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Electronic Supplementary Information

Photofluorochromic Organic Supramolecular Compounds for Multiple Dynamic Anticounterfeiting

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Fig. S17 **(a)** Luminescence spectrum of compound **1** in the initial state and UV-vis diffuse reflectance spectrum of compound **1** in the colored state, **(b)** Luminescence spectrum of compound **2** in the initial state and UV-vis diffuse reflectance spectrum of compound **2** in the colored state.

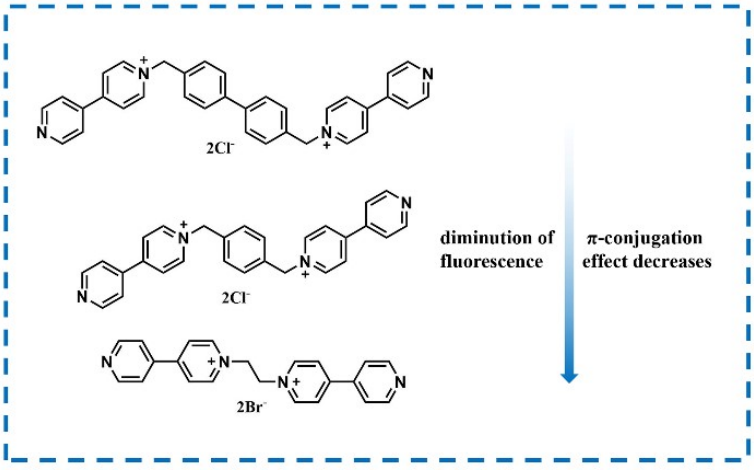
1. Experimental section

Materials and characterization methods

All reagents were purchased commercially and used without further purification. The ligands Bmypd, Pbpy and Bpyen were synthesized as reported. The IR spectra were measured by a Mattson Alpha-Centauri spectrometer. Powder X-ray diffraction (PXRD) patterns were collected on Rigaku Dmax 2000 X-ray diffractometer using Cu Kα radiation (λ = 0.15418 Å) at room temperature in the 2θ range of 5–50°. UV–Vis absorption spectra were measured on a Cary7000 UV-Vis-NIR spectrophotometer. ESR spectra were recorded at X-band frequency (9.867 GHz) on a Bruker ELEXSYS E500 spectrometer. TG analysis was performed on a Perkin-Elmer model TG-7 analyzer from room temperature to 800 °C under nitrogen. A PLSSXE300C 300 W xenon lamp (ca. 2.4 W/cm^2) was used to illuminate samples for achieving various spectra. Fluorescence spectra were obtained with a FLSP920 fluorescence spectrometer equipped with a 450 W Xe lamp and a R928P PMT detector. A UV light (15 W) was used for photofluorescent color change. Elemental analyses were performed on a PerkinElmer 2400 CHN elemental analyzer.

Preparation of anti-counterfeiting images

First, we prepared the "38", "77", "NENU", "sad face" and QR code anti-counterfeiting image model. Different samples are filled up the "38", "77", and "NENU" models for further photo-treat. For hybrid two-dimensional code, compound 1 is filled into the QR code model, sealed with a transparent film, and then a transparent film compound 2 is covered to the first layer of the film. The depth of the model and the film is 0.2mm.



Scheme 1. The molecular structure of (Bmypd)Cl_2, (Pbpy)Cl_2, (Bpyen)Br_2.

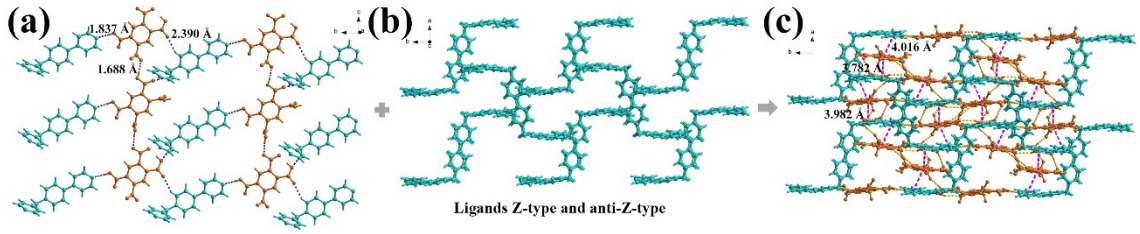


Fig. S1 Structure of compound **1** **(a)** Two-dimensional layer. **(b)** Types of ligands. **(c)** Three-dimensional supramolecule.

