SUPPLEMENTARY INFORMATION

Human Vision Inspired Adaptive Platform for One-on-Multiple Recognition

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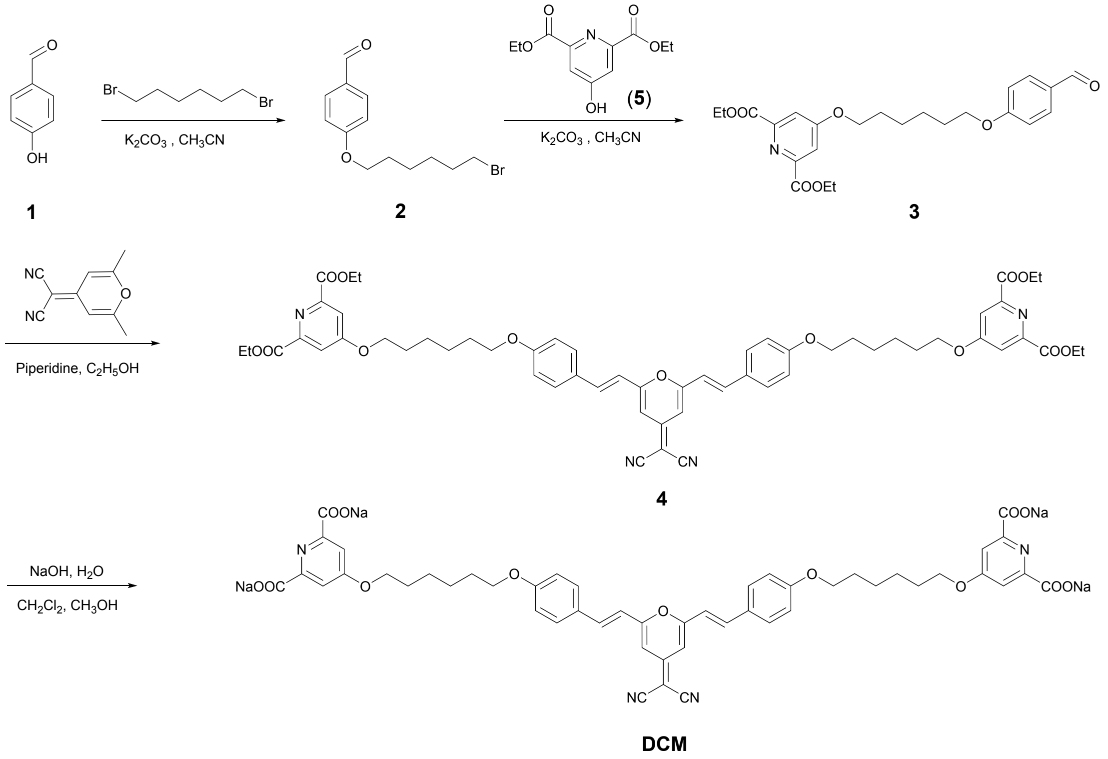
This material includes:

1. Synthesis of DCM



Scheme S1. Synthetic route for DCM.

DCM was prepared by condensation of aldehyde **3** and 4-dicyanomethylene-2,6-dimethyl-4*H*-pyran in the presence of piperidine, followed by a step of hydrolysis. According to the synthetic route depicted in Scheme S1, typical experimental procedures are given below.

Preparation of 4-((6-bromohexyl)oxy)benzaldehyde (**2**).

Synthesis of this compound followed the procedure reported in literature [s1]. Potassium carbonate (10.4 g), 1,6-dibromohexane (18.3 g), and 4-hydroxybenzaldehyde **1** (6.11 g) were mixed in dry CH_3CN (250 mL) at room temperature. The mixture was then stirred and heated to reflux for 24 h under N_2 atmosphere. After filtration and solvent evaporation, the crude product was purified by silica gel chromatography using petroleum ether (PE)/ethyl acetate (EA) mixture (10:1 by volume) as eluent. After dried in vacuum, product **2** was obtained as a white solid (5.40 g, 38%). Melting point: 41 °C. Elemental analysis: Found: C, 54.8; H, 6.2. Calc. for $C_{13}H_{17}BrO_2$: C, 54.75; H, 6.0%. FT-IR (anhydrous KBr, cm^{-1}) v: 2950 (C-H), 1688 (CH=O). ^1H NMR (500 MHz, Chloroform-*d*) δ (ppm): 9.88 (s, 1H), 7.85 – 7.80 (m, 2H), 7.01 – 6.97 (m, 2H), 4.05 (t, *J* = 6.4 Hz, 2H), 3.43 (t, *J* = 6.7 Hz, 2H), 1.90 (tt, *J* = 12.5, 6.2 Hz, 2H), 1.83 (dd, *J* = 13.6, 6.7 Hz, 2H), 1.59 – 1.50 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm): 190.81 , 164.13 , 132.01 , 129.83 , 114.73 , 68.13 , 33.75 , 32.62 , 28.90 , 27.87 , 25.24 . ESI-MS m/z: $[\mathbf{2}+H]^+$ Calcd for $C_{13}H_{18}BrO_2$: 285.0482, found 285.0485.

