Exploring the Chelating Potential of an Easily Synthesized Schiff Base for Copper Sensing

Jesús Sanmartín-Matalobos [1,*], Ana M. García-Deibe [1], Morteza Zarepour-Jevinani [1,2], Pilar Bermejo-Barrera [3], Manuel Aboal-Somoza [3] and Matilde Fondo [1]

[1] Coordination and Supramolecular Chemistry Group (Suprametal), Department of Inorganic Chemistry, Faculty of Chemistry, Universidade de Santiago de Compostela, Avenida das Ciencias s/n, 15782-Santiago de Compostela, Spain; ana.garcia.deibe@usc.es (A.M.G-D.); mortezazarepourjevinani@gmail.com (M.Z-J.); matilde.fondo@usc.es (M.F.)

[2] Department of Chemistry, Sharif University of Technology, PO Box 11155-3516, Tehran, Iran

[3] Trace Element, Speciation and Spectroscopy Group (GETEE) - Health Research Institute of Santiago de Compostela (IDIS), Strategic Grouping in Materials AEMAT, Department of Analytical Chemistry, Nutrition and Bromatology, Faculty of Chemistry, Universidade de Santiago de Compostela, Avenida das Ciencias, s/n, 15782 Santiago de Compostela, Spain; pilar.bermejo@usc.es (P.B-B.); m.aboal@usc.es (M.A-S.)

* Correspondence: jesus.sanmartin@usc.es

Table S1. Crystal data and structure refinement for $Ni(HSB)_2$, $Pd(HSB)_2$ and $Cu(HSB)_2$.

Identification Code	**$Ni(HSB)_2$**	**$Pd(HSB)_2$**	**$Cu(HSB)_2$**
Empirical formula	$C_{42}H_{38}N_4NiO_6S_2$	$C_{42}H_{38}N_4O_6PdS_2$	$C_{42}H_{38}CuN_4O_6S_2$
Formula weight	817.59	865.28	822.42
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 A	0.71073 A	0.71073 Å
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P -1	P -1	P -1
Unit cell dimensions (Å, °)			
a	8.0779(3)	8.2110(3)	8.260(5)
b	10.4541(4)	10.4321(4)	10.485(5)
c	12.4196(6)	12.3276(4)	12.283(5)
α	99.757(3)	99.341(2).	99.103(5).
β	107.032(3)	107.571(2).	108.088(5).
γ	105.90	106.006(2)	106.608(5)
Volume ($Å^3$)	928.17(7)	932.27(6)	932.7(8)
Z	1	1	1
Density (calculated, Mg/m^3)	1.463	1.541 Mg/m^3	1.464
Absorption coefficient	0.691 mm^{-1}	0.665 mm^{-1}	0.753 mm^{-1}
F(000)	426	444	427
Crystal size (mm^3)	0.350 x 0.270 x 0.140	0.160 x 0.110 x 0.020	0.280 x 0.250 x 0.170
θ range for data collection	1.782 to 26.372 deg	1.798 to 26.371 deg	1.812 to 25.349°.
Reflections collected	3786	24950	18296
Independent reflections	3786 [R(int) = 0.000]	3810 [R(int) = 0.0623]	3400 [R(int) = 0.0340]
Completeness to theta	25.242 100.0 %	25.242 100.0 %	25.242° 99.6 %
Max. and min. transmission	0.8878 and 0.7993	1.0000 and 0.8930	1.000 and 0.9229
Data / restraints / parameters	3786 / 0 / 255	3810 / 0 / 251	3400 / 0 / 255
Goodness-of-fit on F^2	1.053	1.021	1.073
Final *R* indices [$I > 2\sigma(I)$]	R_1 = = 0.0392, wR_2 = 0.0817	R_1 = = 0.0416, wR_2= 0.0736	R_1 = 0.0301, wR_2= 0.0688
R indices (all data)	R_1 = 0.0545, wR_2= 0.0871	R_1 = 0.0633, wR_2= 0.0813	R_1 = 0.0351, wR_2 = 0.0708

Largest diff. peak and hole	0.298 and -0.363 e.Å^{-3}	0.550 and -0.852 e.Å^{-3}	0.264 and -0.364 e.Å^{-3}

Table S2.1. Main bond distances [Å] and angles [°] for Ni(HSB)$_2$.