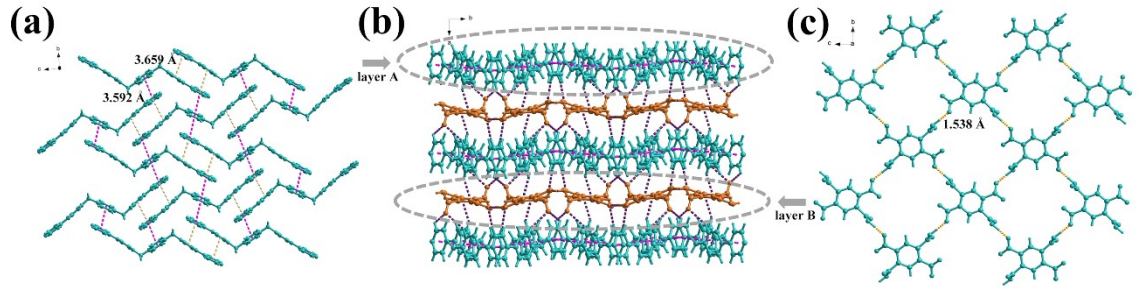


Fig. S2 Structure of compound **2** **(a)** π–π stacking interactions between viologen cations. **(b)** Three-dimensional supramolecule. **(c)** Hydrogen-bonded two-dimensional layer.

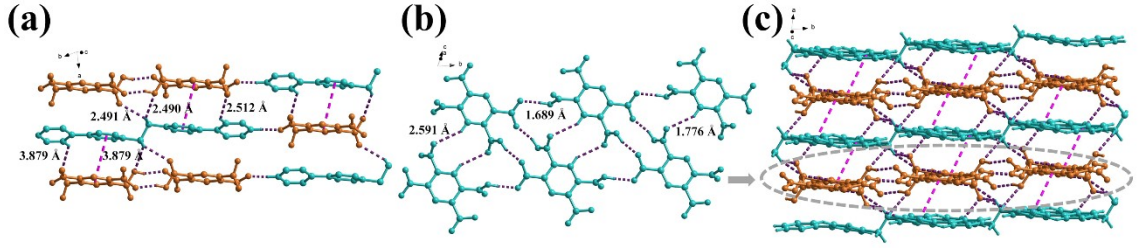


Fig. S3 Structure of compound **3** **(a)** Hydrogen-bond two-dimensional layer and π···π stacking interactions. **(b)** Hydrogen-bonded two-dimensional layer. **(c)** Three-dimensional supramolecule.

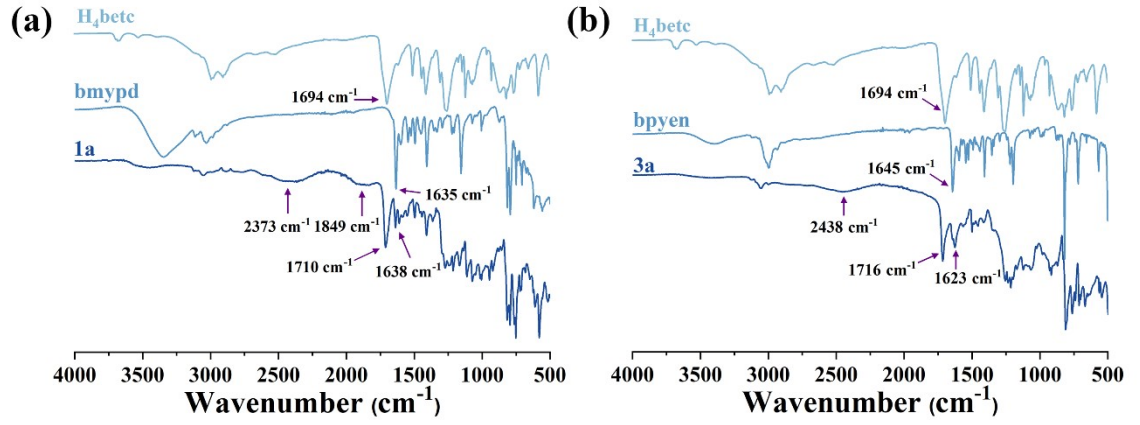


Fig. S4 FT-IR spectra of compounds **1** (**a**) and **3**(**b**). Labels: **1a** and **3a**; bmpyd·HCl and bpyen·HCl; bmpyd and bpyen.

