Supporting Information

Phenanthroimidazole-based gels for information encryption via synergistic acidichromism and light harvesting

Yuehua Liang[a,1], Juan Zhang[a,1], Tingting Zhang[a], Yanyan Li[a], Caiyuan Guo[a], Jiuzhi Wei[a], Xinxian Ma*[a], and Yun Yan*[a,b]

[a] Ningxia Key Laboratory of Green Catalytic Materials and Technology, College of Chemistry and Chemical Engineering, Ningxia Normal University, College of Chemistry and Chemical Engineering, Ningxia Normal University, Guyuan 756099, China.

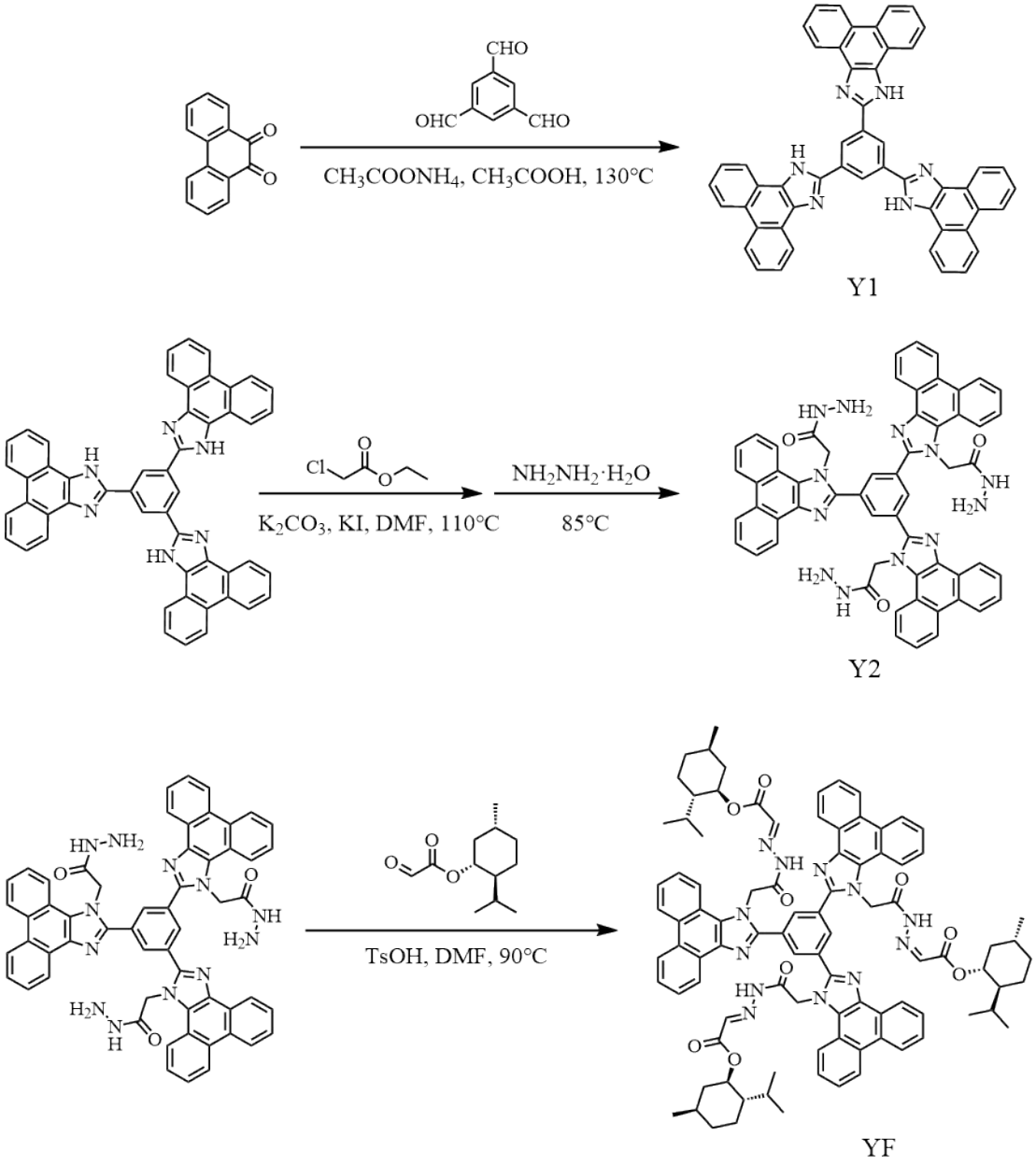
[b] Beijing National Laboratory for Molecular Sciences (BNLMS), College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China.

Corresponding Author

* Xinxian Ma (Email: maxinxian@163.com)

* Yun Yan (Email: cqhuar@126.com; yunyan@pku.edu.cn)

Process of synthesis:



Scheme S1 Synthetic route of molecule YF.

Synthesis of characterization of [Y1]: 9,10-Phenanthraquinone (2.55g, 12.26mmol), ammonium acetate (12.00g, 0.16mol) and 1,3,5-Benzenetricarboxaldehyde (0.66g, 4.07mmol) were dissolved in 60ml of acetic acid, the mixture was stirred at 130 °C for 10h dilute to 1000ml with distilled water, filter, wash with distilled water 4 time. After the product was dried in vacuum, Compound [Y1] was light yellow.

[Y1]: Yield = 57.35%; **^{1}H NMR** (700 MHz, DMSO-d_6) δ(ppm): 14.08 (s, 2H), 14.00 (s, 1H), 8.97 – 8.94 (m, 4H), 8.93 (dd, *J* = 8.4, 5.4 Hz, 3H), 8.90 (d, *J* = 8.4 Hz, 1H), 8.81 (dd, *J* = 7.7, 1.4 Hz, 3H), 8.75 (ddd, *J* = 7.0, 5.7, 1.3 Hz, 3H), 8.67 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.83 (q, *J* = 7.1 Hz, 6H), 7.73 – 7.70 (m, 6H). **Low-resolution ESI-MS:** m/z calculated for $C_{51}H_{31}N_6$ $[M+H]^+$: 727.26; found 727.26.