Ni(1)-O(3)#1	1.8278(15)	O(3)#1-Ni(1)-O(3)	180.00(11)
Ni(1)-O(3)	1.8278(15)	O(3)#1-Ni(1)-N(2)	88.14(7)
Ni(1)-N(2)	1.9181(18)	O(3)-Ni(1)-N(2)	91.86(7)
Ni(1)-N(2)#1	1.9181(18)	O(3)#1-Ni(1)-N(2)#1	91.86(7)
N(2)-C(14)	1.294(3)	O(3)-Ni(1)-N(2)#1	88.14(7)
N(2)-C(13)	1.452(3)	N(2)-Ni(1)-N(2)#1	180.0
O(3)-C(20)	1.318(3)	C(14)-N(2)-C(13)	116.81(19)
C(1)-S(1)	1.764(2)	C(14)-N(2)-Ni(1)	124.77(16)
S(1)-O(2)	1.4342(15)	C(13)-N(2)-Ni(1)	118.30(14)
S(1)-O(1)	1.4344(17)	C(20)-O(3)-Ni(1)	126.68(13)
S(1)-N(1)	1.619(2)	C(6)-C(1)-S(1)	121.03(18)
N(1)-C(7)	1.466(3)	C(2)-C(1)-S(1)	118.67(18)
		O(2)-S(1)-O(1)	120.36(10)
		O(2)-S(1)-N(1)	107.04(10)
		O(1)-S(1)-N(1)	105.86(11)
		O(2)-S(1)-C(1)	107.45(11)
		O(1)-S(1)-C(1)	107.37(10)
		N(1)-S(1)-C(1)	108.28(11)
		C(7)-N(1)-S(1)	117.90(16)
		N(1)-C(7)-C(8)	110.14(19)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+1.

Table S2.2. Hydrogen bonds for Ni(HSB)$_2$ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(3)#1	0.80	2.13	2.891(3)	158.6

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z.

Table S3.1. Main bond lengths [Å] and angles [deg] for $Pd(HSB)_2$.

Pd(1)-O(3)#1	1.981(2)	O(3)#1-Pd(1)-O(3)	180.00(13)
Pd(1)-O(3)	1.981(2)	O(3)#1-Pd(1)-N(2)	89.12(10)
Pd(1)-N(2)	2.025(3)	O(3)-Pd(1)-N(2)	90.88(10)
Pd(1)-N(2)#1	2.025(3)	O(3)#1-Pd(1)-N(2)#1	90.88(10)
N(2)-C(14)	1.292(4)	O(3)-Pd(1)-N(2)#1	89.12(10)
N(2)-C(13)	1.443(4)	N(2)-Pd(1)-N(2)#1	180.0
O(3)-C(20)	1.321(3)	C(14)-N(2)-C(13)	119.0(3)
O(1)-S(1)	1.437(2)	C(14)-N(2)-Pd(1)	123.7(2)
O(2)-S(1)	1.433(2)	C(13)-N(2)-Pd(1)	117.06(18)
S(1)-N(1)	1.620(3)	C(20)-O(3)-Pd(1)	124.32(19)
S(1)-C(1)	1.761(3)	O(2)-S(1)-O(1)	120.17(14)
N(1)-C(7)	1.477(4)	O(2)-S(1)-N(1)	107.24(14)
N(1)-H(1A)	0.9429	O(1)-S(1)-N(1)	105.78(14)
		O(2)-S(1)-C(1)	107.50(15)
		O(1)-S(1)-C(1)	107.46(15)
		N(1)-S(1)-C(1)	108.22(15)
		C(7)-N(1)-S(1)	117.6(2)
		C(7)-N(1)-H(1A)	116.6
		S(1)-N(1)-H(1A)	115.7
		N(1)-C(7)-C(8)	109.8(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z.