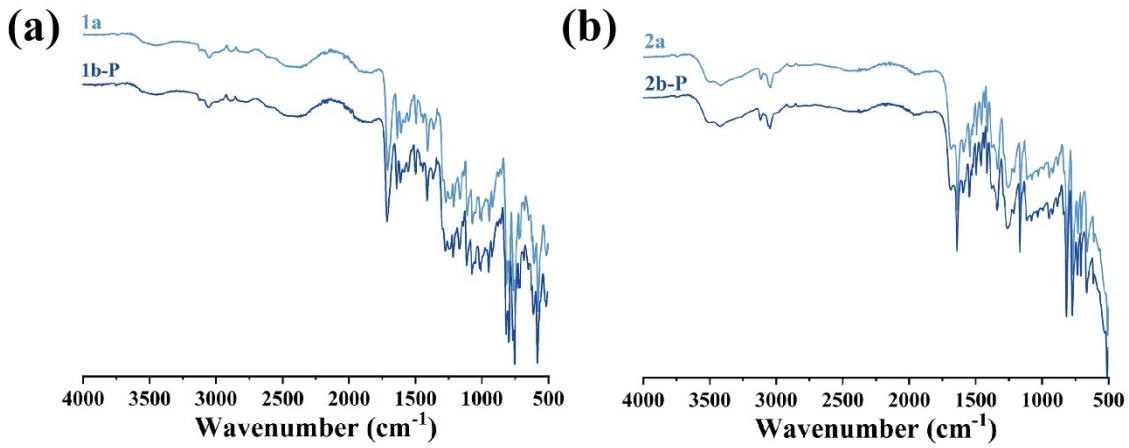


Fig. S5 FT-IR spectra of compounds **1** (**a**) and **2** (**b**). Labels: **1a** and **2a**: before irradiation; **1b-P** and **2b-P**: after photo irradiation.

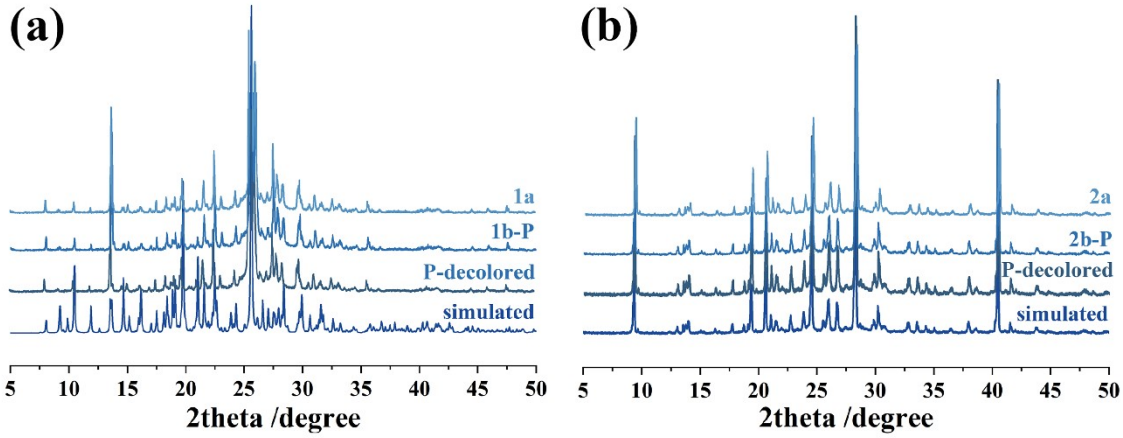


Fig. S6 PXRD patterns of compounds **1** (**a**) and **2** (**b**). Labels: **1a** and **2a**: before irradiation; **1b-P** and **2b-P**: after photo irradiation; **p-decolored (1)**: heating in 120 °C for 0.5 h, and **decolored (2)**: placing in the dark for 7 days, respectively; **simulated**: simulated patterns from single-crystal X-ray structure data.

