Supplemental Information

Ions recognition properties of 2'2-bibenzimidazole regulated by ammonium modified pillar[5]arene

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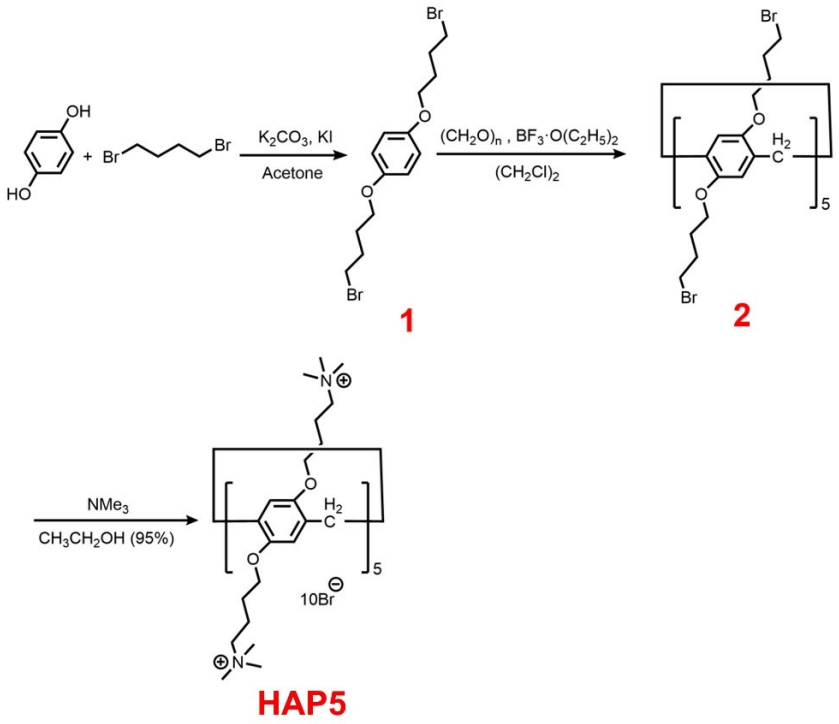
Table of Contents



Scheme S1. Synthesis route of **HAP5**

Synthesis of compound HAP5

We synthesized compound 1 and 2 according to the literature.[1, 2] The compound 2 (1.96 g, 1.0 mmol) and trimethylamine (33% in ethanol, 7.20 mL, 30.0 mmol) were added to ethanol (50 mL). The solution was refluxed over night at 80℃. Then the solvent was removed by evaporation, deionized water (20 mL) was added. After filtration, a clear solution was obtained and then the water was removed by evaporation to obtain HAP5 as a white solid (2.56 g, yield 95%). m.p. 217-219℃. ^{1}H NMR (400 MHz, DMSO-d_6), δ/ppm: δ 6.83 (s, 10H), 4.07 (s, 10H), 3.83 (d, J = 8.3 Hz, 10H), 3.70 (s, 10H), 3.59 (s, 20H), 3.17 (s, 90H), 1.90 (d, J = 46.4 Hz, 40H). ^{13}C NMR (150 MHz, DMSO-d_6.), δ/ppm: 150.12, 129.22, 116.81, 68.46, 65.87, 52.87, 25.78 and 19.46. EMI-MS m/z: calcd for $C_{105}H_{190}N_{10}O_{10}Br_9KNa$ $[HAP5 - Br + K + 3Na]^{5+}$:513.9329, found:513.5933.

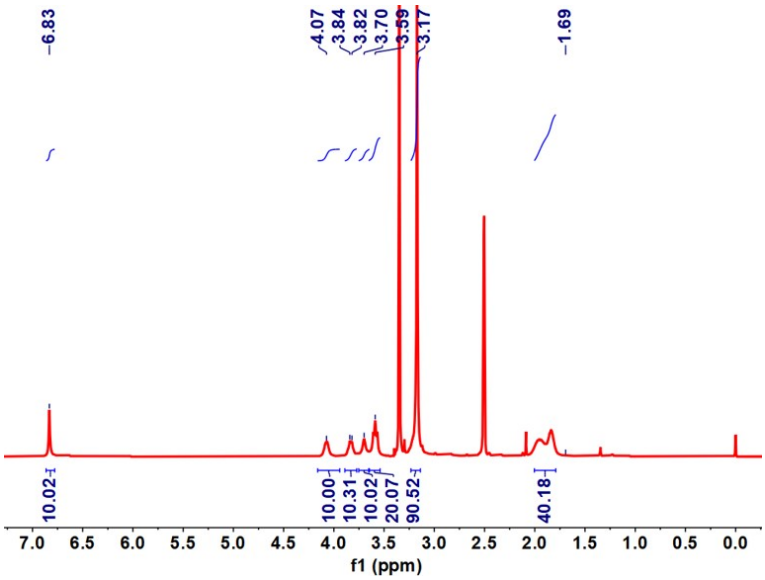


Fig. S1 ^{1}H NMR (400 MHz, 298K) spectra of **HAP5** in DMSO-d_6.

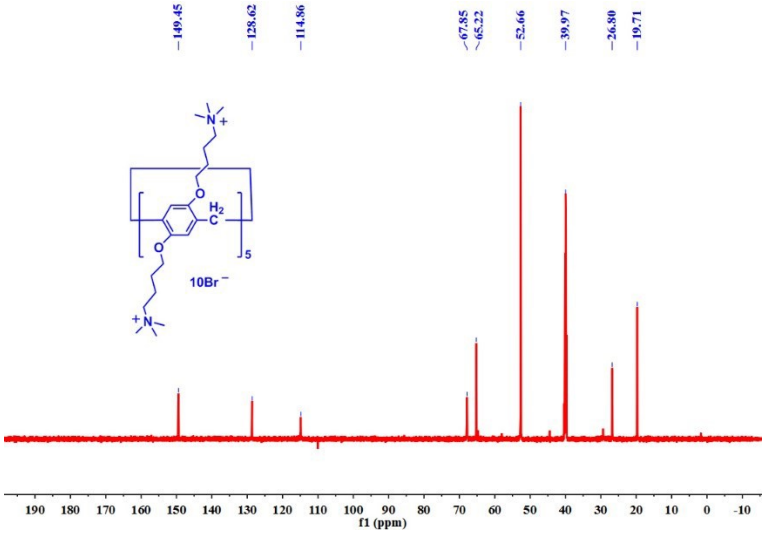


Fig. S2 ^{13}C NMR (150 MHz, 298K) spectra of **HAP5** in D_2O.