Table S3.2. Hydrogen bonds for $Pd(HSB)_2$ [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(3)#1	0.94	1.99	2.881(3)	156.9

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z.

Table S4.1. Main bond lengths [Å] and angles [°] for $Cu(HSB)_2$.

Cu(1)-O(3)#1	1.8834(15)	O(3)#1-Cu(1)-O(3)	180.00(9)
Cu(1)-O(3)	1.8834(15)	O(3)#1-Cu(1)-N(2)#1	90.54(6)
Cu(1)-N(2)#1	2.0098(17)	O(3)-Cu(1)-N(2)#1	89.46(6)
Cu(1)-N(2)	2.0098(17)	O(3)#1-Cu(1)-N(2)	89.46(6)
N(1)-C(7)	1.474(3)	O(3)-Cu(1)-N(2)	90.54(6)
N(1)-S(1)	1.6156(19)	N(2)#1-Cu(1)-N(2)	180.0
N(1)-H(1A)	0.83(2)	C(7)-N(1)-S(1)	117.71(14)
O(3)-C(20)	1.321(2)	C(7)-N(1)-H(1A)	114.5(15)
S(1)-O(2)	1.4312(15)	S(1)-N(1)-H(1A)	114.4(15)
S(1)-O(1)	1.4369(15)	C(20)-O(3)-Cu(1)	126.59(12)
C(13)-N(2)	1.447(2)	O(2)-S(1)-O(1)	120.32(9)
N(2)-C(14)	1.290(2)	O(2)-S(1)-N(1)	107.46(9)
		O(1)-S(1)-N(1)	106.07(10)
		O(2)-S(1)-C(1)	107.36(10)
		O(1)-S(1)-C(1)	107.20(9)
		N(1)-S(1)-C(1)	107.92(9)
		N(1)-C(7)-C(8)	110.10(16)
		C(12)-C(13)-N(2)	117.93(17)
		C(8)-C(13)-N(2)	121.47(17)
		C(14)-N(2)-C(13)	117.90(16)
		C(14)-N(2)-Cu(1)	123.70(13)
		C(13)-N(2)-Cu(1)	118.28(12)
		N(2)-C(14)-C(15)	125.83(17)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z.

Table S4.2. Hydrogen bonds for $Cu(HSB)_2$ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(3)#1	0.83(2)	2.06(2)	2.857(2)	162(2)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z.

