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°C 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 ($\lambda_{ex}$: 380 nm).
Figure S2. $^1$H-$^1$H NOESY NMR spectrum (400 MHz, D$_2$O, 298 K) of PC•2Cl.

Figure S3. $^1$H NMR spectra of PC•2Cl in different concentrations (D$_2$O).
Figure S4. FTIR spectra of (a) PC•2Cl and (b) PC•2Cl@PVA film.
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)

<table>
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<th>Entry</th>
<th>Samples</th>
<th>λ_F (nm)</th>
<th>λ_P (nm)</th>
<th>τ_F (ms)</th>
<th>τ_P (ms)</th>
<th>Φ_F (%)</th>
<th>Φ_P (%)</th>
<th>K_{r,F}(s^{-1})</th>
<th>K_{w,F}(s^{-1})</th>
<th>K_{r,P}(s^{-1})</th>
<th>K_{w,P}(s^{-1})</th>
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<td>92</td>
<td>0</td>
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<td>c</td>
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<td>1.6 × 10^3</td>
<td>369</td>
<td>5.9 × 10^3</td>
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</table>

a: Not detected. b: The radiative decay rate constant of fluorescence \( k_{r,F} = \Phi_F / \tau_F \). c: Not calculated. d: The singlet state nonradiative decay rate constant of fluorescence \( k_{nr,F} = (1 - \Phi_F - \Phi_P) / \tau_F \). e: The radiative decay rate constant of
phosphorescence $k_P^r = \frac{\Phi_P}{\tau_P}$. The triplet state nonradiative decay rate constant $k_{nr}^P = (1 - \Phi_P)/\tau_P$. Data from our previous work.\textsuperscript{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 ($\lambda_{ex}$: 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•2PF₆@PVA film at 520 nm; (b) Photoluminescence spectra of PC•2PF₆@PVA film under 395 nm excitation; (c) Delayed PL spectra of PC•2PF₆@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•2PF₆@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: