Support Informational Material

A new turn-on chemosensor for bio-thiols based on the nanoaggregates of tetraphenylethene-coumarin fluorophore

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Experimental Section

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Experimental Section

General Information

Materials and methods

Tetrahydrofuran (THF) and ethanol are distilled from sodium benzophenone ketyl and magnesium, respectively, under nitrogen immediately prior to use. Zinc dust, titanium(IV) chloride, N,N-dimethylformamide (DMF) and Other chemicals are purchased from Aldrich and used as received without further purification. Water is purified by a Millipore filtration system.

Instruments

^{1}H and ^{13}C NMR spectra are measured on a Bruker ARX 400 NMR spectrometer using $CDCl_3$, D_2O or DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal reference. UV absorption spectra are taken on a Varian Cary spectrometer. Photoluminescence (PL) spectra are recorded on a Perkin-Elmer LS 55 spectrofluorometer. MALDI-TOF mass spectra are recorded on a GCT premier CAB048 mass spectrometer. Particle sizes and Zeta potential of the nanoaggregates are determined using a ZETA-Plus potential Analyzer.

Suitable single crystals of TPE-Cou are grown from dichloromethane with an aliquot of methanol at room temperature in the dark. X-ray diffraction (XRD) intensity data are collected at 173 K on a Bruker-Nonices Smart Apex CCD diffractometer with graphite monochromated Mo Kα radiation. Processing of the intensity data is conducted using the SANT and SADABS routines, and the structure and refinement are carried out using the SHELTL suite of X-ray programs (version 6.10). The ORTEP drawing of TPE-Cou is given in Scheme 1C and its crystal data are summarized in Table S1.

Synthesis and Characterization Data of TPE-Cou

The synthetic route to TPE-Cou is shown in Scheme 1A. Compound 1 and 2 are prepared according to the previously published procedures[1,2]. A solution of compound 1 (173.7 mg, 0.5 mmol) and 2 (122.6 mg, 0.5 mmol) in dry EtOH (30 mL) is refluxed under nitrogen for 24 h. After cooling to room temperature, the precipitates formed are filtered out, washed three times with cold ethanol and recrystallized in ethanol. The product is obtained as a red solid in 62% yield. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 8.51 (s, 1H), 8.45 (s, 1H), 7.64 (d, 1H), 6.94-7.17 (m, 19H), 6.76 (d, 1H), 6.58 (d, 1H), 3.45 (m, 4H), 3.45 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 160.12, 157.16, 152.88, 151.30, 149.69, 143.23, 140.82, 140.27, 140.04, 139.34, 131.36, 130.62, 130.13, 126.90, 126.51, 125.50, 119.69, 114.88, 112.44, 108.66, 108.04, 96.17, 43.87, 11.14. HRMS (MALDI-TOF): *m/z* 574.2622 [$(M+H)^+$, calcd 574.7240].

Preparation of Nanoaggregates

Stock solution of TPE-Cou in THF with a concentration of 1 mM is prepared. Aliquots of the stock solution are transferred to 10 mL volumetric flasks and appropriate amount of THF is added. Water is added dropwise under vigorous stirring to furnish 1 μM TPE-Cou solution with different water contents (0-99 vol %). PL measurement of the resultant solutions is performed immediately.

Preparation for Fluorescent Measurement

A stock solution (1 mM) of TPE-Cou in THF is prepared and used by dilution in water/THF mixtures for fluorescence experiments. A solution of TPE-Cou (2.0 mL) is placed in a quartz cuvette (10.0 mm width). After mixing with appropriate amount of each amino acid (0.1 M), emission spectra are recorded at room temperature.

Table S1. Crystal data and structure refinement for TPE-Cou.