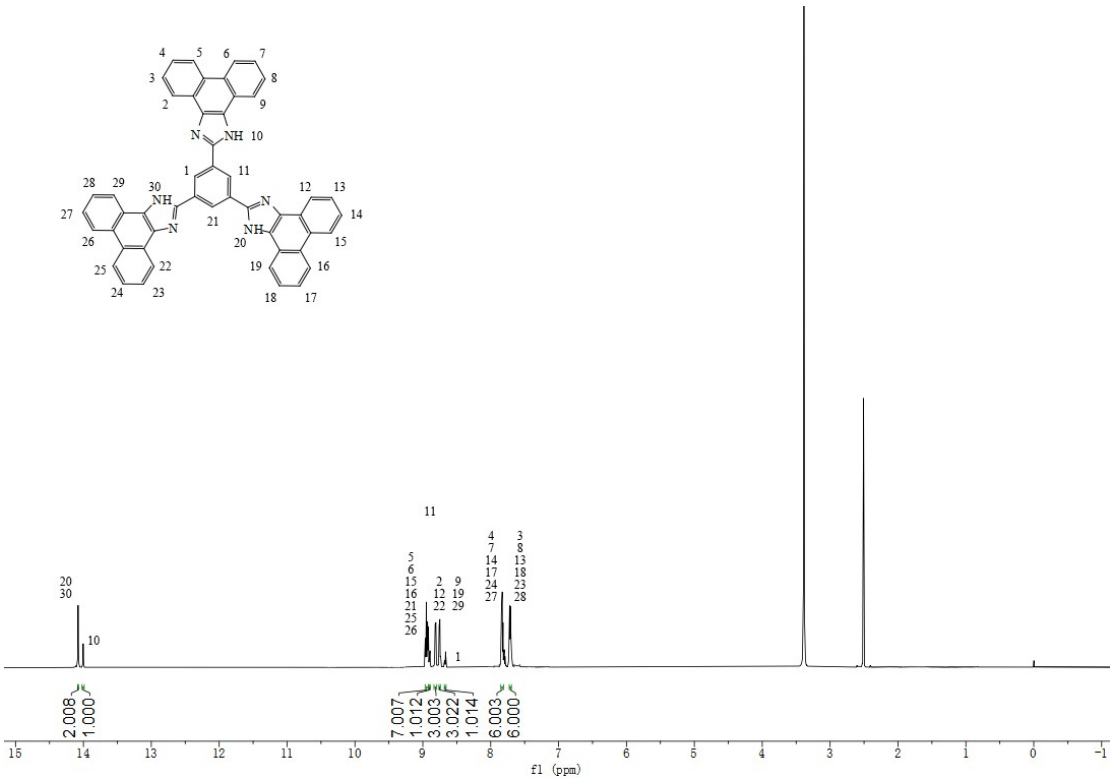
Synthesis of characterization of [Y2]: Compound Y1 (1.20 g, 1.65 mmol) was dissolved in N,N-dimethylformamide (DMF, 40 mL). Potassium carbonate (0.80 g, 5.80 mmol) was then added to the solution, and the mixture was heated and stirred for 40 minutes. Subsequently, potassium iodide (0.2 g, 1.20 mmol) and ethyl chloroacetate (1.30 g, 10.66 mmol) were added. The temperature was raised to 110 °C, and the reaction mixture was stirred for 10 hours. After 10 hours, 7 mL of hydrazine hydrate was added, followed by stirring at 85 °C for another 10 hours. After the reaction was completed, the mixture was cooled to room temperature, and water was added to induce precipitation. The precipitate was collected by suction filtration, washed three times with water and ethanol respectively, and then dried under vacuum, affording a tan solid Y2 (1.37 g, 1.45 mmol) with a yield of 87.88%.

[Y2]: Yield = 87.88%; **^{1}H NMR** (400 MHz, DMSO-d_6) δ(ppm): 9.73 (d, J = 16.2 Hz, 2H), 9.17 – 8.86 (m, 7H), 8.85 – 8.55 (m, 5H), 8.40 – 8.18 (m, 4H), 7.88 – 7.52 (m, 12H), 5.83 (s, 2H), 5.37 (d, J = 44.0 Hz, 4H), 4.51 (s, 4H). **Low-resolution ESI-MS:** m/z calculated for $C_{57}H_{43}N_{12}O_3$ $[M+H]^+$: 943.36; found 943.36.

Synthesis of characterization of [YF]: Compound Y2 (1.00 g, 1.06 mmol) was dissolved in N,N-dimethylformamide (DMF, 20 mL). p-Toluenesulfonic acid (0.02 g, 0.12 mmol) was then added, and the mixture was stirred and gently heated for 10 minutes. Afterwards, L-menthyl glyoxylate (1.30 g, 6.13 mmol) was added, and the mixture was stirred at 90 °C for 9 hours. The product was washed three times with water and ethanol respectively. After being dried under vacuum, a yellow solid YF (1.60 g, 1.05 mmol) was obtained with a yield of 99.06%.

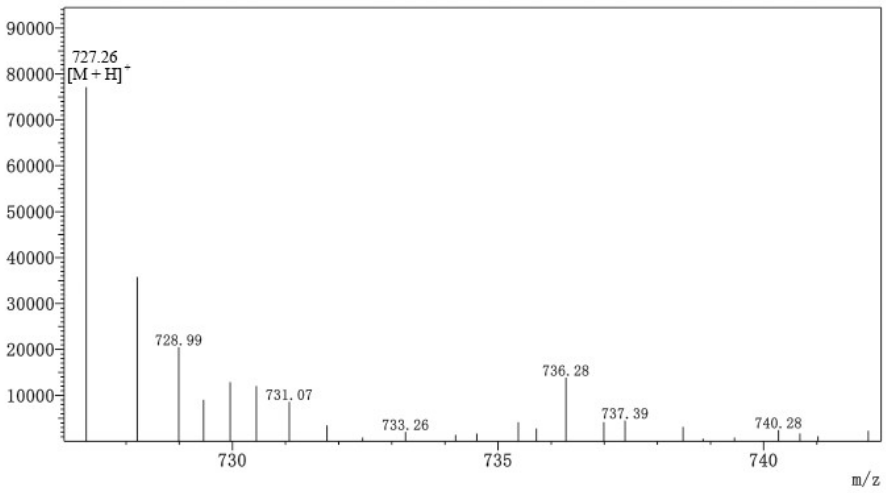
[YF]: Yield = 99.06%; **^{1}H NMR** (400 MHz, DMSO-d_6) δ(ppm):13.94 (s, 1H), 12.75 (d, J = 19.5 Hz, 2H), 9.17 – 7.41 (m, 30H), 6.23 – 5.44 (m, 6H), 4.84 – 4.60 (m, 3H), 1.95 – 1.26 (m, 18H), 1.11 – 0.50 (m, 36H).**^{13}C NMR** (101 MHz, DMSO-d_6) δ(ppm)=170.60, 149.09, 129.33 – 123.79 (m), 122.96 (d, J = 58.8 Hz), 87.45, 73.89, 46.88, 34.07 (d, J = 13.2 Hz), 31.26 (d, J = 4.0 Hz), 25.96, 23.42, 22.29 (d, J = 8.9 Hz), 20.95, 20.81, 17.61 – 16.47 (m); **Low-resolution ESI-MS:** m/z calculated for $C_{93}H_{97}N_{12}O_9$ $[M+H]^+$: 1525.75; found 1525.75.

^{1}H NMR spectra of [Y1]:



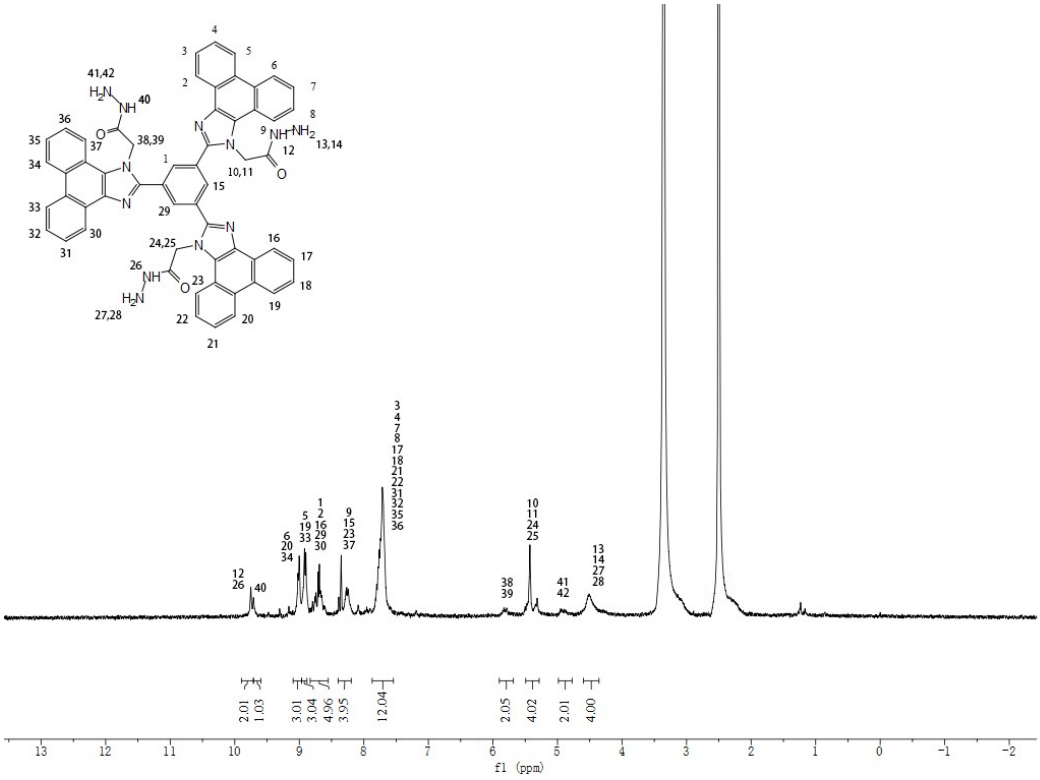
SI Fig.S1: ^{1}H NMR spectrum (700 MHz, DMSO-d_6) of compound Y1.

Mass spectra of [Y1]:



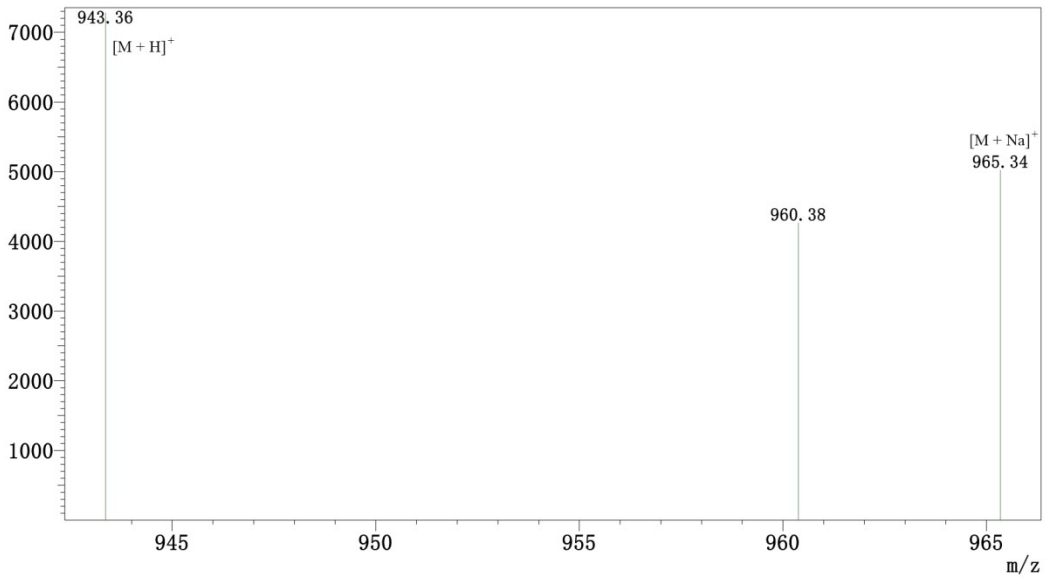
SI Fig.S2: Low-resolution ESI-MS spectrum of compound Y1.