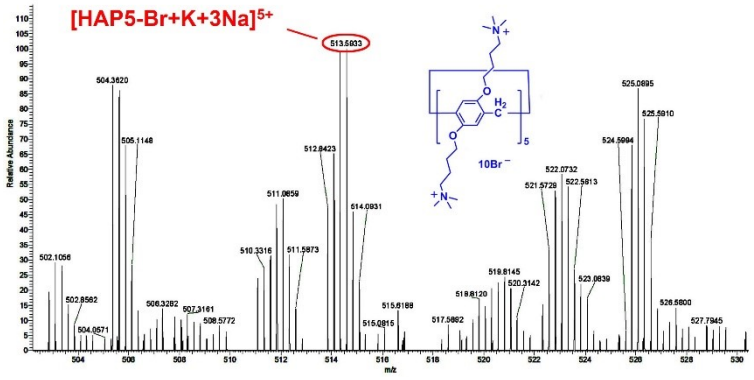
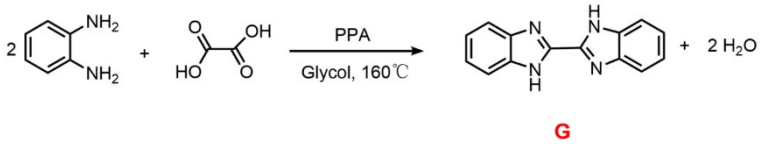


Fig. S3 ESI-MS spectra of **HAP5**



G

Scheme S2. Synthesis route of **G**

Synthesis of compound G

We synthesized compound **G** according to the literature.[3] The amidation reaction was carried out at low temperature by grinding method, and then the ring-closure reaction was completed during reflux. The 1,2-diaminobenzene (7.2 g, 67 mmol), polyphosphoricacid (12 mL) and oxalic acid (4.2 g, 33 mmol) were added to ethylene glycol (50 mL). The solution was refluxed 1.5 h at 160℃. Then cool to room temperature, deionized water (300 mL) was added. After filtration, the product was recrystallized to obtained **G** as a yellow needle-like solid (12.9 g, yield 83.0%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.90 (s, 10H), 4.04 (s, 29H), 3.07 (s, 128H), 1.69 (s, 41H). ^{13}C NMR (150 MHz, DMSO-d_6), δ/ppm: 21.48, 144.19, 172.51. EMI-MS m/z: calcd for $C_{14}H_{10}N_4$ [G-H]$^-$: 234.0905, found: 233.0829.

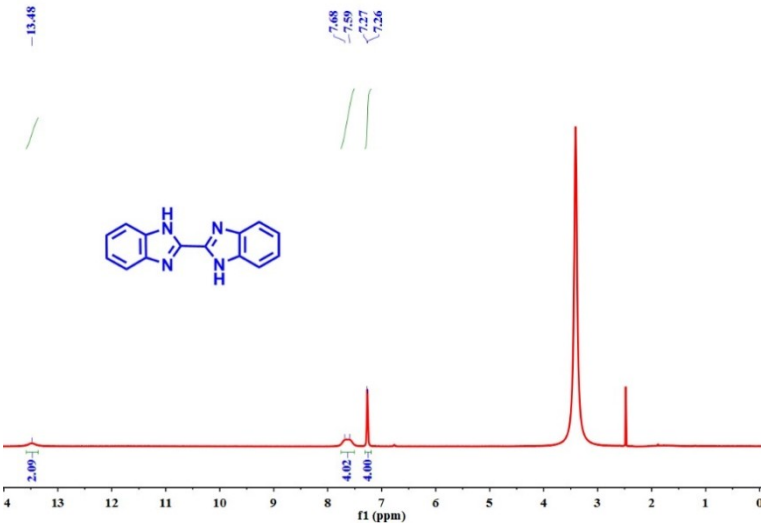


Fig. S4 ^{1}H NMR (400 MHz, 298K) spectra of **G** in DMSO-d_6.

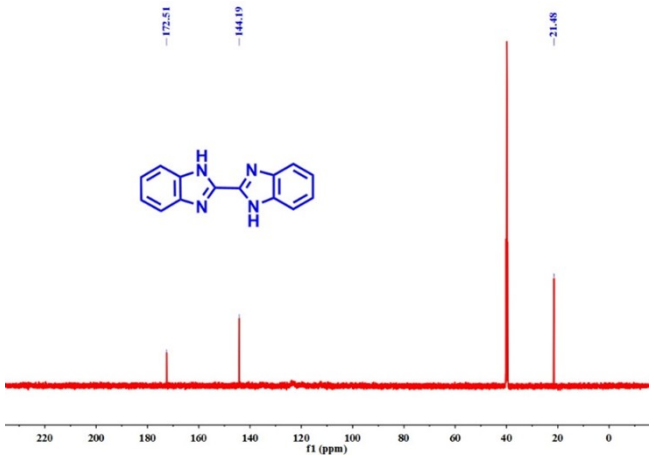


Fig. S5 ^{13}C NMR (150 MHz, 298K) spectra of **G** in DMSO-d_6.