Empirical formula	C40 H34 N2 O2	
Formula weight	574.69	
Temperature	173.00(14) K	
Wavelength	1.5418 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.3623(5) Å	α= 101.052(5)°.
	b = 12.1380(7) Å	β= 95.914(5)°.
	c = 15.3131(8) Å	γ = 96.684(5)°.
Volume	1502.53(15) $Å^3$	
Z	2	
Density (calculated)	1.270 Mg/m^3	
Absorption coefficient	0.609 mm^{-1}	
F(000)	608	
Crystal size	0.2 x 0.12 x 0.03 mm^3	
Theta range for data collection	5.37 to 67.00°.	
Index ranges	-9<=h<=9, -13<=k<=14, -18<=l<=13	
Reflections collected	8527	
Independent reflections	5178 [R(int) = 0.0271]	
Completeness to theta = 66.50°	97.20 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.91049	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5178 / 0 / 399	
Goodness-of-fit on F^2	1.003	
Final R indices [I>2sigma(I)]	R1 = 0.0394, wR2 = 0.1004	
R indices (all data)	R1 = 0.0515, wR2 = 0.1080	
Largest diff. peak and hole	0.170 and -0.183 $e.Å^{-3}$	

Table S2. Bond lengths [Å] and angles [°] for TPE-Cou single crystal structure.

O(1)-C(51)	1.2084(17)	O(2)-C(51)	1.3861(17)
O(2)-C(59)	1.3784(16)	N(1)-C(44)	1.4094(18)
N(1)-C(50)	1.2768(19)	N(2)-C(57)	1.3588(18)
N(2)-C(61)	1.4563(19)	N(2)-C(63)	1.4638(18)
C(1)-C(2)	1.359(2)	C(1)-C(11)	1.4923(19)
C(1)-C(31)	1.5011(19)	C(2)-C(21)	1.4955(19)
C(2)-C(41)	1.4895(19)	C(11)-C(12)	1.399(2)
C(11)-C(12)	1.399(2)	C(11)-C(16)	1.397(2)
C(12)-C(13)	1.387(2)	C(13)-C(14)	1.385(3)
C(14)-C(15)	1.380(3)	C(15)-C(16)	1.383(2)
C(21)-C(22)	1.393(2)	C(21)-C(26)	1.396(2)
C(22)-C(23)	1.388(2)	C(23)-C(24)	1.386(3)
C(24)-C(25)	1.381(3)	C(25)-C(26)	1.385(2)
C(31)-C(32)	1.388(2)	C(31)-C(36)	1.389(2)
C(32)-C(33)	1.392(2)	C(33)-C(34)	1.384(2)
C(34)-C(35)	1.376(2)	C(35)-C(36)	1.395(2)
C(41)-C(42)	1.403(2)	C(41)-C(46)	1.398(2)
C(42)-C(43)	1.388(2)	C(43)-C(44)	1.400(2)
C(44)-C(45)	1.397(2)	C(45)-C(46)	1.378(2)
C(50)-C(52)	1.459(2)	C(51)-C(52)	1.452(2)
C(52)-C(53)	1.362(2)	C(53)-C(54)	1.410(2)
C(54)-C(55)	1.409(2)	C(54)-C(59)	1.400(2)
C(55)-C(56)	1.365(2)	C(56)-C(57)	1.423(2)
C(57)-C(58)	1.4092(19)	C(58)-C(59)	1.373(2)
C(61)-C(62)	1.515(2)	C(63)-C(64)	1.500(2)
C(59)-O(2)-C(51)	122.39(11)	C(50)-N(1)-C(44)	120.50(12)
C(57)-N(2)-C(61)	121.88(12)	C(57)-N(2)-C(63)	121.67(12)
C(61)-N(2)-C(63)	115.72(12)	C(2)-C(1)-C(11)	123.39(12)
C(2)-C(1)-C(31)	122.43(12)	C(1)-C(2)-C(21)	122.09(12)
C(1)-C(2)-C(41)	122.33(12)	C(41)-C(2)-C(21)	115.58(12)
C(12)-C(11)-C(1)	122.63(14)	C(12)-C(11)-C(1)	122.63(14)
C(16)-C(11)-C(1)	119.62(13)	C(16)-C(11)-C(12)	117.74(14)
C(16)-C(11)-C(12)	117.74(14)	C(13)-C(12)-C(11)	120.57(15)

