Supporting Information

Phosphorescence Enhancement of Pyridinium Macrocycles by Poly(vinylalcohol)

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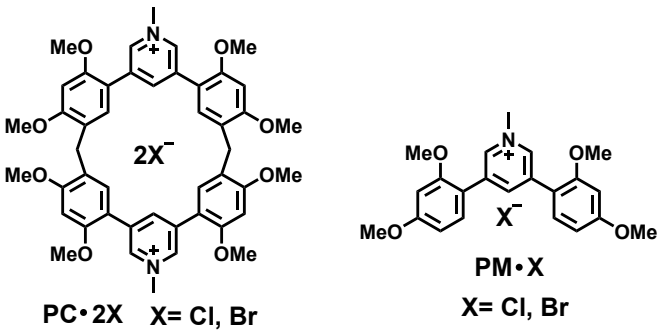
Section I. Materials/Methods/Instrumentation

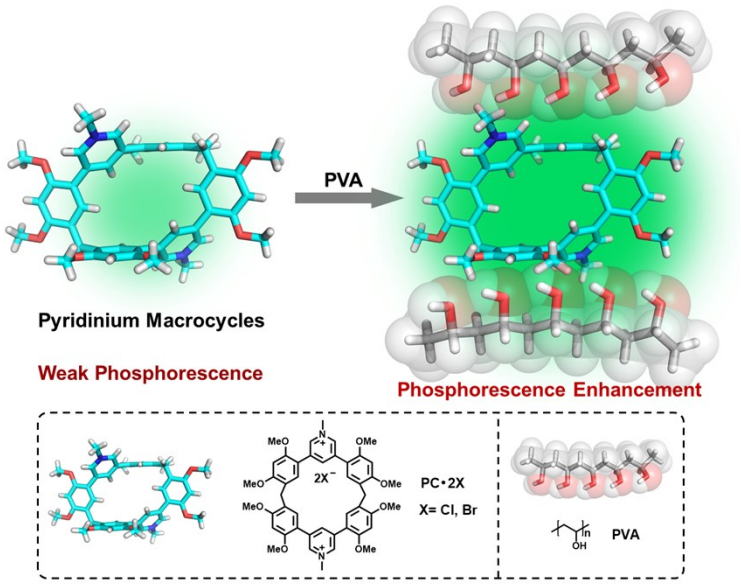
All reagents and solvents were commercially available and used without further purification, unless otherwise noted. ^{1}H NMR spectra were recorded using a Bruker Avance 400 MHz spectrometer. Photoluminescence spectra and lifetime were obtained on FLS1000. Fluorescence and phosphorescence quantum efficiencies were measured on HAMAMATSU C9920-02. The electrostatic potential maps of PC•2Cl and PVA were performed by using Gaussian 09 program with B3LYP-D3(BJ)/6-31G + (d, p) level.



Scheme S1. The structures of macrocycles PC•2X and monomers PM•X (X=Cl, Br).

Preparation of the doped films

In a typical example, 40 mg PVA was dissolved in 100 mL water at 90℃ to obtain an PVA aqueous solution of 40 mg/mL. Different proportions (i.e., 1/200, 1/100, 1/50, 1/25 and 1/10) of films were prepared by dissolving different amount of PC•2Cl (i.e., 0.2, 0.4, 0.8, 1.6, and 4 mg) in 1 mL PVA aqueous solution. Then, the mixed droplets were coated on 20 mm×50 mm glasses and dried at 60 °C to obtain transparent and flexible films.



Scheme S2. Schematic illustration of the phosphorescence enhancement of pyridinium macrocycles by PVA.