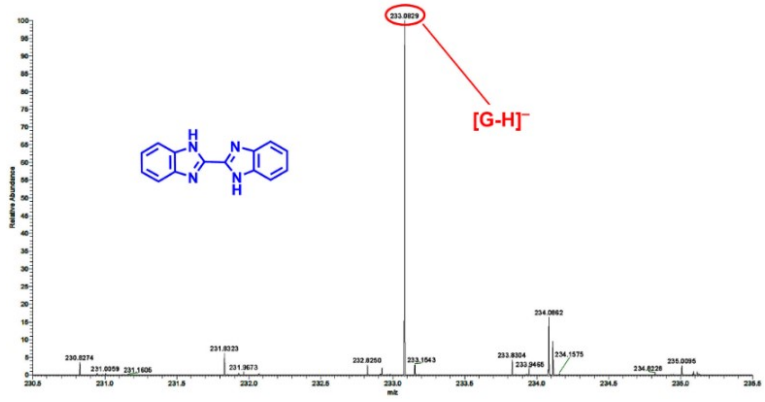


Fig. S6 ESI-MS spectra of **G**

General conditions for fluorescence experiments:

All the fluorescence spectroscopy was carried out in in DMSO/H_2O (1:1, v/v) solution on a Shimadzu RF-5301 spectrometer. All of the solutions prepared fresh and used it at room temperature.

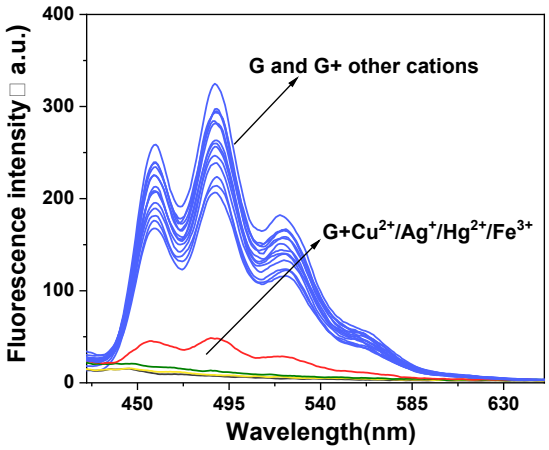


Fig. S7. Fluorescent spectra of **G** (2.0×10^{-5} M) in DMSO/H_2O (1:1, v/v) in the presence of cations (10 equiv.).

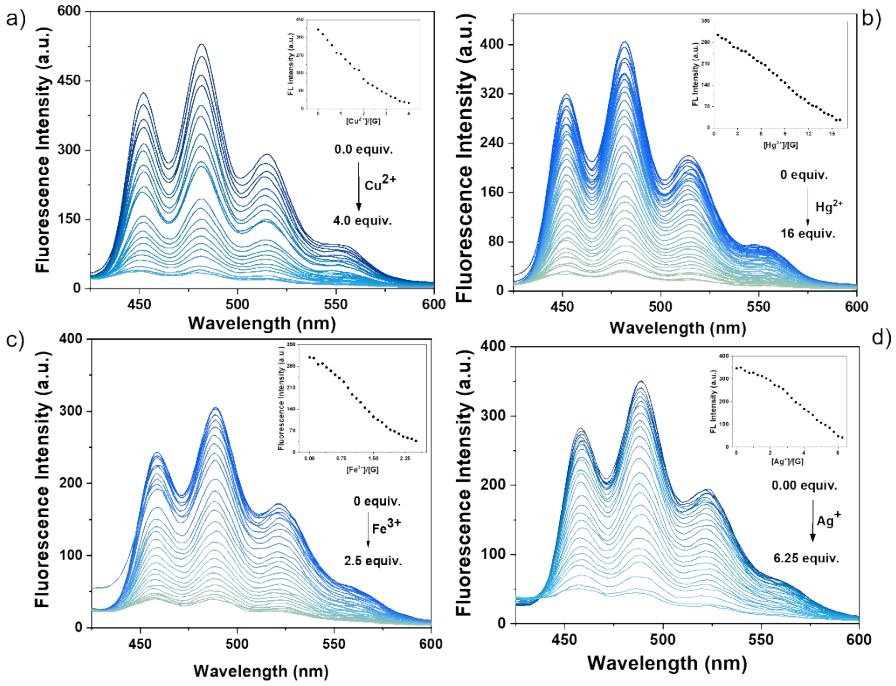


Fig. S8 (**a**) Fluorescence spectrum of **G** (2×10^{-5} M) in the presence of different equivalents of Cu^{2+} in DMSO/H_2O (v/v=1:1) binary solution. (**b**) Fluorescence spectrum of **G** (2×10^{-5} M) in the presence of different equivalents of Hg^{2+} in DMSO/H_2O (v/v=1:1) binary solution. (**c**) Fluorescence spectrum of **G** (2×10^{-5} M) in the presence of different equivalents of Fe^{3+} in DMSO/H_2O (v/v=1:1) binary solution. (**d**) Fluorescence spectrum of **G** (2×10^{-5} M) in the presence of different equivalents of Ag^{+} in DMSO/H_2O (v/v=1:1) binary solution.

