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Aldehyde-functionalized Metal-organic Framework for Selective Sensing of Homocysteine over Cys, GSH and other Natural Amino Acids

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Contents

1. Materials and Methods.

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. 4,4′,4″-tricarboxyltriphenylamine was synthesised from literature methods,[S1] 1H-Pyrrolo[2,3-b]pyridine-2-carbaldehyde was purchased from J&K Scientific, natural amino acids and GSH were purchased from Beijing Innochem Science & Technology Co.,Ltd.

The elemental analyses of C, H and N were performed on a Vario EL III elemental analyzer.

^{1}HNMR spectra were measured on a Bruker-400 spectrometer with Me_4Si as an internal standard.

X-Ray powder diffraction (XRD) patterns of the Cd–PPCA was recorded on a Rigaku D/max-2400 X−ray powder diffractometer (Japan) using Cu $K\alpha$ (l =1.5405 Å) radiation.

Thermogravimetric analysis (TGA) was carried out at a ramp rate of 5 °C/min in a nitrogen flow with a Mettler-Toledo TGA/SDTA851 instrument.

FT-IR spectra were recorded as KBr pellets on Bruker Optics TENSOR 27 FT-IR spectrophotometer.

The solution fluorescent spectra were measured on Hitachi F-4500. Both excitation and emission slit widths were 2.5 nm. The Cd–PPCA emulsion was prepared by introducing 1 mg of Cd–PPCA powder into 3.00 mL of 0.1 M NaCl buffer aqueous solution, the intensity was recorded at 450 nm, excitation at 350 nm. For natural amino acids and GSH molecular detection, the high concentration stock solutions of related analysts (2.0×10^{-2} M) were prepared directly in water solvents.

2. Synthesis of Cd–PPCA.

A mixture of 4,4',4''-tricarboxyltriphenylamine (H_3tca) (4.5 mg, 3.0 mM), 1H-Pyrrolo[2,3-b]pyridine-2-carbaldehyde (ppca) (3.5 mg, 6.0 mM), NaOH (1.5 mg, 9.0 mM) and $Cd(NO_3)_2 \cdot 6H_2O$ (8.3 mg, 6.0 mM) were dissolved in dimethylformamide/methanol/water (2/1/1, 4 mL) in a screw capped vial. The resulting mixture was placed in an oven at 80 ºC for 1 day. Light yellow crystals with block-shape were obtained after filtration. Yield: 75 % (based on H_3tca). Anal calc. for $(C_{21}H_{12}NO_6)_2(C_8H_6NO_2)_2Cd_3$: C 50.55, H 2.63, N 6.10%; Found: C 50.60, H 2.69, N 6.06%.

3. X-ray Crystallography (Single-crystal diffraction) and Characterizations.

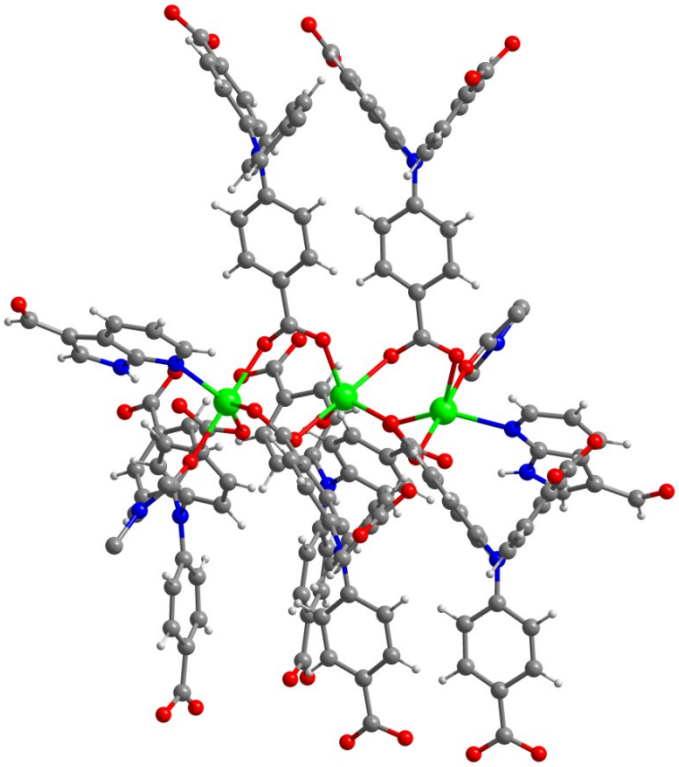
3.1 Crystal data of Cd–PPCA:

$C_{69}H_{54}N_9O_{21}Cd_3$, M = 1682.41, Orthorhombic, space group *Pnna*, a = 25.500(5), b = 20.600(4), c = 13.700(3) Å, α = 90.00, β = 90.00, γ = 90.00, V = 7179.7(19) Å^3, Z = 4, *D*c = 1.553 g cm^{-3}, μ(Mo-Kα) = 0.957 mm^{-1}, *T* = 123(2) K. 6339 unique reflections [R_{int} = 0.0954]. Final R_1[with $I > 2\sigma(I)$] = 0.0953 wR_2(all data) = 0.2579, GOOF = 1.078. CCDC number: 1582652.

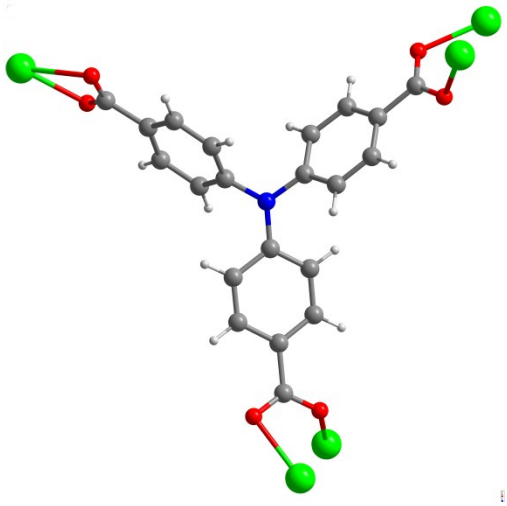
3.2 Crystallography:

Intensities were collected on a Bruker SMART APEX CCD diffractometer with graphitemonochromated Mo-Kα (λ = 0.71073 Å) using the SMART and SAINT programs. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL *version* 5.1. Non-hydrogen atoms of the ligand backbones were refined anisotropically. Hydrogen atoms within the ligand backbones were fixed geometrically at calculated positions and allowed to ride on the parent non-hydrogen atoms.

3.3 Figure S1 The coordination configuration of the Cd centres in Cd–PPCA. The asymmetric mode: A, x, 0.5-y, -0.5-z; B: -0.5+x, 0.5-y, 0.5+z.



3.4 Figure S2 The coordination mode of the tca^{3-} in Cd–PPCA.

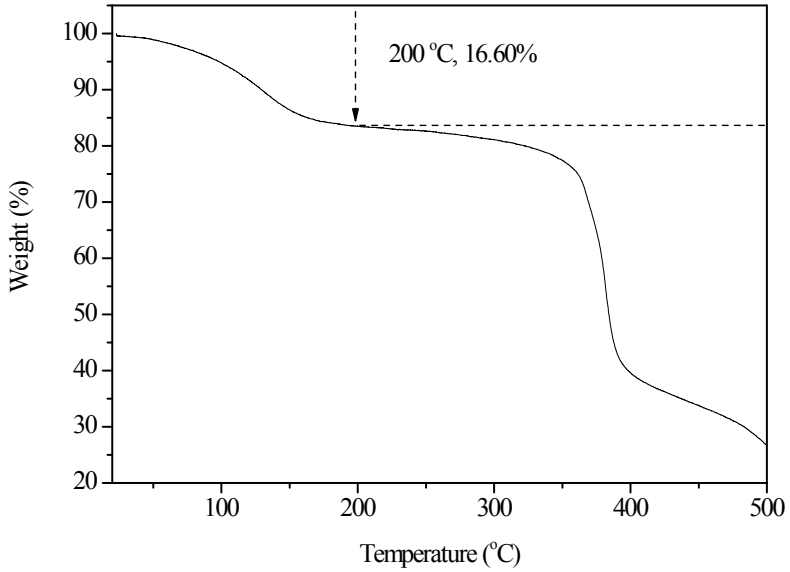


3.5 Selective bond distance (Å) and angle (°) in Cd–PPCA.

Selective bond distance (Å): Cd(1)-O(5) 2.279(6), Cd(1)-O(4) 2.290(7), Cd(1)-O(8) 2.295(8), Cd(1)-N(2) 2.333(7), Cd(1)-O(1) 2.346(7), Cd(1)-O(2) 2.528(8), Cd(1)-O(6) 2.615(8), Cd(2)-O(2w) 2.156(14), Cd(2)-O(3A) 2.207(7), Cd(2)-O(2) 2.324(8), Cd(2)-O(3B) 2.207(7), Cd(2)-O(2B) 2.324(8).

