Electronic Supplementary Information

Multicolor Luminescent Supramolecular Hydrogels Based on Cucurbit[8]uril and OPV Derivative

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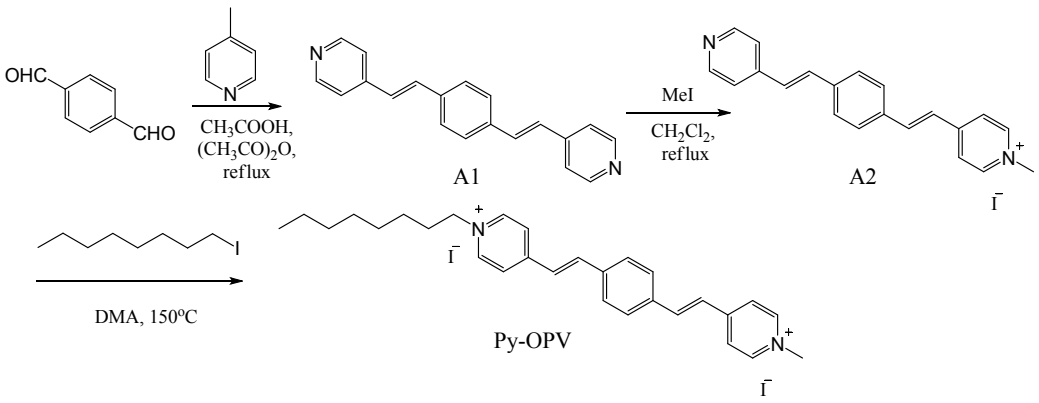
1. Instrumentation and methods

All the reagents and solvents were commercially available and used as received unless otherwise specified purification. All aqueous solutions were prepared in distilled water. Column chromatography was performed on 200-300 mesh silica gel. NMR spectra were recorded on a Bruker AV400 instrument. UV/vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer in a quartz cell at 25 °C. Steady state fluorescence emission spectra were recorded in a conventional quartz cell at 25 °C on a Varian Cary Eclipse equipped with a Varin Cary single-cell peltier accessory to control temperature. The fluorescence lifetimes were measured by time correlated single photon counting on a FLS920 instrument (Edinburg Instruments Ltd., Livingstone, UK) with a H2 pulse lamp. SEM images were recorded on a JEOL JSM-7500F scanning electronic microscope operating at an accelerating voltage of 30 keV.

2. Synthesis and characterization of intermediates and products

Synthetic route of Py-OPV



Scheme S1. Synthetic routes of oligo (phenylenevinylene) derivative (Py-OPV)

2.1 NMR and mass spectrum data of A2

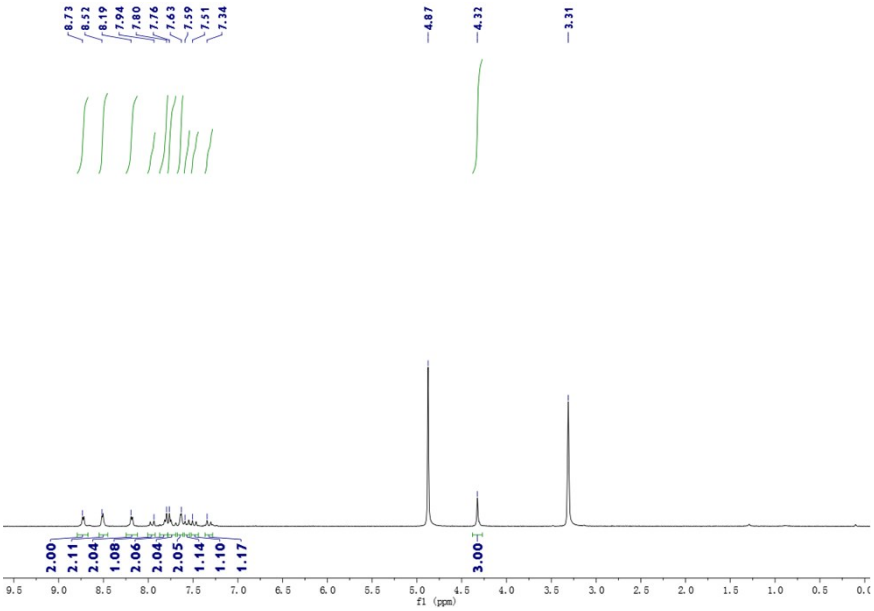


Figure S1 ^{1}H NMR spectrum (400 MHz, CD_3OD, 298 K) of A2.

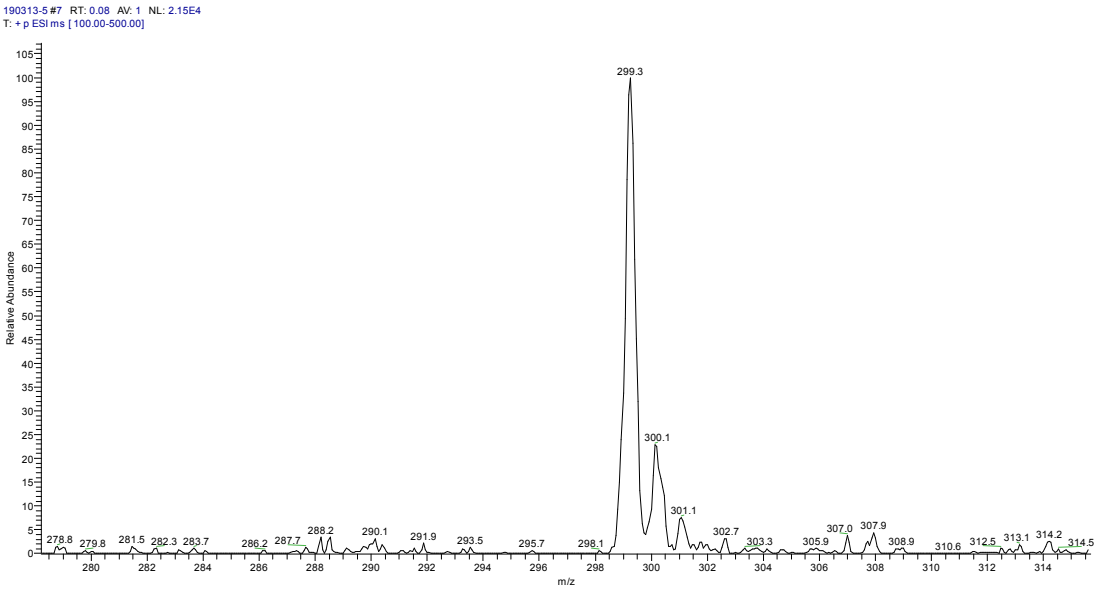


Figure S2 ESI-MS spectrum of A2 (*m/z*): calculated for $C_{21}H_{19}N_2^+$: 299.4, found: 299.2