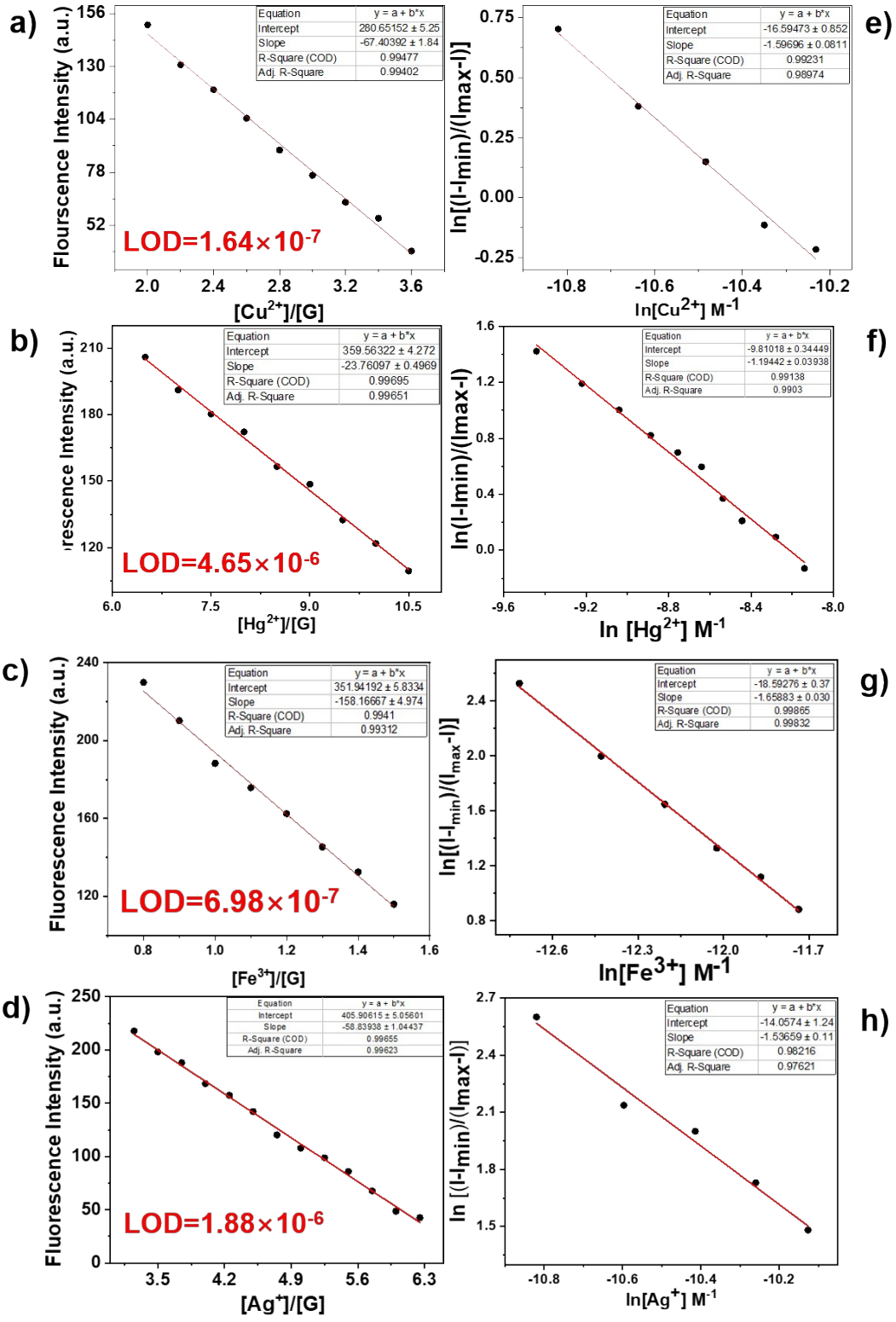


Fig. S9 (**a-d**) Fluorescent spectrum linear range for Cu^{2+}, Hg^{2+}, Fe^{3+}, and Ag^{+} by addition of various concentrations of Cu^{2+}, Hg^{2+}, Fe^{3+}, and Ag^{+} into **G**. (**d-f**) The photograph of the linear range based on Bensi-Hildebrand equation to calculated K_a between Cu^{2+}, Hg^{2+}, Fe^{3+}, and Ag^{+} with **G.**

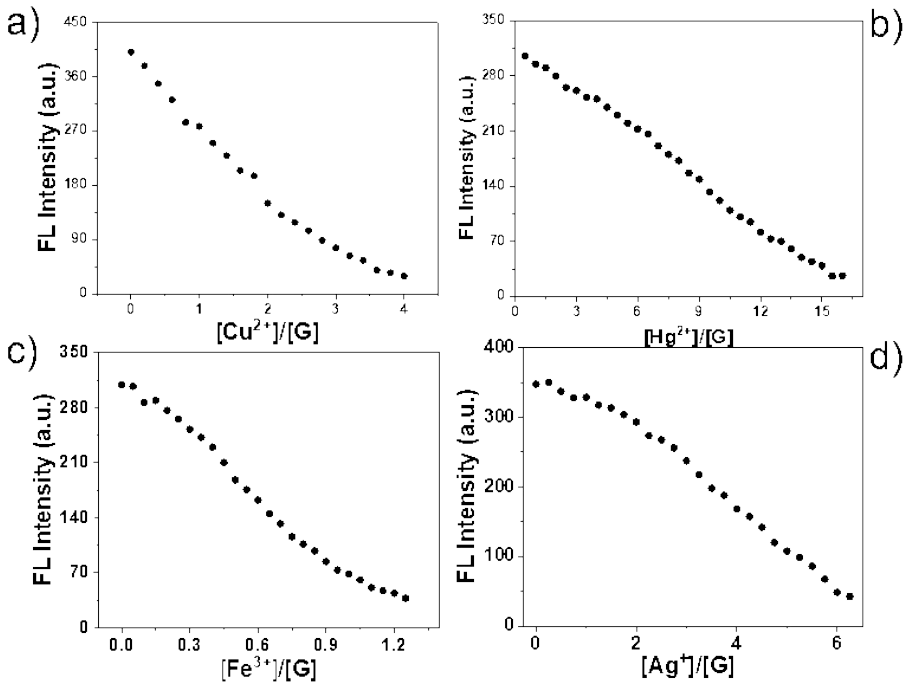


Fig. S10 A plot of fluorescent intensity depending on the concentration of Cu^{2+}, Hg^{2+}, Fe^{3+} and Ag^{+} in the range from different equivalents: (**a**) **G-Cu^{2+}**, (**b**) **G-Hg^{2+}**, (**c**) **G-Fe^{3+}** and (**d**) **G-Ag^{+}**.

Tab. S1 Calculation formula and related date of the detection limits of **G** for Cu^{2+}, Hg^{2+}, Fe^{3+} and Ag^{+}.