C(14)-C(13)-C(12)	120.77(16)	C(15)-C(14)-C(13)	119.21(15)
C(14)-C(15)-C(16)	120.38(16)	C(15)-C(16)-C(11)	121.29(15)
C(22)-C(21)-C(2)	120.94(13)	C(22)-C(21)-C(26)	118.19(13)
C(26)-C(21)-C(2)	120.84(13)	C(23)-C(22)-C(21)	120.79(15)
C(24)-C(23)-C(22)	119.99(15)	C(25)-C(24)-C(23)	119.96(15)
C(24)-C(25)-C(26)	119.91(16)	C(25)-C(26)-C(21)	121.04(15)
C(32)-C(31)-C(1)	121.09(13)	C(32)-C(31)-C(36)	118.79(13)
C(36)-C(31)-C(1)	119.86(13)	C(31)-C(32)-C(33)	120.58(15)
C(31)-C(32)-C(33)	120.58(15)	C(34)-C(33)-C(32)	120.16(15)
C(35)-C(34)-C(33)	119.70(14)	C(34)-C(35)-C(36)	120.28(15)
C(31)-C(36)-C(35)	120.47(14)	C(42)-C(41)-C(2)	120.66(13)
C(46)-C(41)-C(2)	121.93(13)	C(46)-C(41)-C(42)	117.38(13)
C(43)-C(42)-C(41)	121.39(14)	C(42)-C(43)-C(44)	120.45(14)
C(43)-C(44)-N(1)	124.66(13)	C(45)-C(44)-N(1)	116.95(13)
C(45)-C(44)-C(43)	118.27(13)	C(46)-C(45)-C(44)	120.96(13)
C(45)-C(46)-C(41)	121.54(13)	N(1)-C(50)-C(52)	121.09(13)
O(1)-C(51)-O(2)	116.18(13)	O(1)-C(51)-C(52)	126.67(13)
O(2)-C(51)-C(52)	117.15(12)	C(51)-C(52)-C(50)	117.25(12)
C(53)-C(52)-C(50)	122.86(13)	C(53)-C(52)-C(51)	119.88(13)
C(52)-C(53)-C(54)	121.88(13)	C(55)-C(54)-C(53)	125.37(13)
C(59)-C(54)-C(53)	118.17(13)	C(59)-C(54)-C(55)	116.46(13)
C(56)-C(55)-C(54)	121.69(13)	C(55)-C(56)-C(57)	121.15(13)
N(2)-C(57)-C(56)	121.13(12)	N(2)-C(57)-C(58)	121.27(13)
C(58)-C(57)-C(56)	117.60(13)	C(59)-C(58)-C(57)	119.74(13)
O(2)-C(59)-C(54)	120.44(12)	C(58)-C(59)-O(2)	116.28(12)
C(58)-C(59)-C(54)	123.27(12)	N(2)-C(61)-C(62)	113.25(14)
N(2)-C(63)-C(64)	113.52(14)		

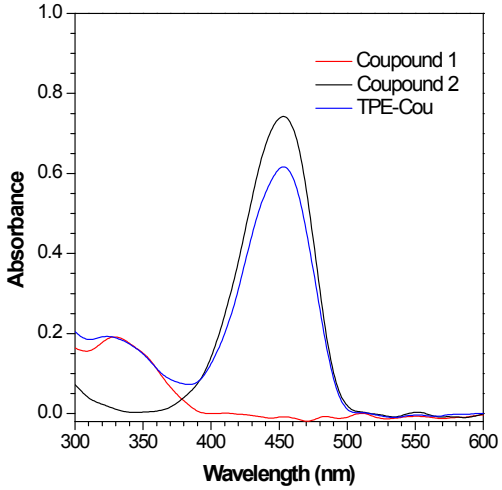

Fig. S1 Absorption spectra of Compound 1, Compound 2 and TPE-Cou (20 μM).

