Appendix A

Supporting Information

A simple fluorescent probe for detection of Ag^+ and Cd^{2+} and its Cd^{2+} complex for sequential recognition of S^{2-}

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1. Experimental

1.1. Materials and instruments

The raw materials were purchased from Aladdin and Energy Chemical Reagents Ltd. and used with no further purification. Compounds **1** and **2** were synthesized according to the previous studies. [1, 2] NMR spectra were acquired on a Bruker AVANCE III spectrometer (Switzerland) in $CDCl_3$ solution at 400 and 100 MHz, respectively. ESI-MS spectras were measured on a Bruker Solarix XR Fourier transform-ion cyclotron resonance (FT-ICR) mass spectrometer. The melting point of probe **DQT** was determined on a WRS-C1 microcomputer melting point instrument. The pH values were determined on a PHS-3C pH meter.

1.2. Synthesis

Briefly, 278 mg of 1 mmol compound **1**, 277 mg of 1.1 mmol compound **2**, 276 mg of 2 mmol anhydrous potassium carbonate and 30 mL of anhydrous CH_3CN were added to a 100 mL three-necked flask with magneton and reflux for 12 h for TLC monitoring. Then, the mixture was cooled to 25 ºC, and the organic layer was evaporated. The crude product was purified by column chromatography using CH_2Cl_2 as the eluent to obtain 400 mg of white solid with a yield of 89%. mp: 198.1-198.6 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ (ppm) 8.54 (d, 1H, J = 8.4 Hz, ArH), 8.33 (s, 2H, ArH), 8.29 (d, 1H, J = 8.4 Hz, ArH), 8.15 (d, 1H, J = 8 Hz, ArH), 8.01 (d, 1H, J = 8 Hz, ArH), 7.51-7.55 (m, 1H, ArH), 7.43-7.50 (m, 5H, ArH), 7.22 (dd, 1H, J_1 = 6.8 Hz, J_2 = 2.4 Hz, ArH), 7.11 (dd, 1H, J_1 = 6.8 Hz, J_2 = 2 Hz, ArH), 5.78 (s, 2H, $-CH_2-$), 4.14 (s, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ (ppm): 170.3, 157.3, 155.0, 154.5, 154.4, 150.2, 140.1, 139.5, 137.2, 137.0, 136.6, 130.3, 128.9, 128.1, 126.5, 126.3, 125.9, 123.8, 122.1, 120.2, 119.8, 119.6, 118.8, 111.0, 107.9, 72.2, 56.2. HRMS (ESI): m/z calcd for $C_{27}H_{20}N_3O_2S$ $[(M+H)^+]$: 450.1278, found 450.1270; $C_{27}H_{19}N_3NaO_2S$ $[(M+Na)^+]$: 472.1096, found 472.1104.

1.3. Recording of fluorescence spectra

The fluorescence spectra were measured on a HITACHI F-2700 spectrophotometer in CH_3OH/HEPES (9:1 v/v, pH=7.30) buffer system (λ_{ex}=344 nm). The probe was formulated into a mother liquor of 1×10^{-3} M using DMSO as a solvent, and stock solutions of ions (1×10^{-2} mol/L) were prepared in deionized water. The concentration of probe **DQT** was 10 μM. The emission spectra were determined using 5×5 nm slits. In this test, cations included: Na^+, Ni^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Cs^+, Ag^+, Mg^{2+}, Ca^{2+}, Li^+, K^+, Hg^{2+}, Pb^{2+}, Ba^{2+}, Al^{3+} and Fe^{3+}; anions included: S^{2-}, HCO_3^-, F^-, CO_3^{2-}, Cl^-, OAc^-, Br^-, I^-, HSO_3^-, SO_3^{2-}, SO_4^{2-}, NO_3^- and NO_2^-.

1.4. Fluorescence quantum yield experiment

According to Eq. 3, the relative fluorescence quantum yields were calculated when quinine sulfate ($\emptyset = 0.577$) was used as the reference solution.

1.5. X-ray crystallography

The crystal of probe **DQT** for X-ray structure analysis was acquired by slow volatilizing acetonitrile solvent. The X-ray crystal diffraction data of probe **DQT** were collected on a Bruker D8 VENTURE diffractometer using Mo-Kα radiation (λ=0.71073 Å). Integration and scaling of intensity data were accomplished with the SAINT program, and the data sets were corrected by SADABS. The structures were solved by direct method and refined with full-matrix least-squares technique using SHELX-2014 software. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in calculated positions and refined with a riding model.

2. Determination of detection limit

The limit of detection (LOD) of probe **DQT** for Ag^+, Cd^{2+} and S^{2-} was calculated based on the fluorescence titration and determined from the following equation:

$$\text{LOD} = 3\sigma/m \qquad \text{Eq. 1}$$

where σ is the standard deviation of the blank solution; m is the slope of the calibration curve.

3. Determination of association constant

The association constants (Ka) were also determined based on the fluorescent titration curve using the equation as follows:

$$\frac{1}{F-F_0}=\frac{1}{F_{max}-F_0}\left[\frac{1}{K_a[X]}+1\right] \quad \text{Eq. 2}$$

Where F and F_0 represent the intensity of host in the presence and absence of ions, respectively, F_{max} is the saturated intensity of host in the presence of excess amount of ions; [X] is the concentration of ions added.

4. Fluorescence quantum yield

The fluorescence quantum yield ($\emptyset$) of **DQT**, **DQT-**Ag^{+}, **DQT-**Cd^{2+}, **DQT-**Cd^{2+}+S^{2-} were determined based on the equation as follows:

$$\emptyset=\emptyset_{fr}\left(\frac{1-10^{-A_rL_r}}{1-10^{-AL}}\right)\left(\frac{n}{n_r}\right)^2\left(\frac{D}{D_r}\right) \quad \text{Eq. 3}$$

Where $\emptyset$-fluorescence quantum yield of the test sample; $\emptyset_{fr}$-fluorescence quantum yield of the reference substance; A-absorbance of the test solution; A_r-absorbance of the reference solution; D-integrated fluorescence intensity of the test solution; D_r-integrated fluorescence intensity of the reference solution; n-refractive index of the solvent of the test solution; n_r-refractive index of the solvent of the reference solution; L and L_r-width of the cuvette.