2.2 NMR and mass spectrum data of Py-OPV

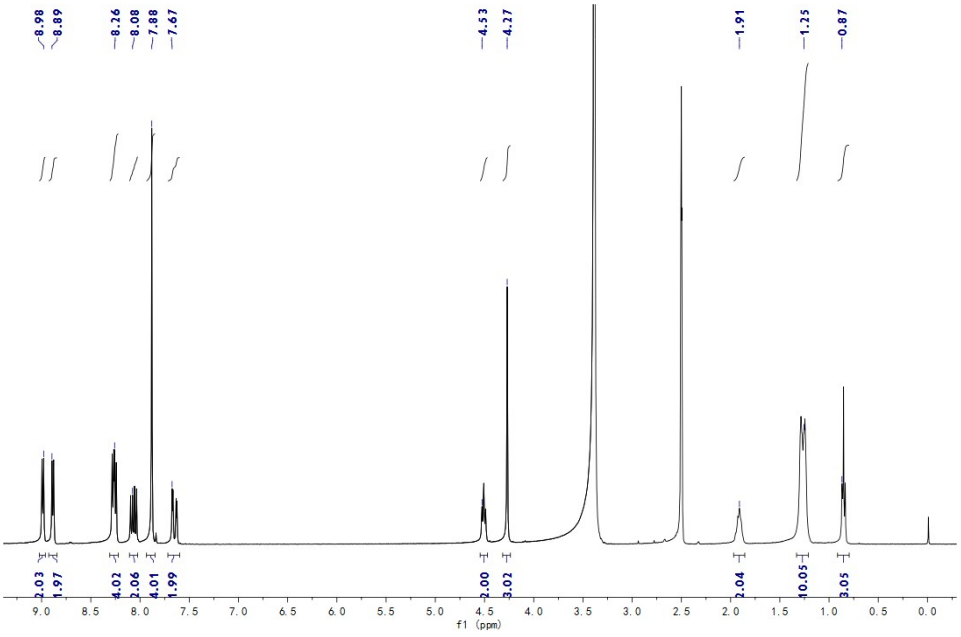


Figure S3 ^{1}H NMR spectrum (400 MHz, CD_3OD, 298 K) of Py-OPV

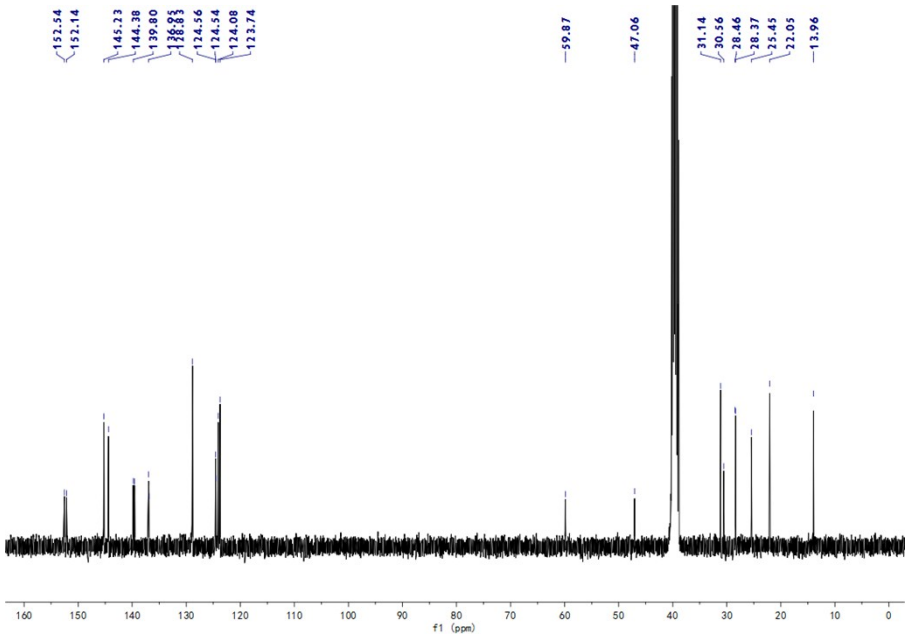


Figure S4 ^{13}C NMR spectrum (400 MHz, CD_3OD, 298 K) of Py-OPV

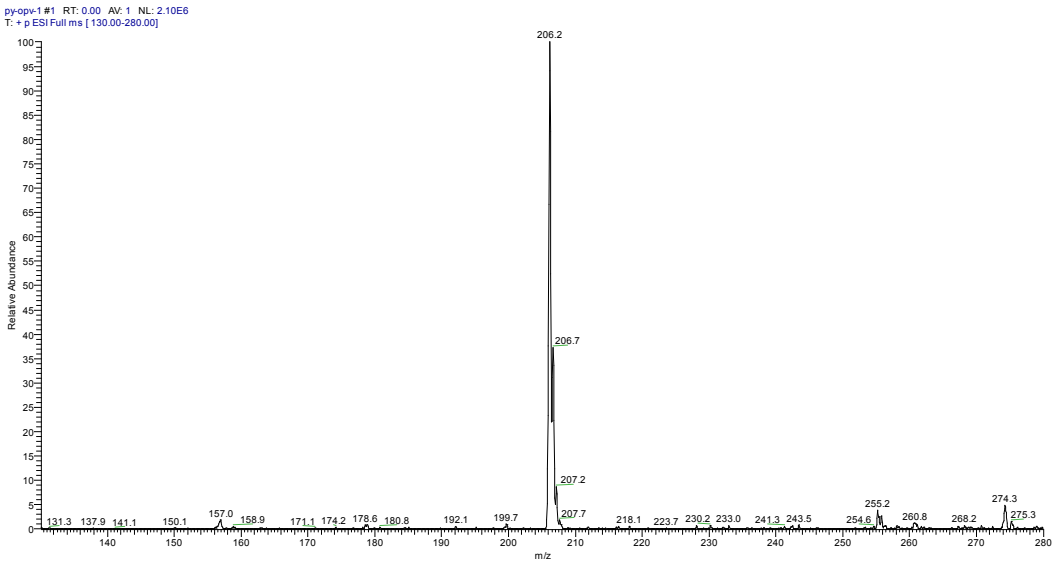


Figure S5 ESI-MS spectrum of Py-OPV (*m/z*): calculated for $C_{29}H_{36}N_2^{2+}$: 206.3, found: 206.2

3. Characterization of Py-OPV

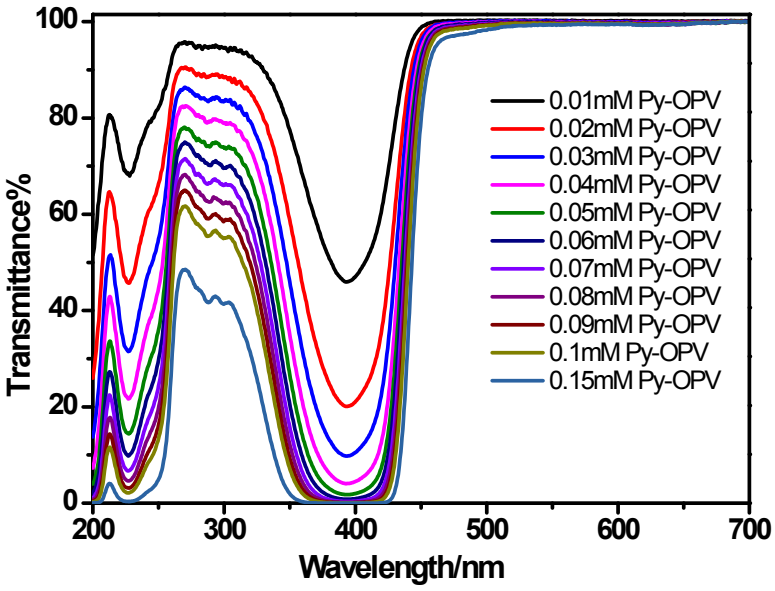


Figure S6. Optical transmittance of Py-OPV at different concentrations in water at 25 °C.

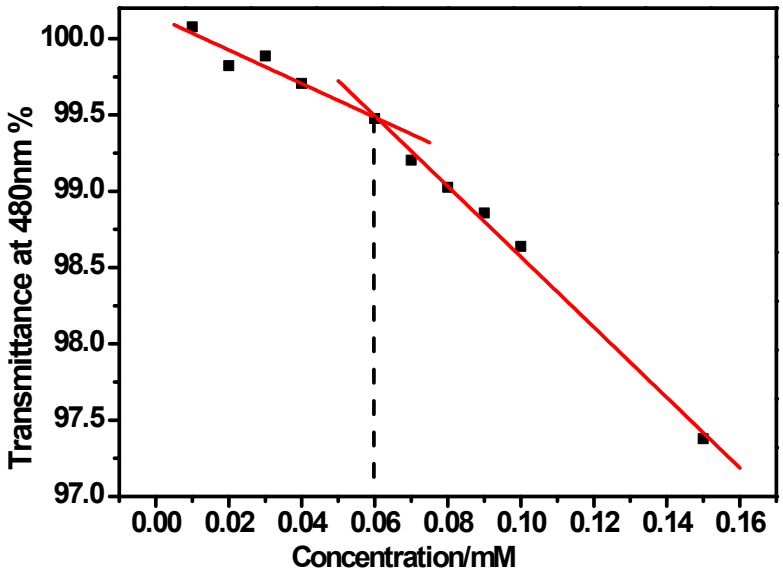


Figure S7. Dependence of the optical transmittance at 480 nm at different concentrations of Py-OPV.

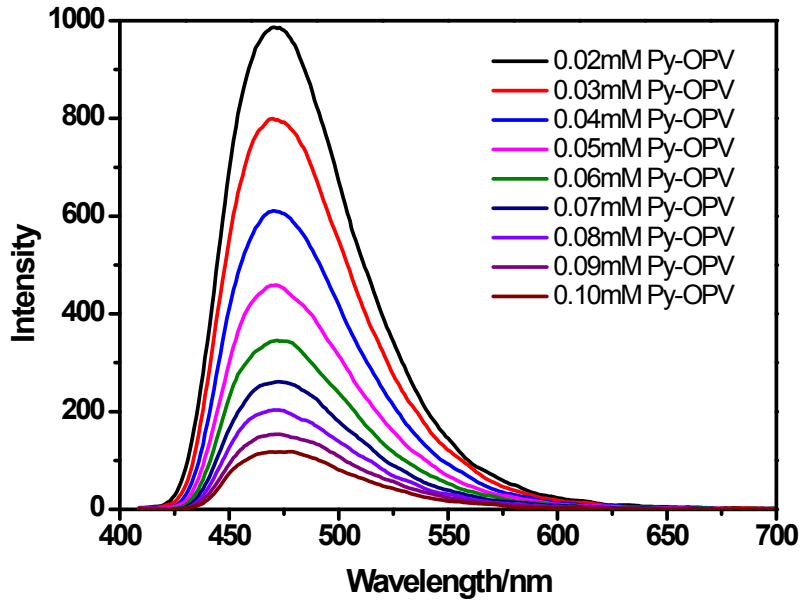


Figure S8. Fluorescence spectra of Py-OPV at different concentrations in water at 25 °C (λ_{ex} = 391 nm)

4. Characterization of Py-OPV with CB[7]

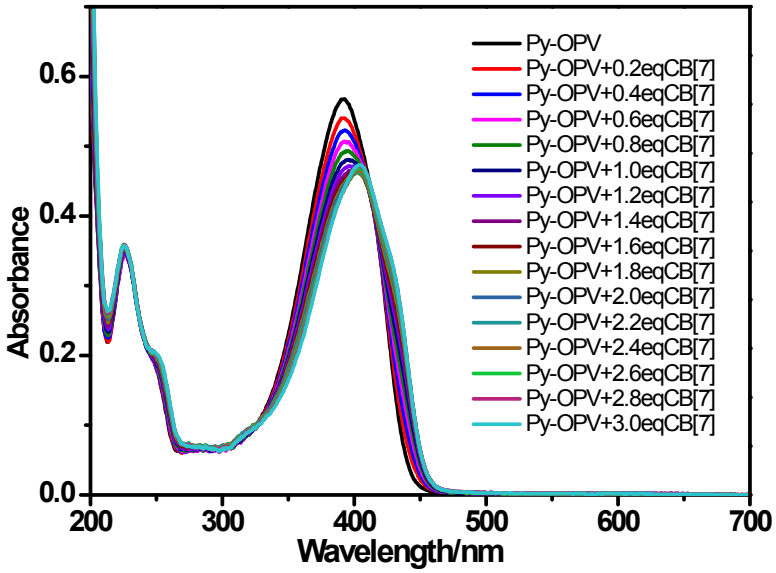


Figure S9. UV-vis absorption spectrum of Py-OPV (10.0 μM) upon addition of increasing concentrations of CB[7] in aqueous solution (0-3.0 equiv) at 25 °C.