Section II. Photophysical properties

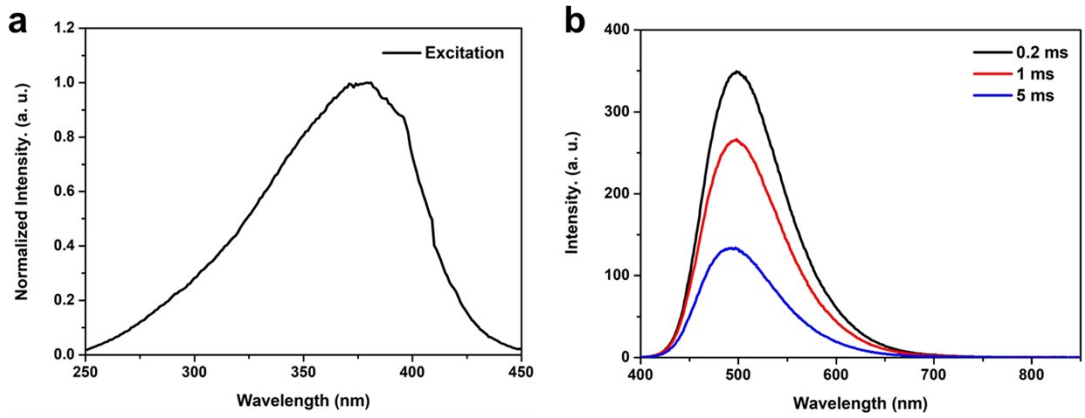


Figure S1. (a) Excitation spectra of PC•2Cl@PVA film at 498 nm; (b) Delayed PL spectra of PC•2Cl@PVA film with delay time of 0.2, 1 and 5 ms at 298 K (λ_{ex}: 380 nm).

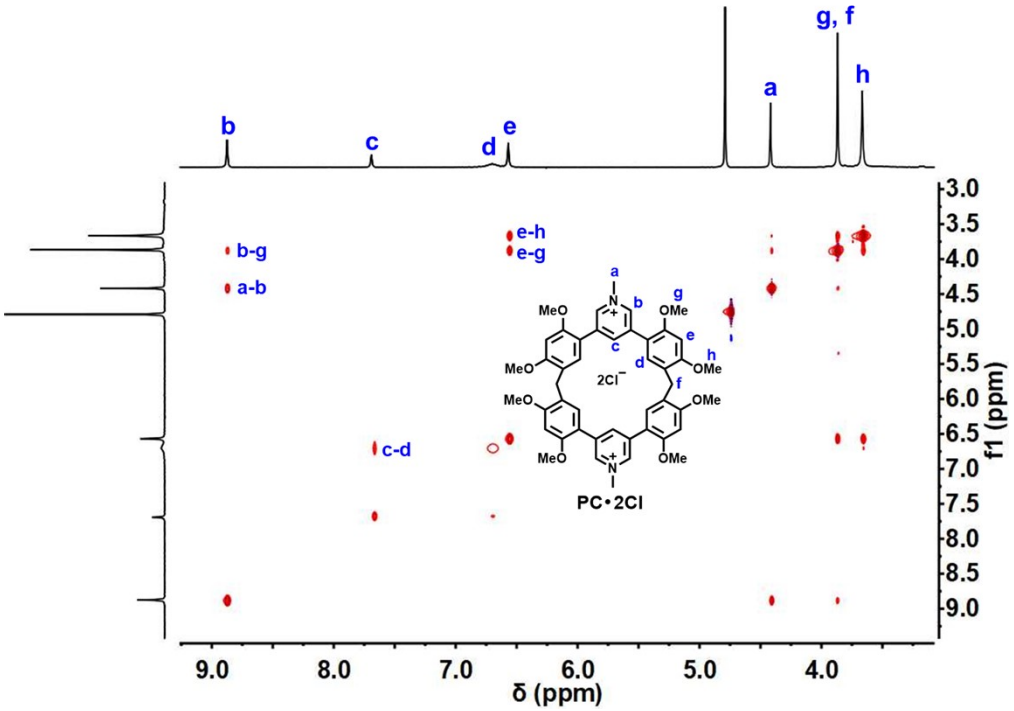


Figure S2. ^{1}H-^{1}H NOESY NMR spectrum (400 MHz, D_2O, 298 K) of PC•2Cl.

