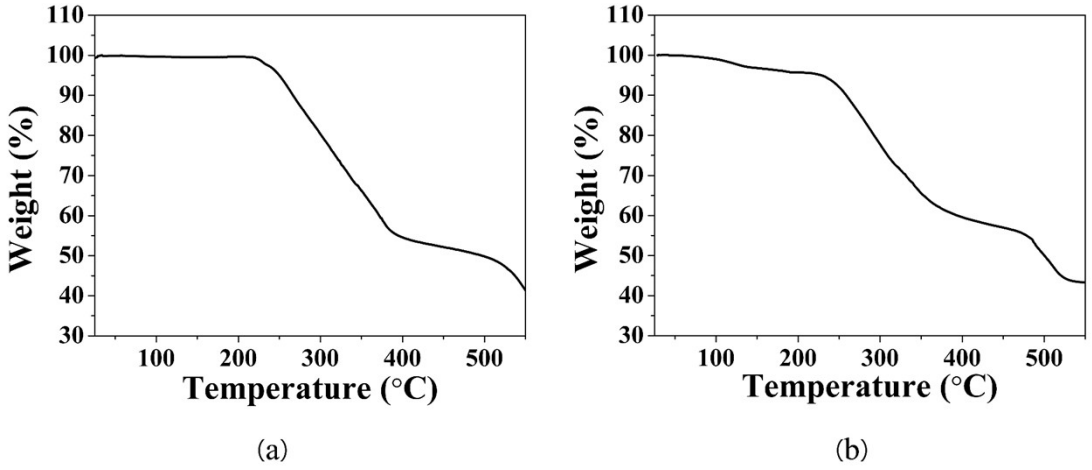


Figure S9. Thermogravimetric curves of Compounds **1**(a) and **2**(b).

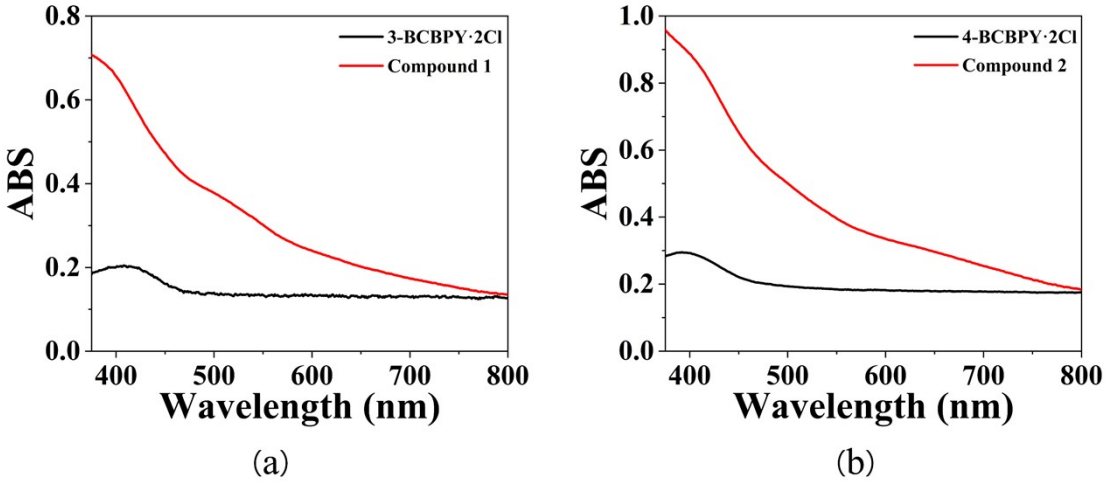
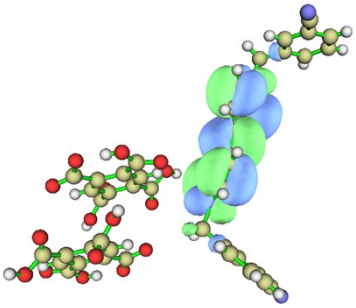
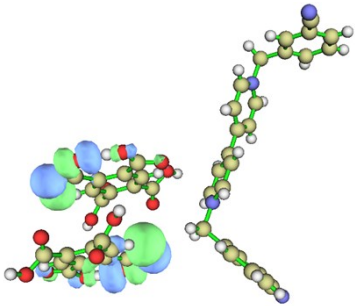


Figure S10. (a) UV-Vis spectra of 3-BCBPY.2Cl and compound **1**; (b) UV-Vis spectra of 4-BCBPY.2Cl and compound **2**.