^{1}H NMR spectra of [Y2]:



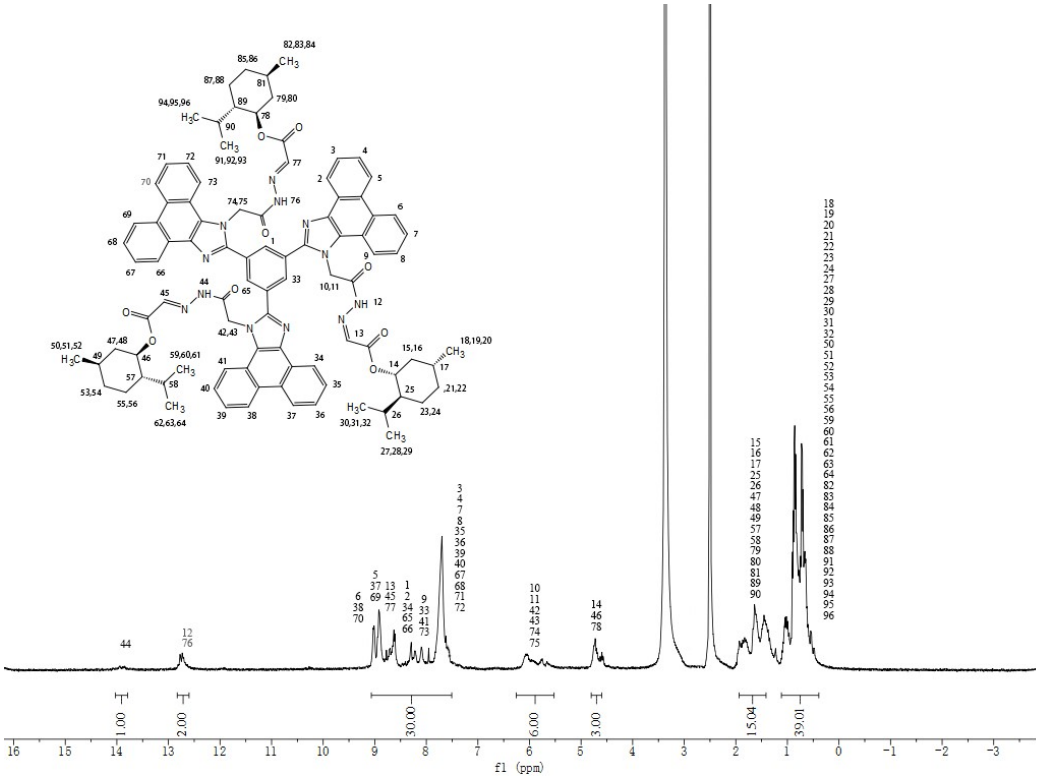
SI Fig.S3: ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound Y2.

Mass spectra of [Y2]:

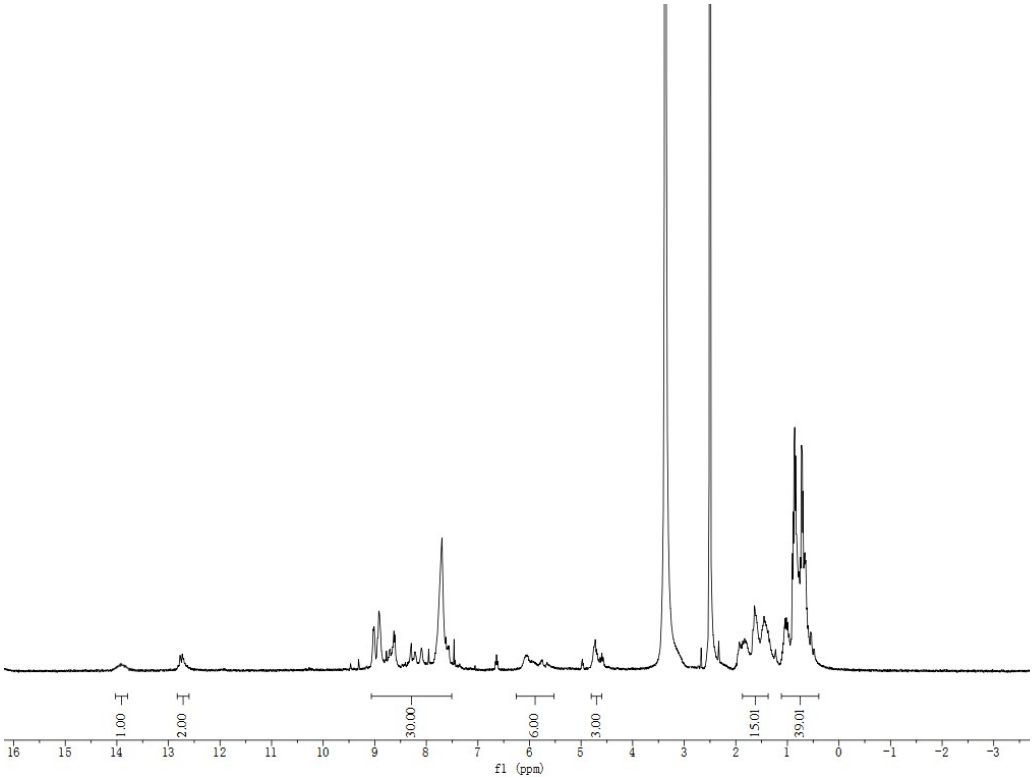


SI Fig.S4: Low-resolution ESI-MS spectrum of compound Y2.