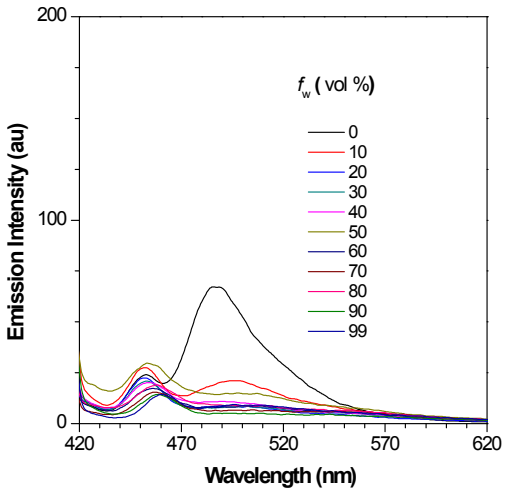

Fig. S2 Emission spectra of TPE-Cou (10 μM) in THF/water mixtures with different volume fractions of water (f_w). Excitation wavelength: 390 nm.

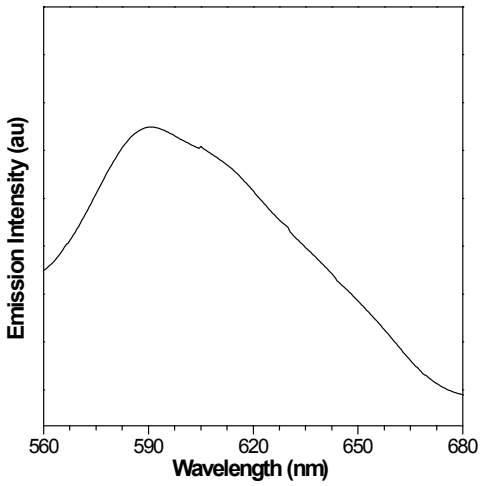

Fig. S3 Emission spectrum of TPE-Cou in solid state.

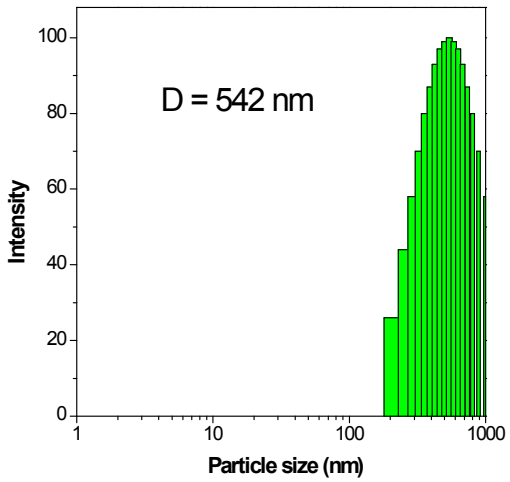

Fig. S4 Particle size distribution of TPE-Cou in a water/THF mixture (7:3, v/v).

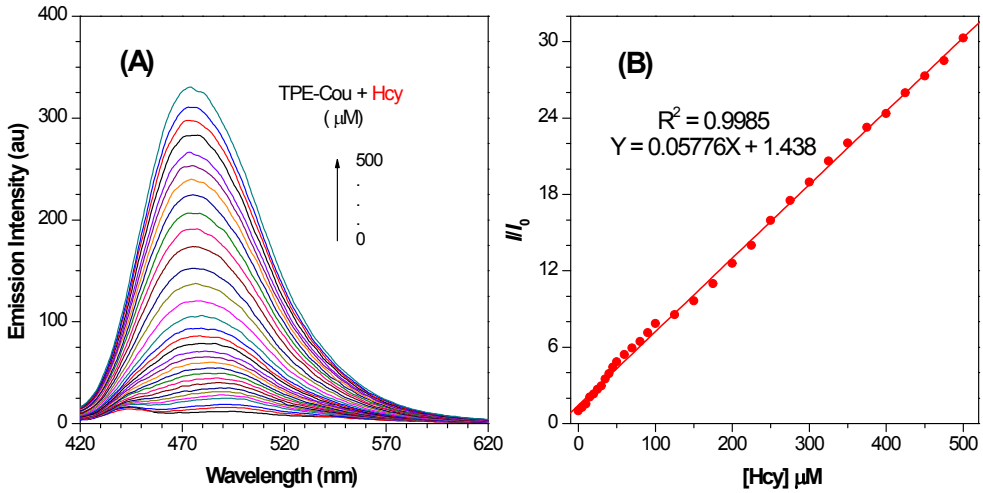

Fig. S5 (A) Emission spectra of TPE-Cou (1 μM) in the presence of different concentrations of Hcy. (B) Plot of emission intensity at 473 nm versus the concentration of Hcy. Each spectrum is acquired in a water/THF mixture (7:3, v/v) at 25 °C. Excitation wavelength: 390 nm.