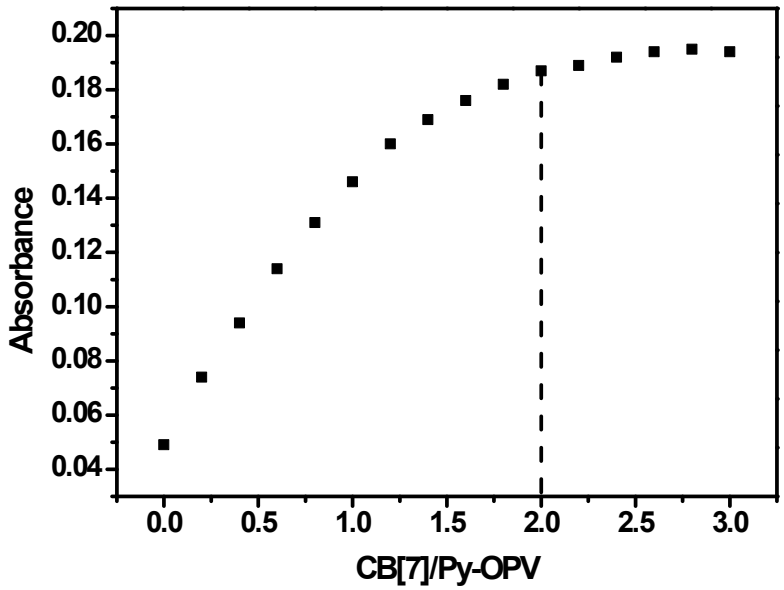


Figure S10. The absorbance intensity of Py-OPV (10.0 μ M) at 440nm upon addition of increasing concentrations of CB[7] in aqueous solution (0-3.0 equiv) at 25 °C.

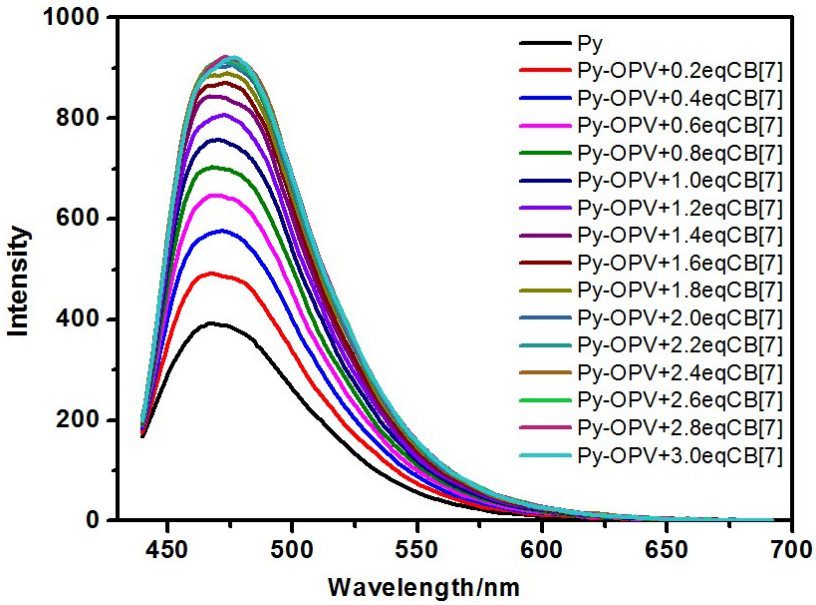


Figure S11. Fluorescence spectra of Py-OPV (10.0 μM) upon addition of increasing concentrations of CB[7] in aqueous solution (0-3.0 equiv) at 25 °C (λ_{ex} = 430 nm)

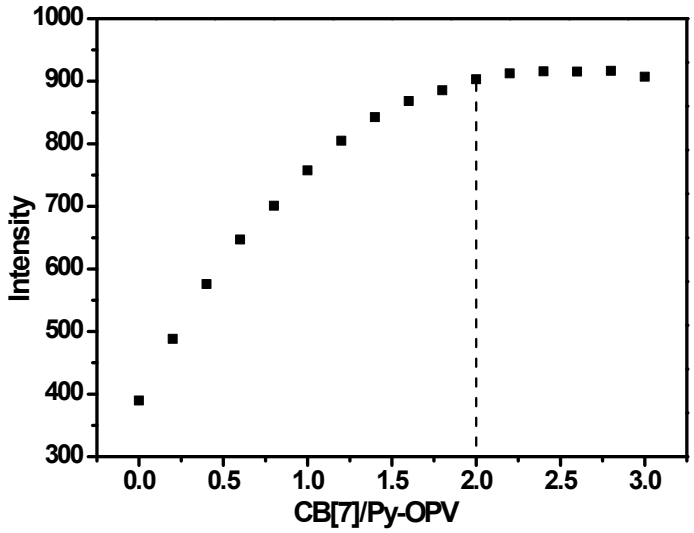


Figure S12. The fluorescence intensity of Py-OPV (10.0 μM) at 471nm upon addition of increasing concentrations of CB[7].

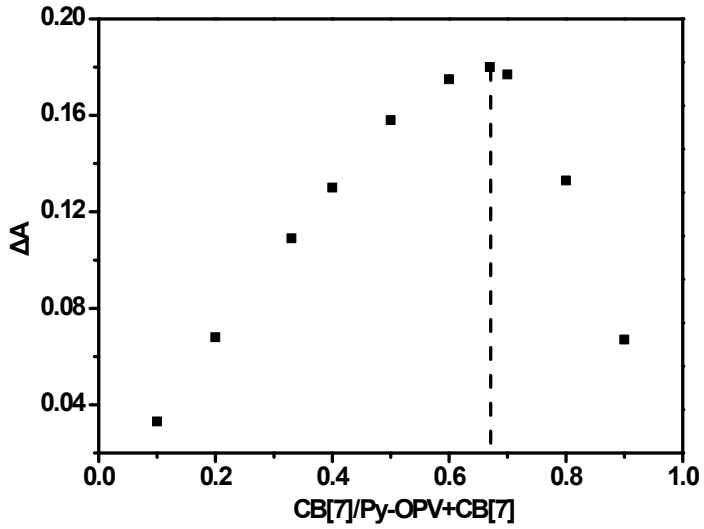


Figure S13. Job's plot for the binding of Py-OPV and CB[7] in water at 25 °C. The total concentration was fixed at 2×10^{-5} M.

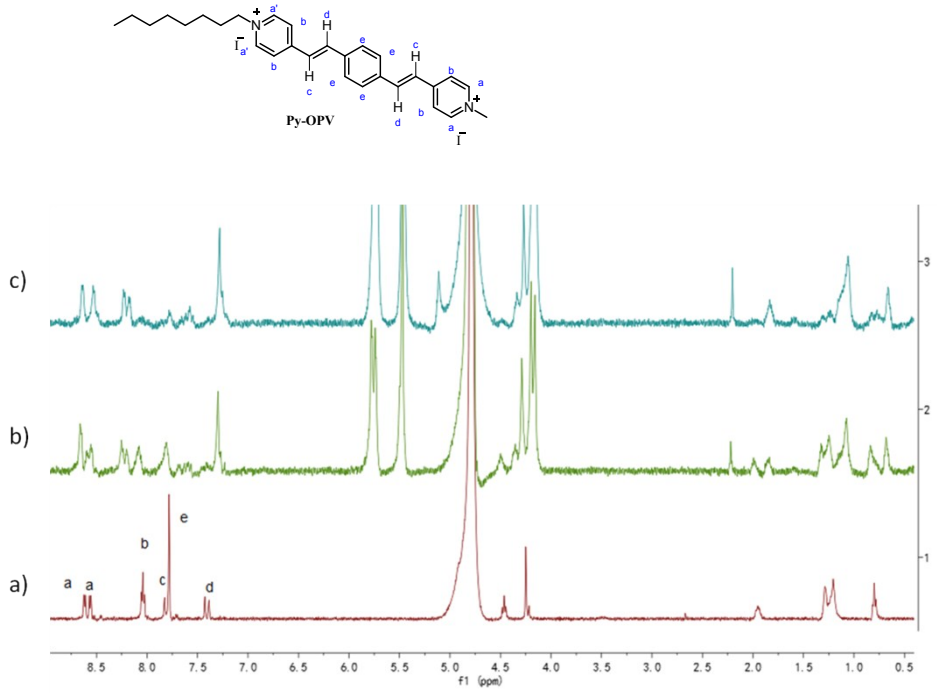


Figure S14. ^{1}H NMR titration of the CB[7]/G system in D_2O at 298 K. (a) Resonance signals for the free Py-OPV (1.0 mM). (b−c) Changes in resonance signals of Py-OPV in the presence of 1.0, 2.0, equiv of CB[7].