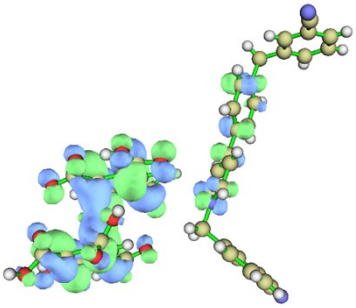
Compound **1**



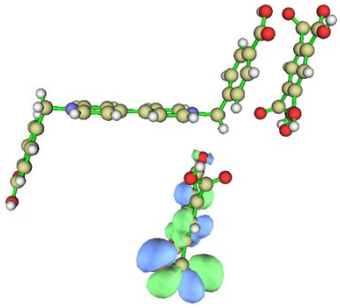
LUMO



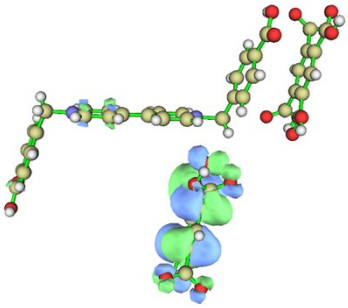
HOMO-1



LUMO+1

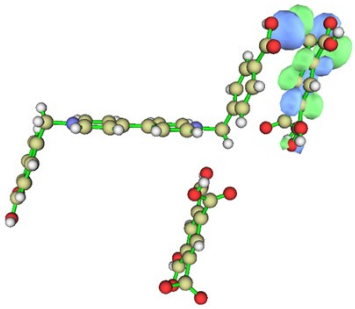


HOMO

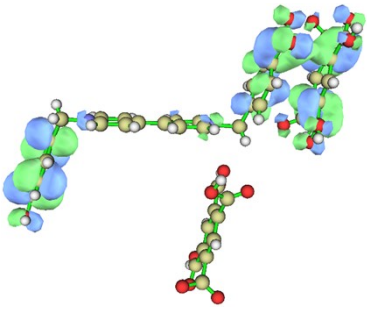


LUMO+4

Compound **2**



HOMO-1



LUMO+3

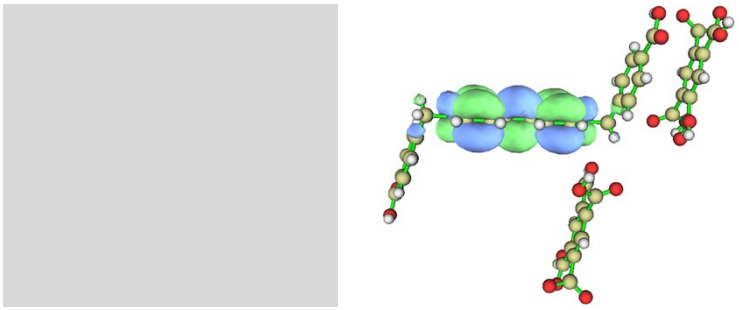


Figure S11. Caluclated HOMO and LUMO orbitals of compounds **1** and **2**.

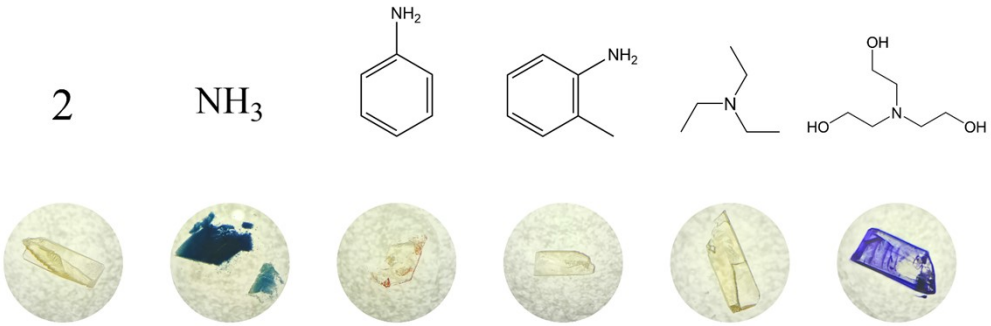


Figure S12. Photographs of Compound **2** before and after exposure to different amines.