Preparation of diethyl 4-((6-(4-formylphen-oxy)hexyl)oxy)pyridine-2,6-dicarboxylate (**3**).

Diethyl 4-hydroxypyridine-2,6-dicarboxylate (**5**) was synthesized according to the procedure previously reported by our group [s2]. Potassium carbonate (3.93 g), compound **2** (5.40 g) and compound **5** (4.53 g) were mixed in dry CH_3CN (100 mL) at room temperature. The mixture was then stirred and heated to reflux for 24 h under N_2 atmosphere. After filtration and solvent evaporation, the crude product was purified by silica gel chromatography using PE/EA mixture (3:1-1:1 by volume) as eluent. Product **3** was obtained as a white solid (6.80 g, 81%). Melting point: 104 °C. Elemental analysis: Found: C, 65.1; H, 6.9; N, 3.1. Calc. for $C_{24}H_{29}NO_7$: C, 65.0; H, 6.6; N, 3.2%. FT-IR (anhydrous KBr, cm^{-1}) v: 2943 (=CH), 1733 (C=O), 1686 (CH=O), 1592 (C=N), 1250 (C-OEt). ^1H NMR (500 MHz, Chloroform-*d*) δ (ppm): 9.88 (s, 1H), 7.83 – 7.81 (m, 2H), 7.77 (s, 2H), 7.00 – 6.97 (m, 2H), 4.46 (qd, *J* = 7.1, 3.9 Hz, 4H), 4.17 – 4.14 (m, 2H), 4.06 (dd, *J* = 10.5, 4.1 Hz, 2H), 1.93 – 1.79 (m, 4H), 1.63 – 1.53 (m, 4H), 1.45 (td, *J* = 7.1, 3.8 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm): 190.77 , 166.93 , 164.79 , 164.10 , 150.15 , 131.98 , 129.82 , 114.71 , 114.29 , 68.78 , 68.11 , 62.39 , 28.96 , 28.68 , 25.72 , 25.67 , 14.20 . ESI-MS m/z: $[\mathbf{3}+H]^+$ Calcd for $C_{24}H_{30}NO_7$: 444.2026, found 444.2017.

Preparation of ethyl ester of **DCM** (**4**).

A mixture of **3** (6.8 g), 4-dicyanomethylene-2,6-dimethyl-4*H*-pyran (1.29 g), piperidine (1.6 g), and absolute ethanol (75 mL) were refluxed under N_2 for 24 h. After filtration and solvent evaporation, the crude product was purified by silica gel chromatography using

PE/EA mixture (3:2-1:1 by volume) as eluent. Product **4** was obtained as a yellow solid (2.22 g, 29%). Melting point: 158 °C. Elemental analysis: Found: C, 67.9; H, 6.2; N, 5.4. Calc. for $C_{58}H_{62}N_4O_{13}$: C, 68.1; H, 6.1; N, 5.5%. FT-IR (anhydrous KBr, cm^{-1}) ν: 2952 (=CH), 2210 (C≡N), 1730 (C=O), 1647 (C=C), 1590 (C=N), 1246 (C-OEt). ^1H NMR (500 MHz, DMSO-*d₆*) δ (ppm): 7.78 (s, 4H), 7.53 (d, *J* = 8.7 Hz, 4H), 7.48 (d, *J* = 16.0 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 4H), 6.65 (s, 2H), 6.63 (d, *J* = 16.5 Hz, 2H), 4.47 (q, *J* = 7.1 Hz, 8H), 4.16 (t, *J* = 6.3 Hz, 4H), 4.05 (t, *J* = 6.3 Hz, 4H), 1.95 – 1.80 (m, 8H), 1.59 (s, 8H), 1.46 (t, *J* = 7.1 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-d) δ (ppm): 166.93 , 164.76 , 161.06 , 158.57 , 150.12 , 137.58 , 129.54 , 127.12 , 115.93 , 115.50 , 115.07 , 114.29 , 106.32 , 68.80 , 67.96 , 62.36 , 29.04 , 28.68 , 25.74 , 25.67 , 14.20 . ESI-MS m/z: [**4**+H]$^+$ Calcd for $C_{58}H_{63}N_4O_{13}$: 1023.4365, found 1023.4386.