^{1}H NMR spectra of [YF]:

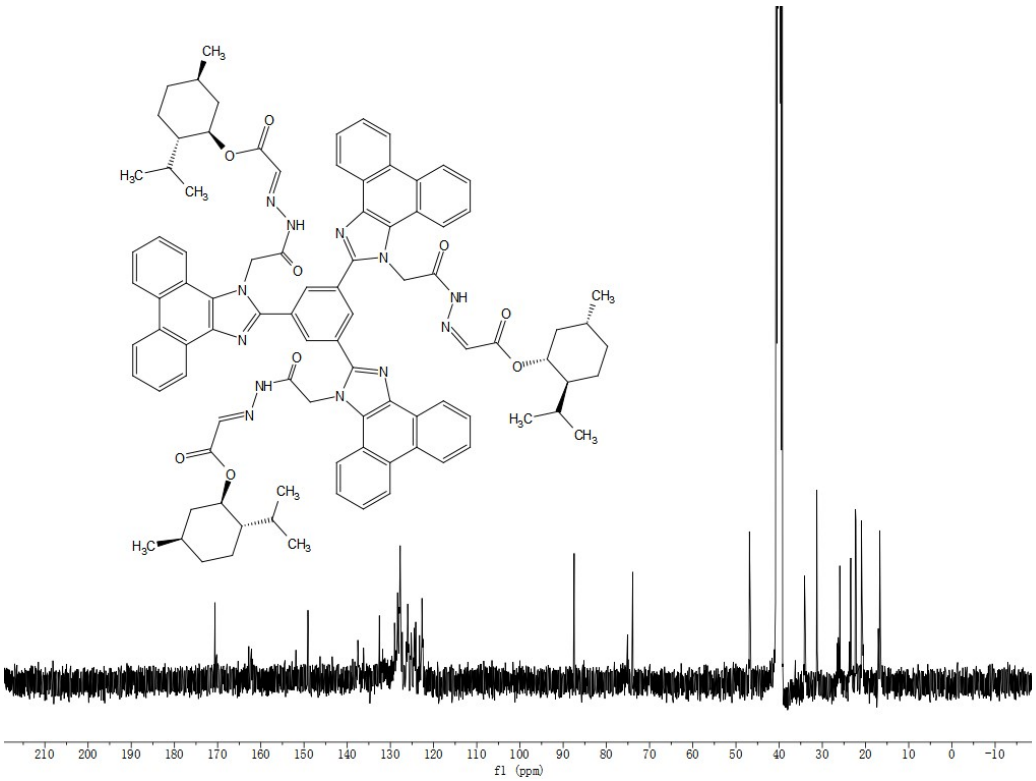


SI Fig.S5: ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound YF.



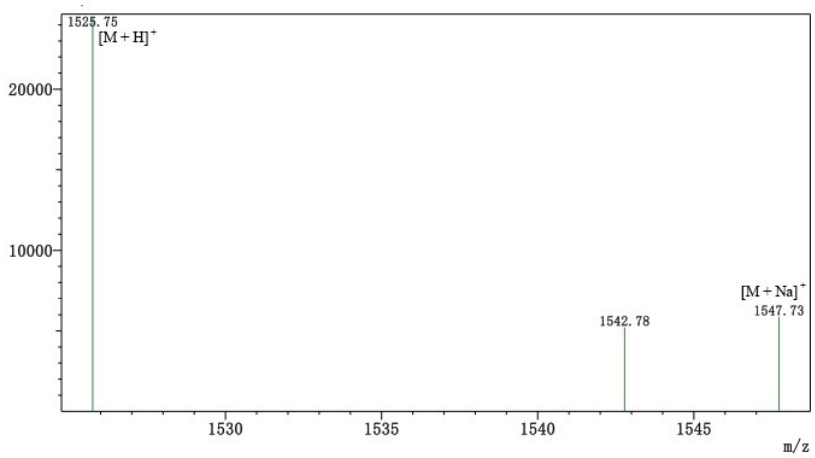
SI Fig.S6: ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound YF after heating to 120 °C and cooling to room temperature.

^{13}C NMR spectra of [YF]:



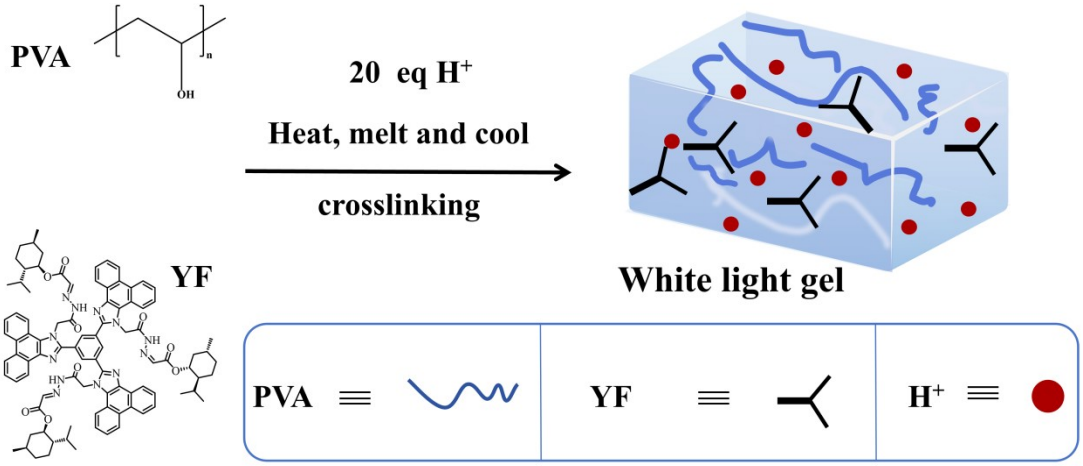
SI Fig.S7: ^{13}C NMR spectrum (101 MHz, DMSO-d_6) of compound YF.