Cation	**A(Slope)**	**B(Intercept)**	**R^2**	**δ**	***S***	**LOD**
Cu^{2+}	67.4039	280.6515	0.994	3.683	6.74×10^{6}	1.64×10^{-6}
Hg^{2+}	23.7610	359.5632	0.996	3.683	2.38×10^{7}	4.65×10^{-6}
Fe^{3+}	158.1667	351.9419	0.994	3.683	1.58×10^{8}	6.98×10^{-7}
Ag^{+}	58.8394	405.9061	0.996	3.683	5.88×10^{7}	1.88×10^{-6}
Liner Equation ***y=A x+ B***						
Calculation formula	$\delta=\sqrt{\frac{\Sigma(F-\bar{F})2}{(N-1)}}$ N=20 K=3 S=A×10^{6}					
LOD=K×δ/*S*						

Tab. S2 Association constants of the **G** treated by Cu^{2+}, Hg^{2+}, Fe^{3+} and Ag^{+}, calculation formula and related data.

Compand	Metal ions	A(Slope)	B(Intercept)	R^2	*Ka*/M^{-1}
G	Cu^{2+}	1.59	16.59	0.989	1.60×10^{7}
G	Hg^{2+}	1.19	9.81	0.990	1.82×10^{4}
G	Fe^{3+}	1.66	18.59	0.998	1.18×10^{8}
G	Ag^{+}	1.54	14.06	0.976	1.28×10^{6}

Calculation formula

Liner Equation $y=Ax+B$ $\qquad In\frac{I-Imin}{Imax-I} = -InKa - nIn[M^{2+}]$

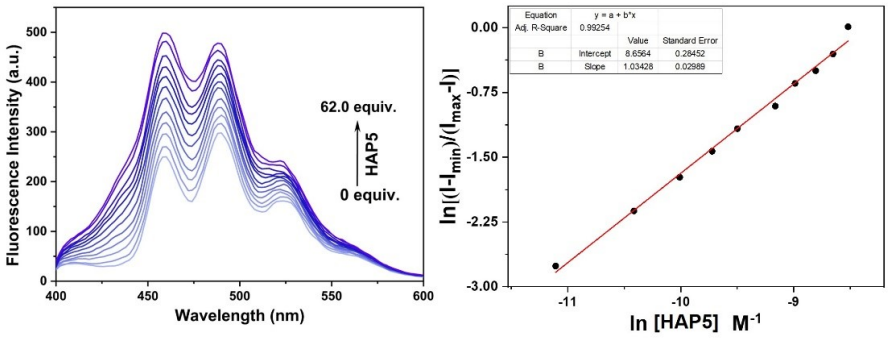


Fig. S11. Fluorescence titration of **G** (2.0×10^{-5} M) in DMSO/water aqueous solution system (1:1, v/v) upon addition of increasing with **HAP5**.

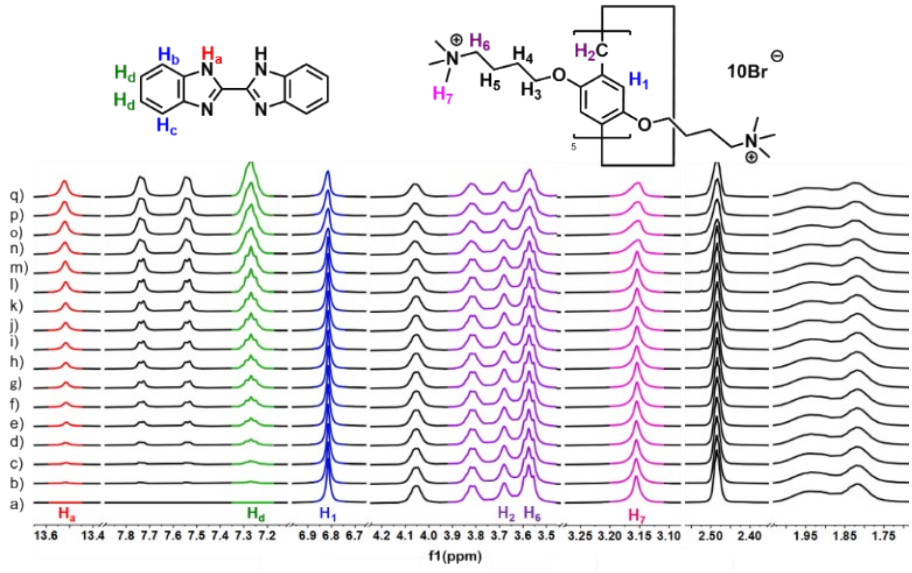


Fig. S12 ^{1}H NMR spectra of **HAP5** (DMSO–d_6) and in the presence of varying amounts of **G** from 0 equiv. to 2 equiv.