5. Characterization of Py-OPV with CB[8]

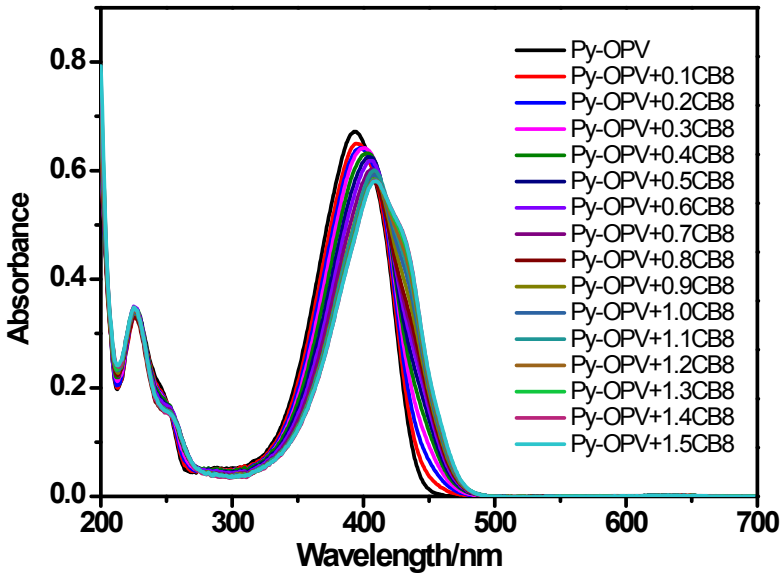


Figure S15. UV-vis absorption spectrum of Py-OPV (10.0 μM) upon addition of increasing concentrations of CB[8] in aqueous solution at 25 °C

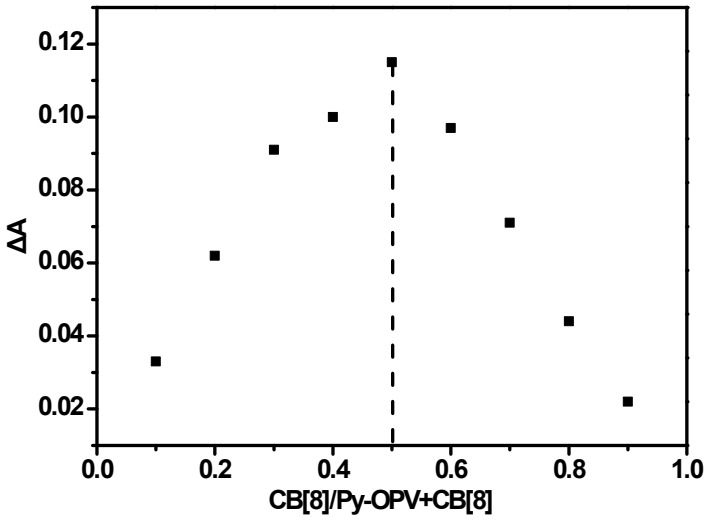


Figure S16. Job's plot for the binding of Py-OPV and CB[8] in water at 25 °C. The total concentration was fixed at 1×10^{-5} M.

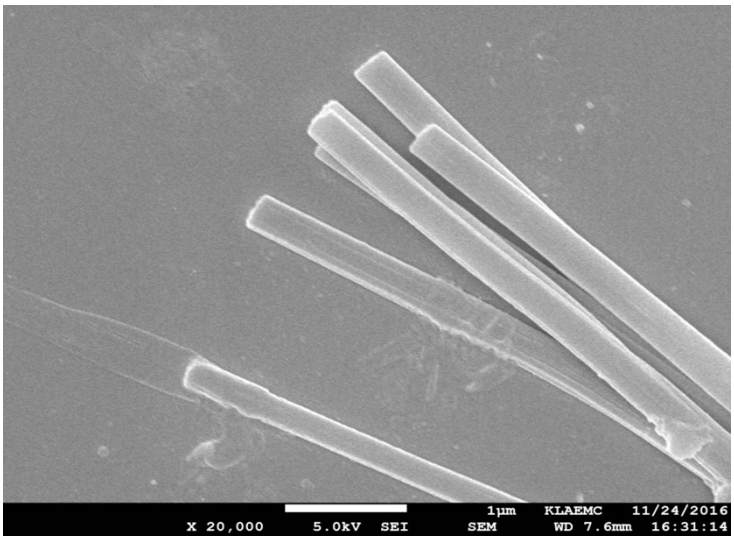


Figure S17. Magnified SEM images of Py-OPV (×20000).

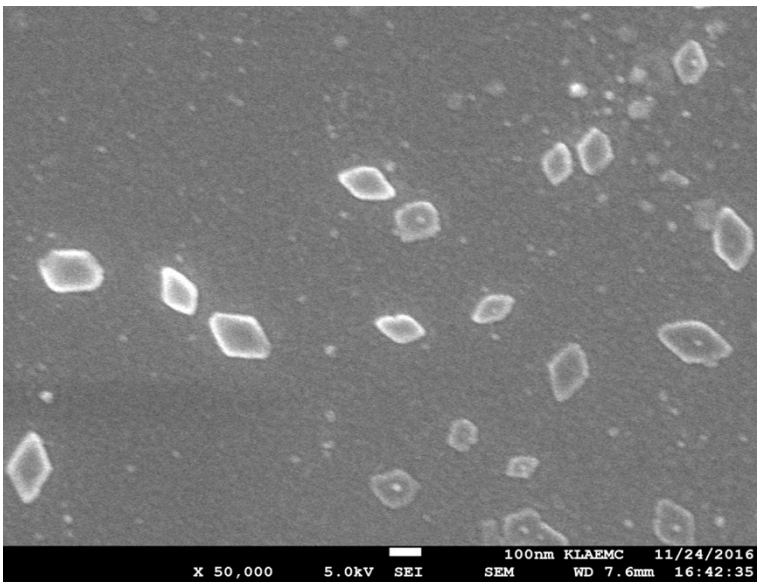


Figure S18. Magnified SEM images of the assembly of Py-OPV and CB[8] (×50000).

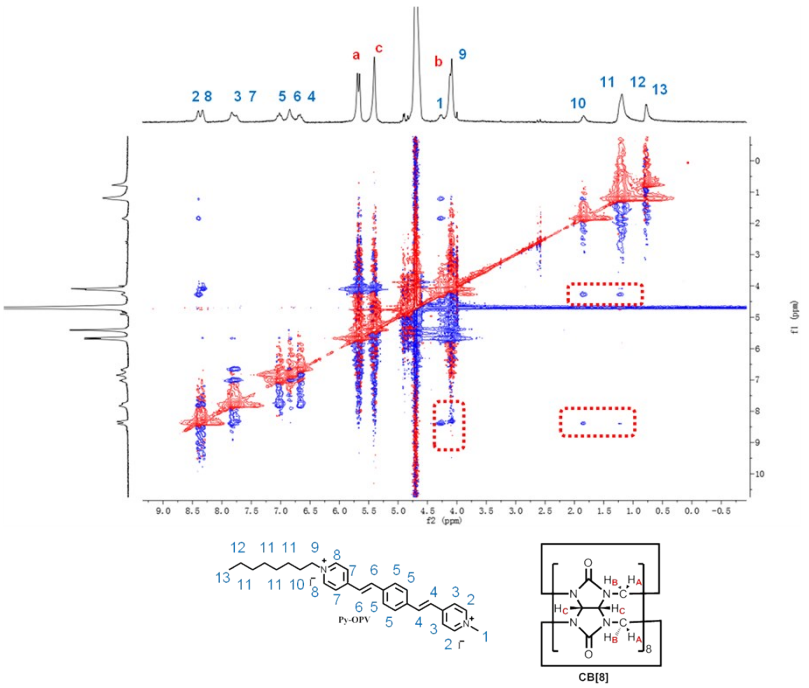


Figure S19. 2D ROESY spectrum (400 MHz, D_2O, 298 K) of Py-OPV and CB[8].

6. Characterization of Py-OPV with other hosts

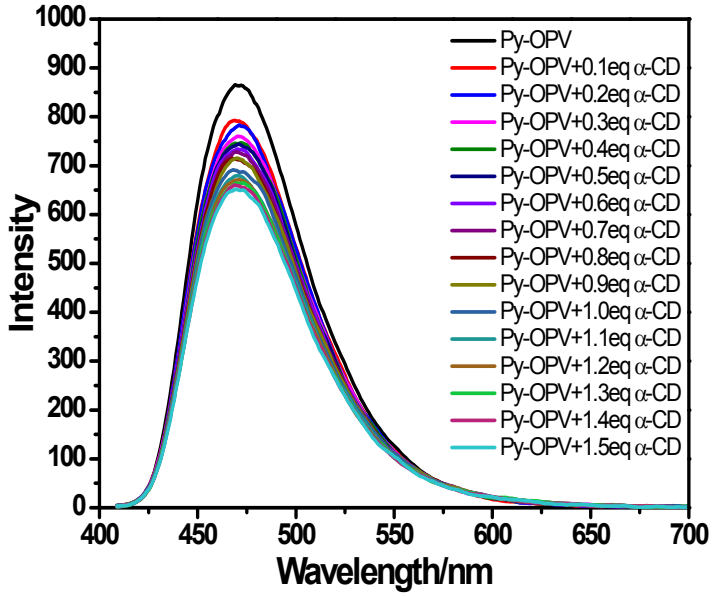


Figure S20. Fluorescence spectrum of Py-OPV (10.0 μM) upon addition of increasing concentrations of α-CD in aqueous solution (λ_{ex} = 391nm).