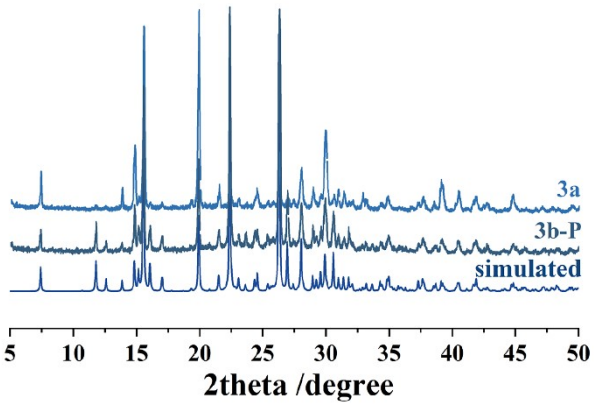


Fig. S7 PXRD patterns of compound **3**. Labels: **3a**: before irradiation; **3b-P**: after photo irradiation.

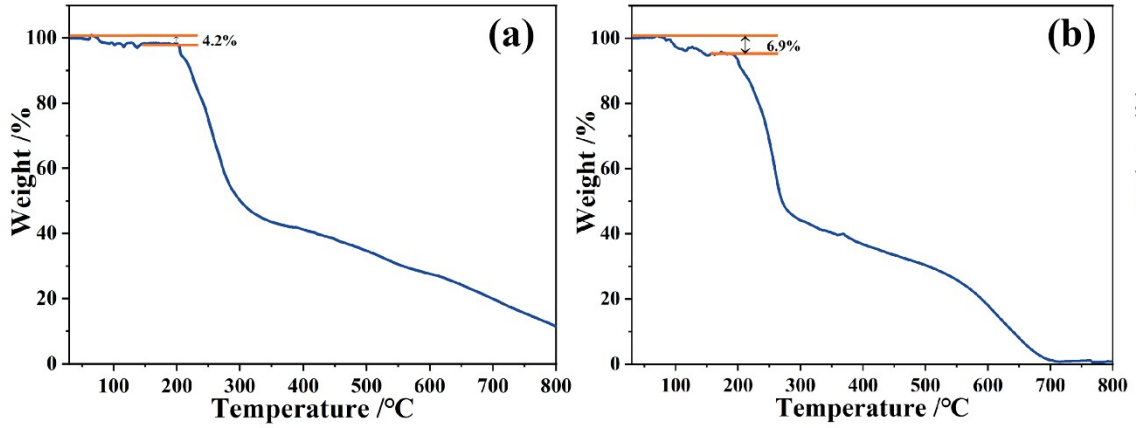


Fig. S8 TGA curve of compound **1 (a)**, compound **2 (b)** was investigated using powder samples under N_2. The corresponding weight loss values are 4.2% and 6.9% (calc. 5.0% and 7.4 %) corresponding to the loss of three free H_2O molecules.

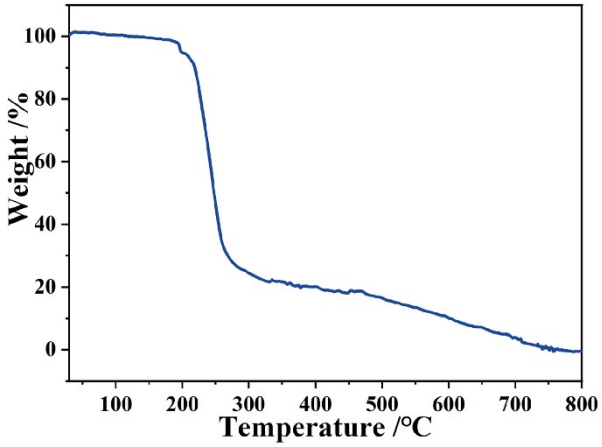


Fig. S9 TGA curve of compound **3** was investigated using powder samples under N_2.