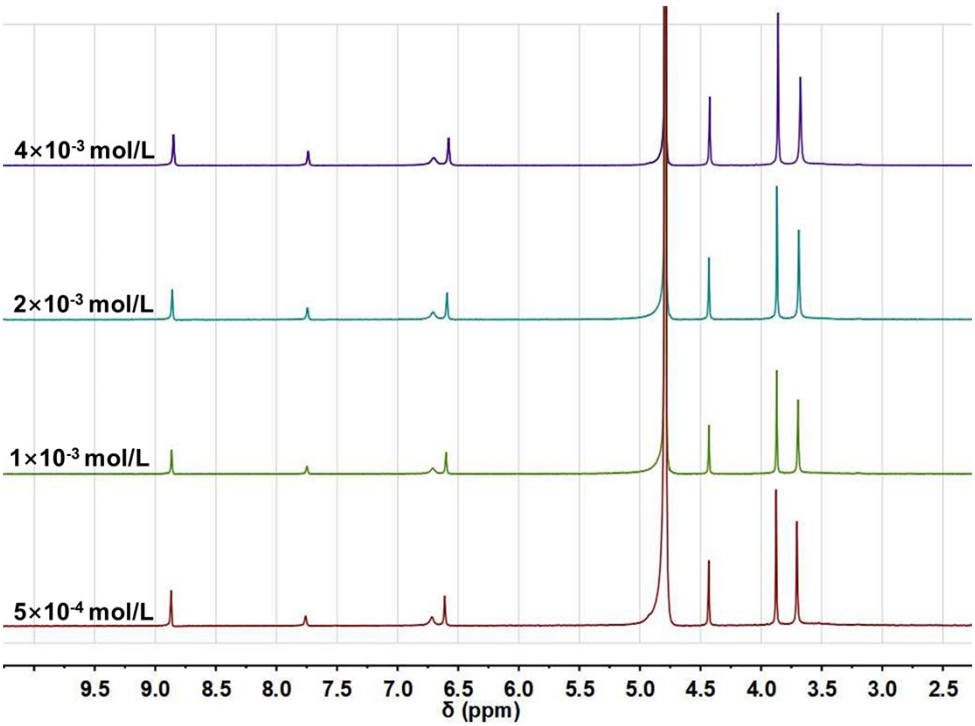


Figure S3. ^{1}H NMR spectra of PC•2Cl in different concentrations (D_2O).

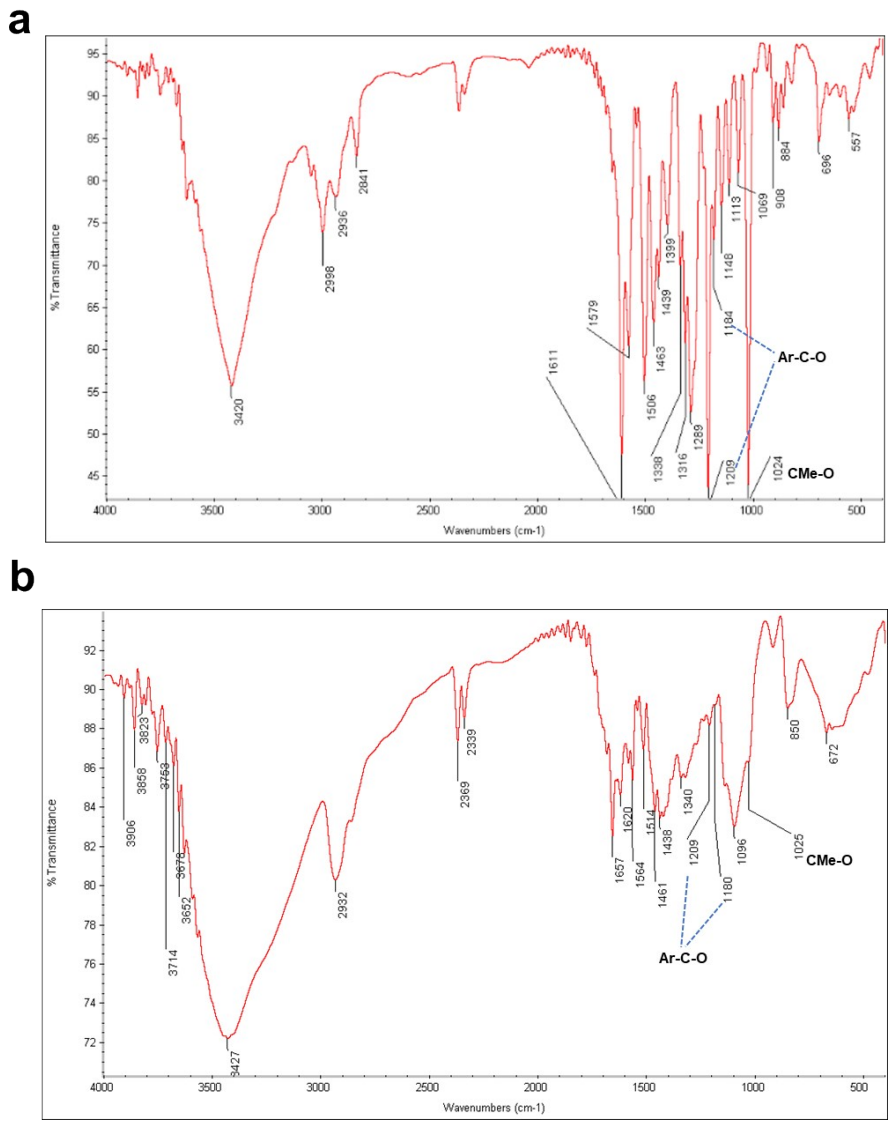


Figure S4. FTIR spectra of (a) PC•2Cl and (b) PC•2Cl@PVA film.