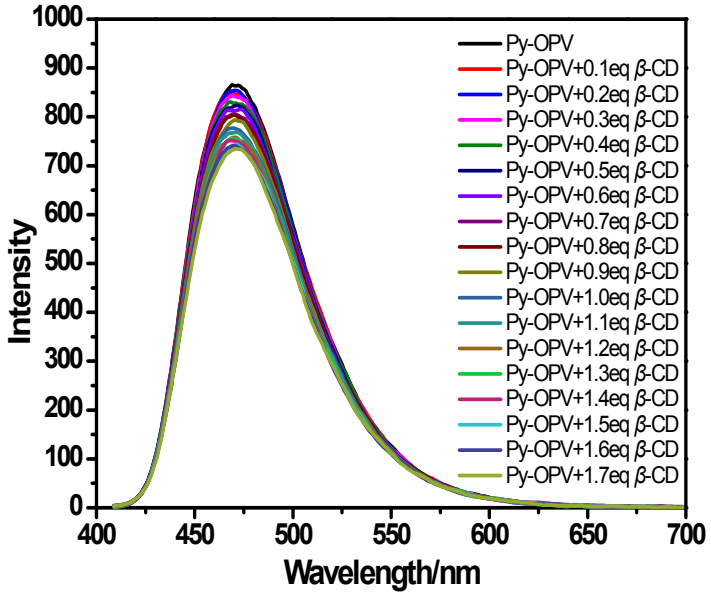


Figure S21. Fluorescence spectrum of Py-OPV (10.0 μM) upon addition of increasing concentrations of β-CD in aqueous solution (λ_{ex} = 391nm).

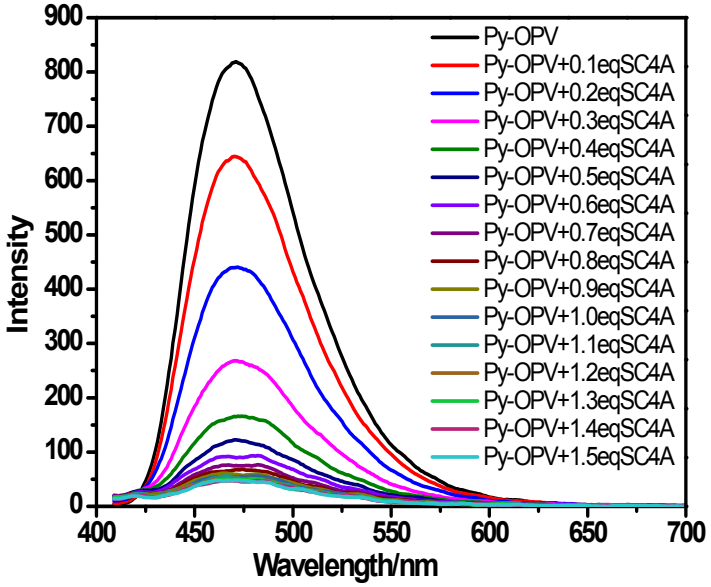
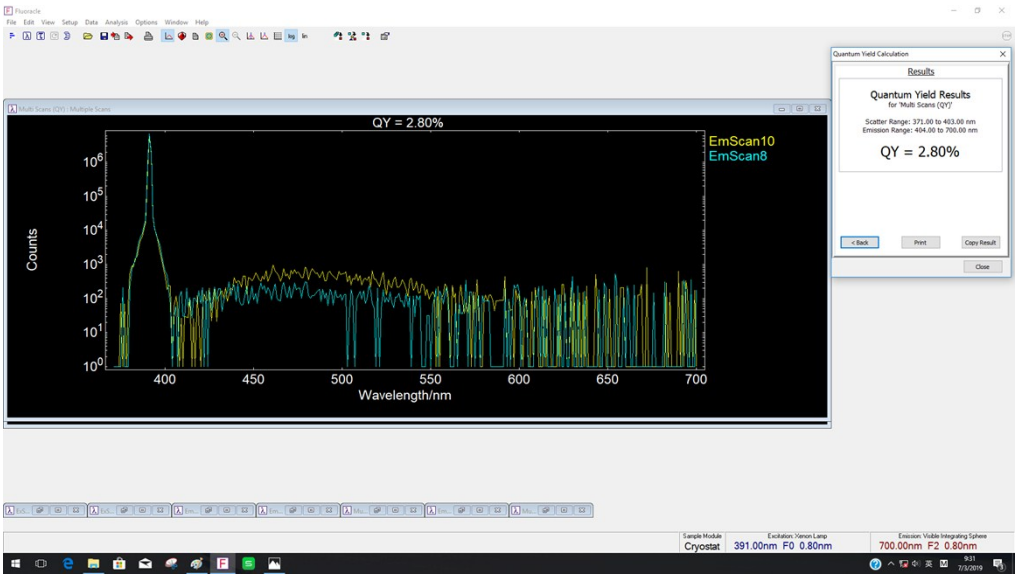


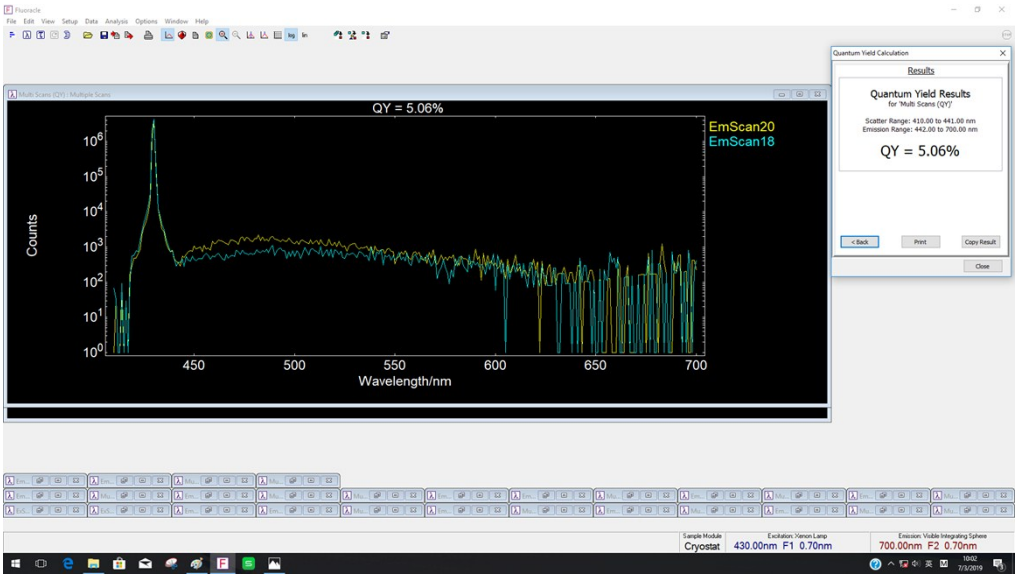
Figure S22. Fluorescence spectrum of Py-OPV (10.0 μM) upon addition of increasing concentrations of SC4Ain aqueous solution. (λ_{ex} = 391nm)

7. Fluorescence quantum yield and decay traces of Py-OPV with CB[7] and CB[8]

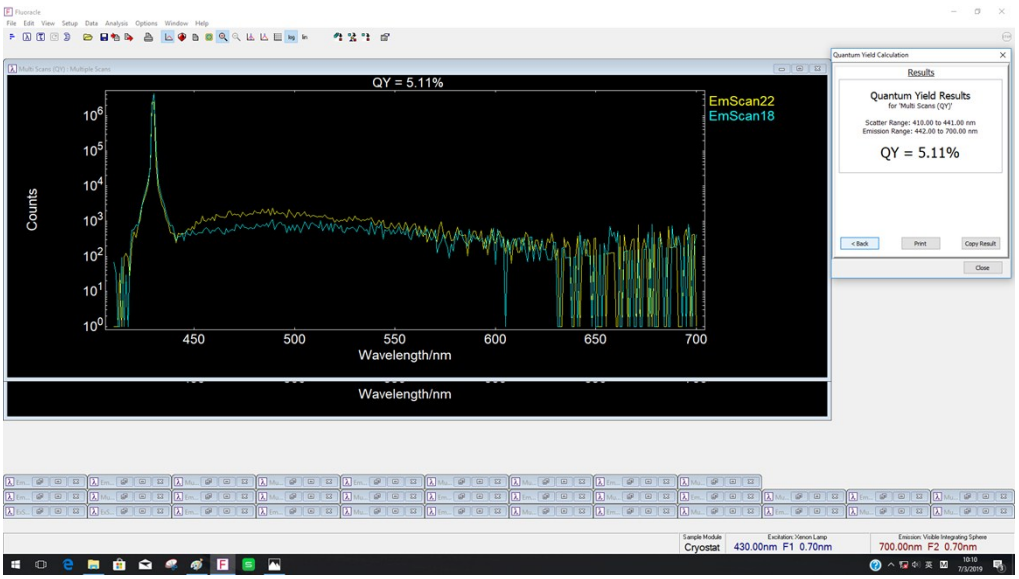
a)



b)