5. [1]H NMR spectra of probe **DQT**

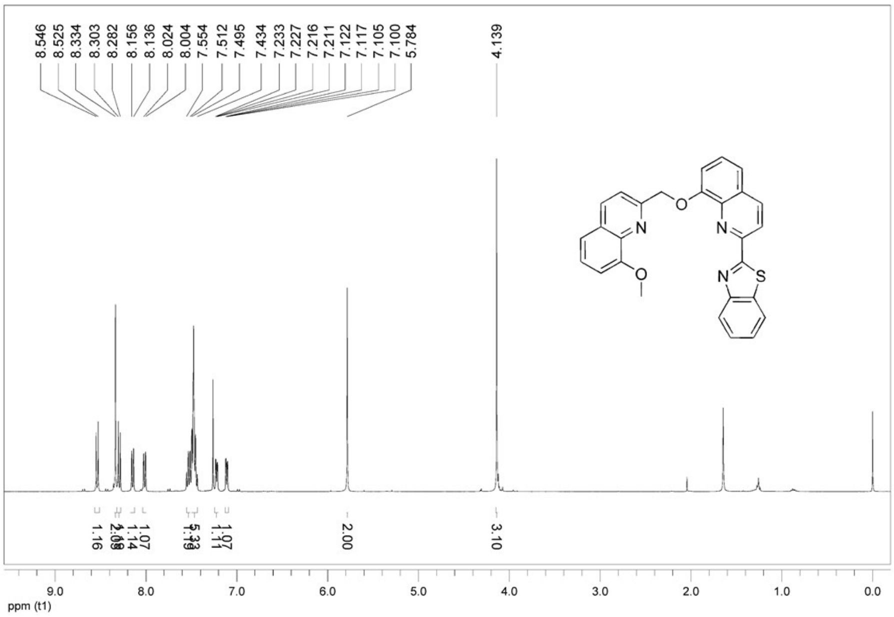

Fig. S1. [1]H NMR spectra of probe **DQT**

6. [13]C NMR spectra of probe **DQT**

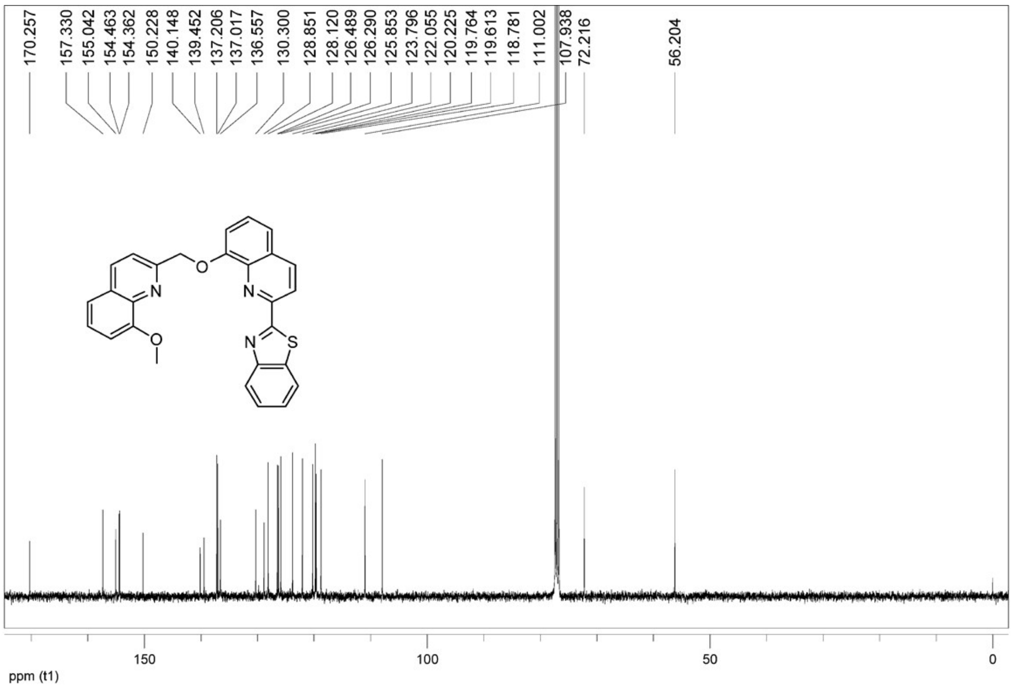

Fig. S2. [13]C NMR spectra of probe **DQT**

7. SI-MS spectra of probe **DQT**

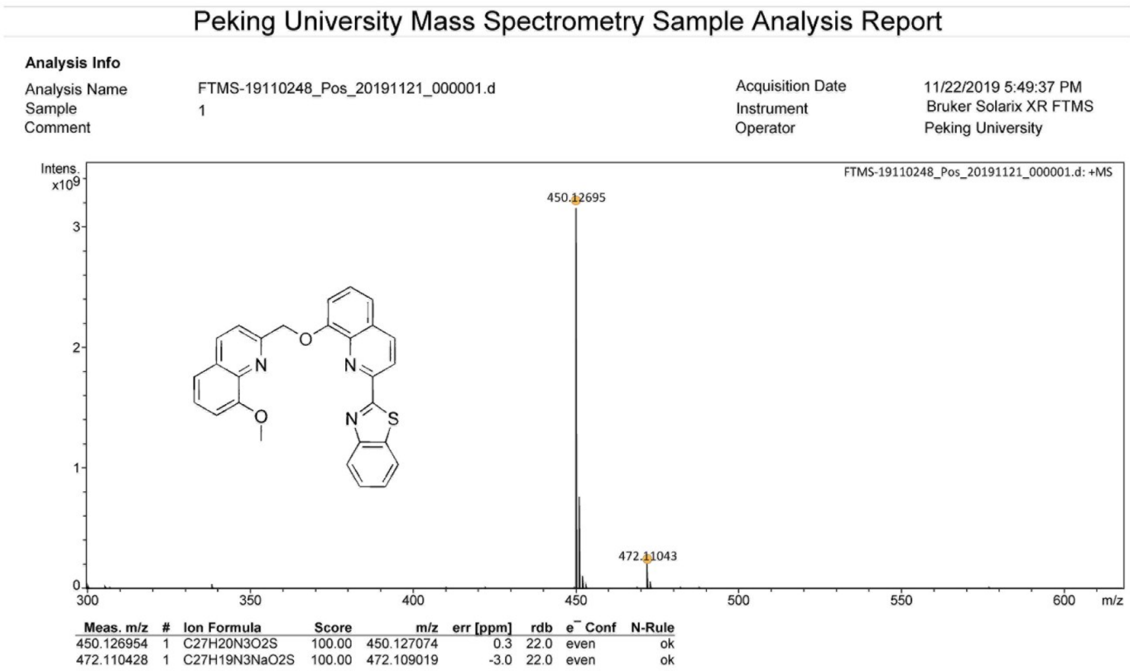

Fig. S3. ESI-MS spectra of probe **DQT**

8. Calculation of binding constant Ka with Ag^+

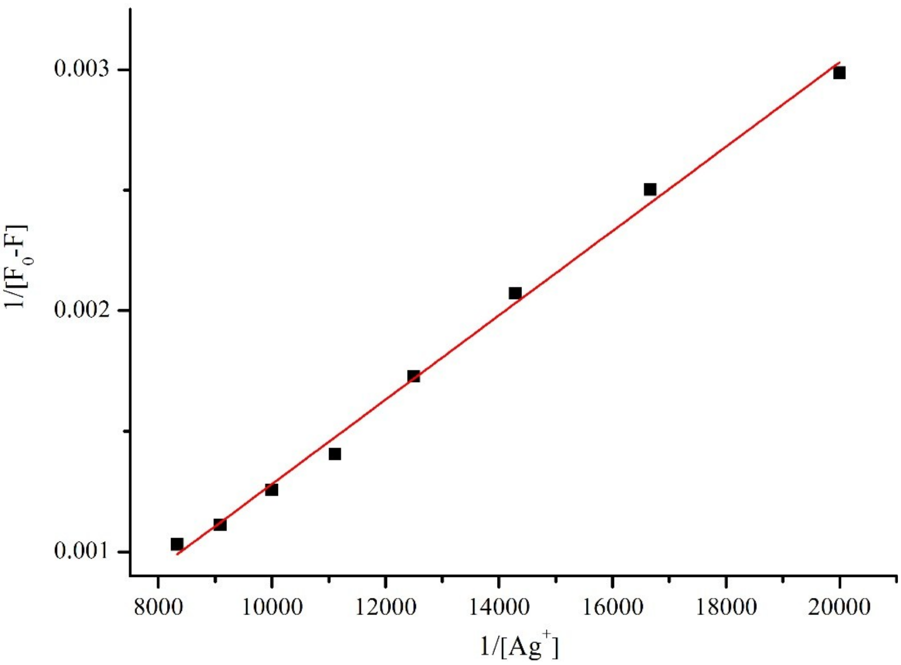

Fig. S4. The Benesi-Hilderbrand plot of probe **DQT** with Ag^+. Linear Equation: $Y=1.75\times10^{-7}\times X-4.69\times10^{-4}$, $R^2=0.9953$, $Ka=2.68\times10^3\ M^{-1}$.