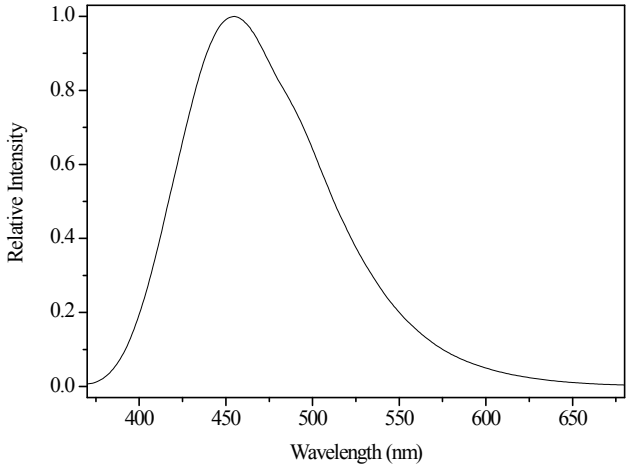
Selective bond angle (°): O(5)-Cd(1)-O(4) 89.8(3), O(5)-Cd(1)-O(8) 83.7(3), O(4)-Cd(1)-O(8) 173.4(3), O(5)-Cd(1)-N(2) 142.1(3), O(4)-Cd(1)-N(2) 94.1(3), O(8)-Cd(1)-N(2) 90.7(4), O(1)-Cd(1)-O(5) 132.4(3), O(4)-Cd(1)-O(1) 98.4(3), O(8)-Cd(1)-O(1) 86.6(3), N(2)-Cd(1)-O(1) 84.3(3), O(5)-Cd(1)-O(2) 79.6(2), O(4)-Cd(1)-O(2) 90.1(3), O(8)-Cd(1)-O(2) 89.4(4), N(2)-Cd(1)-O(2) 138.0(3), O(1)-Cd(1)-O(2) 53.8(2), O(5)-Cd(1)-O(6) 52.8(2), O(4)-Cd(1)-O(6) 97.2(3), O(8)-Cd(1)-O(6) 78.2(3), N(2)-Cd(1)-O(6) 89.3(3), O(1)-Cd(1)-O(6) 163.5(3), O(2)-Cd(1)-O(6) 131.6(2), O(2W)-Cd(2)-O(3A) 128.5(2), O(2W)-Cd(2)-O(3B) 128.5(2), O(3A)-Cd(2)-O(3B) 103.1(4), O(2W)-Cd(2)-O(2B) 87.54(16), O(3A)-Cd(2)-O(2B) 88.8(3), O(3B)-Cd(2)-O(2B) 94.2(3), O(3B)-Cd(2)-O(2B) 87.54(16), O(3A)-Cd(2)-O(2) 88.8(3), O(2B)-Cd(2)-O(2) 175.1(3).