Preparation of **DCM**.

To the solution of compound **4** (0.80 g) in 1-1 dichloromethane-methanol mixture (20 mL), sodium hydroxide (0.19 g) and water (1.5 mL) was added. The mixture was then stirred and heated to reflux for 2 h under N_2 atmosphere. After filtration, the crude product was first acidified in water and filtered, then converted to sodium salts in ethanol using sodium hydroxide. The precipitates were collected and dried in vacuum. Such process was repeated for 3 times. The final product **DCM** was obtained as a yellow powder (0.35 g, 45%). Elemental analysis: Found: C, 55.9; H, 4.8; N, 5.1. Calc. for $C_{50}H_{42}N_4Na_4O_{13}\cdot 4H_2O$: C, 56.1; H, 4.7; N, 5.2%. FT-IR (anhydrous KBr, cm^{-1}) ν: 2939 (=CH), 2207 (C≡N), 1634 (C=O), 1423 (C-O$^-$). ^1H NMR (500 MHz, DMSO-*d₆*) δ (ppm): 7.76 (d, *J* = 8.6 Hz, 4H), 7.74 (d, *J* = 16.1 Hz, 2H), 7.67 (s, 4H), 7.24 (d, *J* = 16.1, 2H), 7.03 (d, *J* = 8.6 Hz, 4H), 6.82 (s, 2H), 4.27 (t, *J* = 6.5 Hz, 4H), 4.10 – 4.03 (m, 4H), 1.78 (m, 4H), 1.51 (m, 4H). ^{13}C NMR (125 MHz, DMSO-*d₆*) δ (ppm): 160.94 , 150.16 , 130.44 , 128.08 , 117.11 , 115.41 , 113.16 , 106.76 , 69.49 , 68.12 , 61.11 , 28.98 , 28.56 , 25.75 , 25.60 , 25.47. ESI-MS m/z: [**DCM**-H]$^-$ Calcd for $C_{50}H_{46}N_4O_{13}$: 909.2989, found. 909.2938.