9. Calculation of binding constant Ka with Cd^{2+}

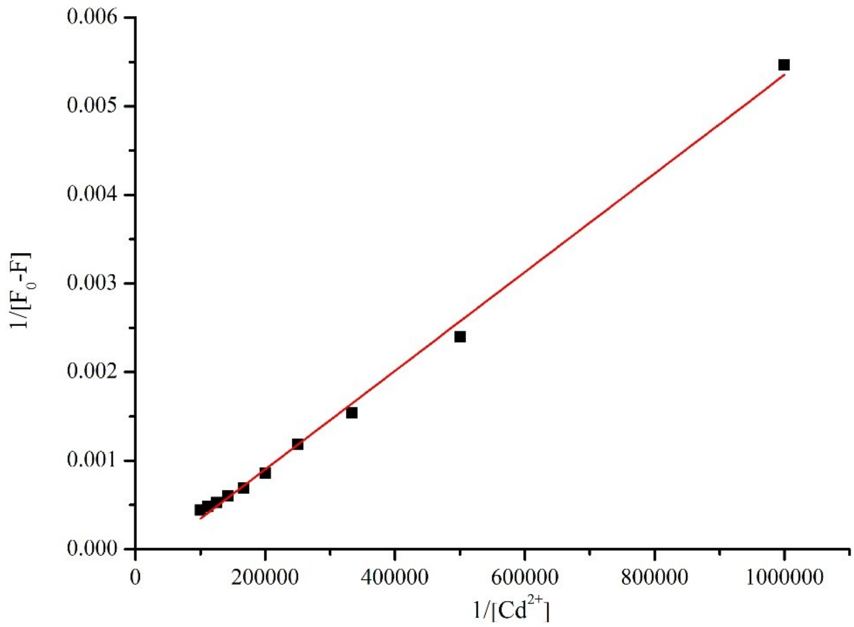

Fig. S5. The Benesi-Hilderbrand plot of probe **DQT** with Cd^{2+}. Linear Equation: $Y=3.91\times10^{-8}\times X+8.72\times10^{-4}$, $R^2=0.9967$, $Ka=2.23\times10^4\ M^{-1}$.

10. Determination of detection limit of Ag^+

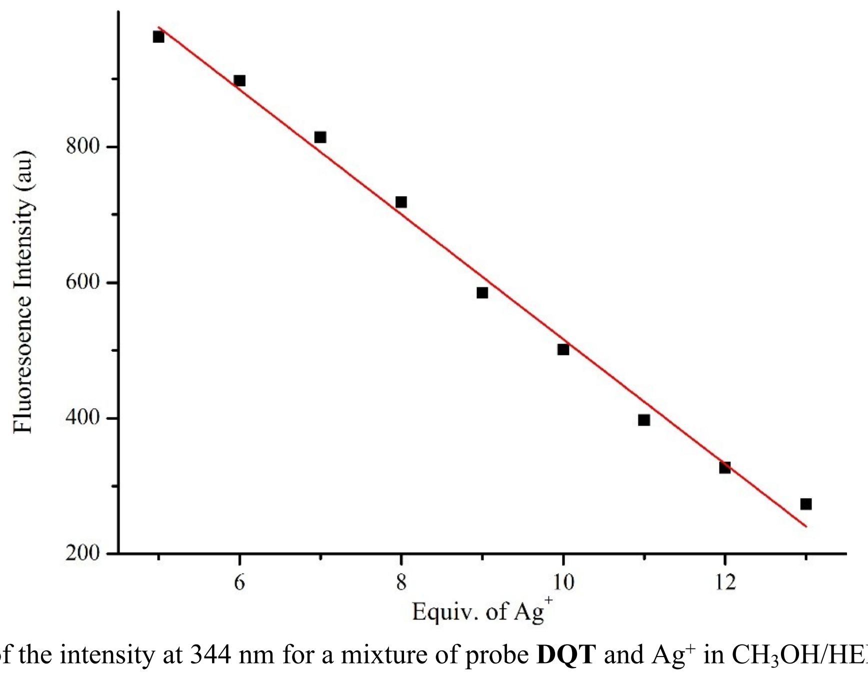

Fig. S6. Plot of the intensity at 344 nm for a mixture of probe **DQT** and Ag^+ in CH_3OH/HEPES (9:1 v/v, pH=7.30) buffer system in the range 5~13 equiv. Linear Equation: $Y=-91.99\times X+1436.26$, $R^2=0.9916$.The calculated detection limit of **DQT** for Ag^+ is 0.42 μM.

11. Determination of detection limit of Cd^{2+}

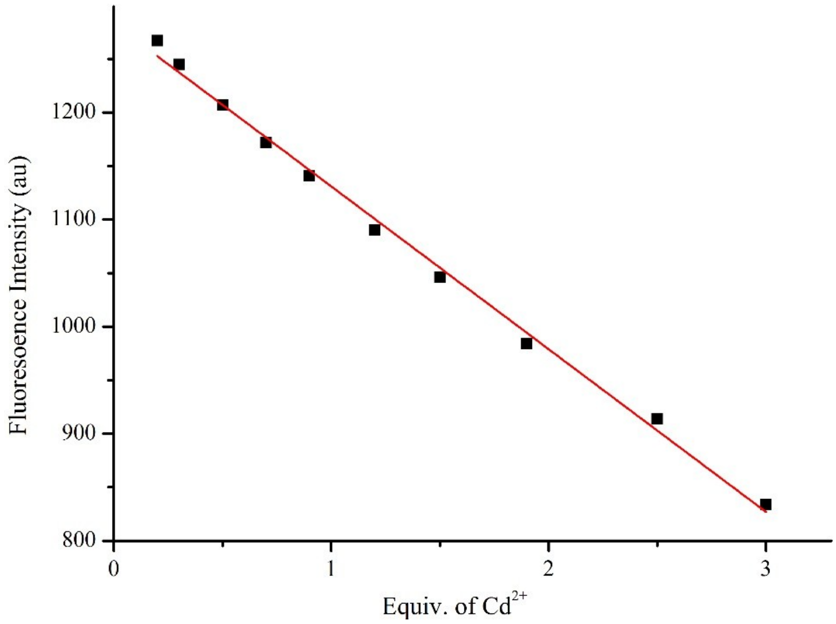

Fig. S7. Plot of the intensity at 344 nm for a mixture of probe **DQT** and Cd^{2+} in CH_3OH/HEPES (9:1 v/v, pH=7.30) buffer system in the range 0.2~3 equiv. Linear Equation: Y=-152.11×X+1283.18, R^2=0.9954.The calculated detection limit of **DQT** for Cd^{2+} is 0.26 μM.

12. Fluorescence intensity of **DQT**-Cd^{2+} towards S^{2-} -selective probe

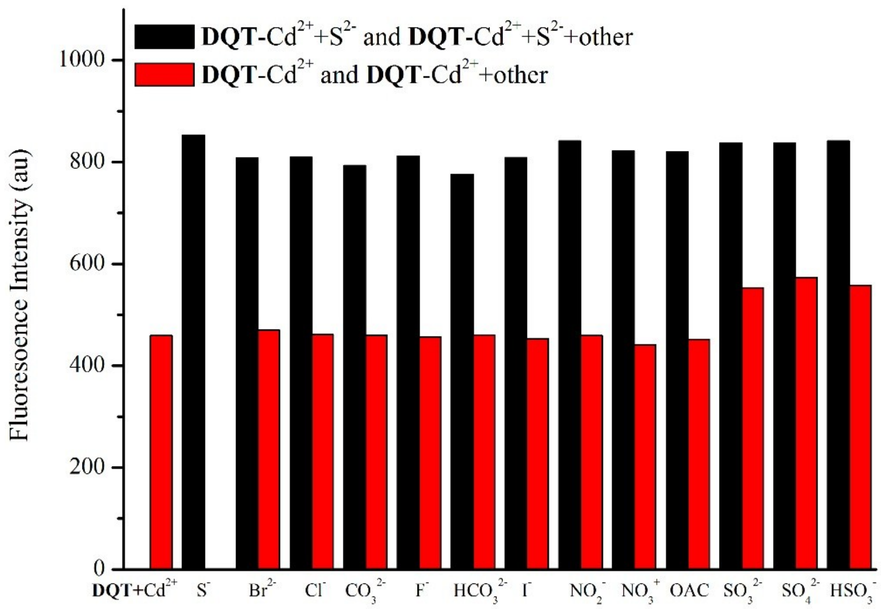

Fig. S8. Fluorescence intensity of **DQT**-Cd^{2+} (10 μM) with selected anions (20 equiv.) in the absence (red bars) or presence (black bars) of S^{2-} (20 equiv.).