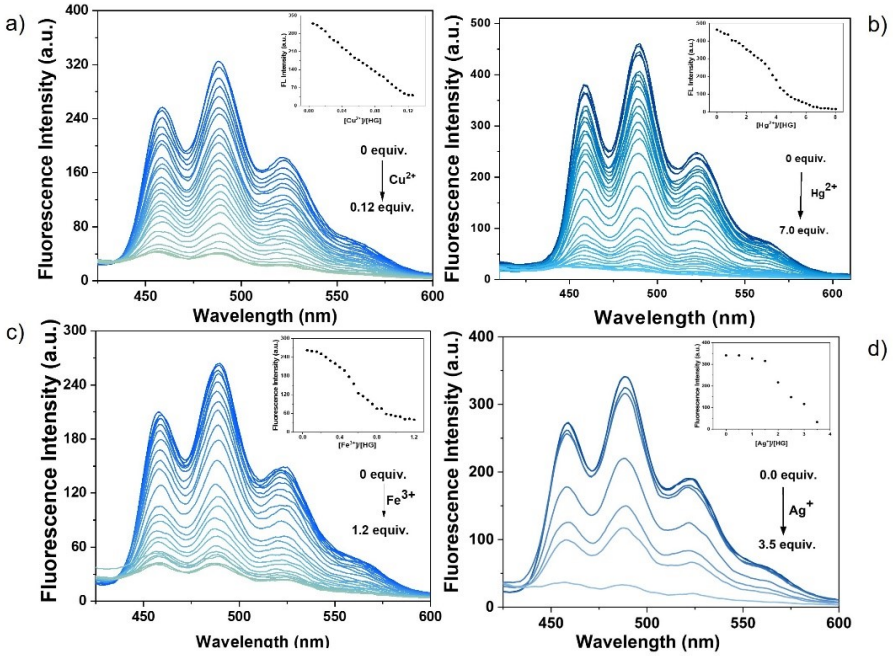


Fig. S13 (**a**) Fluorescence spectrum of **HG** (2×10^{-5} M) in the presence of different equivalents of Cu^{2+} in DMSO/H_2O (v/v=1:1) binary solution. (**b**) Fluorescence spectrum of **HG** (2×10^{-5} M) in the presence of different equivalents of Hg^{2+} in DMSO/H_2O (v/v=1:1) binary solution. (**c**) Fluorescence spectrum of **HG** (2×10^{-5} M) in the presence of different equivalents of Fe^{3+} in DMSO/H_2O (v/v=1:1) binary solution. (**d**) Fluorescence spectrum of **HG** (2×10^{-5} M) in the presence of different equivalents of Ag^{+} in DMSO/H_2O (v/v=1:1) binary solution.

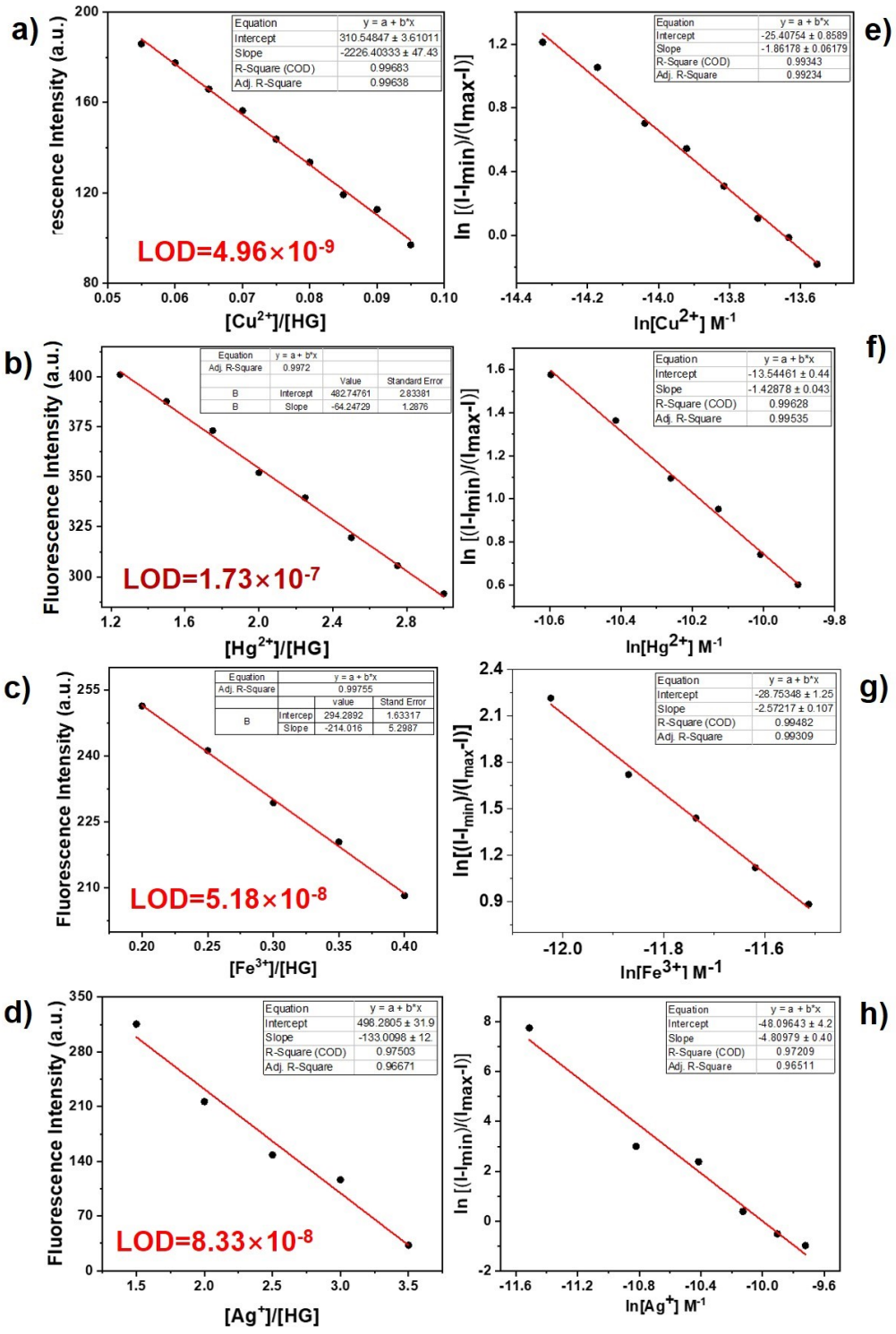


Fig. S14 (**a-d**) Fluorescent spectrum linear range for Cu^{2+}, Hg^{2+}, Fe^{3+}, and Ag^{+} by addition of various concentrations of Cu^{2+}, Hg^{2+}, Fe^{3+}, and Ag^{+} into **HG**. (**d-f**) The photograph of the linear range based on Bensi-Hildebrand equation to calculated K_a between Cu^{2+}, Hg^{2+}, Fe^{3+}, and Ag^{+} with **HG.**