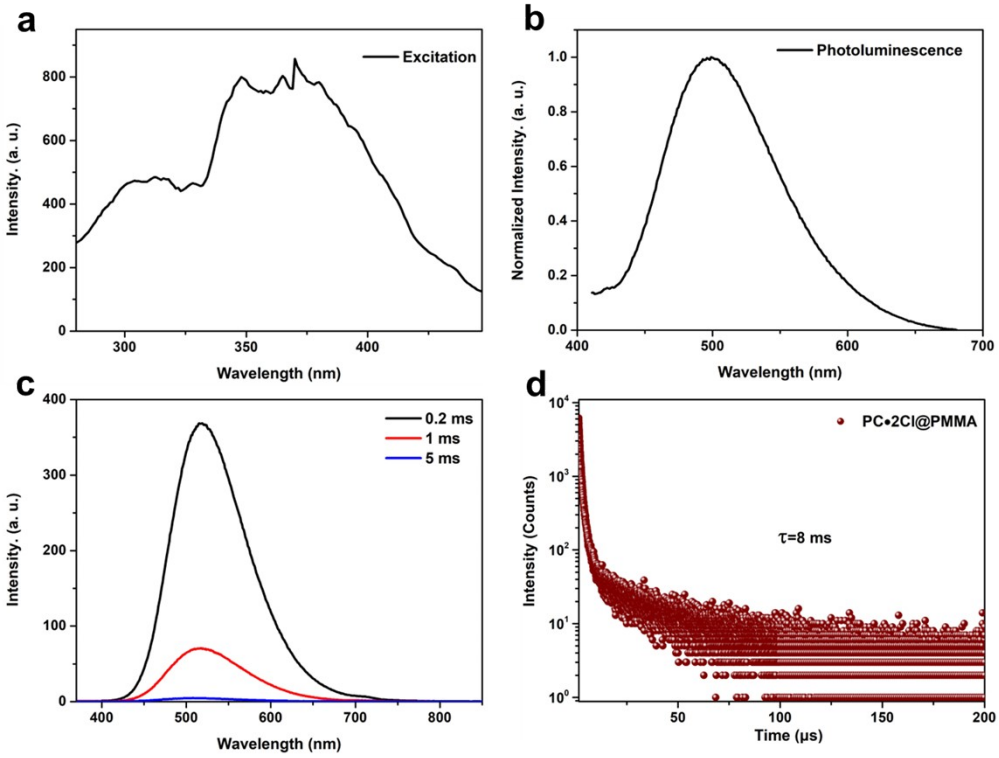


Figure S5. (a) Excitation spectra of PC•2Cl@PMMA film at 498 nm; (b) Photoluminescence spectra of PC•2Cl@PMMA film under 350 nm excitation; (c) Delayed PL spectra of PC•2Cl@PMMA film with delay time of 0.2, 1 and 5 ms at 298 K under 350 nm excitation; (d) Time-resolved PL decay of PC•2Cl@PMMA film @520 nm in solid state at room temperature.

To evaluate other polymers, we have prepared and tested the photophysical properties of PC•2Cl@PMMA and PC•2Cl@EVOH films with the proportion of 1/100. PC•2Cl@PMMA has a lifetime of 8 ms, indicated that PMMA is not a good matrix, possibly because weaker hydrogen-bonding interactions (Figure S5). For PC•2Cl@EVOH, the lifetime is only 68 ms, shorter than PC•2Cl@PVA (92 ms), proved that the reduction of hydrogen-bonding ratio is detrimental to phosphorescence (Figure S6). All results revealed that PVA is the best matrix because of multiple hydrogen bonding sites.