2. Optical behaviors of DCM

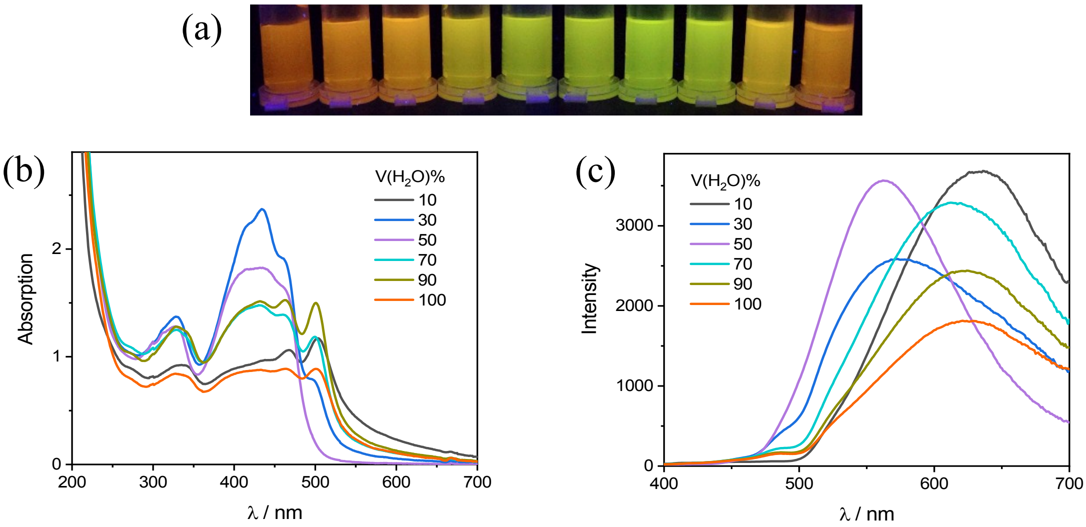


Figure S1. (a) Fluorescent pictures of DCM solutions in mixed H_2O-EtOH solvent under 365nm UV lamp, water volume fraction (%) are 100, 90, 80, 70, 60, 50, 40, 30, 20, 10 from left to right, [DCM] = 50 μM. (b) Absorption spectrum of DCM solutions in mixed H_2O-EtOH solvent. (c) Emission spectrum of DCM solutions in mixed H_2O-EtOH solvent, the excitation wavelength is 365 nm. [DCM] = 50 μM.

The fluorescence of **DCM** can be regulated by changing solvent polarity. The absorption and emission maximums are both greatly red-shifted when it is dispersed in water or ethanol rich solvents, which indicate the formation of ICT complexes.

3. Binding ratio between DCM and metal ions

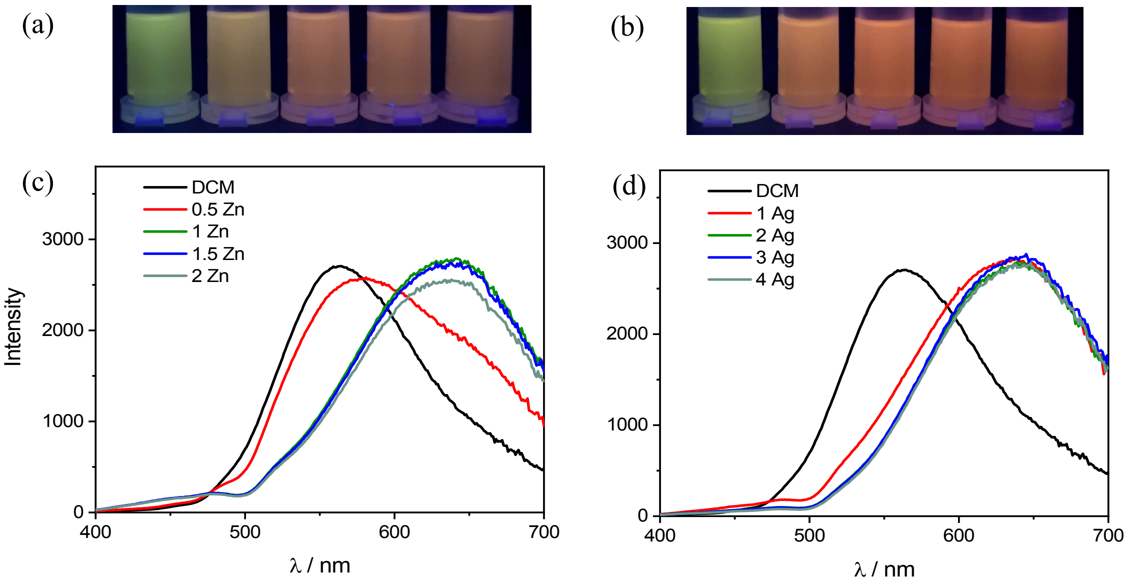


Figure S2. Fluorescent pictures of 50 μM DCM with (a) 0, 25, 50, 75, 100 μM Zn^{2+} and (b) 0, 50, 100, 150, 200 μM Ag^{+} in 1-1 water-ethanol mixed solvents under 365nm UV lamp. (c) and (d) are corresponding fluorescent spectrums.

The detemination of molar ratios between **DCM** and metal ions was simply based on fluorescent results. Generally, divalent metal ions, represented by Zn^{2+}, can afford stable fluorescent regulation with the addition of equivalent amount. Ag^{+} need two equivalent to achieve similar results. Therefore, such molar ratios were selected for the following experiments.