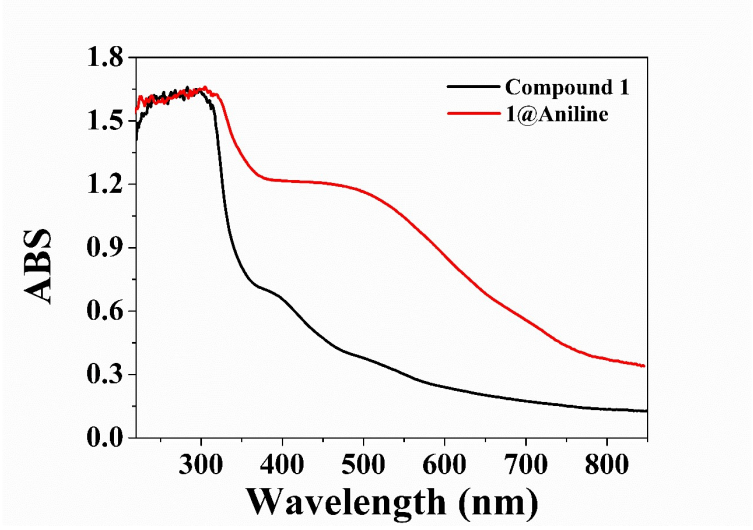


Figure S13. The UV-Vis spectra of Compounds **1** and **1**@Aniline.

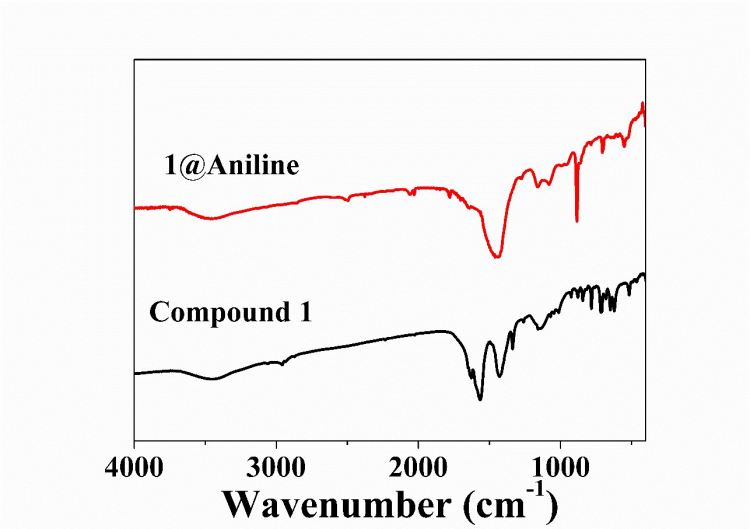


Figure S14. FT-IR spectra of Compound **1** and **1**@Aniline.

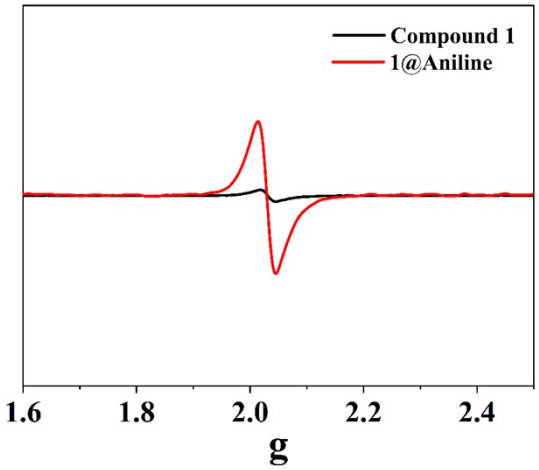


Figure S15. ESR spectra of Compounds **1** and **1**@Aniline.

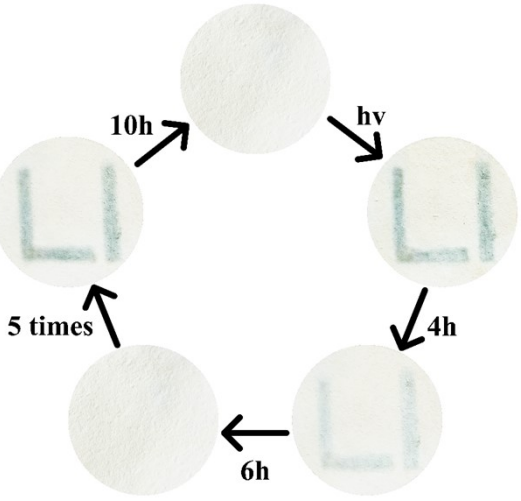


Figure S16. Photograph of **1**@ethanol after repeated printing.