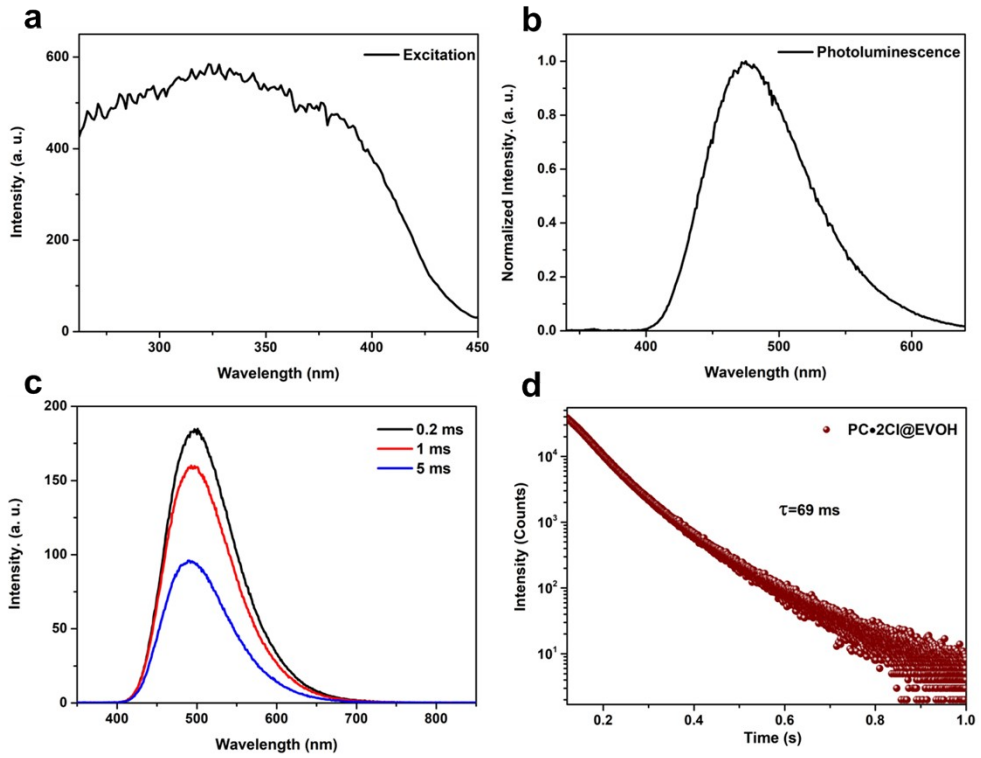


Figure S6. (a) Excitation spectra of PC•2Cl@EVOH film at 475 nm; (b) Photoluminescence spectra of PC•2Cl@EVOH film under 325 nm excitation; (c) Delayed PL spectra of PC•2Cl@EVOH film with delay time of 0.2, 1 and 5 ms at 298 K under 325 nm excitation; (d) Time-resolved PL decay of PC•2Cl@EVOH film @500 nm in solid state at room temperature.

Table S1. Photophysical data of macrocycles and monomers in the solid states (PC•2Cl/Br and PM•Cl/Br) and in the PVA films (PC•2Cl/Br@PVA and PM•Cl/Br@PVA)

Entry	Samples	λ_F (nm)	λ_P (nm)	τ_F (ns)	τ_P (ms)	Φ_F (%)	Φ_P (%)	$K^F_{r(s^{-1})}$ [b]	$K^F_{nr(s^{-1})}$ [d]	$K^P_{r(s^{-1})}$ [e]	$K^P_{nr(s^{-1})}$ [f]
1	PC•2Cl@PVA	-[a]	498	-[a]	92	0	32	-[c]	-[c]	3.5	7.4
2	PC•2Cl[g]	470	518	9.45	16.7	14.6	18.6	1.5×10^7	7.1×10^7	11	49
3	PM•Cl@PVA	458	487	8.2	218	14.1	24.3	1.7×10^7	7.5×10^7	1.1	3.5
4	PM•Cl[g]	470	500	14.1	0.29	10.4	17.3	7.4×10^6	5.1×10^7	597	2.8×10^3
5	PC•2Br@PVA	-[a]	498	-[a]	110	0	28	-[c]	-[c]	2.6	6.6
6	PC•2Br[g]	481	522	8.0	7.00	4.2	7.2	5.2×10^6	1.1×10^8	10	133
7	PM•Br@PVA	464	487	8.6	286	14	23.6	1.6×10^7	7.3×10^7	0.8	2.7
8	PM•Br[g]	470	503	5.6	0.16	3.9	5.9	7.0×10^6	1.6×10^8	369	5.9×10^3

a: Not detected. b: The radiative decay rate constant of fluorescence $k^F_r = \Phi_F/\tau_F$. c: Not calculated. d: The singlet state nonradiative decay rate constant of fluorescence $k^F_{nr} = (1- \Phi_F - \Phi_P)/\tau_F$. e: The radiative decay rate constant of

phosphorescence $k_r^p = \Phi_P/\tau_p$. f: The triplet state nonradiative decay rate constant $k_{nr}^p = (1-\Phi_P)/\tau_p$. g: Data from our previous work.[1]