3.6 Figure S3 TGA traces of Cd−PPCA ranging from room temperature to 500 °C.

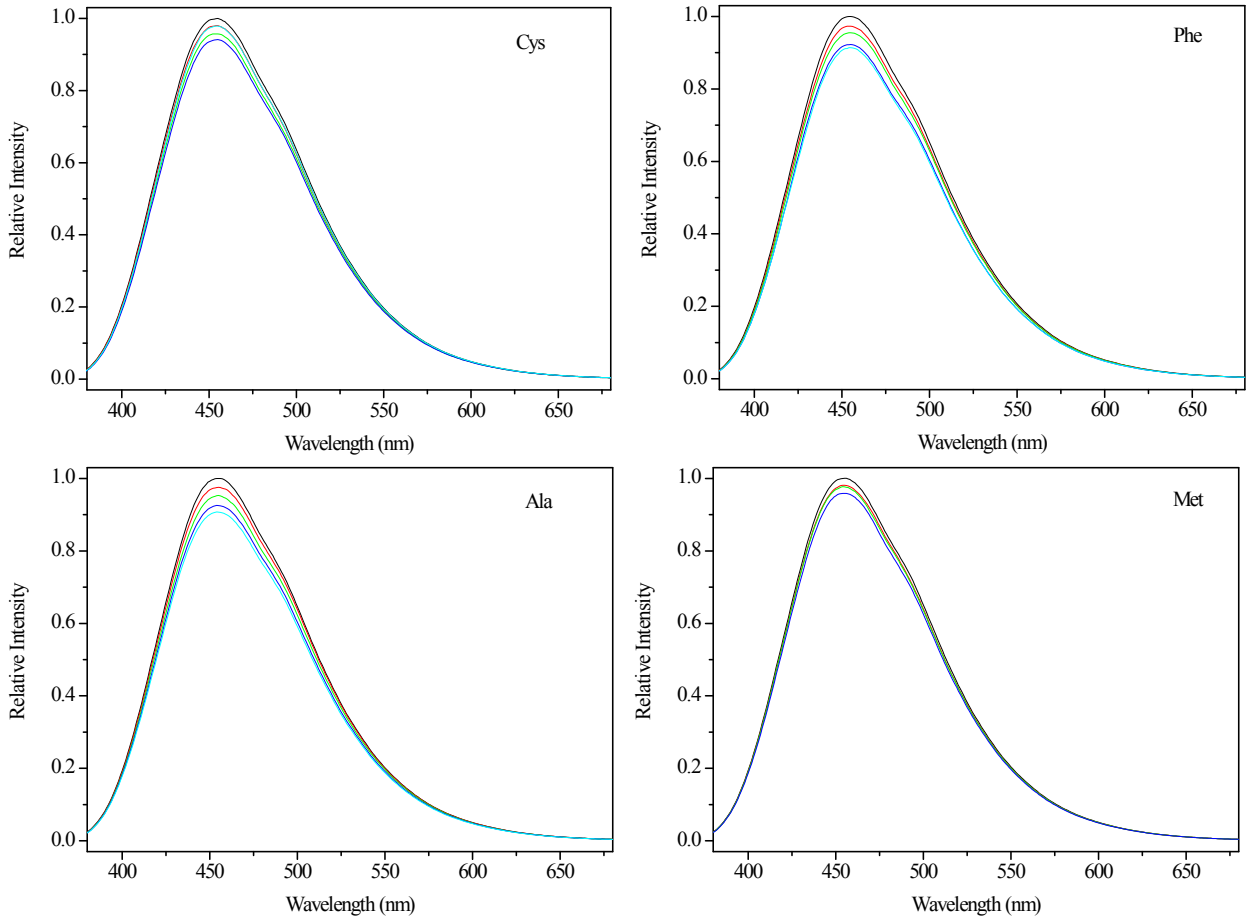


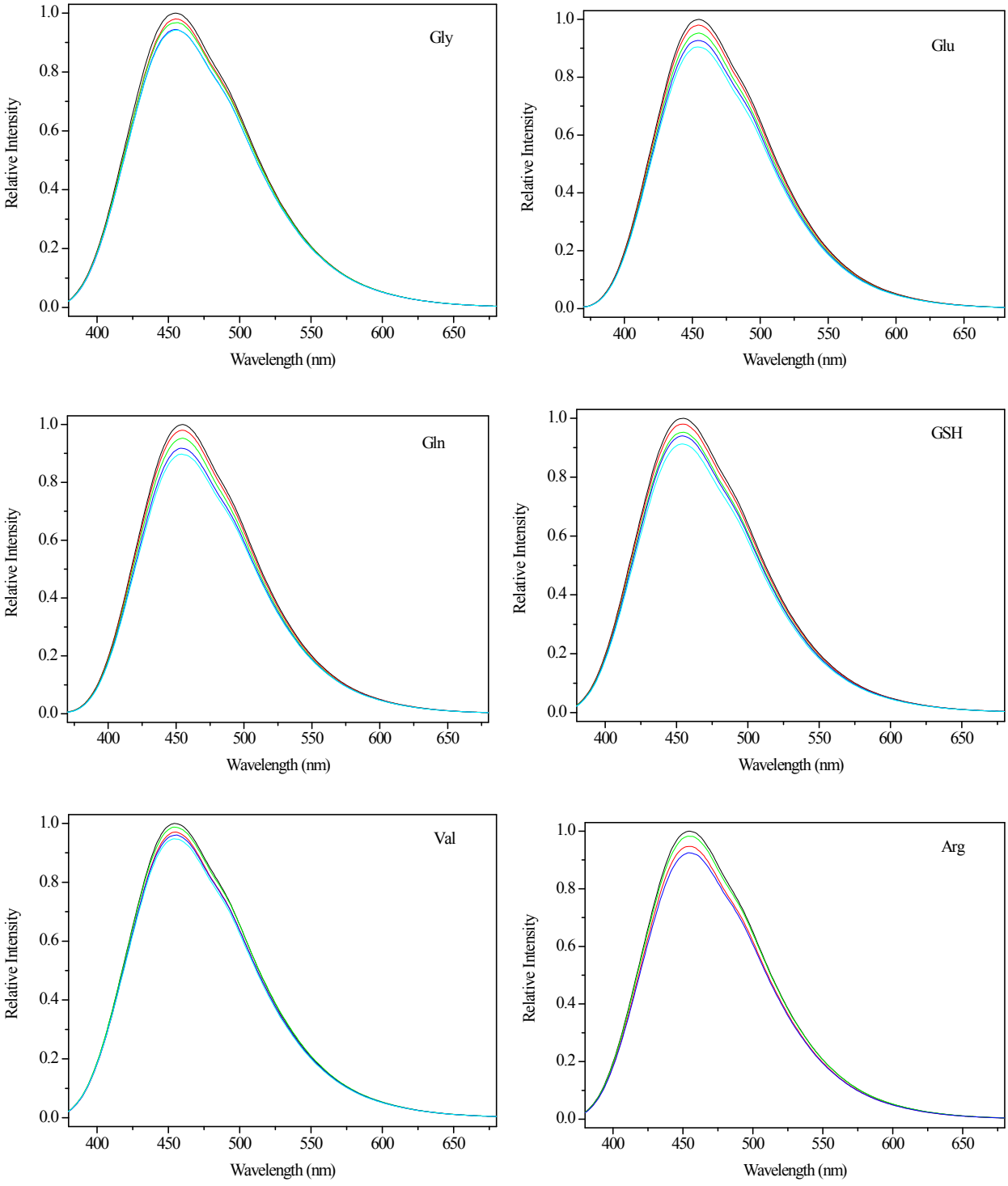
4. Studies on the natural amino acids sensing based on Cd–PPCA.