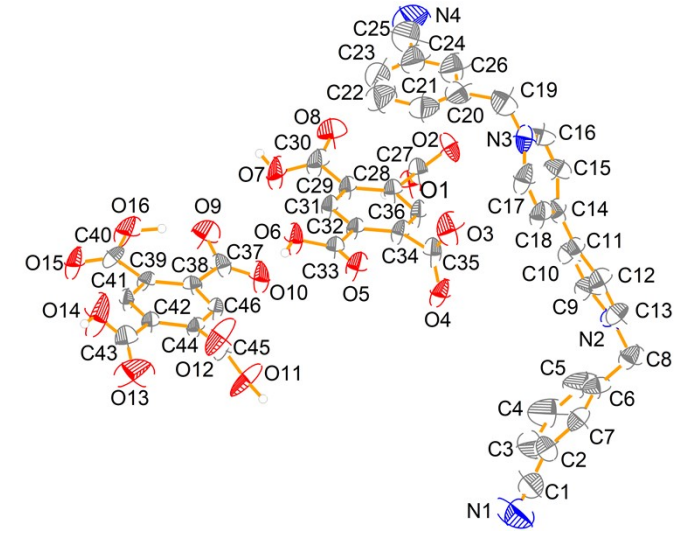


Figure S17. The asymmetric units of the structures (thermal ellipsoids) for Compound **1**.

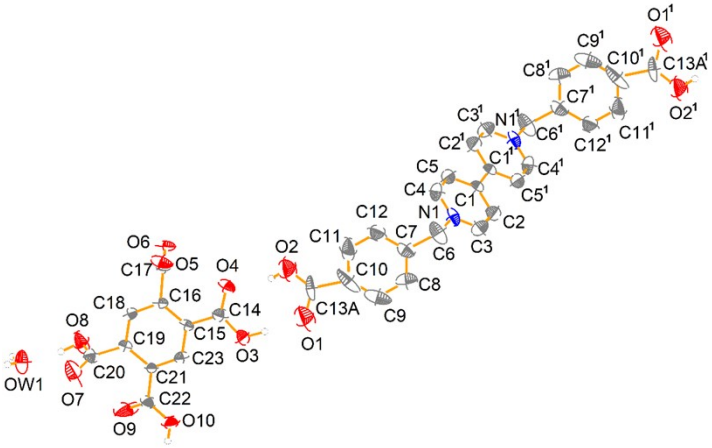


Figure S18. The asymmetric units of the structures (thermal ellipsoids) for Compound **2**

(Symmetry code: [1]2-x, -y, -z).

Table S1. Crystal data and structure refinement for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{46}H_{29.58}N_4O_{16}$	$C_{46}H_{35}N_2O_{21}$
Formula weight	894.32	951.76
Temperature/K	296.15	296.15
Crystal system	triclinic	monoclinic
Space group	*P-1*	*P2₁/c*
a/Å	9.7493(16)	9.6809(14)
b/Å	14.816(2)	15.526(2)
c/Å	14.827(2)	13.6809(17)
α/°	81.262(3)	90
β/°	81.825(3)	94.407(3)
γ/°	72.098(3)	90
Volume/Å^3	2003.9(5)	2050.2(5)
Z	2	2
ρ_{calc}g/cm^3	1.482	1.542
μ/mm^{-1}	0.114	0.124
2*θ* range for data collection/°	2.908 to 54.868	3.974 to 55.382
Goodness-of-fit on F^2	1.036	1.062
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0910$, $wR_2 = 0.2500$	$R_1 = 0.0896$, $wR_2 = 0.1823$
Final R indexes [all data]	$R_1 = 0.1507$, $wR_2 = 0.2980$	$R_1 = 0.2066$, $wR_2 = 0.2192$

Table S2. O/C−H···O interactions Geometry (Å, °) for **1** and **2**.