13. Determination of detection limit of S^{2-}

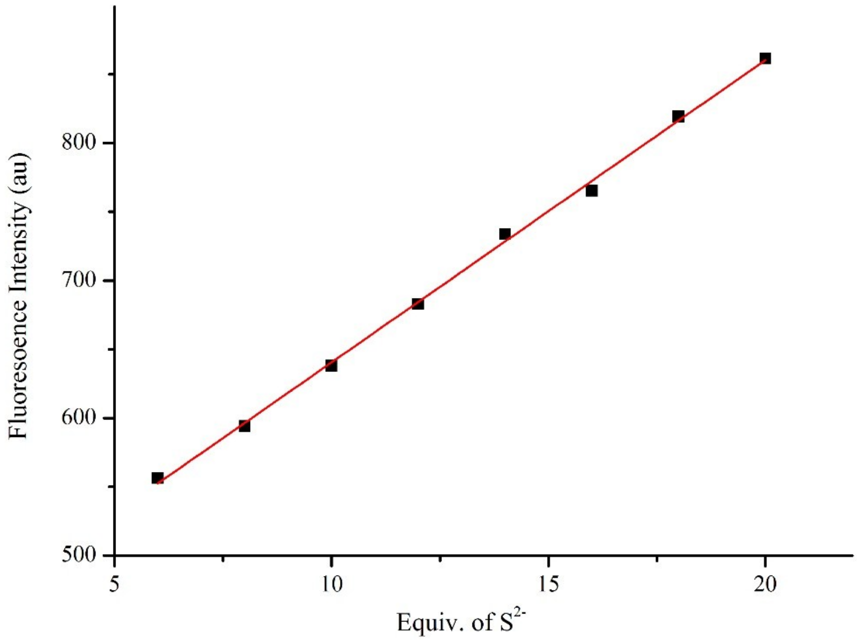

Fig. S9. Plot of the intensity at 344 nm for a mixture of **DQT-**Cd^{2+} and S^{2-} in CH_3OH/HEPES (9:1 v/v, pH=7.30) buffer system in the range 6~20 equiv. Linear Equation: Y=21.99×X+420.56, R^2=0.9983. The detection limit of **DQT-**Cd^{2+} for S^{2-} is 11.50 μM.

References

[1] J. F. Li, H. J. Jin, H. Y. Zhou, J Rothfuss, Z. D. Tu. Med. Chem. Commun. 4(2013) 443.

[2] K. Aich, S. Goswami, S. Das, C. D. Mukhopadhyay, C. K. Quah, Ho. K. Fun. Inorg. Chem. 54(2015) 7309-7315.

Appendix B

Table S1. Crystal date and structure refinement for **DQT**

Compound	**DQT**
Empirical formula	$C_{27}H_{19}N_3O_2S$
Formula weight	449.51
Temperature	170.0 K
Crystal system	Monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 21.767(3) Å, α = 90°
	b = 4.8042(8) Å, β = 103.866(7)°
	c = 42.042(7) Å, γ = 90°
Volume	4268.4(12) Å^3
Z	8
Density (calculated)	1.399 Mg/m^3
Absorption coefficient	0.183 mm^{-1}
F(000)	1872
Crystal size	0.08 ×0.05 × 0.02 mm^3
Reflections collected	26795
Independent reflections	7500 [R(int) = 0.1074]
Goodness-of-fit on F^2	1.014
Final *R* indices [*I*>2sigma(*I*)]	R_1 = 0.0808, wR_2 = 0.1869
R indices (all data)	R_1 = 0.1748, wR_2 = 0.2420

Table S2 Bond lengths (Å) for **DQT**

S(1)-C(21)	1.745(14)	C(15A)-C(16A)	1.40(2)	C(34)-H(34C)	0.98
S(1)-C(23)	1.701(14)	C(16)-C(17)	1.43(2)	C(35)-C(36)	1.364(7)
S(1A)-C(21A)	1.743(16)	C(16)-C(18)	1.44(2)	C(35)-C(40)	1.441(7)
S(1A)-C(22)	1.718(13)	C(16A)-C(17A)	1.43(2)	C(36)-H(36)	0.95
O(3)-C(11)	1.427(5)	C(16A)-C(18A)	1.39(2)	C(36)-C(37)	1.395(7)
O(3)-C(12)	1.365(6)	C(18)-H(18)	0.95	C(37)-H(37)	0.95
O(4)-C(1)	1.438(6)	C(18)-C(19)	1.356(17)	C(37)-C(38)	1.387(8)
O(4)-C(2)	1.362(6)	C(18A)-H(18A)	0.95	C(38)-H(38)	0.95
N(1)-C(7)	1.375(6)	C(18A)-C(19A)	1.35(2)	C(38)-C(39)	1.413(7)
N(1)-C(10)	1.328(6)	C(19)-H(19)	0.95	C(39)-C(40)	1.407(7)
N(2)-C(17)	1.352(19)	C(19)-C(20)	1.449(17)	C(39)-C(41)	1.409(7)
N(2)-C(20)	1.355(19)	C(19A)-H(19A)	0.95	C(41)-H(41)	0.95
N(2A)-C(17A)	1.35(2)	C(19A)-C(20A)	1.38(2)	C(41)-C(42)	1.357(7)
N(2A)-C(20A)	1.32(2)	C(20)-C(21)	1.451(18)	C(42)-H(42)	0.95
N(5)-C(21A)	1.288(19)	C(20A)-C(21A)	1.47(2)	C(42)-C(43)	1.408(7)
N(5)-C(24)	1.416(15)	C(23)-C(25)	1.390(17)	C(43)-C(44)	1.501(7)
N(6)-C(21)	1.313(17)	C(23)-C(33)	1.400(16)	C(44)-H(44A)	0.99