Mass spectra of [YF]:



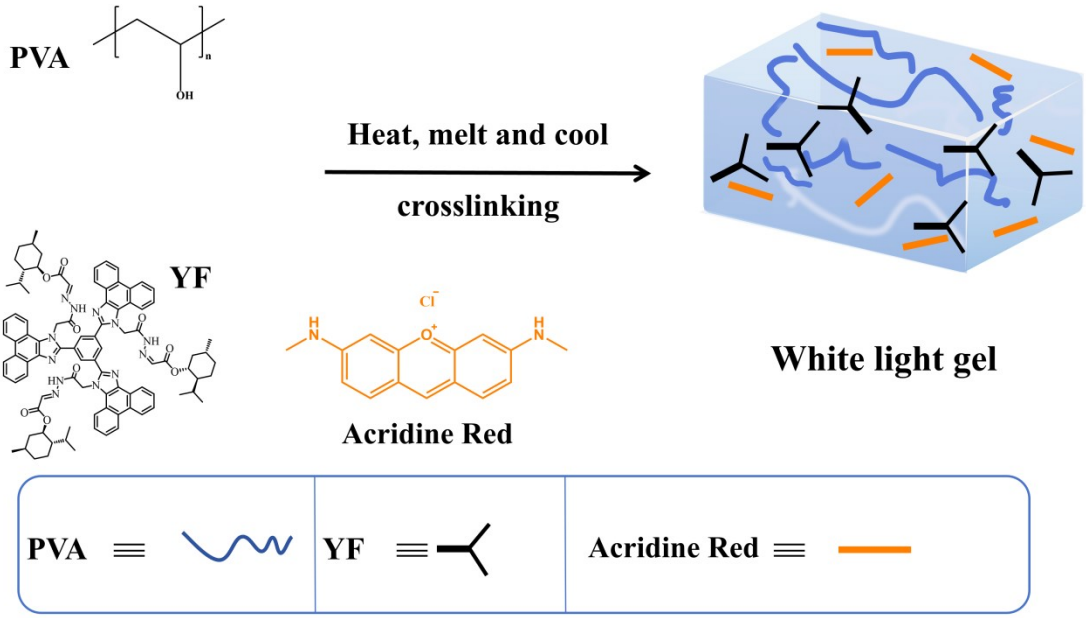
SI Fig.S8: Low-resolution ESI-MS spectrum of compound YF.

Schematic diagram of the preparation of PYFS and PYFF gels:



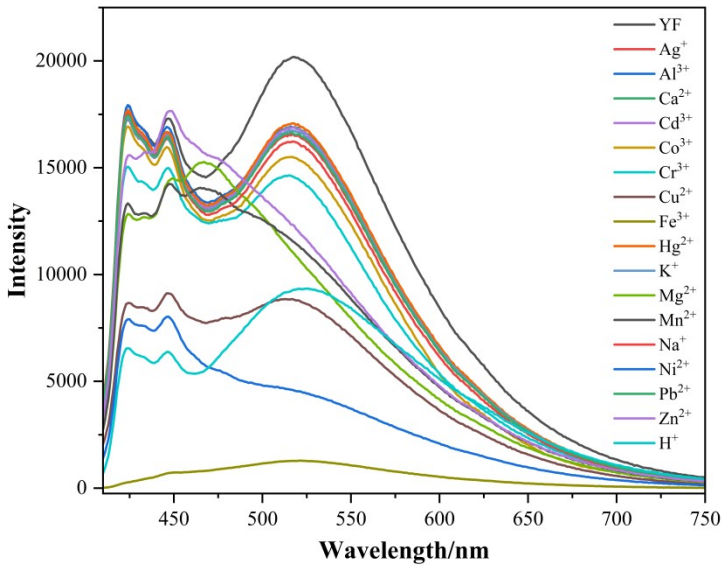
SI Fig.S9: Schematic diagram of the preparation of PYFS gel.

A solution of YF in dimethyl sulfoxide (DMSO) (10 mL, [YF] = 1 × 10^{-4} mol/L), PVA (2.2 g), and concentrated sulfuric acid (50 μL) were mixed. The mixture was heated at 120°C and stirred for 7 h, and it was then poured into a petri dish while still hot and spread evenly. Next, the mixture was cooled to 25°C and placed in a refrigerator at −20°C for 12 h to obtain a PYFS white-light-emitting gel.

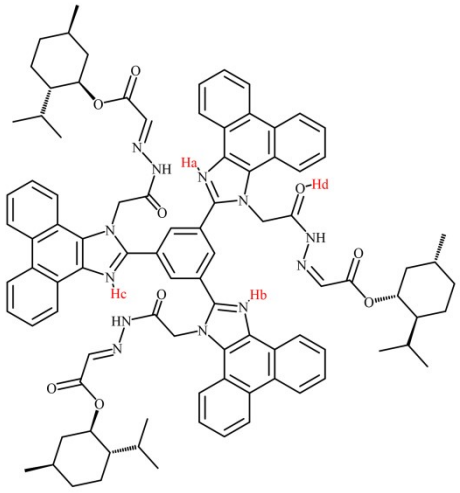


SI Fig.S10: Schematic diagram of the preparation of PYFF gel.

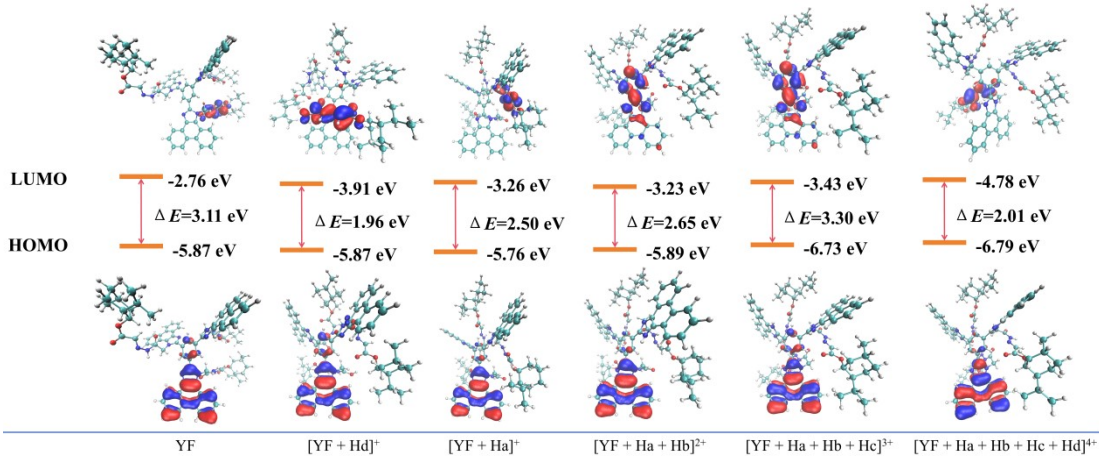
A solution of YF and Acridine Red in DMSO (10 mL, YF:Acridine Red molar ratio = 50:1) and PVA (2.2 g) were mixed at [YF] = 1 × 10^{-3} mol/L. After the mixture was heated at 120°C and stirred for 7 h, it was poured (while still hot) into a petri dish and spread evenly. The mixture was then cooled to room temperature and placed in a refrigerator at −20°C for 12 h to obtain a PYFF white-light gel.