c)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EmScan22
EmScan18
Counts
Wavelength/nm
Quantum Yield Calculation
Results
Quantum Yield Results
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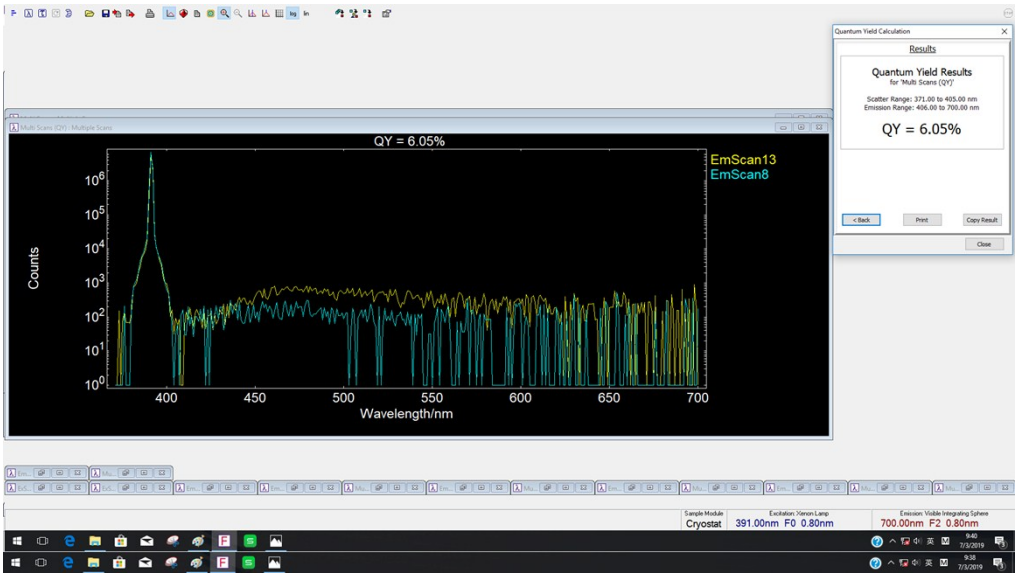
Emission Range: 442.00 to 700.00 nm
QY = 5.11%
< Back
Print
Copy Result
Close
Cryostat
430.00nm F1 0.70nm
700.00nm F2 0.70nm

d)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EmScan13
EmScan8
Counts
Wavelength/nm
Quantum Yield Calculation
Results
Quantum Yield Results
for 'Multi Scans (QY)'
Scatter Range: 371.00 to 405.00 nm
Emission Range: 406.00 to 700.00 nm
QY = 6.05%
< Back
Print
Copy Result
Close
Cryostat
391.00nm F0 0.80nm
700.00nm F2 0.80nm

e)

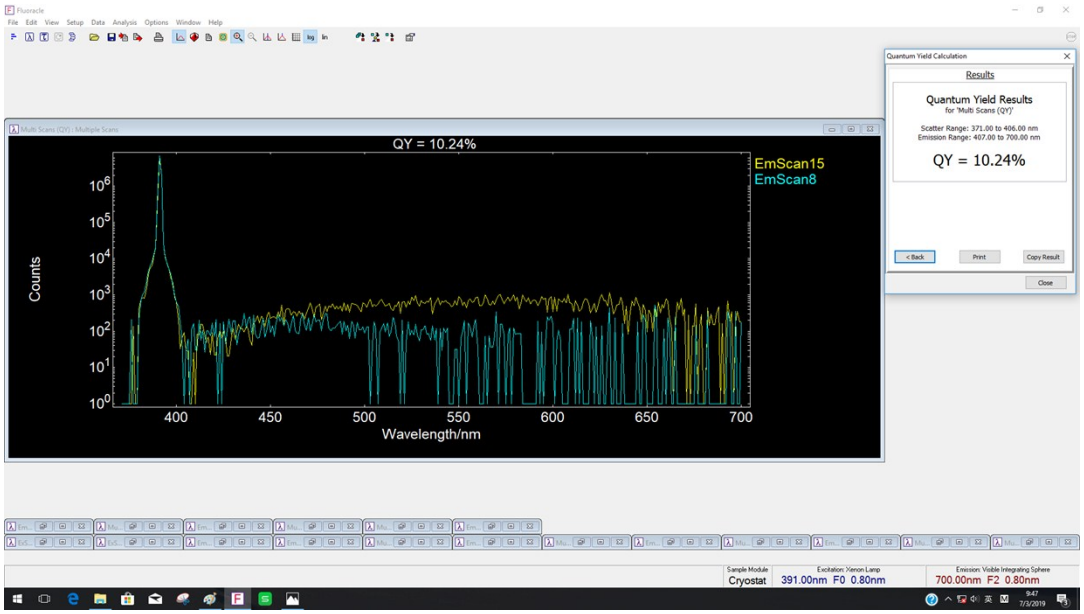
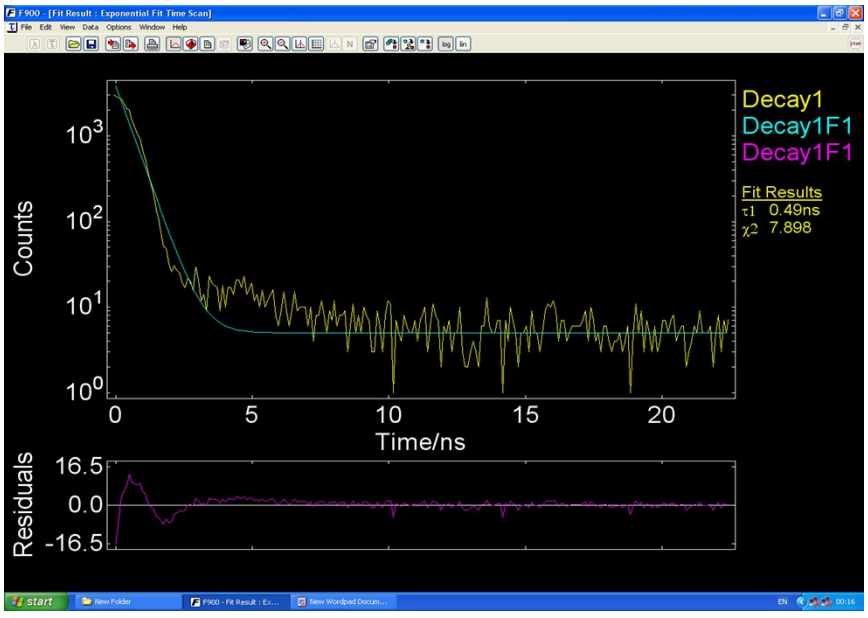


Figure S23. (a) Absolute fluorescence quantum yield ($\Phi_{f(abs)}$) of Py-OPV (10.0 μM) (λ_{ex} = 391 nm) in aqueous solution. (b-c) Absolute fluorescence quantum yield ($\Phi_{f(abs)}$) of Py-OPV (10.0 μM) (λ_{ex} = 430 nm) in aqueous solution after addition of 1 and 2 equiv of CB[7]. (d-e) Absolute fluorescence quantum yield ($\Phi_{f(abs)}$) of Py-OPV (10.0 μM) (λ_{ex} = 391 nm) in aqueous solution after addition of 0.2 and 1 equiv of CB[8].

a)