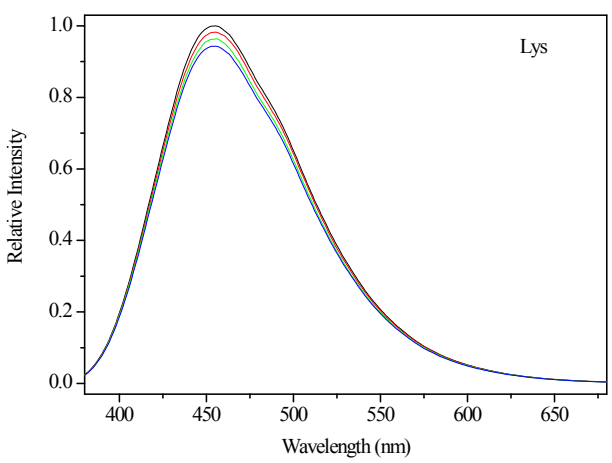
4.1 FigureS4 The PL spectra of Cd–PPCA in HEPES buffer solution when excited at 350 nm.

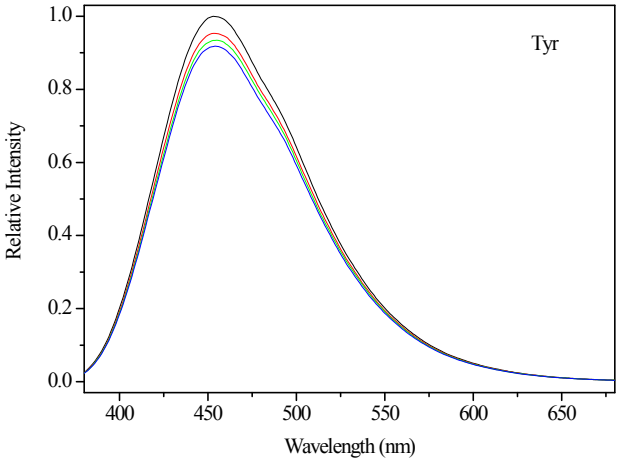


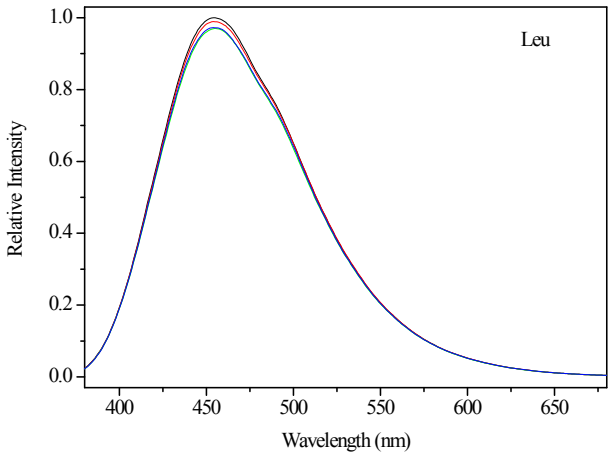
4.2 Figure S5 Families of various fluorescence spectra of 0.3 mM Cd–PPCA in HEPES buffer solution upon the addition of 0.3 mM of different selected amino acids.