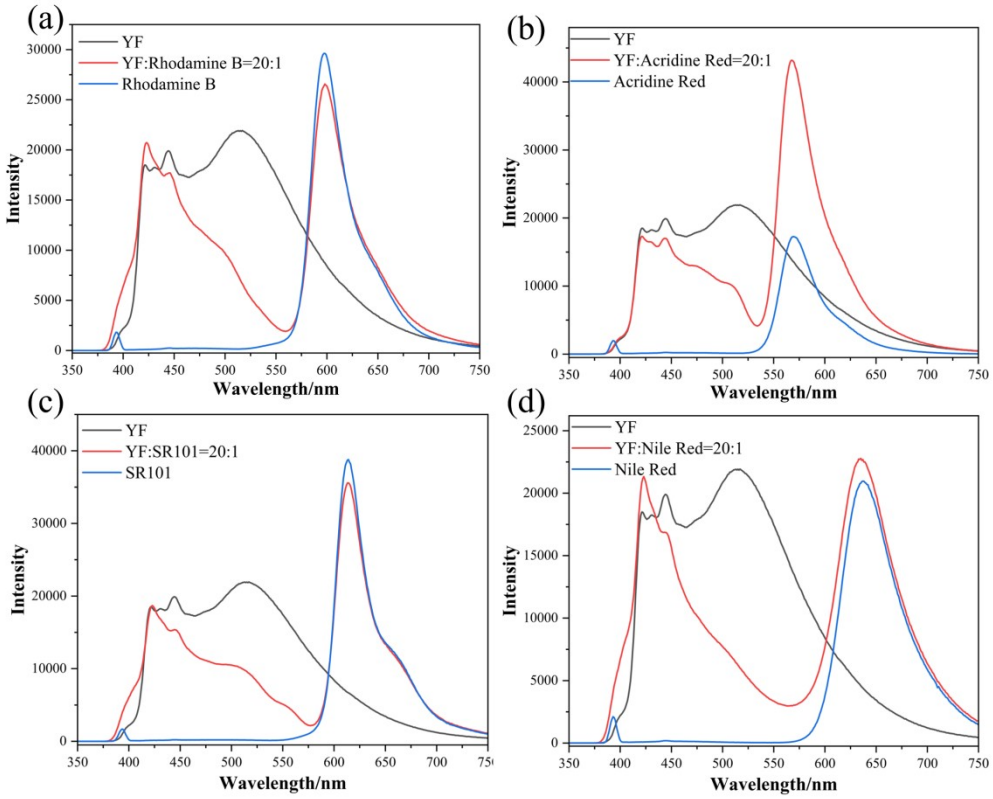
SI Fig.S11: The cation recognition detection curve of YF.



SI Fig.S12: YF–H^+ binding schematic.



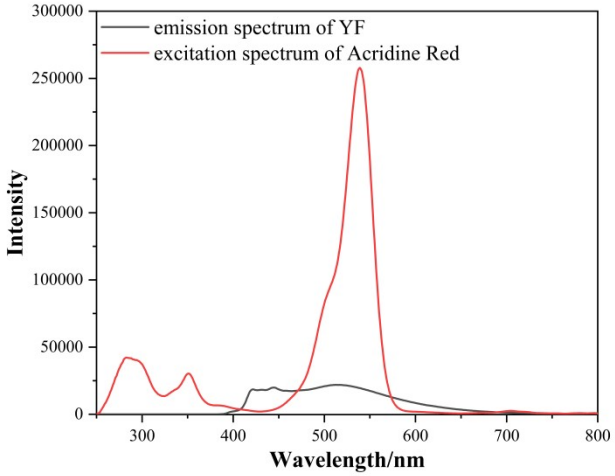
SI Fig.S13: Calculated HOMO–LUMO levels of YF at varied H^+ binding extents.



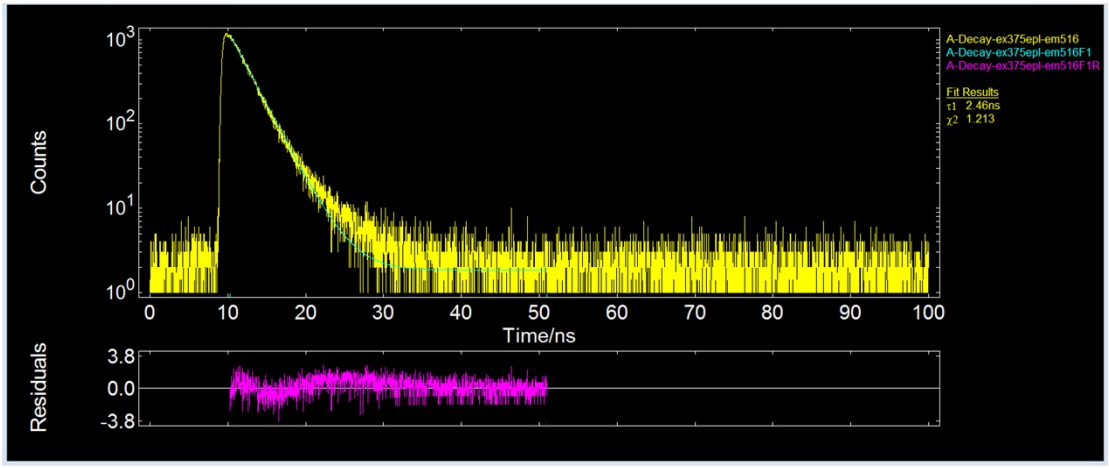
SI Fig.S14: Fluorescence performance tests were conducted for (a), (b), (c), and (d), which correspond to the donor YF paired with four acceptors—namely Rhodamine B, Acridine Red, SR101, and Nile Red, respectively. The tests were carried out at a donor/acceptor molar ratio of 20:1, with the following concentrations: [YF] = 1×10^{-3} mol/L, and [Rhodamine B] = [Acridine Red] = [SR101] = [Nile Red] = 0.5×10^{-5} mol/L.