N(6)-C(25)	1.381(15)	C(25)-C(27)	1.445(16)	C(44)-H(44B)	0.99
C(1)-H(1A)	0.98	C(27)-H(27)	0.95	C(45)-C(46)	1.362(6)
C(1)-H(1B)	0.98	C(27)-C(29)	1.371(18)	C(45)-C(50)	1.428(6)
C(1)-H(1C)	0.98	C(29)-H(29)	0.95	C(46)-H(46)	0.95
C(2)-C(3)	1.370(7)	C(29)-C(32)	1.366(18)	C(46)-C(47)	1.412(7)
C(2)-C(7)	1.440(7)	C(31)-H(31)	0.95	C(47)-H(47)	0.95
C(3)-H(3)	0.95	C(31)-C(22)	1.39	C(47)-C(48)	1.361(7)
C(3)-C(4)	1.409(7)	C(31)-C(30)	1.39	C(48)-H(48)	0.95
C(4)-H(4)	0.95	C(22)-C(24)	1.39	C(48)-C(49)	1.402(6)
C(4)-C(5)	1.368(8)	C(24)-C(26)	1.39	C(49)-C(50)	1.424(6)
C(5)-H(5)	0.95	C(26)-H(26)	0.95	C(49)-C(51)	1.418(6)
C(5)-C(6)	1.411(7)	C(26)-C(28)	1.39	C(51)-H(51)	0.95
C(6)-C(7)	1.403(6)	C(28)-H(28)	0.95	C(51)-C(52)	1.353(7)
C(6)-C(8)	1.411(7)	C(28)-C(30)	1.39	C(52)-H(52)	0.95
C(8)-H(8)	0.95	C(30)-H(30)	0.95	C(52)-C(53)	1.406(7)
C(8)-C(9)	1.362(7)	C(32)-H(32)	0.95	C(53)-C(54)	1.468(7)
C(9)-H(9)	0.95	C(32)-C(33)	1.385(16)	C(55)-C(56)	1.317(9)
C(9)-C(10)	1.399(6)	C(33)-H(33)	0.95	C(55)-C(62)	1.480(19)
C(10)-C(11)	1.500(7)	S(2)-C(54)	1.744(7)	C(55)-C(62A)	1.45(2)
C(11)-H(11A)	0.99	S(2)-C(55)	1.737(7)	C(56)-C(57)	1.478(17)
C(11)-H(11B)	0.99	S(2A)-C(54)	1.718(7)	C(56)-C(58)	1.441(17)
C(12)-C(13)	1.42(4)	S(2A)-C(55)	1.797(8)	C(57)-H(57)	0.95
C(12)-C(13A)	1.30(4)	O(1)-C(44)	1.426(5)	C(57)-C(59)	1.45(5)
C(12)-C(17)	1.46(2)	O(1)-C(45)	1.366(5)	C(58)-H(58)	0.95
C(12)-C(17A)	1.44(3)	O(2)-C(34)	1.433(6)	C(58)-C(60)	1.38(3)
C(13)-H(13)	0.95	O(2)-C(35)	1.366(6)	C(59)-H(59)	0.95
C(13)-C(14)	1.29(5)	N(3)-C(40)	1.361(6)	C(59)-C(61)	1.11(5)
C(13A)-H(13A)	0.95	N(3)-C(43)	1.331(6)	C(60)-H(60)	0.95
C(13A)-C(14A)	1.53(5)	N(4)-C(50)	1.365(6)	C(60)-C(61)	1.42(3)
C(14)-H(14)	0.95	N(4)-C(53)	1.324(6)	C(61)-H(61)	0.95
C(14)-C(15)	1.34(3)	N(7)-C(54)	1.317(15)	C(61)-H(61A)	0.95
C(14A)-H(14A)	0.95	N(7)-C(56)	1.430(16)	C(61)-C(62)	1.38(2)
C(14A)-C(15A)	1.41(3)	N(7A)-C(54)	1.306(14)	C(61)-C(62A)	1.45(2)
C(15)-H(15)	0.95	N(7A)-C(56)	1.435(16)	C(62)-H(62)	0.95
C(15)-C(16)	1.419(18)	C(34)-H(34A)	0.98	C(62A)-H(62A)	0.95
C(15A)-H(15A)	0.95	C(34)-H(34B)	0.98		

Table S3 Angles (deg) for **DQT**

C(23)-S(1)-C(21)	89.1(8)	C(16A)-C(18A)-H(18A)	119.7	N(3)-C(40)-C(39)	123.8(5)
C(22)-S(1A)-C(21A)	88.0(8)	C(19A)-C(18A)-C(16A)	120.5(17)	C(39)-C(40)-C(35)	118.5(5)
C(12)-O(3)-C(11)	120.3(4)	C(19A)-C(18A)-H(18A)	119.7	C(39)-C(41)-H(41)	119.7
C(2)-O(4)-C(1)	115.7(4)	C(18)-C(19)-H(19)	120.4	C(42)-C(41)-C(39)	120.6(5)
C(10)-N(1)-C(7)	116.7(4)	C(18)-C(19)-C(20)	119.1(14)	C(42)-C(41)-H(41)	119.7
C(17)-N(2)-C(20)	116.6(13)	C(20)-C(19)-H(19)	120.4	C(41)-C(42)-H(42)	120.7
C(20A)-N(2A)-C(17A)	116.9(14)	C(18A)-C(19A)-H(19A)	119.6	C(41)-C(42)-C(43)	118.6(5)
C(21A)-N(5)-C(24)	108.9(12)	C(18A)-C(19A)-C(20A)	120.7(17)	C(43)-C(42)-H(42)	120.7
C(21)-N(6)-C(25)	109.7(11)	C(20A)-C(19A)-H(19A)	119.6	N(3)-C(43)-C(42)	123.4(5)
O(4)-C(1)-H(1A)	109.5	N(2)-C(20)-C(19)	124.1(13)	N(3)-C(43)-C(44)	114.1(4)