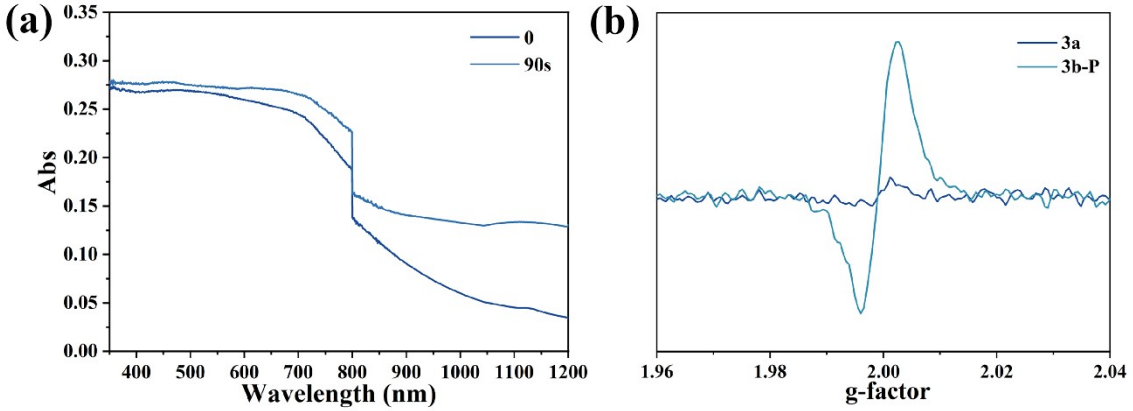


Fig. S10 (a) UV–vis spectra of compound **3**, **(b)** before and after Xe lamp irradiation. EPR spectra of compound **3**.

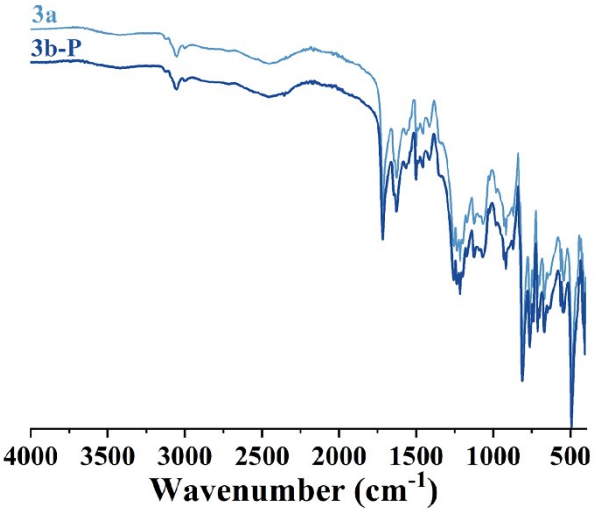


Fig. S11 FT-IR spectra of compound **3**. Labels: **3a**: before irradiation; **3b-P**: after photo irradiation.

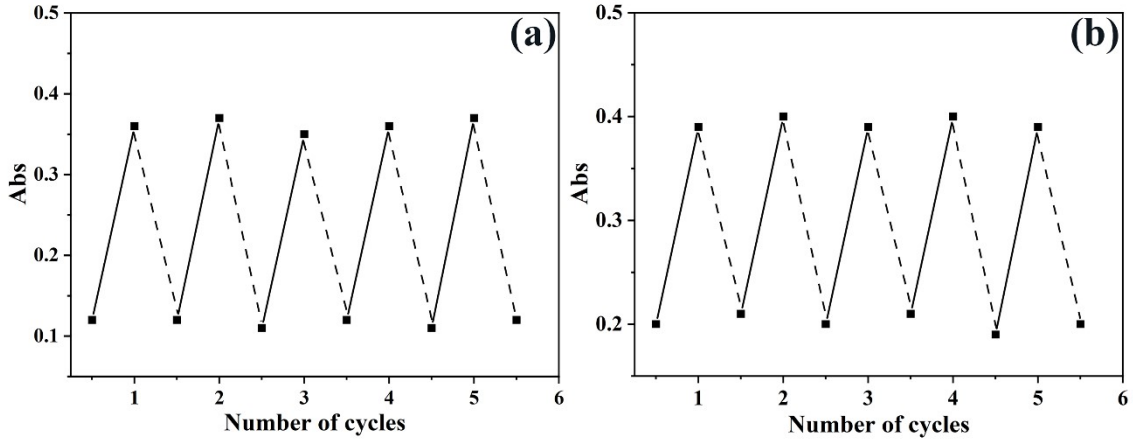


Fig. S12 (a) Cyclability of compound **1**, **(b)** cyclability of compound **2**.