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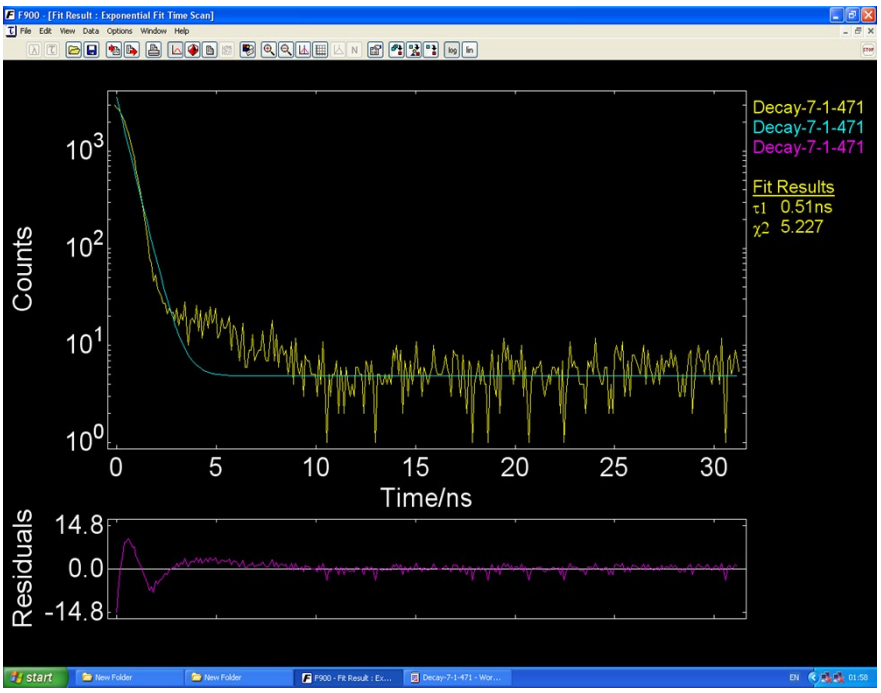
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Fit Results
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χ2 5.227
Counts
10^3
10^2
10^1
10^0
0
5
10
15
20
25
30
Time/ns
Residuals
14.8
0.0
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start
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New Folder
F900 - Fit Result : Ex...
Decay-7-1-471 - Wor...
EN
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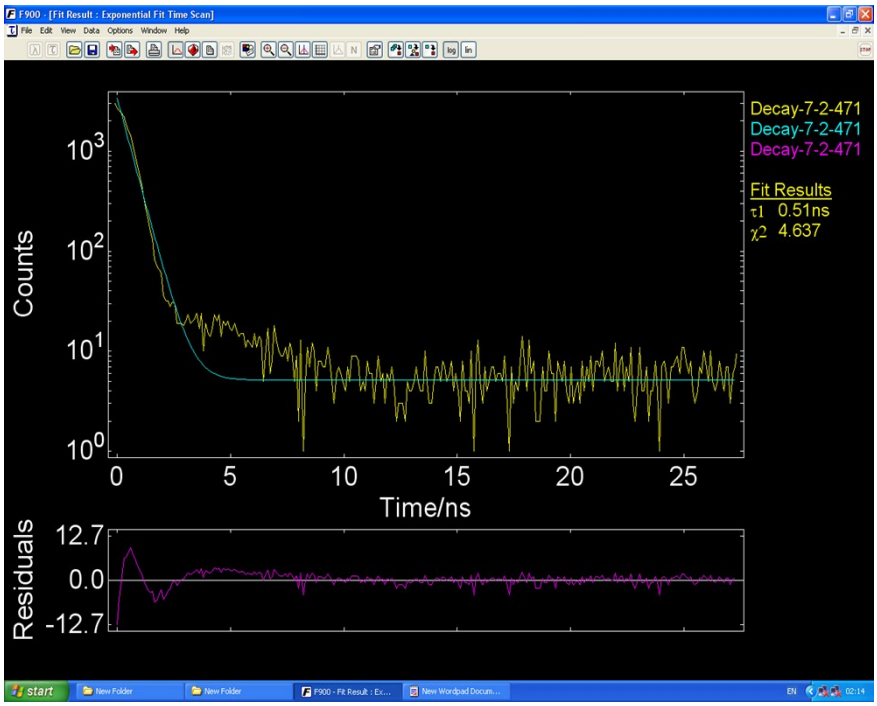
c)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File Edit View Data Options Window Help
Decay-7-2-471
Decay-7-2-471
Decay-7-2-471
Fit Results
τ1 0.51ns
χ2 4.637
Counts
10^3
10^2
10^1
10^0
0
5
10
15
20
25
Time/ns
Residuals
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start
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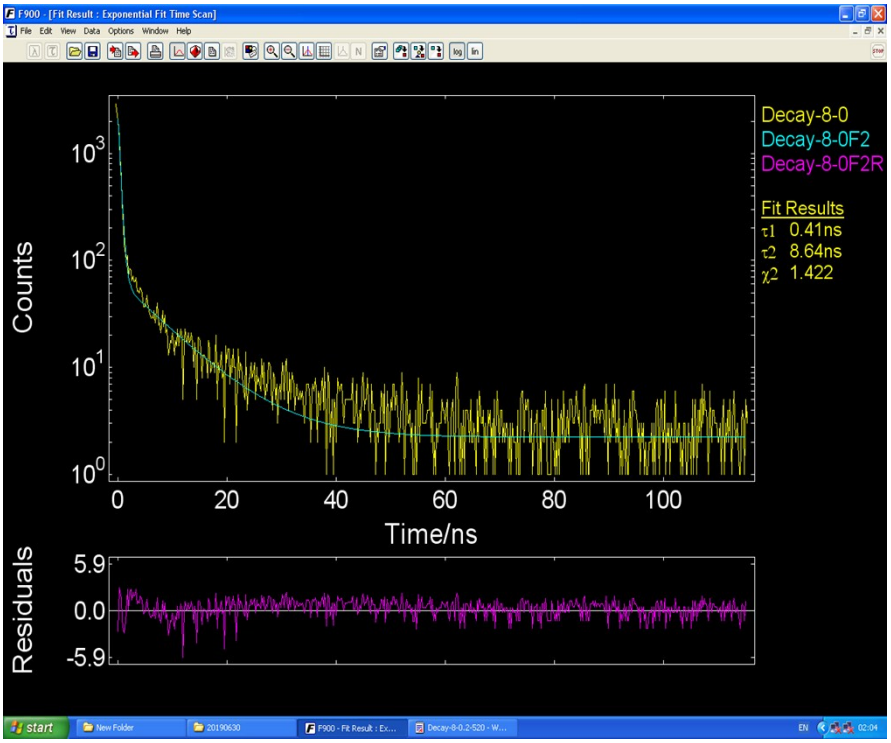
d)



e)

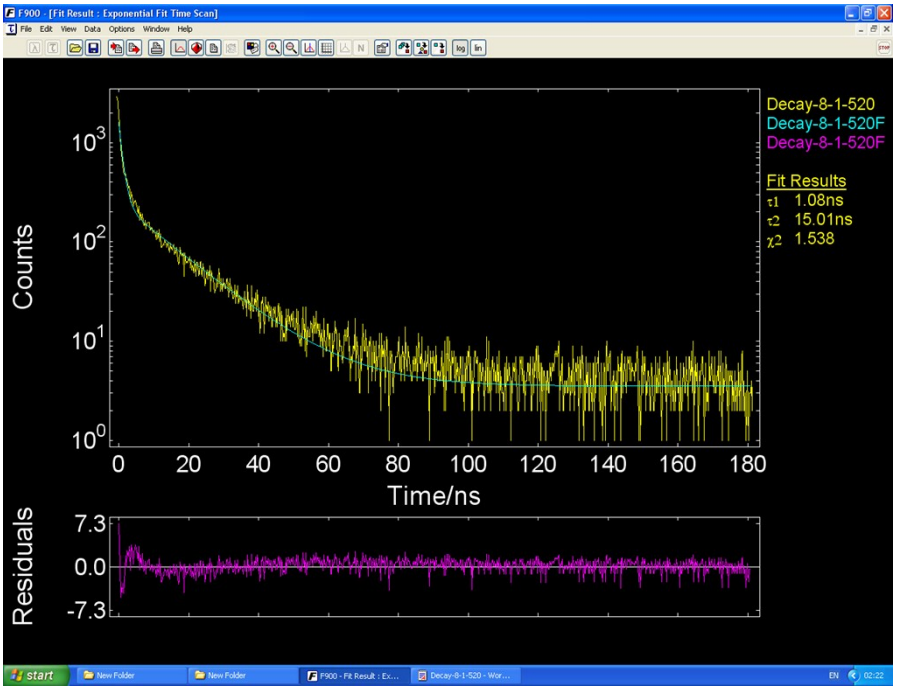
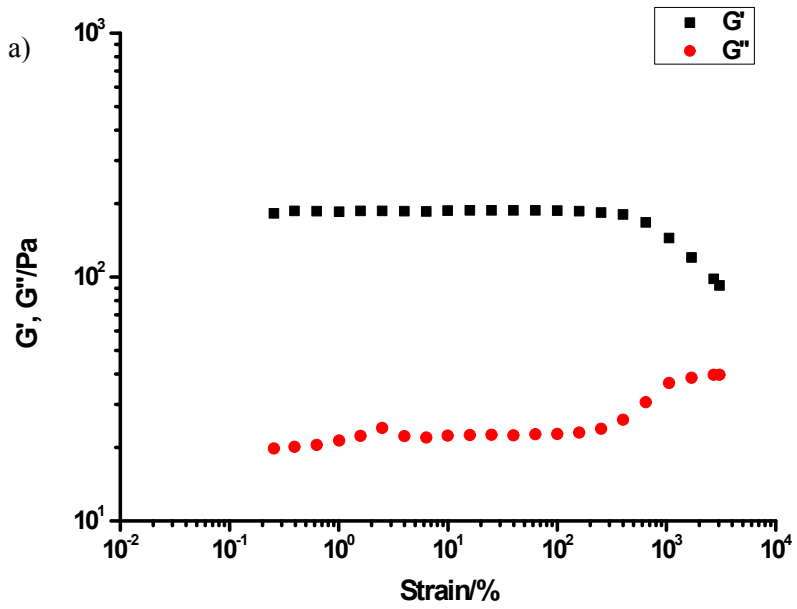


Figure S24. (a) Fluorescence decay traces of Py-OPV (10.0 μM) at 471 nm (λ_{ex} = 380 nm) in aqueous solution. (b-c) Fluorescence decay traces of Py-OPV (10.0 μM) at 471 nm (λ_{ex} = 380 nm) in aqueous solution upon addition of 1 and 2 equiv of CB[7], respectively. (d-e) Fluorescence decay traces of Py-OPV (10.0 μM) at 520 nm (λ_{ex} = 380 nm) in aqueous solution upon addition of 0.2 and 1 equiv of CB[8], respectively.

8. Synthesis of hydrogels

The aqueous solution of Py-OPV (250 μL, 0.1 mM) was added with the aqueous solution of CB[8] (0, 25, 50, 75, 125, 250 μL, 0.1 mM) and then was added with water to 500 μL. On the other hand, acrylamide (0.9384 g, monomers), N,N-methylenebis(acrylamide) (0.564 mg, cross-linkers), ammonium persulfate (1.598 mg, photo initiator) and N,N,N',N'-tetramethylethylenediamine (5 μL, cross-linking accelerator) were dissolved in 6 mL water.[2] After slightly stirring, each 1 mL of the mixture was added into the above assembly solution. Then after 5 minutes of exposure to sunlight, they became transparent and elastic hydrogels.

9. Characterization of the hydrogels



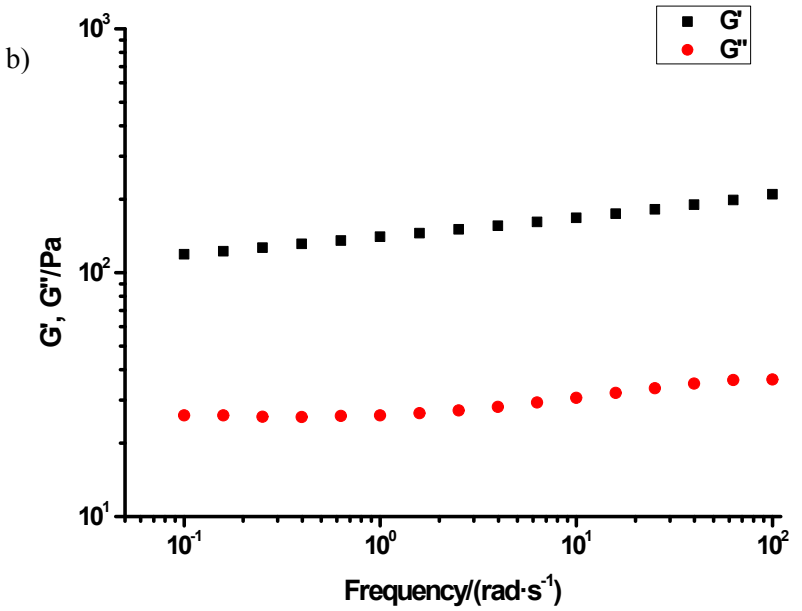
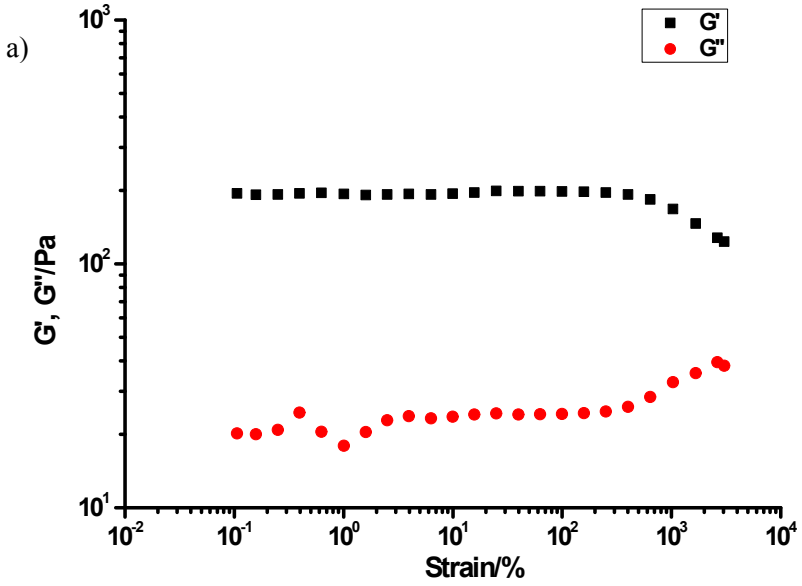


Figure S25. Rheological characterization of hydrogel without CB[8]. a) Dynamic strain sweep curves at fixed angular frequency of 10 rad/s. b) Dynamic frequency sweep curves at fixed strain of 1%.



b)

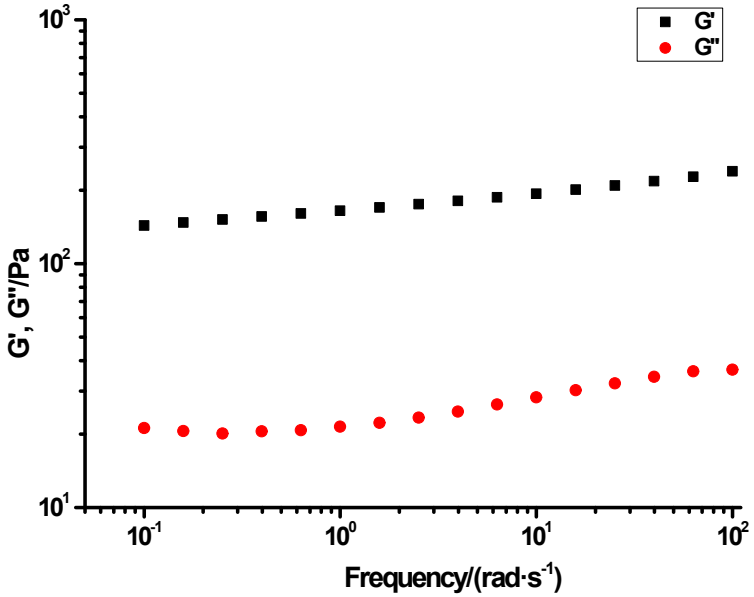


Figure S26. Rheological characterization of hydrogel upon addition of 1 equiv of CB[8]. a) Dynamic strain sweep curves at fixed angular frequency of 10 rad/s. b) Dynamic frequency sweep curves at fixed strain of 1%.

a)

b)

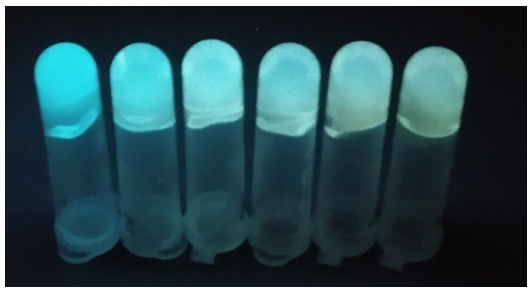


Figure S27. a) Photographs of the hydrogels upon the addition of 0, 0.1, 0.2, 0.3, 0.5, and 1.0 equiv of CB[8] under UV light at 365 nm. b) Photographs of the hydrogels upon the addition of 0, 0.1, 0.2, 0.3, 0.5, and 1.0 equiv of CB[8] after a month in the dark under UV light at 365 nm.

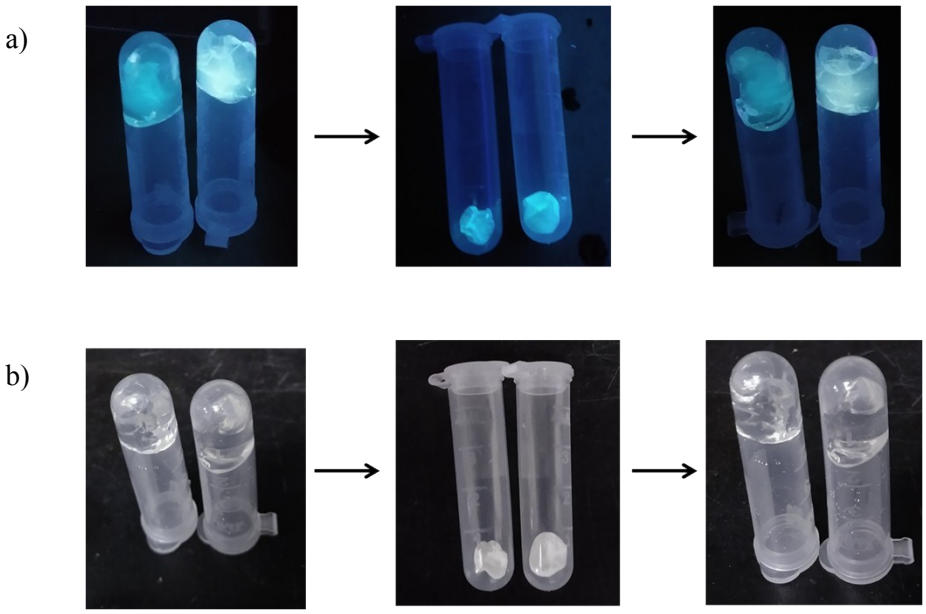


Figure S28. a) Photographs of the hydrogels upon the addition of 0 and 1.0 equiv of CB[8] under UV light at 365 nm, then after being lyophilized, and finally after being **s**oaked in water overnight. b) Photographs of the hydrogels upon the addition of 0 and 1.0 equiv of CB[8], then after being lyophilized, and finally after being **s**oaked in water overnight.

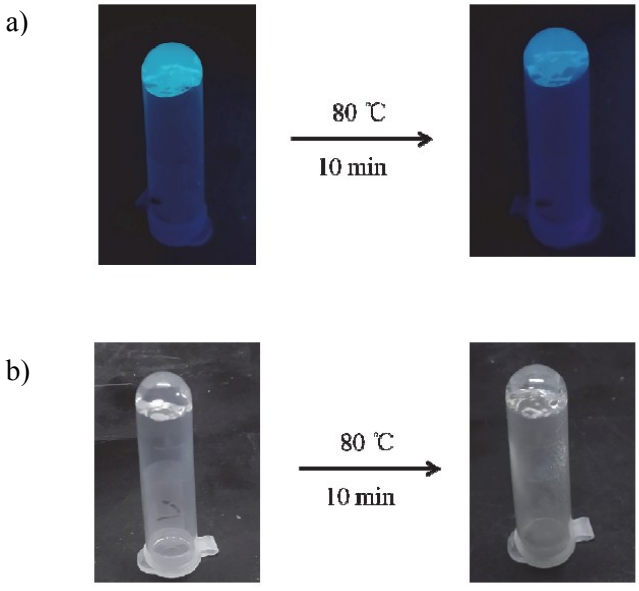


Figure S29. a) Photographs of the hydrogels upon the addition of 1.0 equiv of CB[8] under UV light at 365 nm, then after being soaked in hot water at 80 ℃ for up to 10 minutes. b) Photographs of the hydrogels upon the addition of 1.0 equiv of CB[8], then after being soaked in hot water at 80 ℃ for up to 10 minutes.

REFERENCES

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