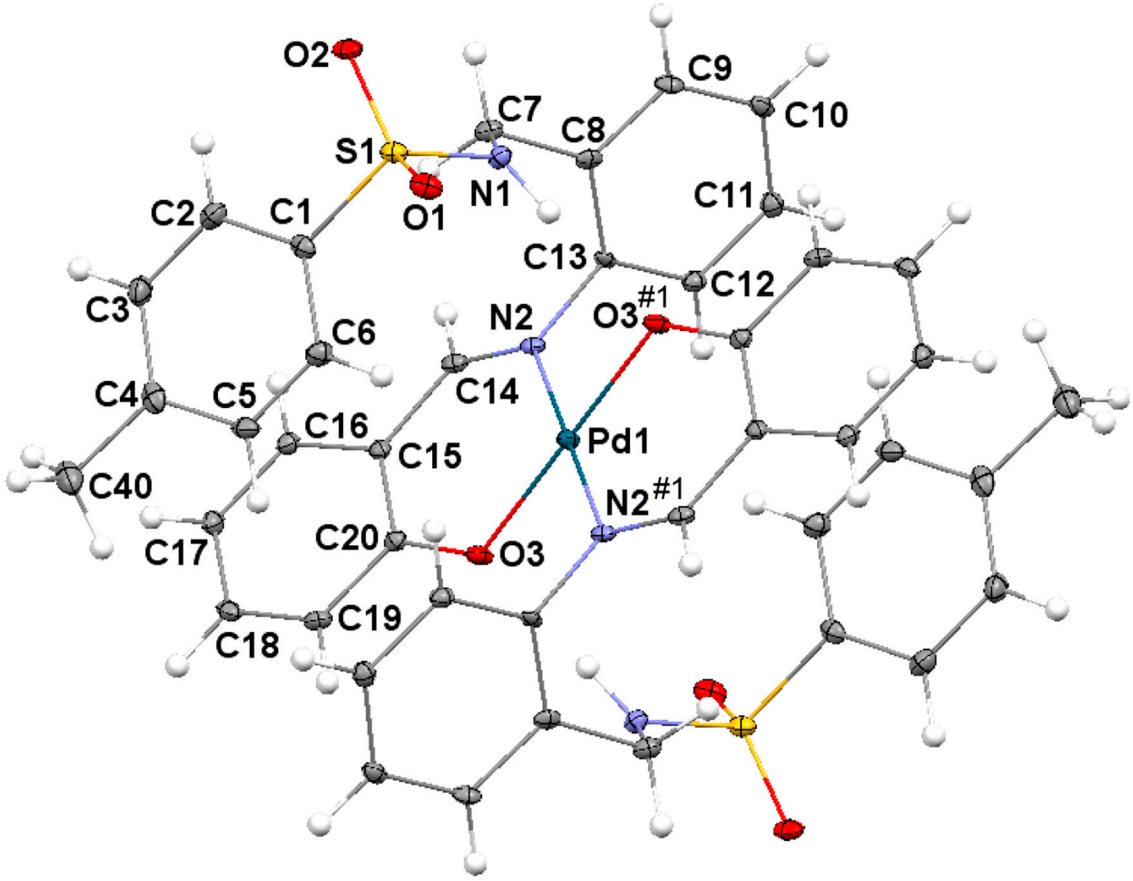

Figure S1. Molecular structure of $Pd(HSB)_2$.

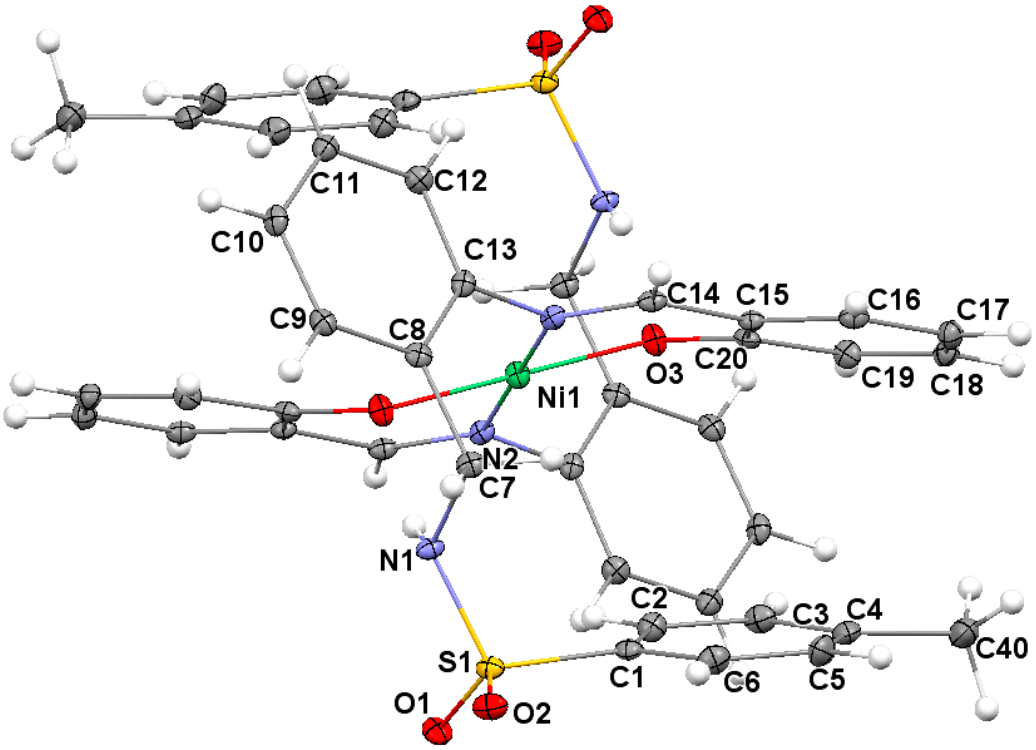

Figure S2. Molecular structure of Ni(HSB)2.