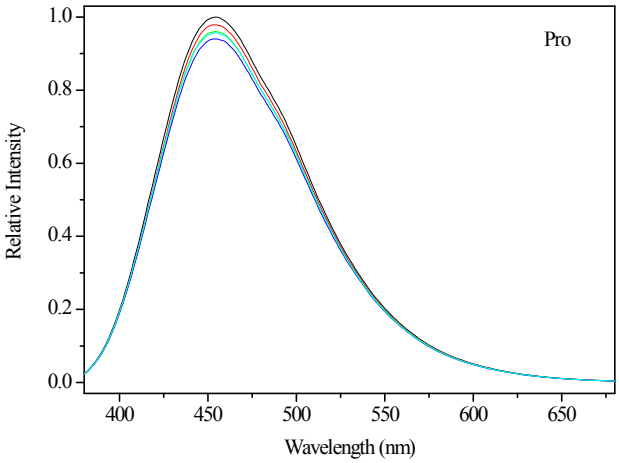


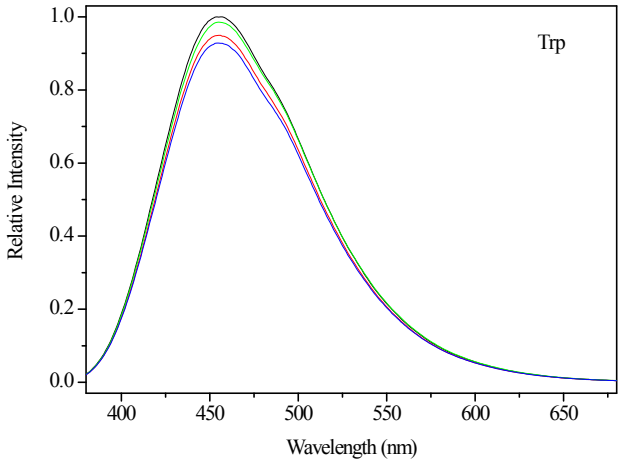

Gly
Glu
Gln
GSH
Val
Arg
Relative Intensity
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
400
450
500
550
600
650

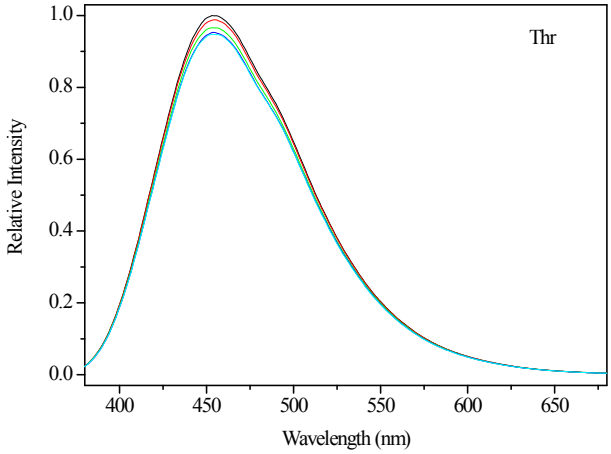

Lys
Relative Intensity
Wavelength (nm)

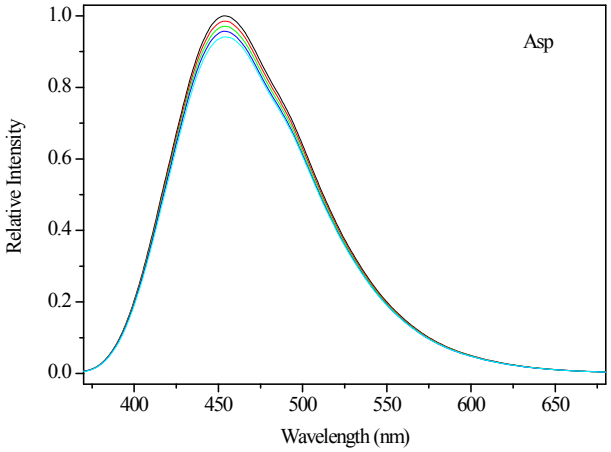

Tyr
Relative Intensity
Wavelength (nm)


Leu
Relative Intensity
Wavelength (nm)


Pro
Relative Intensity
Wavelength (nm)


Trp
Relative Intensity
Wavelength (nm)


Thr
Relative Intensity
Wavelength (nm)


Asp
Relative Intensity
Wavelength (nm)
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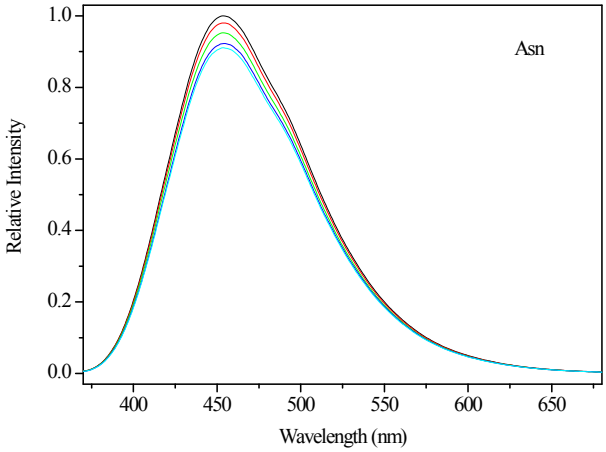
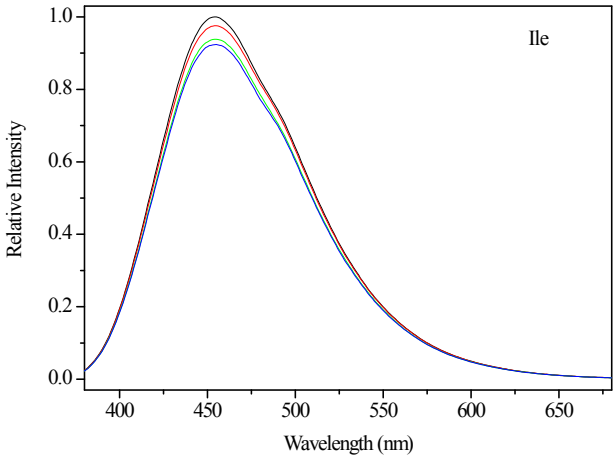
0.6
0.4
0.2
0.0
400
450
500
550
600
650