4. IR spectrum of some DCM-Metal ions complex

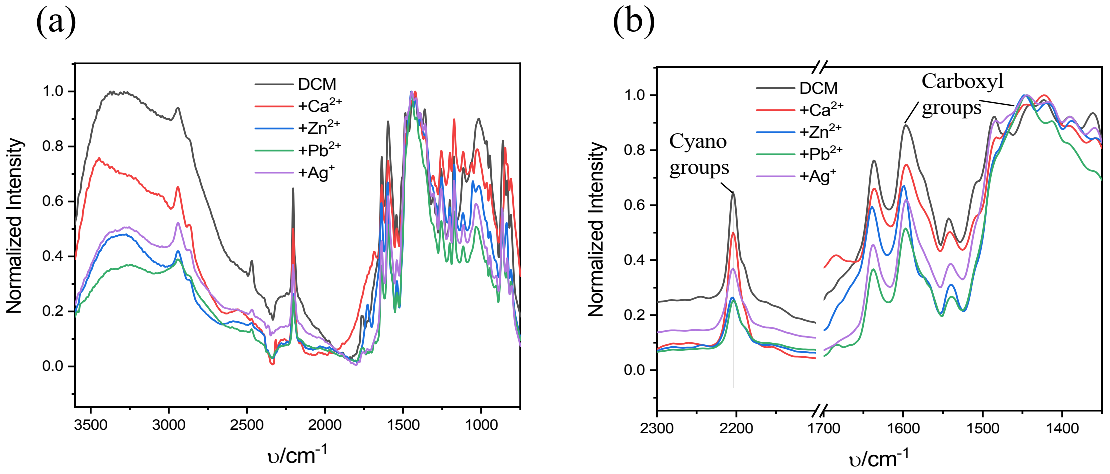


Figure S3. (a) IR spectrums of DCM+M^{n+} systems that exhibit ICT emission. (b) Detailed spectrums about cyano groups in the fluorophore and carboxyls groups in the head groups.

The cyano groups are possible coordinative sites with metal ions, but their vibrational peaks at around 2200 cm^{-1} remain unaffected in different systems. In contrast, the C-O vibration peaks of carboxyls groups are changed, indicating a binding of metal ions.

5. Selectivity in the detection of TETA

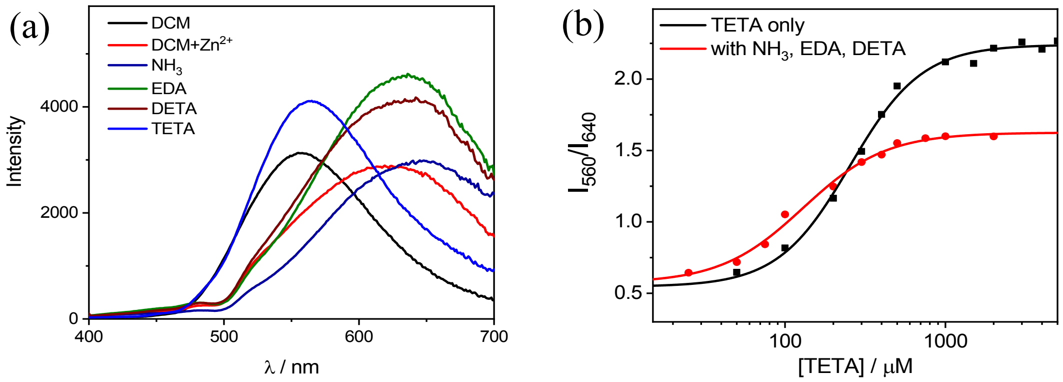


Figure S4. (a) Emission spectrums of DCM-Zn^{2+} in the presence of various amines. (b) Detection of TETA with co-existence of NH_3, EDA and DETA. [DCM] = [Zn^{2+}] = 50 μM, [NH_3] = [EDA] = [DETA] = [TETA] = 1 mM if not mentioned.

Under equivalent concentration, the detection of TETA was barely affected by other amine species or common Zn^{2+}-binding species.