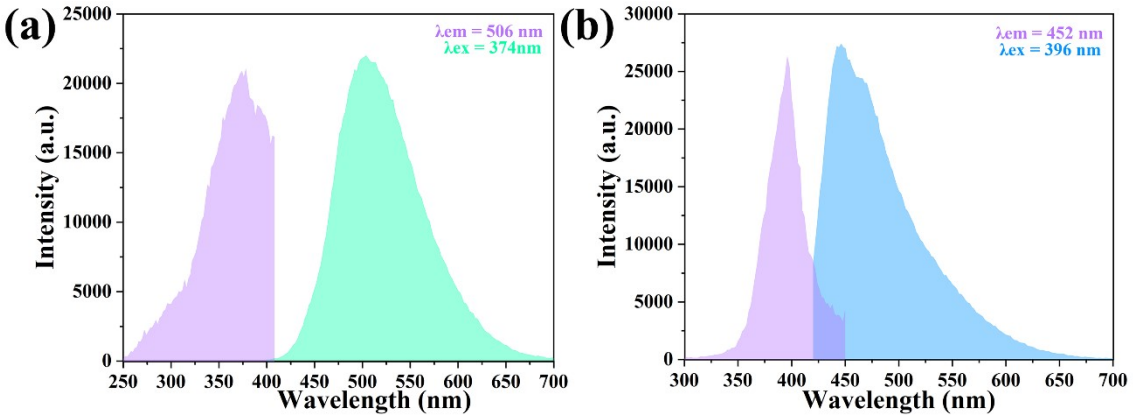


Fig. S13 (a) PL emission and excitation spectra of the compound **1**, **(b)** PL emission and excitation spectra of the compound **2**.

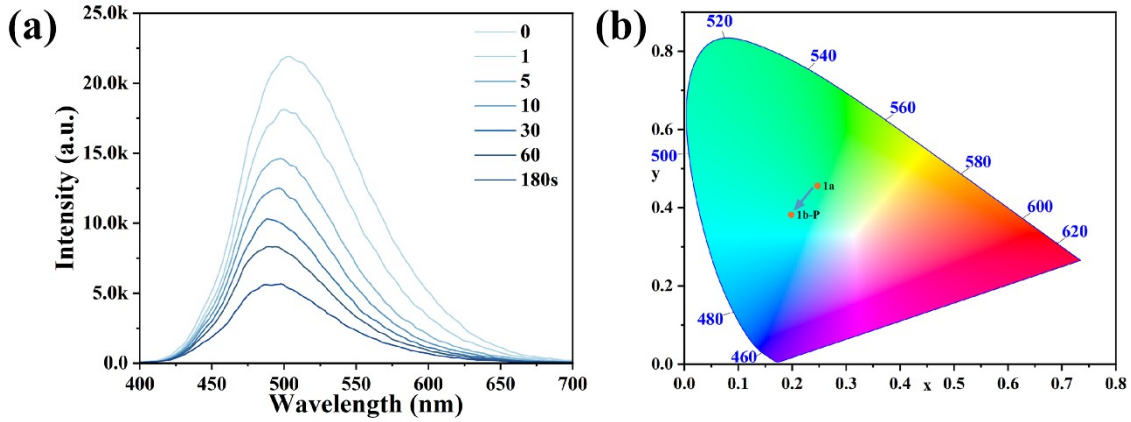


Fig. S14 (a) Steady-state emission spectra of compound **1** after irradiation, **(b)** CIE coordinates of compound **1** before and after irradiation at room temperature.