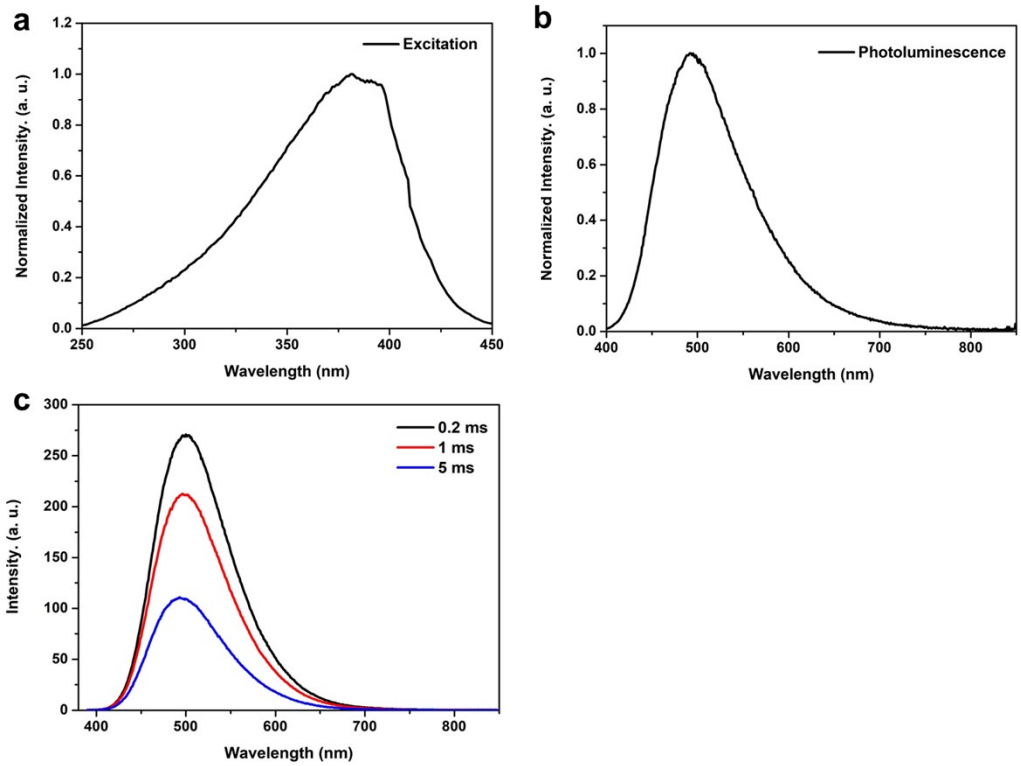


Figure S7. (a) Excitation spectra of PC•2Br@PVA film at 498 nm; (b) Photoluminescence spectra of PC•2Br@PVA film under 380 nm excitation; (c) Delayed PL spectra of PC•2Br@PVA film with delay time of 0.2, 1 and 5 ms at 298 K (λ_{ex}: 380 nm).

Figure S8. Luminescence photographs of PC•2PF_6@PVA film under 365 nm light and at different time intervals after ceasing irradiation.