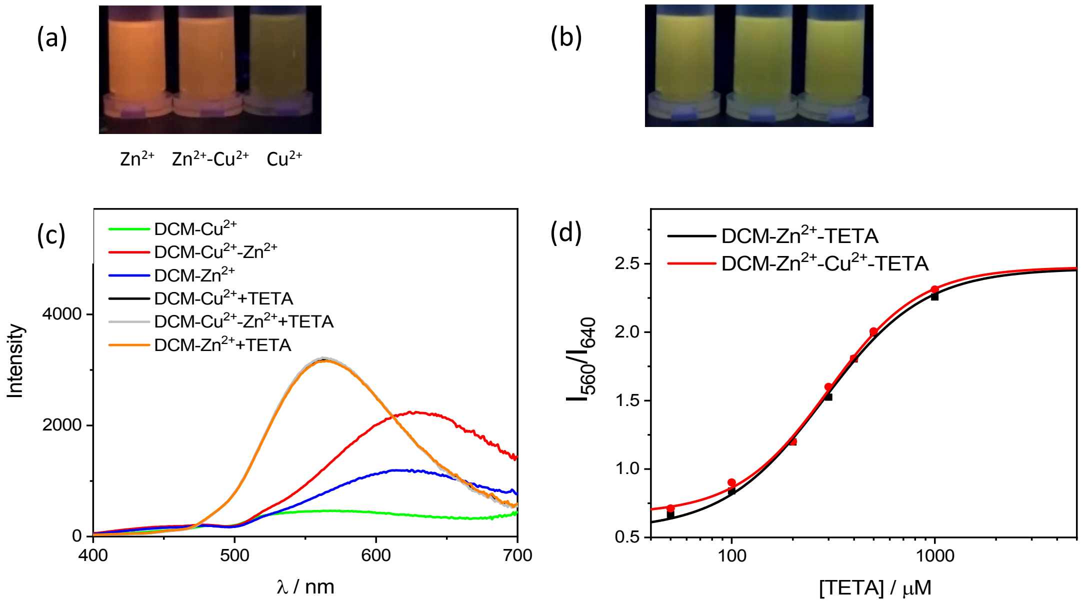


Figure S5: Fluorescent pictures of DCM-Zn^{2+}、DCM-Zn^{2+}-Cu^{2+}、DCM-Cu^{2+} (a) without TETA, (b) with TETA, and (c) corresponding emission spectrum. (d) Ratiometric response of DCM-Zn^{2+} and DCM-Zn^{2+}-Cu^{2+} towards TETA.