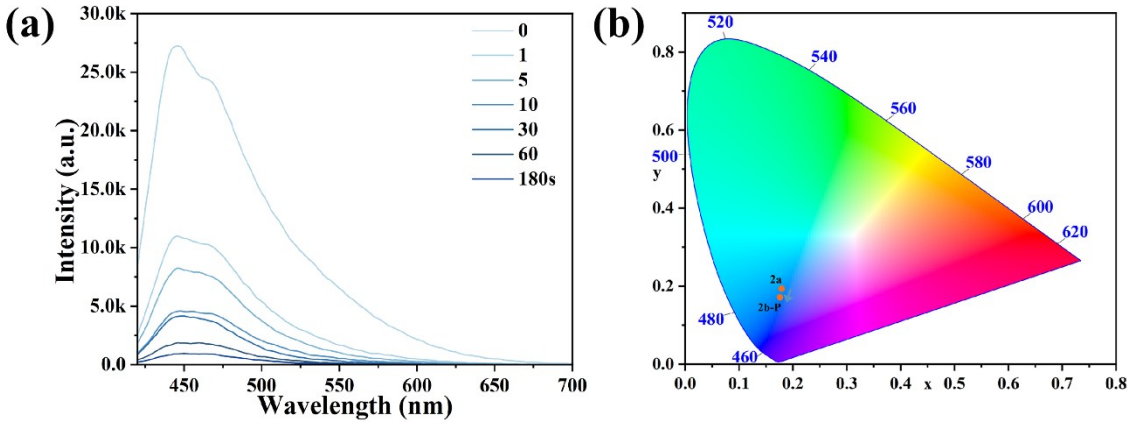


Fig. S15 (a) Steady-state emission spectra of compound **2** after irradiation, **(b)** CIE coordinates of compound **2** before and after irradiation at room temperature.

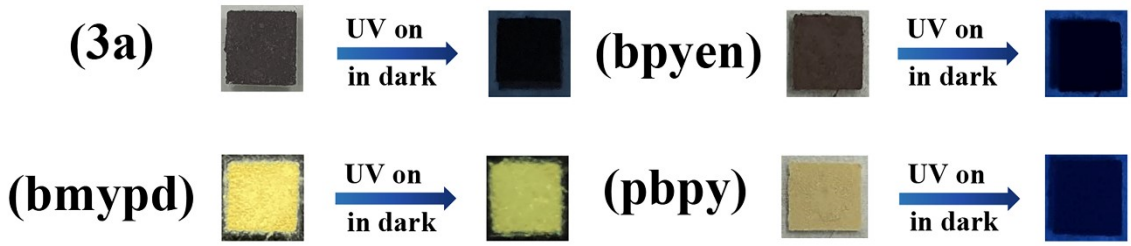


Fig. S16 Photographs of compound **3**, bpyen, pbpy and bmypd before and after UV irradiation (365 nm) at room temperature.

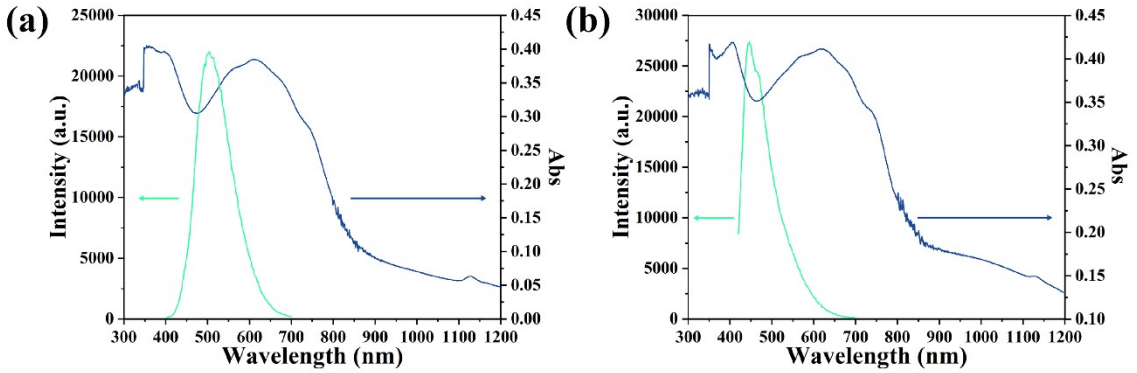


Fig. S17 (a) Luminescence spectrum of compound **1** in the initial state and UV-vis diffuse reflectance spectrum of compound **1** in the colored state, **(b)** Luminescence spectrum of compound **2** in the initial state and UV-vis diffuse reflectance spectrum of compound **2** in the colored state.

Tables.