O(4)-C(1)-H(1B)	109.5	N(2)-C(20)-C(21)	115.4(11)	C(42)-C(43)-C(44)	122.5(4)
O(4)-C(1)-H(1C)	109.5	C(19)-C(20)-C(21)	120.3(13)	O(1)-C(44)-C(43)	108.4(4)
H(1A)-C(1)-H(1B)	109.5	N(2A)-C(20A)-C(19A)	122.6(14)	O(1)-C(44)-H(44A)	110
H(1A)-C(1)-H(1C)	109.5	N(2A)-C(20A)-C(21A)	112.3(15)	O(1)-C(44)-H(44B)	110
H(1B)-C(1)-H(1C)	109.5	C(19A)-C(20A)-C(21A)	125.1(17)	C(43)-C(44)-H(44A)	110
O(4)-C(2)-C(3)	124.1(5)	N(6)-C(21)-S(1)	115.4(11)	C(43)-C(44)-H(44B)	110
O(4)-C(2)-C(7)	116.1(4)	N(6)-C(21)-C(20)	125.9(13)	H(44A)-C(44)-H(44B)	108.4
C(3)-C(2)-C(7)	119.8(5)	C(20)-C(21)-S(1)	118.7(11)	O(1)-C(45)-C(50)	114.5(4)
C(2)-C(3)-H(3)	119.5	N(5)-C(21A)-S(1A)	117.8(13)	C(46)-C(45)-O(1)	125.0(4)
C(2)-C(3)-C(4)	121.0(5)	N(5)-C(21A)-C(20A)	121.8(14)	C(46)-C(45)-C(50)	120.5(4)
C(4)-C(3)-H(3)	119.5	C(20A)-C(21A)-S(1A)	120.0(14)	C(45)-C(46)-H(46)	119.8
C(3)-C(4)-H(4)	119.8	C(25)-C(23)-S(1)	110.4(9)	C(45)-C(46)-C(47)	120.4(5)
C(5)-C(4)-C(3)	120.5(5)	C(25)-C(23)-C(33)	120.3(10)	C(47)-C(46)-H(46)	119.8
C(5)-C(4)-H(4)	119.8	C(33)-C(23)-S(1)	129.2(10)	C(46)-C(47)-H(47)	119.7
C(4)-C(5)-H(5)	120.2	N(6)-C(25)-C(23)	115.3(10)	C(48)-C(47)-C(46)	120.6(5)
C(4)-C(5)-C(6)	119.7(5)	N(6)-C(25)-C(27)	125.7(12)	C(48)-C(47)-H(47)	119.7
C(6)-C(5)-H(5)	120.2	C(23)-C(25)-C(27)	119.0(11)	C(47)-C(48)-H(48)	119.8
C(5)-C(6)-C(8)	122.3(5)	C(25)-C(27)-H(27)	121	C(47)-C(48)-C(49)	120.5(5)
C(7)-C(6)-C(5)	121.0(5)	C(29)-C(27)-C(25)	118.1(13)	C(49)-C(48)-H(48)	119.8
C(7)-C(6)-C(8)	116.7(5)	C(29)-C(27)-H(27)	121	C(48)-C(49)-C(50)	119.9(4)
N(1)-C(7)-C(2)	118.4(4)	C(27)-C(29)-H(29)	118.6	C(48)-C(49)-C(51)	123.7(4)
N(1)-C(7)-C(6)	123.6(5)	C(32)-C(29)-C(27)	122.8(13)	C(51)-C(49)-C(50)	116.4(4)
C(6)-C(7)-C(2)	118.1(5)	C(32)-C(29)-H(29)	118.6	N(4)-C(50)-C(45)	118.7(4)
C(6)-C(8)-H(8)	119.9	C(22)-C(31)-H(31)	120	N(4)-C(50)-C(49)	123.3(4)
C(9)-C(8)-C(6)	120.1(5)	C(22)-C(31)-C(30)	120	C(49)-C(50)-C(45)	118.1(4)
C(9)-C(8)-H(8)	119.9	C(30)-C(31)-H(31)	120	C(49)-C(51)-H(51)	119.8
C(8)-C(9)-H(9)	120.5	C(31)-C(22)-S(1A)	128.9(7)	C(52)-C(51)-C(49)	120.4(5)
C(8)-C(9)-C(10)	119.0(5)	C(24)-C(22)-S(1A)	111.1(7)	C(52)-C(51)-H(51)	119.8
C(10)-C(9)-H(9)	120.5	C(24)-C(22)-C(31)	120	C(51)-C(52)-H(52)	120.8
N(1)-C(10)-C(9)	123.8(5)	C(22)-C(24)-N(5)	114.2(8)	C(51)-C(52)-C(53)	118.4(5)
N(1)-C(10)-C(11)	114.6(4)	C(22)-C(24)-C(26)	120	C(53)-C(52)-H(52)	120.8
C(9)-C(10)-C(11)	121.5(4)	C(26)-C(24)-N(5)	125.8(8)	N(4)-C(53)-C(52)	124.8(4)
O(3)-C(11)-C(10)	106.3(4)	C(24)-C(26)-H(26)	120	N(4)-C(53)-C(54)	115.5(4)
O(3)-C(11)-H(11A)	110.5	C(24)-C(26)-C(28)	120	C(52)-C(53)-C(54)	119.6(4)
O(3)-C(11)-H(11B)	110.5	C(28)-C(26)-H(26)	120	N(7)-C(54)-S(2)	115.5(8)
C(10)-C(11)-H(11A)	110.5	C(26)-C(28)-H(28)	120	N(7)-C(54)-C(53)	122.1(8)
C(10)-C(11)-H(11B)	110.5	C(30)-C(28)-C(26)	120	N(7A)-C(54)-S(2A)	118.0(8)
H(11A)-C(11)-H(11B)	108.7	C(30)-C(28)-H(28)	120	N(7A)-C(54)-C(53)	122.9(8)
O(3)-C(12)-C(13)	129.1(18)	C(31)-C(30)-H(30)	120	C(53)-C(54)-S(2)	122.3(4)
O(3)-C(12)-C(17)	105.4(8)	C(28)-C(30)-C(31)	120	C(53)-C(54)-S(2A)	119.1(4)
O(3)-C(12)-C(17A)	121.6(10)	C(28)-C(30)-H(30)	120	C(56)-C(55)-S(2)	109.8(5)
C(13)-C(12)-C(17)	125.4(18)	C(29)-C(32)-H(32)	120.1	C(56)-C(55)-S(2A)	109.3(5)
C(13A)-C(12)-O(3)	123.0(18)	C(29)-C(32)-C(33)	119.8(12)	C(56)-C(55)-C(62)	116.7(8)
C(13A)-C(12)-C(17A)	115(2)	C(33)-C(32)-H(32)	120.1	C(56)-C(55)-C(62A)	118.5(11)
C(12)-C(13)-H(13)	122.2	C(23)-C(33)-H(33)	120	C(62)-C(55)-S(2)	124.8(9)
C(14)-C(13)-C(12)	116(4)	C(32)-C(33)-C(23)	120.0(12)	C(62A)-C(55)-S(2A)	122.1(12)
C(14)-C(13)-H(13)	122.2	C(32)-C(33)-H(33)	120	N(7)-C(56)-C(57)	119.4(11)
C(12)-C(13A)-H(13A)	116.8	C(55)-S(2)-C(54)	87.1(3)	N(7A)-C(56)-C(58)	117.2(12)

C(12)-C(13A)-C(14A)	126(3)	C(54)-S(2A)-C(55)	86.0(4)	C(55)-C(56)-N(7)	112.7(8)
C(14A)-C(13A)-H(13A)	116.8	C(45)-O(1)-C(44)	117.0(4)	C(55)-C(56)-N(7A)	113.0(8)
C(13)-C(14)-H(14)	117.6	C(35)-O(2)-C(34)	115.4(4)	C(55)-C(56)-C(57)	116.0(9)
C(13)-C(14)-C(15)	125(3)	C(43)-N(3)-C(40)	117.1(4)	C(55)-C(56)-C(58)	119.6(8)
C(15)-C(14)-H(14)	117.6	C(53)-N(4)-C(50)	116.6(4)	C(56)-C(57)-H(57)	124.5
C(13A)-C(14A)-H(14A)	121.9	C(54)-N(7)-C(56)	106.7(10)	C(59)-C(57)-C(56)	111(2)
C(15A)-C(14A)-C(13A)	116(3)	C(54)-N(7A)-C(56)	107.1(11)	C(59)-C(57)-H(57)	124.5
C(15A)-C(14A)-H(14A)	121.9	O(2)-C(34)-H(34A)	109.5	C(56)-C(58)-H(58)	122.8
C(14)-C(15)-H(15)	118.8	O(2)-C(34)-H(34B)	109.5	C(60)-C(58)-C(56)	114.4(17)
C(14)-C(15)-C(16)	122.4(19)	O(2)-C(34)-H(34C)	109.5	C(60)-C(58)-H(58)	122.8
C(16)-C(15)-H(15)	118.8	H(34A)-C(34)-H(34B)	109.5	C(57)-C(59)-H(59)	115.9
C(14A)-C(15A)-H(15A)	121	H(34A)-C(34)-H(34C)	109.5	C(61)-C(59)-C(57)	128(4)
C(16A)-C(15A)-C(14A)	118(2)	H(34B)-C(34)-H(34C)	109.5	C(61)-C(59)-H(59)	115.9
C(16A)-C(15A)-H(15A)	121	O(2)-C(35)-C(40)	114.5(4)	C(58)-C(60)-H(60)	120.6
C(15)-C(16)-C(17)	118.7(16)	C(36)-C(35)-O(2)	125.7(5)	C(58)-C(60)-C(61)	118.8(19)
C(15)-C(16)-C(18)	122.0(15)	C(36)-C(35)-C(40)	119.7(5)	C(61)-C(60)-H(60)	120.6
C(17)-C(16)-C(18)	119.2(13)	C(35)-C(36)-H(36)	119.5	C(59)-C(61)-H(61)	118.6
C(15A)-C(16A)-C(17A)	122.1(18)	C(35)-C(36)-C(37)	121.0(5)	C(59)-C(61)-C(62)	123(3)
C(18A)-C(16A)-C(15A)	123.2(18)	C(37)-C(36)-H(36)	119.5	C(60)-C(61)-H(61A)	120.1
C(18A)-C(16A)-C(17A)	114.6(19)	C(36)-C(37)-H(37)	119.4	C(60)-C(61)-C(62A)	119.9(15)
N(2)-C(17)-C(12)	124.3(14)	C(38)-C(37)-C(36)	121.2(5)	C(62)-C(61)-H(61)	118.6
N(2)-C(17)-C(16)	122.8(16)	C(38)-C(37)-H(37)	119.4	C(62A)-C(61)-H(61A)	120.1
C(16)-C(17)-C(12)	112.6(14)	C(37)-C(38)-H(38)	120.6	C(55)-C(62)-H(62)	122.9
N(2A)-C(17A)-C(12)	113.3(17)	C(37)-C(38)-C(39)	118.7(5)	C(61)-C(62)-C(55)	114.2(14)
N(2A)-C(17A)-C(16A)	125(2)	C(39)-C(38)-H(38)	120.6	C(61)-C(62)-H(62)	122.9
C(16A)-C(17A)-C(12)	122.0(15)	C(40)-C(39)-C(38)	120.7(5)	C(55)-C(62A)-C(61)	111.5(18)
C(16)-C(18)-H(18)	121	C(40)-C(39)-C(41)	116.4(5)	C(55)-C(62A)-H(62A)	124.3
C(19)-C(18)-C(16)	117.9(13)	C(41)-C(39)-C(38)	122.8(5)	C(61)-C(62A)-H(62A)	124.3
C(19)-C(18)-H(18)	121	N(3)-C(40)-C(35)	117.8(5)		