Asn
Relative Intensity
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
400
450
500
550
600
650


Ile
Relative Intensity
Wavelength (nm)
1.0
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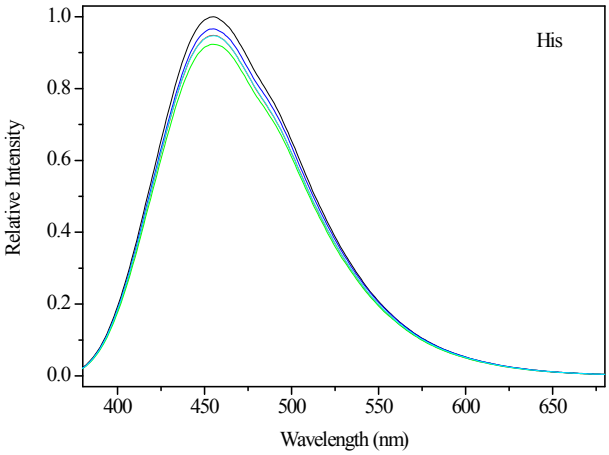
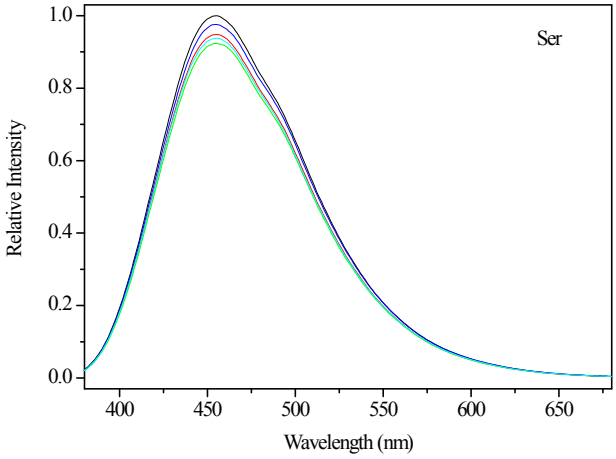
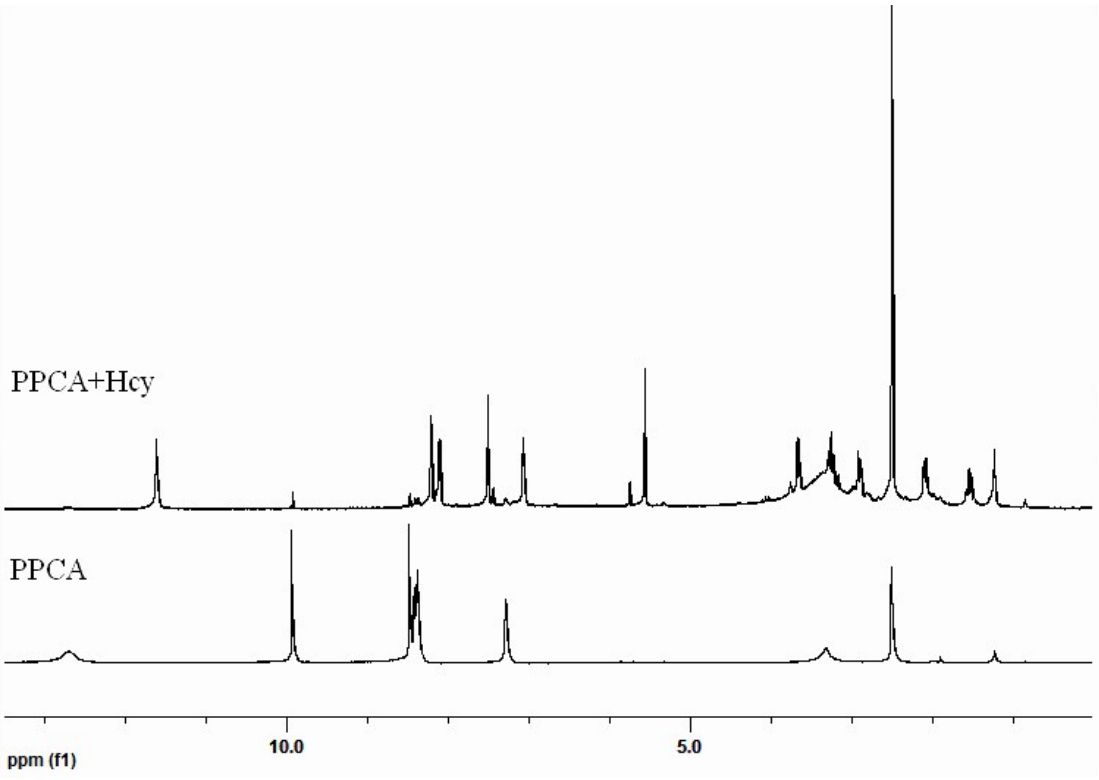
0.6
0.4
0.2
0.0
400
450
500
550
600
650