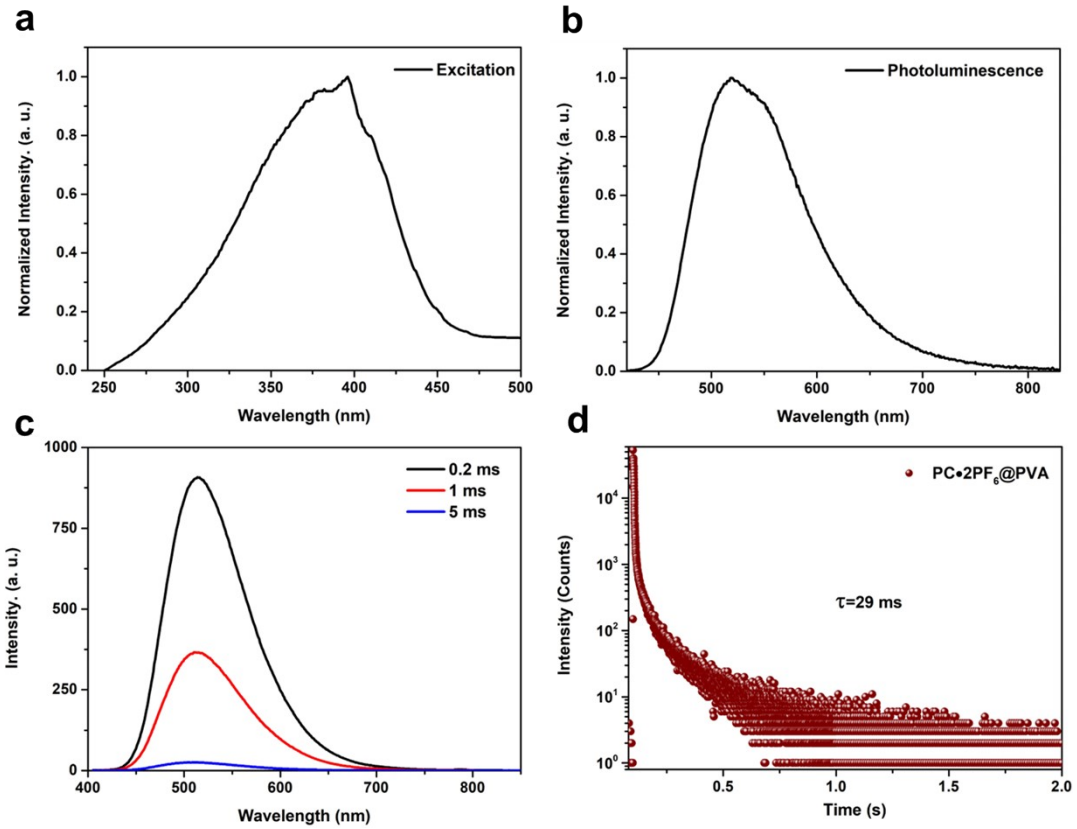


Figure S9. (a) Excitation spectra of PC•2PF_6@PVA film at 520 nm; (b) Photoluminescence spectra of PC•2PF_6@PVA film under 395 nm excitation; (c) Delayed PL spectra of PC•2PF_6@PVA film with delay time of 0.2, 1 and 5 ms at 298 K under 395 nm excitation; (d) Time-resolved PL decay of PC•2PF_6@PVA film @520 nm in solid state at room temperature.

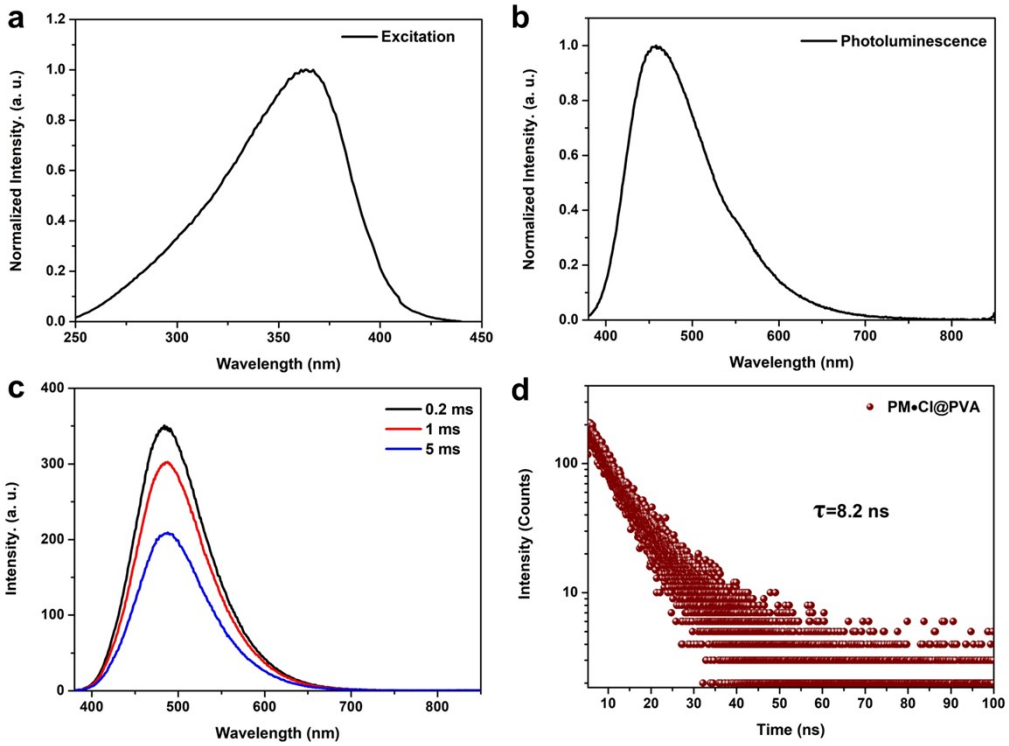


Figure S10. (a) Excitation spectra of PM•Cl@PVA film at 458 nm; (b) Photoluminescence spectra of PM•Cl@PVA film under 364 nm excitation; (c) Delayed PL spectra of PM•Cl@PVA film with delay time of 0.2, 1 and 5 ms at 298 K under 364 nm excitation; (d) Time-resolved PL decay of PM•Cl@PVA film @458 nm in solid at room temperature.

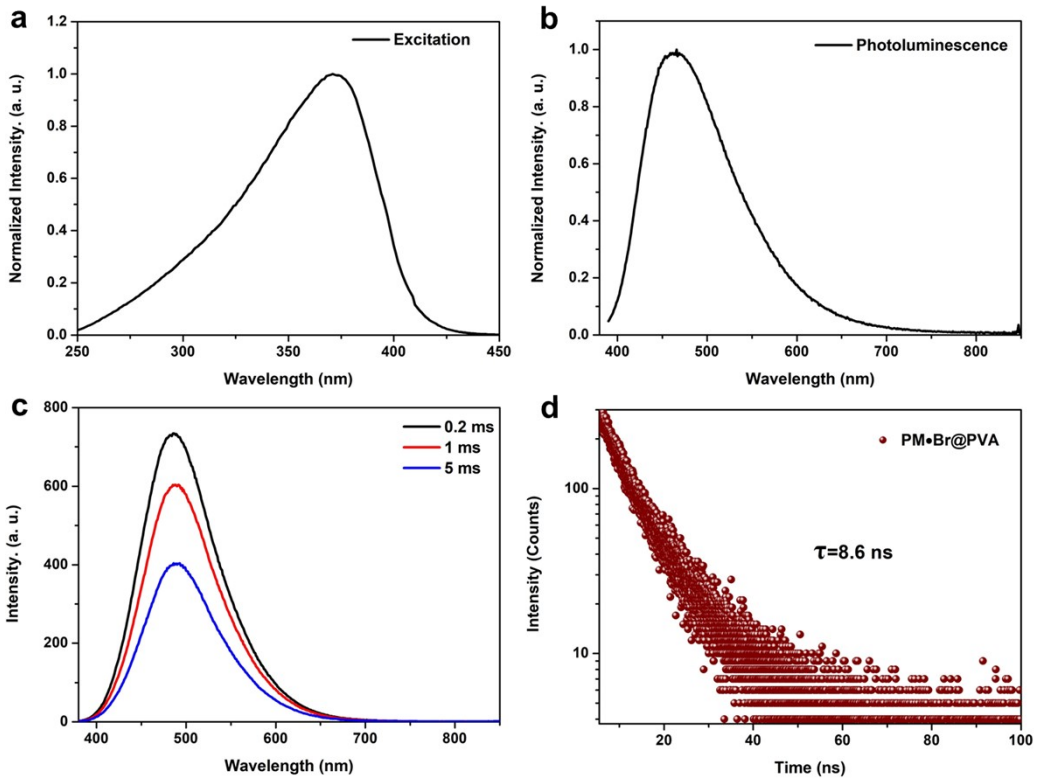


Figure S11. (a) Excitation spectra of PM•Br@PVA film at 469 nm; (b) Photoluminescence spectra of PM•Br@PVA film under 371 nm excitation; (c) Delayed PL spectra of PM•Br@PVA film with delay time of 0.2, 1 and 5 ms at 298 K under 371 nm excitation; (d) Time-resolved PL decay of PM•Cl@PVA film @464 nm.

Figure S12. Luminescence photographs of information encryption.

Reference:

1. S. Li, Z.-Y. Zhang, J.-F. Lv, L. Li, J. Li and C. Li, *J. Mater. Chem. A.*, 2023, **11**, 4957-4962.