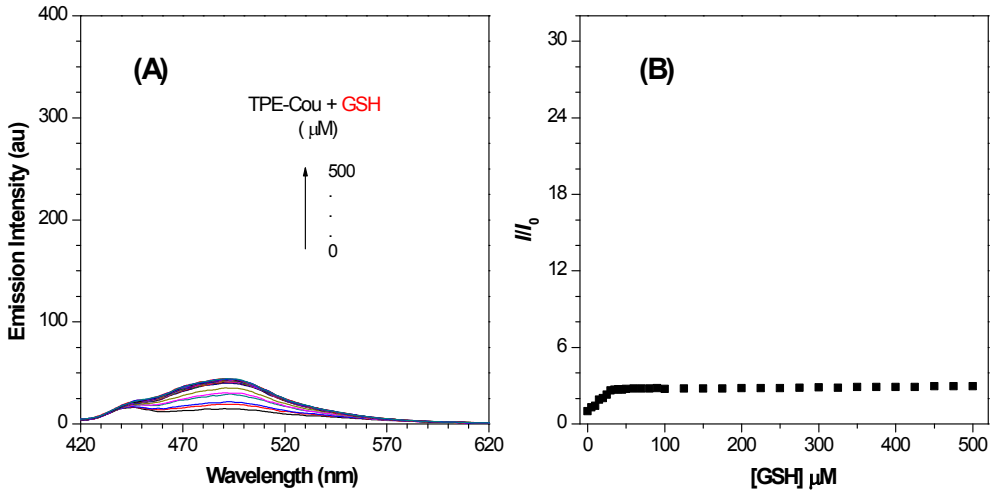

Fig. S6 (A) Emission spectra of TPE-Cou (1 μM) in the presence of different concentrations of GSH. (B) Plot of emission intensity at 473 nm versus the concentration of GSH. Each spectrum is acquired in a water/THF mixture (7:3, v/v) at 25 °C. Excitation wavelength: 390 nm.

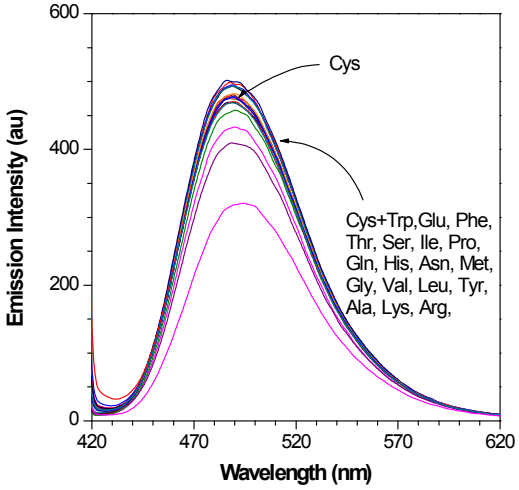

Fig. S7 Emission spectra of TPE-Cou (1 μM) in the presence of Cys and different amino acids (500 μM) in a water/THF mixture (7:3, v/v).

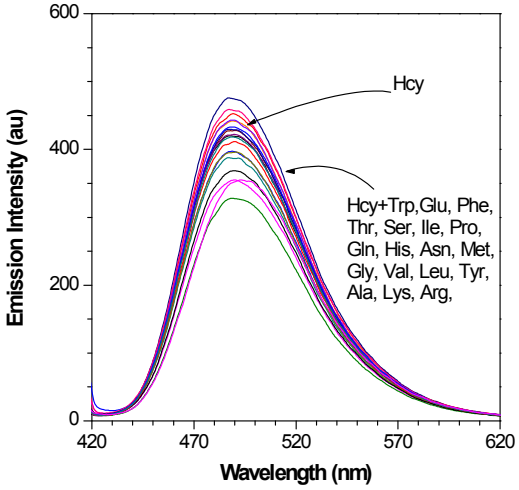

Fig. S8 Emission spectra of TPE-Cou (1 μM) in the presence of Hcy and different amino acids (500 μM) in a water/THF mixture (7:3, v/v).