	D-H...A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
Compound 1	C13-H13…O5[1]	0.93	2.34	3.175(5)	148.6
	C13-H13…O1[2]	0.93	2.63	3.201(6)	120.1
	C12-H12…O1[2]	0.93	2.55	3.161(6)	123.5
	C12-H12…O1A[2]	0.93	2.24	3.143(9)	163.3
	C10-H10…O13[3]	0.93	2.16	3.088(6)	173.1
	C18-H18…O82	0.93	2.23	3.120(5)	159.6
	C7-H7…O5[1]	0.93	2.57	3.402(6)	149.3
	C7-H7…O3[1]	0.93	2.58	3.313(6)	135.9
	C9-H9…O9[4]	0.93	2.31	3.220(6)	165.2
	C15-H15…O12[3]	0.93	2.42	3.332(6)	165.5
	C15-H15…O13[3]	0.93	2.75	3.380(7)	126.0
	C8-H8A…O5[1]	0.97	2.59	3.389(5)	139.3
	C17-H17…O3	0.93	2.42	3.043(7)	124.1
	O1-H1…O4[4]	0.82	1.62	2.373(6)	151.7
	C16-H16…N4[5]	0.93	2.35	3.219(10)	156.0
	C5-H5…O9[4]	0.93	2.59	3.351(6)	139.6
	O16-H16A…O9	1.04(5)	1.34(5)	2.364(5)	168(4)
	O6-H6…O10	0.88(6)	1.76(6)	2.627(4)	170(6)
	O11-H11…O15[2]	1.00(7)	1.72(7)	2.704(4)	168(6)
	O11-H11…O16[2]	1.00(7)	2.52(7)	3.152(5)	121(5)
	O14-H14…O2[6]	0.86(2)	1.79(2)	2.649(6)	177(7)
	O14-H14…O1[6]	0.86(2)	2.54(6)	3.093(7)	123(5)
	O14-H14…O2A[6]	0.86(2)	2.03(4)	2.797(10)	148(6)
	O14-H14…O1A[6]	0.86(2)	2.36(5)	3.009(9)	133(6)
	O7-H7A…O4[7]	0.84(2)	1.91(5)	2.678(4)	152(9)
Compound 2	OW1-HW1A...O5[1]	0.85	1.86	2.685(5)	162.3
	OW1-HW1B...O6[2]	0.85	1.99	2.798(4)	158.3
	O2-H2A...O4	0.82	1.91	2.697(8)	159.6
	O8-H8A...OW1	0.92(5)	1.77(6)	2.644(5)	158(5)
	O10-H10...O6[3]	0.84(6)	1.74(6)	2.572(4)	171(6)
	O3-H3A...O1	0.98(7)	1.75(7)	2.727(5)	176(6)

Symmetry codes of 1: [1]2-x, 1-y, 1-z; [2]1+x, +y, +z; [3]+x, -1+y, 1+z; [4]1-x, 1-y, 1-z; [5]1-x, -y, 1-z; [6]+x, 1+y, -1+z; [7]-1+x, +y, +z.

Symmetry codes of 2: [1]1-x, 2-y, 1-z; [2]1-x, 1/2+y, 1/2-z; [3]-1+x, +y, +z.

Table S3. Atomic Occupancy for **1** and **2**.

	Atom	**Occupancy**
Compound 1	O1	0.584(8)
	O1A	0.416(8)
	O2	0.584(8)
	O2A	0.416(8)
	H1	0.584(8)
Compound 2	C13A	0.497(11)
	C13B	0.503(11)
	O2	0.5
	H2A	0.5

Table S4. Results of the TDDFT/B3LYP-lanl2dz calculations related to **1** and **2**.

	Excited states	Orbital description	λ_{max} / nm		f
			Exp.	Calc.	
Compound **1**	8	$HOMO_{-1}$→$LUMO$ (51.20%)	404	364	0.0034
	2	$HOMO_{-1}$→$LUMO_{+1}$ (54.24%)	618	514	0.0001
Compound **2**	8	$HOMO$→$LUMO_{+4}$ (64.78%)	406	377	0.0737
	7	$HOMO_{-1}$→$LUMO_{+3}$ (46.67%)		379	0.0651
	1	$HOMO$→$LUMO$ (70.67%)	624	622	0.0001