6. Selectivity in the detection of Cys

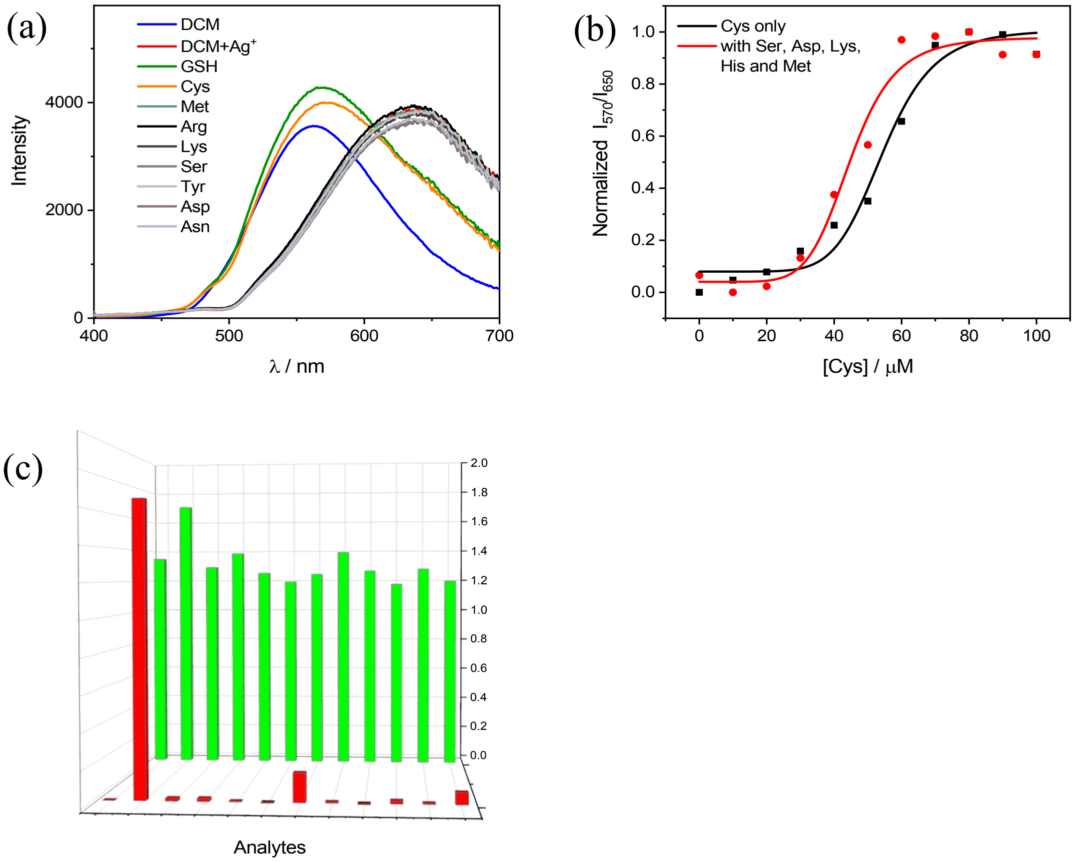


Figure S6. (a) Emission spectrums of **DCM-Ag$^+$** in the presence of polar amino acids. (b) Detection of Cys with co-existence of Ser, Asp, Lys, His and Met.(c) Ratiometric response of **DCM-Ag$^+$** towards various competing species without (Red bar) or with (Green bar) additional GSH. From left to right: None, GSH, Cys-Cys, Met, Lys, Arg, His, Asp, Asn, Glu, Tyr, BSA (Bovine serum albumin). [DCM] = [Ag$^+$]/2 = 50 μM, [Amino acids] = 100 μM if not mentioned.

Under equivalent concentration, the detection of Cys was barely affected by other amino acids. Similar results can be obtained if Cys was replaced with GSH (Figure S5c).

7. Selectivity in the detection of H_2S

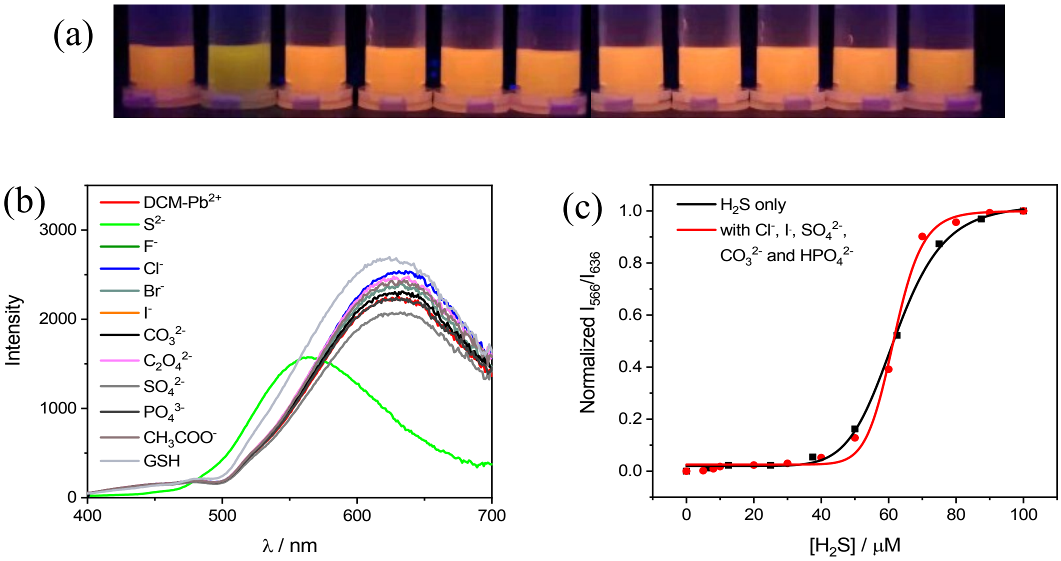


Figure S7. (a) Fluorescent pictures of DCM-Pb^{2+} system in the existence of various anions under 365nm UV lamp. From left to right, anions are OH^-, S^{2-}, F^-, Cl^-, Br^-, I^-, CO_3^{2-}, $C_2O_4^{2-}$, SO_4^{2-}, PO_4^{3-}, CH_3COO^-. (b) Emission spectrum of DCM-Pb^{2+} system in the existence of various competitors. (c) Detection of H_2S with the co-existence of Cl^-, I^-, SO_4^{2-}, CO_3^{2-} and HPO_4^{2-}. [DCM] = [Pb^{2+}] = 50 μM, [Analytes] = 150 μM if not mentioned.

Under same concentration, the detection of H_2S was barely affected by common anions and thiols, indicating the good selectivity of DCM-Pb^{2+} towards H_2S.

References:

S1. H. Zhang, Y. Qu, Y. Gao, J. Hua, J. Li and B. Li, *Tetrahedron Lett.*, 2013, **54**, 909-912.

S2. L. Zhao, X. Cheng, Y. Ding, Y. Yan and J. B. Huang, *Soft Matter*, 2012, **8**, 10472-10478.