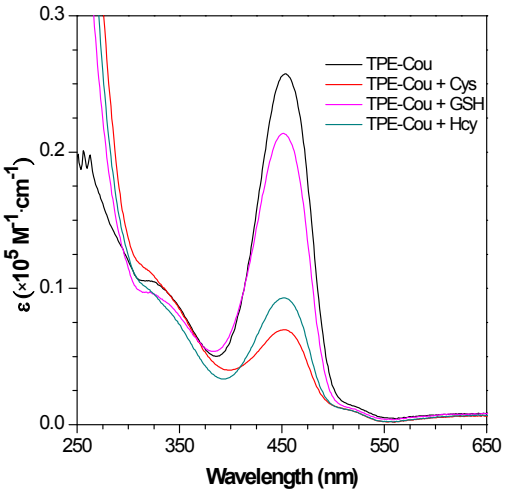

Fig. S9 Absorption spectra of TPE-Cou (20 μM) after addition of Cys, Hcy or GSH in a water/THF mixture (7:3, v/v).

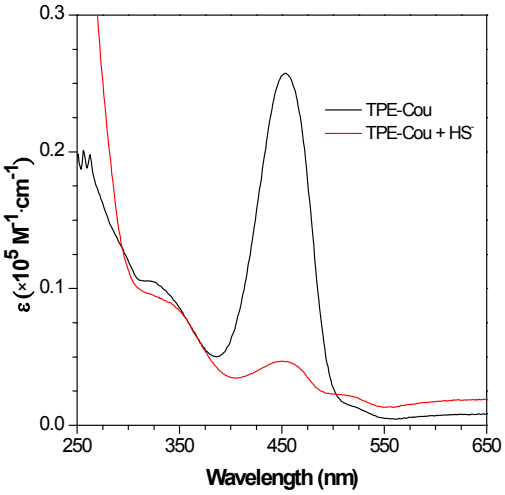

Fig. S10 Absorption spectra of TPE-Cou (20 μM) after addition of SH^- in a water/THF mixture (7:3, v/v).

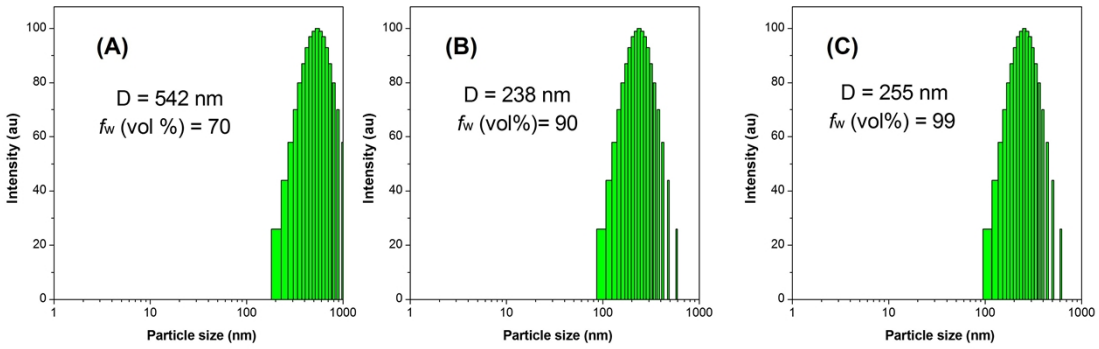

Fig. S11 Particle size distribution of TPE-Cou in THF/water mixtures with different volume fractions of water (f_w).

References

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2 J. Y. Shao, H. Y. Sun, H. M. Guo, S. M. Ji, C. L. Zhang, T. D. James, Chem. Sci., 2012, 3, 1049-1061.