His
Relative Intensity
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
400
450
500
550
600
650


Ser
Relative Intensity
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
400
450
500
550
600
650

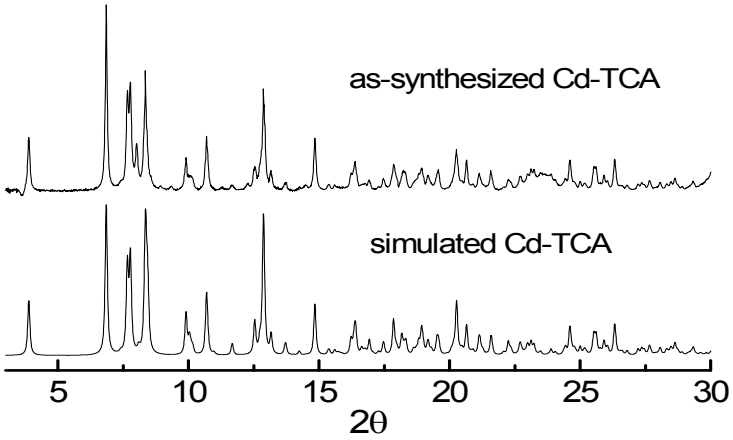
4.3 Figure S6 ^{1}H NMR spectra of PPCA and PPCA+Hcy in DMSO-d_6. The resonances centered at 9.95 and 5.56 *ppm* are assigned to the aldehyde hydrogens of PPCA and the methine protons of the thiazolidine of PPCA+Hcy, respectively.



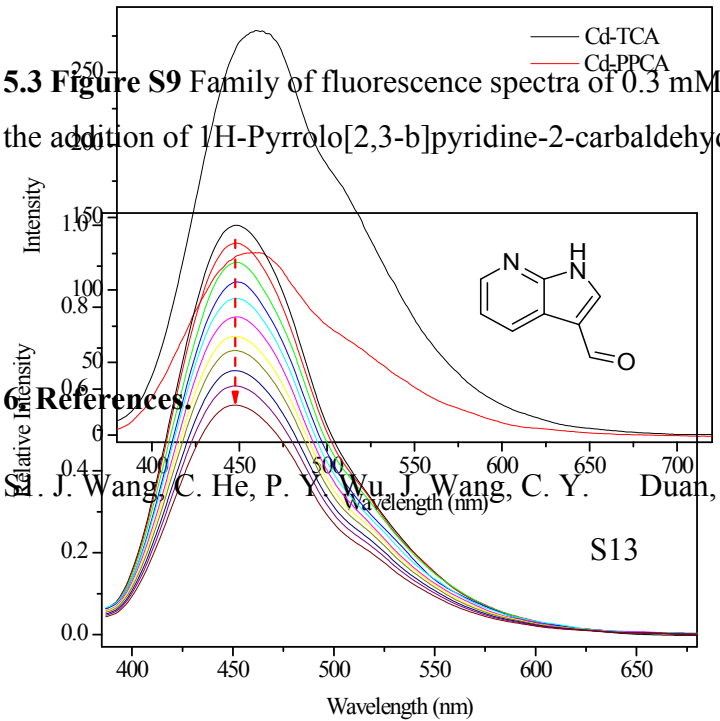
5. Synthesis and luminescent properties of Cd–TCA.

Cd–TCA was synthesized according to the literature method[S2]: The mixture of $CdCl_2 \cdot 6H_2O$ (45 mg, 0.2 mmol), and H_3tca (18 mg, 0.05 mmol) in 3 mL of N,N-dimethylformamide (DMF) and 2 drops of NaOH (2 M) was sealed in a 15 mL vial and heated to 100 ºC for 3 days, and then cooled to room temperature. The light yellow crystals obtained were washed with ethanol, and dried at room temperature.

5.1 Figure S7 Powder X-ray diffraction (XRD) profiles for simulated and as-synthesized Cd–TCA.



5.2 Figure S8 The PL spectra of Cd–TCA and Cd–PPCA in HEPES buffer when excited at 350 nm.



5.3 Figure S9 Family of fluorescence spectra of 0.3 mM Cd–TCA in HEPES buffer solution upon the addition of 1H-Pyrrolo[2,3-b]pyridine-2-carbaldehyde.

6. References.

S1. J. Wang, C. He, P. Y. Wu, J. Wang, C. Y. Duan, *J. Am. Chem. Soc.*, 2011, **133**, 12402.

S2. X. L. Hu, C. Qin, X. L. Wang, K. Z. Shao, Z. M. Su, *New J. Chem.*, 2015, **39**, 7858.