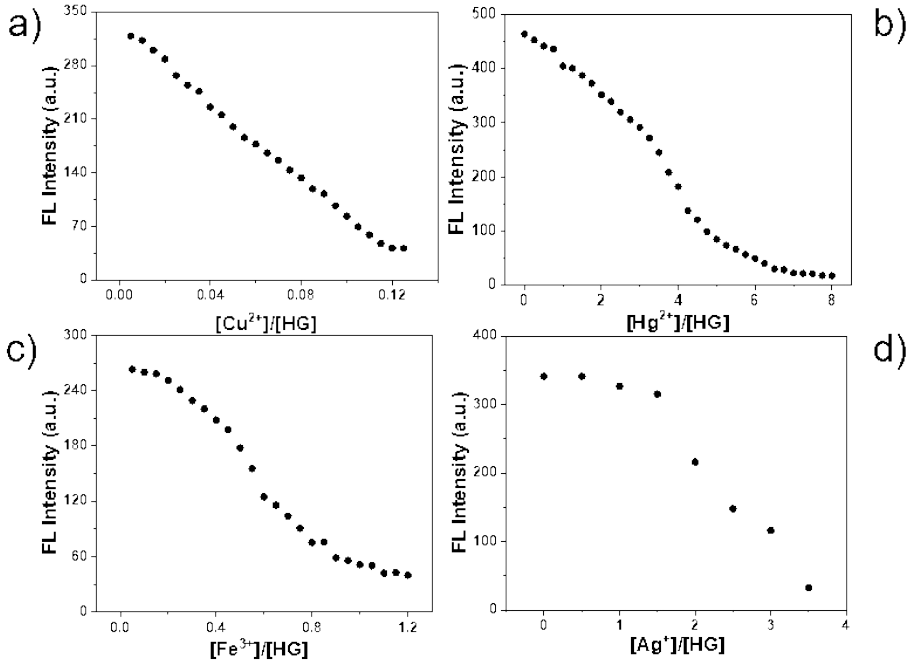


Fig. S15 A plot of fluorescent intensity depending on the concentration of Cu^{2+}, Hg^{2+}, Fe^{3+} and Ag^{+} in the range from different equivalents: (**a**) **HG-Cu^{2+}**, (**b**) **HG-Hg^{2+}**, (**c**) **HG-Fe^{3+}** and (**d**) **HG-Ag^{+}**.

Tab. S3 Calculation formula and related date of the detection limits of **HG** for Cu^{2+}, Hg^{2+}, Fe^{3+} and Ag^{+}.

Cation	**A(Slope)**	**B(Intercept)**	**R^2**	**δ**	***S***	**LOD**
Cu^{2+}	2226.40	310.55	0.997	3.694	2.23×10^{9}	**4.96×10^{-9}**
Hg^{2+}	64.24	482.75	0.997	3.694	6.42×10^{7}	1.73×10^{-7}
Fe^{3+}	214.01	294.29	0.998	3.694	2.14×10^{8}	5.18×10^{-8}
Ag^{+}	133.01	133.01	0.966	3.694	1.33×10^{8}	8.33×10^{-8}
		Liner Equation ***y=A x+ B***				
Calculation formula		$\delta=\sqrt{\frac{\Sigma(F-\bar{F})2}{(N-1)}}$		N=20	K=3	*S*=A×10^{6}
		LOD=K×δ/*S*				

Tab. S4 Association constants of the **HG** treated by Cu^{2+}, Hg^{2+}, Fe^{3+} and Ag^{+}, calculation formula and related data.

Compand	Metal ions	A(Slope)	B(Intercept)	R^2	Ka/M^{-1}
HG	Cu^{2+}	1.86	25.41	0.992	1.08×10^{11}
HG	Hg^{2+}	1.43	13.54	0.995	7.59×10^{5}
HG	Fe^{3+}	2.57	28.75	0.993	3.06×10^{12}
HG	Ag^{+}	4.81	48.09	0.965	7.68×10^{20}

Calculation formula

Liner Equation $y=Ax+B$ $\quad In\frac{I-Imin}{Imax-I} = -InKa - nIn[M^{2+}]$

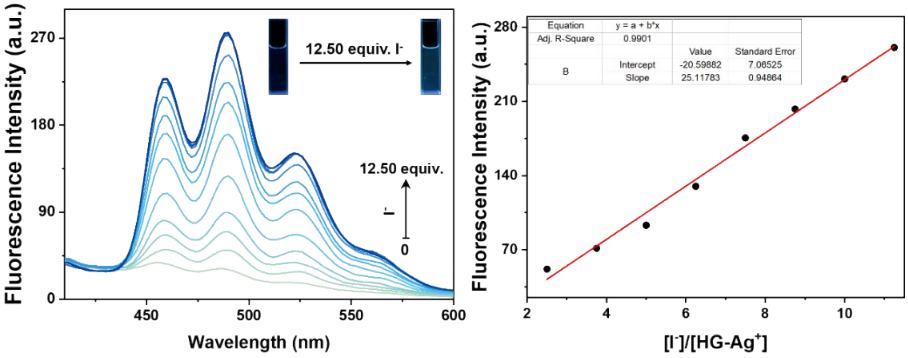


Fig. S16 (**left**) Fluorescence spectrum of **HG-Ag**$^{+}$ (2×10^{-5} M, 3.5 equiv. Ag^{+}) in the presence of different equivalents of I^{-} in DMSO/H_2O (v/v=1:1) binary solution; (**right**) Fluorescent spectrum linear range for I^{-} by addition of various concentrations of I^{-}, into **HG-Ag**$^{+}$.