Table S4 Torsion angles (deg) for **DQT**

S(1)-C(23)-C(25)-N(6)	-1.8(16)	C(22)-S(1A)-C(21A)-N(5)	-1.1(16)
S(1)-C(23)-C(25)-C(27)	179.3(13)	C(22)-S(1A)-C(21A)-C(20A)	-174.1(15)
S(1)-C(23)-C(33)-C(32)	-178.6(12)	C(22)-C(31)-C(30)-C(28)	0
S(1A)-C(22)-C(24)-N(5)	-0.4(11)	C(22)-C(24)-C(26)-C(28)	0
S(1A)-C(22)-C(24)-C(26)	179.1(11)	C(24)-N(5)-C(21A)-S(1A)	1(2)
O(3)-C(12)-C(13)-C(14)	177(3)	C(24)-N(5)-C(21A)-C(20A)	173.9(16)
O(3)-C(12)-C(13A)-C(14A)	-180(4)	C(24)-C(26)-C(28)-C(30)	0
O(3)-C(12)-C(17)-N(2)	-2(3)	C(26)-C(28)-C(30)-C(31)	0
O(3)-C(12)-C(17)-C(16)	-176.2(18)	C(30)-C(31)-C(22)-S(1A)	-178.9(13)
O(3)-C(12)-C(17A)-N(2A)	5(3)	C(30)-C(31)-C(22)-C(24)	0
O(3)-C(12)-C(17A)-C(16A)	-178(2)	C(33)-C(23)-C(25)-N(6)	-178.4(13)
O(4)-C(2)-C(3)-C(4)	179.2(4)	C(33)-C(23)-C(25)-C(27)	2.7(19)
O(4)-C(2)-C(7)-N(1)	0.3(6)	S(2)-C(55)-C(56)-N(7)	-31.0(13)
O(4)-C(2)-C(7)-C(6)	-179.5(4)	S(2)-C(55)-C(56)-C(57)	-173.8(9)
N(1)-C(10)-C(11)-O(3)	175.1(4)	S(2)-C(55)-C(62)-C(61)	-177.8(9)
N(2)-C(20)-C(21)-S(1)	5(2)	S(2A)-C(55)-C(56)-N(7A)	27.5(12)

N(2)-C(20)-C(21)-N(6)	-175.4(19)	S(2A)-C(55)-C(56)-C(58)	172.0(10)
N(2A)-C(20A)-C(21A)-S(1A)	-6(3)	S(2A)-C(55)-C(62A)-C(61)	177.7(8)
N(2A)-C(20A)-C(21A)-N(5)	-179(2)	O(1)-C(45)-C(46)-C(47)	-178.9(4)
N(5)-C(24)-C(26)-C(28)	179.4(16)	O(1)-C(45)-C(50)-N(4)	1.8(6)
N(6)-C(25)-C(27)-C(29)	179.6(15)	O(1)-C(45)-C(50)-C(49)	-179.5(4)
C(1)-O(4)-C(2)-C(3)	2.2(7)	O(2)-C(35)-C(36)-C(37)	179.6(5)
C(1)-O(4)-C(2)-C(7)	-179.0(4)	O(2)-C(35)-C(40)-N(3)	1.8(6)
C(2)-C(3)-C(4)-C(5)	-0.1(8)	O(2)-C(35)-C(40)-C(39)	-178.4(4)
C(3)-C(2)-C(7)-N(1)	179.2(4)	N(3)-C(43)-C(44)-O(1)	-174.0(4)
C(3)-C(2)-C(7)-C(6)	-0.7(7)	N(4)-C(53)-C(54)-S(2)	-22.3(8)
C(3)-C(4)-C(5)-C(6)	0.1(8)	N(4)-C(53)-C(54)-S(2A)	9.3(8)
C(4)-C(5)-C(6)-C(7)	-0.3(8)	N(4)-C(53)-C(54)-N(7)	152.8(9)
C(4)-C(5)-C(6)-C(8)	-179.8(5)	N(4)-C(53)-C(54)-N(7A)	-170.9(9)
C(5)-C(6)-C(7)-N(1)	-179.2(4)	N(7)-C(56)-C(57)-C(59)	-165.5(18)
C(5)-C(6)-C(7)-C(2)	0.6(7)	N(7A)-C(56)-C(58)-C(60)	178.9(16)
C(5)-C(6)-C(8)-C(9)	179.2(5)	C(34)-O(2)-C(35)-C(36)	0.7(8)
C(6)-C(8)-C(9)-C(10)	-0.5(7)	C(34)-O(2)-C(35)-C(40)	-177.1(4)
C(7)-N(1)-C(10)-C(9)	-1.4(6)	C(35)-C(36)-C(37)-C(38)	1.4(9)
C(7)-N(1)-C(10)-C(11)	177.6(4)	C(36)-C(35)-C(40)-N(3)	-176.1(5)
C(7)-C(2)-C(3)-C(4)	0.4(7)	C(36)-C(35)-C(40)-C(39)	3.6(7)
C(7)-C(6)-C(8)-C(9)	-0.3(7)	C(36)-C(37)-C(38)-C(39)	-1.1(8)
C(8)-C(6)-C(7)-N(1)	0.3(7)	C(37)-C(38)-C(39)-C(40)	2.1(8)
C(8)-C(6)-C(7)-C(2)	-179.8(4)	C(37)-C(38)-C(39)-C(41)	-179.9(5)
C(8)-C(9)-C(10)-N(1)	1.4(7)	C(38)-C(39)-C(40)-N(3)	176.4(5)
C(8)-C(9)-C(10)-C(11)	-177.5(4)	C(38)-C(39)-C(40)-C(35)	-3.4(7)
C(9)-C(10)-C(11)-O(3)	-5.9(6)	C(38)-C(39)-C(41)-C(42)	-176.7(5)
C(10)-N(1)-C(7)-C(2)	-179.3(4)	C(39)-C(41)-C(42)-C(43)	0.7(8)
C(10)-N(1)-C(7)-C(6)	0.5(6)	C(40)-N(3)-C(43)-C(42)	2.3(7)
C(11)-O(3)-C(12)-C(13)	5(3)	C(40)-N(3)-C(43)-C(44)	-176.1(4)
C(11)-O(3)-C(12)-C(13A)	7(2)	C(40)-C(35)-C(36)-C(37)	-2.7(8)
C(11)-O(3)-C(12)-C(17)	-171.1(14)	C(40)-C(39)-C(41)-C(42)	1.3(8)
C(11)-O(3)-C(12)-C(17A)	-175.7(18)	C(41)-C(39)-C(40)-N(3)	-1.7(7)
C(12)-O(3)-C(11)-C(10)	-179.7(4)	C(41)-C(39)-C(40)-C(35)	178.5(4)
C(12)-C(13)-C(14)-C(15)	5(7)	C(41)-C(42)-C(43)-N(3)	-2.6(8)
C(12)-C(13A)-C(14A)-C(15A)	-4(7)	C(41)-C(42)-C(43)-C(44)	175.6(5)
C(13)-C(12)-C(17)-N(2)	-179(3)	C(42)-C(43)-C(44)-O(1)	7.6(6)
C(13)-C(12)-C(17)-C(16)	7(4)	C(43)-N(3)-C(40)-C(35)	179.7(4)
C(13)-C(14)-C(15)-C(16)	-3(7)	C(43)-N(3)-C(40)-C(39)	-0.1(7)
C(13A)-C(12)-C(17A)-N(2A)	-178(3)	C(44)-O(1)-C(45)-C(46)	-5.4(6)
C(13A)-C(12)-C(17A)-C(16A)	-1(4)	C(44)-O(1)-C(45)-C(50)	175.0(4)
C(13A)-C(14A)-C(15A)-C(16A)	3(6)	C(45)-O(1)-C(44)-C(43)	-178.3(4)
C(14)-C(15)-C(16)-C(17)	4(4)	C(45)-C(46)-C(47)-C(48)	-2.6(7)
C(14)-C(15)-C(16)-C(18)	180(3)	C(46)-C(45)-C(50)-N(4)	-177.8(4)
C(14A)-C(15A)-C(16A)-C(17A)	-1(5)	C(46)-C(45)-C(50)-C(49)	1.0(7)
C(14A)-C(15A)-C(16A)-C(18A)	175(3)	C(46)-C(47)-C(48)-C(49)	2.9(7)
C(15)-C(16)-C(17)-N(2)	-179(3)	C(47)-C(48)-C(49)-C(50)	-1.3(7)
C(15)-C(16)-C(17)-C(12)	-5(3)	C(47)-C(48)-C(49)-C(51)	178.4(5)
C(15)-C(16)-C(18)-C(19)	-178(2)	C(48)-C(49)-C(50)-N(4)	178.1(4)