Table S1. Crystal Data and Structure Refinements for **1**, **2**, **3**

Empirical formula	$C_{54}H_{46}N_4O_{19}$ **(1)**	$C_{38}H_{36}N_4O_{11}$**(2)**	$C_{42}H_{32}N_4O_{16}$**(3)**
Formula	1052.93	722.69	846.70
T (K)	295	295	284
Crystal system	monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a (Å)	13.9394(15)	9.191(3)	8.0044(2)
b (Å)	17.884(2)	12.609(4)	9.6508(2)
c (Å)	19.2029(17)	14.370(4)	12.8662(3)
α (°)	90	90	71.243(1)
β (°)	94.343(3)	94.56(2)	73.948(1)
γ (°)	90	90	73.077(1)
V(Å^3)	4773.4(9)	1660.1(9)	881.82(4)
Z	4	2	1
D_x/Mg m^{-3}	1.465	1.450	1.598
F(000)	2192	756	438
U(mm^{-1})	0.113	0.900	1.060
GOF	1.017	1.008	1.038
R_1 [I > 2σ(I)]	0.0747	0.0602	0.0429
wR_2 [I > 2σ(I)]	0.2126	0.1706	0.1235
CCDC	2304097	2372803	2372809

Table S2. Selected bond lengths (Å) and angles (deg) for **1**.

bond lengths (Å)		**angles (deg)**	
C(1)-C(2)	1.384(6)	C(1)-N(1)-C(5)	117.5(4)
C(2)-C(3)	1.375(6)	C(2)-C(3)-C(4)	116.4(4)
C(3)-C(4)	1.338(6)	C(3)-C(2)-C(1)	119.5(4)
C(4)-C(5)	1.373(6)	C(4)-C(3)-C(6)	121.0(4)
N(1)- C(1)	1.312(6)	N(1)-C(1)-C(2)	123.6(4)
N(2)- C(11)	1.476(5)	N(2)-C(9)-C(10)	120.6(4)
N(3)- C(24)	1.481(5)	O(1)-C(44)-C(36)	114.4(3)
O(1)-C(44)	1.297(5)	O(1)-C(44)-C(36)	121.4(4)

O(2)-C(44)	1.200(5)	O(3)-C(43)-C(37)	120.7(4)
O(3)-C(43)	1.215(6)	O(3)-C(43)-O(4)	126.9(4)

Table S3. Selected bond lengths (Å) and angles (deg) for **2**.

bond lengths (Å)		**angles (deg)**	
C(1)-C(4)[1]	1.390(3)	C(1)1-C(4)-C(6)	122.1(2)
C(2)-C(12)[2]	1.377(5)	C(2)2-C(12)-C(7)	120.9(3)
C(3)-C(15)	1.363(5)	C(3)-C(14)-C(16)	122.2(3)
C(6)-C(8)	1.517(4)	C(4)-C(6)-C(8)	119.5(2)
N(1)-C(5)	1.332(4)	N(1)-C(5)-C(19)	121.1(3)
N(2)-C(9)	1.330(5)	N(1)-C(7)-C(12)	111.3(3)
O(1)-C(10)	1.292(3)	N(2)-C(17)-C(11)	124.0(4)
O(1)-C(10)	1.292(3)	O(1)-C(10)-C(1)	113.7(2)
O(3)-C(8)	1.222(4)	O(3)-C(8)-O(4)	125.1(3)
O(4)-C(8)	1.249(4)	O(4)-C(8)-C(6)	116.1(3)

Table S4. Selected bond lengths (Å) and angles (deg) for **3**.

bond lengths (Å)		**angles (deg)**	
C(2)-C(1)	1.376(3)	C(1)-C(2)-C(3)	120.0(2)
C(4)-C(5)	1.382(3)	C(2)-C(3)-C(4)	118.15(18)
C(6)-C(3)	1.486(3)	C(4)-C(3)-C(6)	122.22(18)
C(7)-C(8)	1.369(3)	C(5)-C(4)-C(3)	118.9(2)
N(1)-C(1)	1.326(3)	N(1)-C(1)-C(2)	120.7(2)
N(1)-C(5)	1.334(3)	N(1)-C(5)-C(4)	121.2(2)
N(2)-C(8)	1.338(3)	N(2)-C(8)-C(7)	120.53(18)

O(1)-C(16)	1.273(3)	O(1)-C(16)-C(15)	112.12(18)
O(2)-C(16)	1.215(3)	O(2)-C(16)-C(15)	120.96(18)
O(3)-C(18)	1.289(2)	O(3)-C(18)-C(17)	113.38(16)