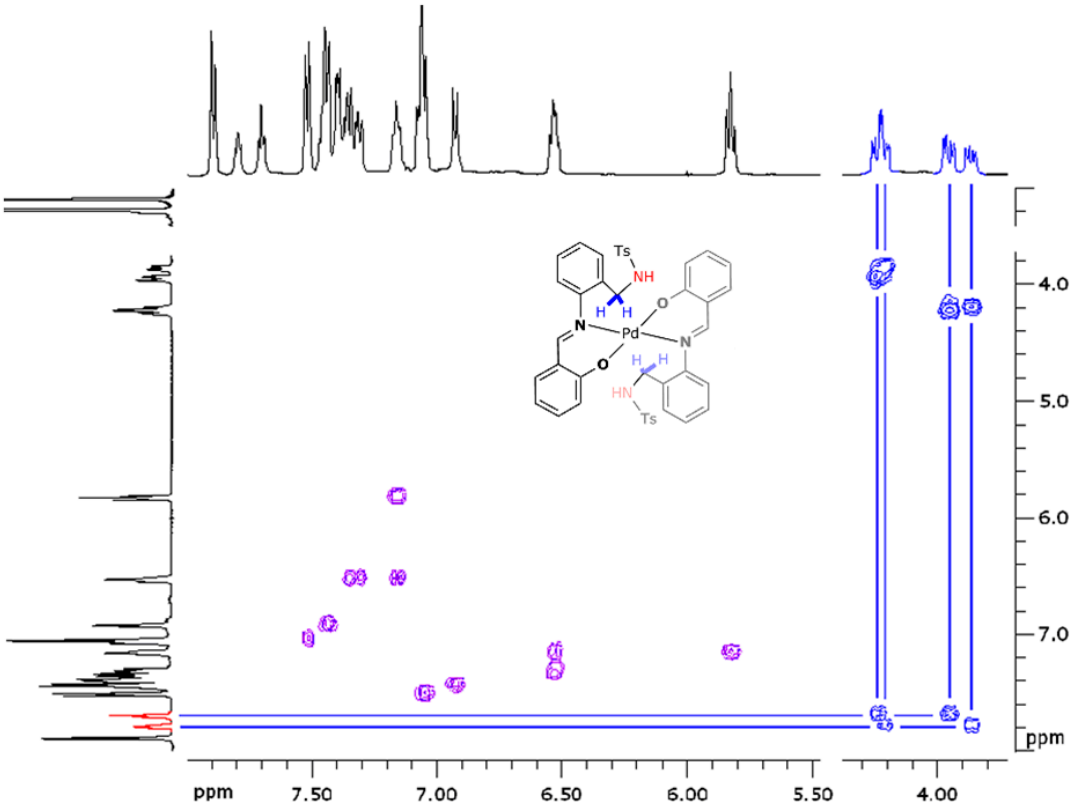

Figure S3. 2 D COSY spectrum of Pd(HSB)2.