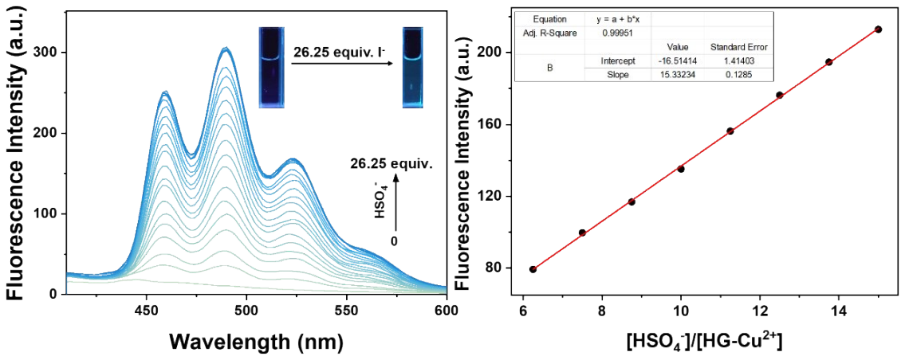


Fig. S17 (**left**) Fluorescence spectrum of **HG-Cu**$^{2+}$ (2×10^{-5} M, 6.5 equiv. Hg^{2+}) in the presence of different equivalents of I^{-} in DMSO/H_2O (v/v=1:1) binary solution; (**right**) Fluorescent spectrum linear range for I^{-} by addition of various concentrations of I^{-} into **HG-Cu**$^{2+}$.

Tab. S5 Association constants of the **HG-M (**M= Hg^{2+}, Ag^{+} and Cu^{2+}**)** treated by I^-， I^-, and HSO_4^-, calculation formula and related data.

Cation	A(Slope)	B(Intercept)	R^2	δ	*S*	LOD
HG-Hg^{2+}-I^-	11.65	53.36	0.995	3.683	1.16×10^{7}	9.48×10^{-7}
HG-Ag^{+}-I^-	25.12	20.60	0.990	3.683	2.51×10^{7}	4.40×10^{-7}
HG-Cu^{2+}-HSO_4^-	15.33	16.51	0.999	3.683	1.53×10^{7}	7.21×10^{-7}
		Liner Equation ***y=A x+ B***				
Calculation formula	$\delta=\sqrt{\frac{\Sigma(F-\bar{F})2}{(N-1)}}$		N=20	K=3	*S*=A×10^6	
	LOD=K×δ/*S*					

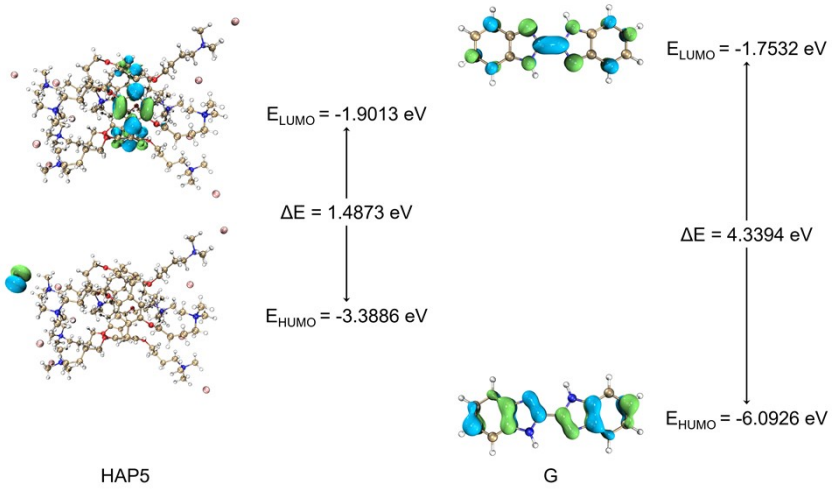


Fig. S18 Frontier molecular orbital amplitude plots and electronic properties of **HAP5** and **G**.

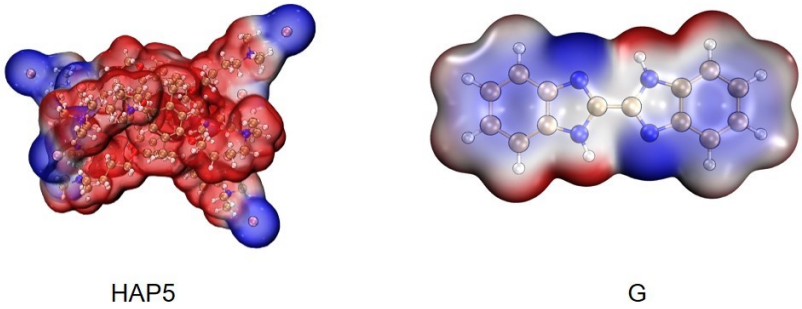


Fig. S19 The electrostatic potential surface of **HAP5** and **G**.

Tab. S6 Comparative result of I^- chemosensors

Entry	Compounds of probe	LOD for I^-	solvent	Ref.
1	HG-Ag^{+}	4.40×10^{-7}	DMSO/H_2O (v/v, 1/1)	This work

2	2	4.74×10^{-6}	THF/H_2O (v/v, 9/1)	51
3	1-Ag	5.31×10^{-6}	H_2O	49
4	2	5.20×10^{-4}	THF/H_2O (v/v, 2/1)	52

Tab. S7 Comparative result of HSO_4^-chemosensors

Entry	Compounds of probe	LOD for I^-	solvent	Ref.
1	HG-Cu^{2+}	7.21×10^{-7}	DMSO/H_2O (v/v, 1/1)	This work
2	1	7.79×10^{-7}	DMSO/H_2O (v/v, 1/1)	50
3	1	3.72×10^{-6}	MeOH	53
4	T-Zn^{2+}	3.84×10^{-6}	CH_3CN	48

Notes and references

1. Q. Lin, Y.-Q. Fan, P.-P. Mao, L. Liu, J. Liu, Y.-M. Zhang, H. Yao and T.-B. Wei, *Chemistry – A European Journal*, 2018, **24**, 777-783.
2. Q. Lin, L. Liu, F. Zheng, P.-P. Mao, J. Liu, Y.-M. Zhang, H. Yao and T.-B. Wei, *RSC Advances*, 2017, **7**, 34411-34414.
3. T. Wei, J. Liu, H. Yao, Q. Lin, Y. Xie, B. Shi, P. Zhang, X. You and Y. Zhang, *Chinese Journal of Chemistry*, 2013, **31**, 515-519.