Table S1. Fluorescence properties of YF, YF/Rhodamine B,YF/Acridine red, YF/SR101 and YF/Nile Red. ([YF] = 1×10^{-3} mol/L, [SR101] = 0.5×10^{-5} mol/L, [Acridine red] = 0.5×10^{-5} mol/L, [Nile Red] = 0.5×10^{-5} mol/L, [Rhodamine B] = 0×10^{-5} mol/L, respectively).

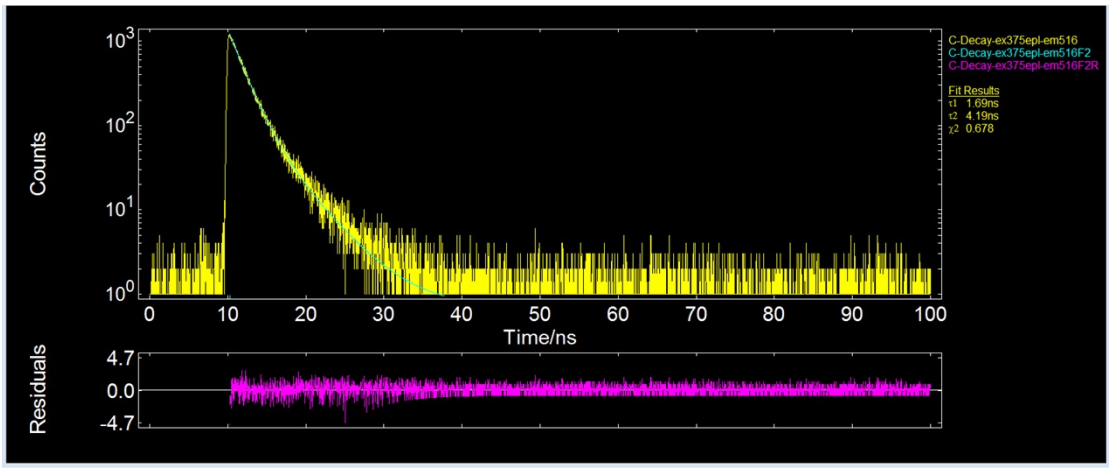
sample	chromaticity coordinate	energy transfer efficiency [%]
YF	(0.25,0.33)	—
YF/Rhodamine B	(0.36,0.24)	67.89
YF/Acridine red	(0.27,0.36)	58.57
YF/SR101	(0.38,0.26)	56.14
YF/Nile Red	(0.34,0.21)	71.54



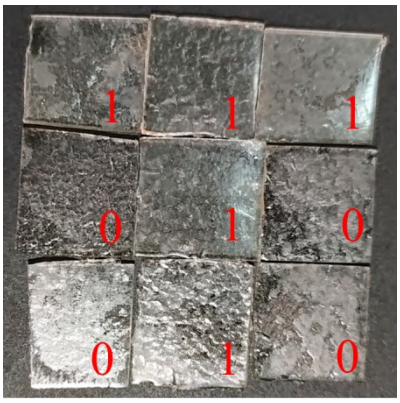
SI Fig.S15: Comparison of the optimal emission spectrum of YF (1×10^{-3} mol/L in DMF) and the optimal excitation spectrum of Acridine Red (5×10^{-5} mol/L in DMF).



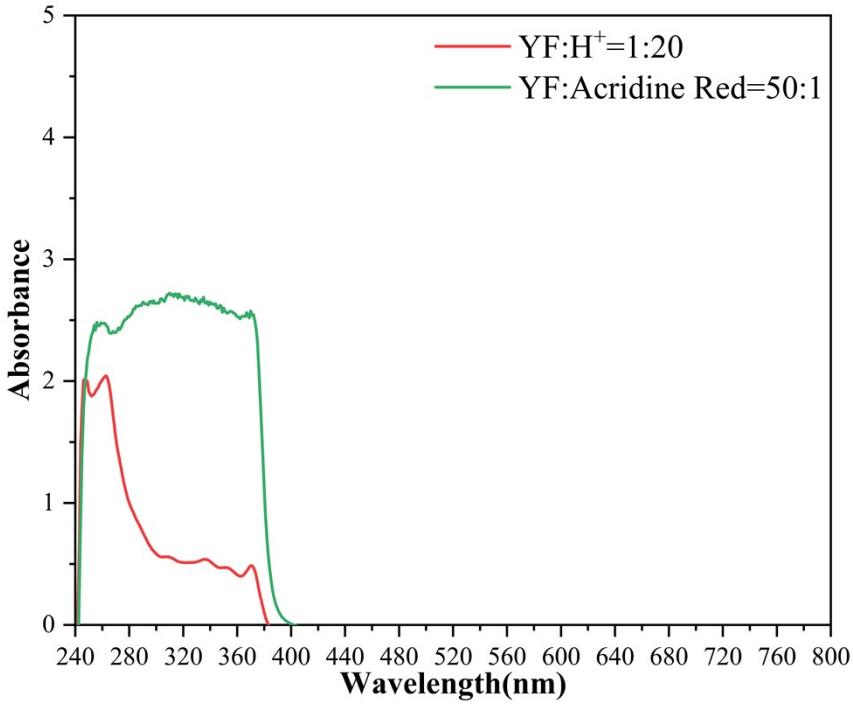
SI Fig.S16: Fluorescence lifetime of YF ([YF] = 1×10^{-3} mol/L. Monitored at 516nm upon excitation at 375nm).



SI Fig.S17: Fluorescence lifetime of YF/Acridine red ([YF] = 1×10^{-3} mol/L, [Acridine red] = 2.0×10^{-5} mol/L. Monitored at 516nm upon excitation at 375nm).



SI Fig.S18: Images of the PYFS and PYFF gels under natural light. Here, 1 represents the PYFF gel and 0 represents the PYYS gel.



SI Fig.S19: UV–vis absorption spectra of PYFS and PYFF gels.