C(15A)-C(16A)-C(17A)-N(2A)	177(3)	C(48)-C(49)-C(50)-C(45)	-0.6(7)
C(15A)-C(16A)-C(17A)-C(12)	0(4)	C(48)-C(49)-C(51)-C(52)	-178.3(5)
C(15A)-C(16A)-C(18A)-C(19A)	-178(3)	C(49)-C(51)-C(52)-C(53)	0.7(7)
C(16)-C(18)-C(19)-C(20)	0(3)	C(50)-N(4)-C(53)-C(52)	2.7(7)
C(16A)-C(18A)-C(19A)-C(20A)	2(4)	C(50)-N(4)-C(53)-C(54)	-175.8(4)
C(17)-N(2)-C(20)-C(19)	3(3)	C(50)-C(45)-C(46)-C(47)	0.6(7)
C(17)-N(2)-C(20)-C(21)	-180(2)	C(50)-C(49)-C(51)-C(52)	1.4(7)
C(17)-C(12)-C(13)-C(14)	-7(6)	C(51)-C(49)-C(50)-N(4)	-1.6(7)
C(17)-C(16)-C(18)-C(19)	-2(3)	C(51)-C(49)-C(50)-C(45)	179.7(4)
C(17A)-N(2A)-C(20A)-C(19A)	0(4)	C(51)-C(52)-C(53)-N(4)	-2.9(8)
C(17A)-N(2A)-C(20A)-C(21A)	-180(2)	C(51)-C(52)-C(53)-C(54)	175.5(5)
C(17A)-C(12)-C(13A)-C(14A)	3(5)	C(52)-C(53)-C(54)-S(2)	159.1(6)
C(17A)-C(16A)-C(18A)-C(19A)	-1(4)	C(52)-C(53)-C(54)-S(2A)	-169.3(6)
C(18)-C(16)-C(17)-N(2)	4(4)	C(52)-C(53)-C(54)-N(7)	-25.8(11)
C(18)-C(16)-C(17)-C(12)	178(2)	C(52)-C(53)-C(54)-N(7A)	10.6(11)
C(18)-C(19)-C(20)-N(2)	-1(3)	C(53)-N(4)-C(50)-C(45)	178.4(4)
C(18)-C(19)-C(20)-C(21)	-177.7(18)	C(53)-N(4)-C(50)-C(49)	-0.3(7)
C(18A)-C(16A)-C(17A)-N(2A)	0(4)	C(54)-S(2)-C(55)-C(56)	18.9(8)
C(18A)-C(16A)-C(17A)-C(12)	-176(3)	C(54)-S(2)-C(55)-C(62)	165.1(10)
C(18A)-C(19A)-C(20A)-N(2A)	-1(4)	C(54)-S(2A)-C(55)-C(56)	-17.0(8)
C(18A)-C(19A)-C(20A)-C(21A)	178(2)	C(54)-S(2A)-C(55)-C(62A)	-161.7(11)
C(19)-C(20)-C(21)-S(1)	-178.2(13)	C(54)-N(7)-C(56)-C(55)	28.6(14)
C(19)-C(20)-C(21)-N(6)	2(3)	C(54)-N(7)-C(56)-C(57)	169.9(10)
C(19A)-C(20A)-C(21A)-S(1A)	174.5(17)	C(54)-N(7A)-C(56)-C(55)	-25.5(13)
C(19A)-C(20A)-C(21A)-N(5)	2(3)	C(54)-N(7A)-C(56)-C(58)	-170.8(10)
C(20)-N(2)-C(17)-C(12)	-178(2)	C(55)-S(2)-C(54)-N(7)	-2.4(7)
C(20)-N(2)-C(17)-C(16)	-5(4)	C(55)-S(2)-C(54)-C(53)	173.0(5)
C(20A)-N(2A)-C(17A)-C(12)	177(2)	C(55)-S(2A)-C(54)-N(7A)	2.4(7)
C(20A)-N(2A)-C(17A)-C(16A)	1(4)	C(55)-S(2A)-C(54)-C(53)	-177.7(5)
C(21)-S(1)-C(23)-C(25)	0.5(12)	C(55)-C(56)-C(57)-C(59)	-25(2)
C(21)-S(1)-C(23)-C(33)	176.7(14)	C(55)-C(56)-C(58)-C(60)	36(2)
C(21)-N(6)-C(25)-C(23)	2.5(19)	C(56)-N(7)-C(54)-S(2)	-13.2(11)
C(21)-N(6)-C(25)-C(27)	-178.7(16)	C(56)-N(7)-C(54)-C(53)	171.4(7)
C(21A)-S(1A)-C(22)-C(31)	179.7(11)	C(56)-N(7A)-C(54)-S(2A)	11.5(11)
C(21A)-S(1A)-C(22)-C(24)	0.7(9)	C(56)-N(7A)-C(54)-C(53)	-168.4(6)
C(21A)-N(5)-C(24)-C(22)	-0.4(17)	C(56)-C(55)-C(62)-C(61)	-33.7(18)
C(21A)-N(5)-C(24)-C(26)	-179.9(12)	C(56)-C(55)-C(62A)-C(61)	36.1(19)
C(23)-S(1)-C(21)-N(6)	0.9(15)	C(56)-C(57)-C(59)-C(61)	12(5)
C(23)-S(1)-C(21)-C(20)	-179.0(15)	C(56)-C(58)-C(60)-C(61)	-27(3)
C(23)-C(25)-C(27)-C(29)	-2(2)	C(57)-C(59)-C(61)-C(62)	-11(6)
C(25)-N(6)-C(21)-S(1)	-2.0(19)	C(58)-C(60)-C(61)-C(62A)	26(3)
C(25)-N(6)-C(21)-C(20)	177.9(16)	C(59)-C(61)-C(62)-C(55)	20(3)
C(25)-C(23)-C(33)-C(32)	-2.7(19)	C(60)-C(61)-C(62A)-C(55)	-28(2)
C(25)-C(27)-C(29)-C(32)	1(2)	C(62)-C(55)-C(56)-N(7)	179.7(10)
C(27)-C(29)-C(32)-C(33)	-1(2)	C(62)-C(55)-C(56)-C(57)	36.9(18)
C(29)-C(32)-C(33)-C(23)	2(2)	C(62A)-C(55)-C(56)-N(7A)	173.7(11)
C(31)-C(22)-C(24)-N(5)	-179.5(14)	C(62A)-C(55)-C(56)-C(58)	-42(2)
C(31)-C(22)-C(24)-C(26)	0		