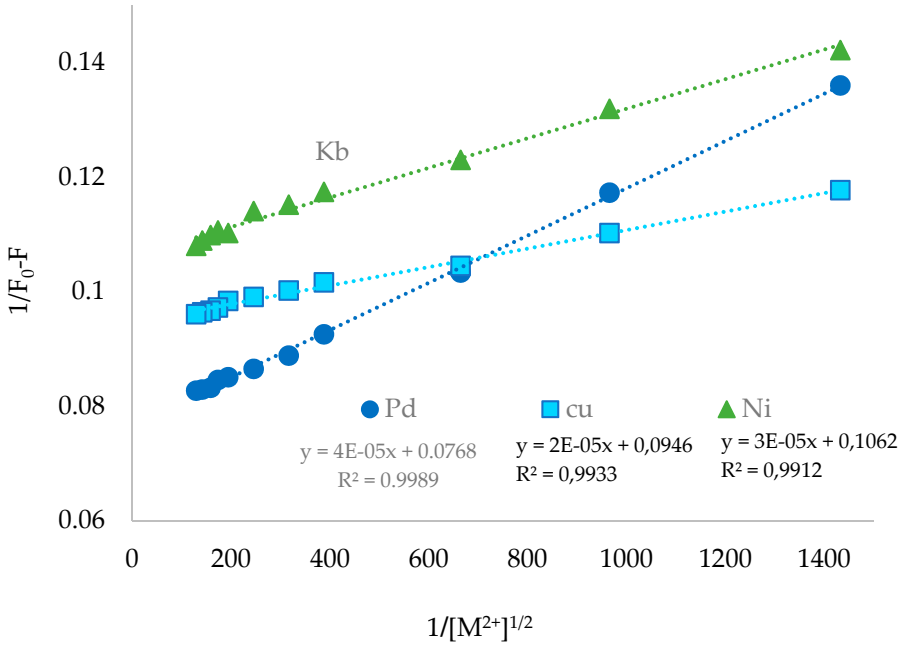

Figure S4. Benesi–Hildebrand plot from fluorescence titration data of H_2SB (100 μM) with Pd^{2+}, Ni^{2+} and Cu^{2+}: Determination of binding constants in $Pd(HSB)_2$, $Ni(HSB)_2$ and $Cu(HSB)_2$.

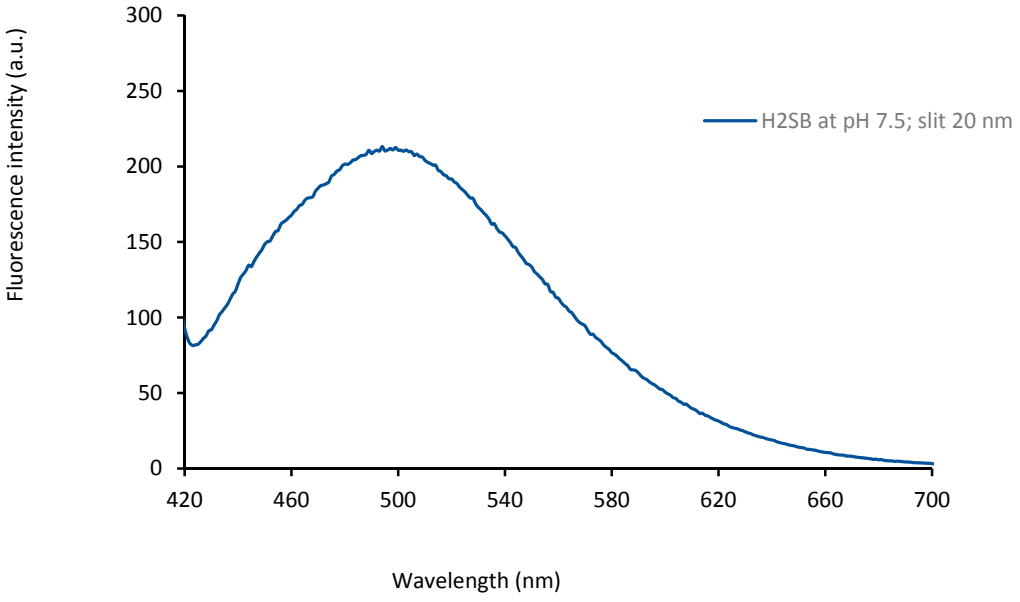

Figure S5.1. Fluorescence spectrum of H_2SB (100 μM,) measured in methanol-water in 80:20 v/v.

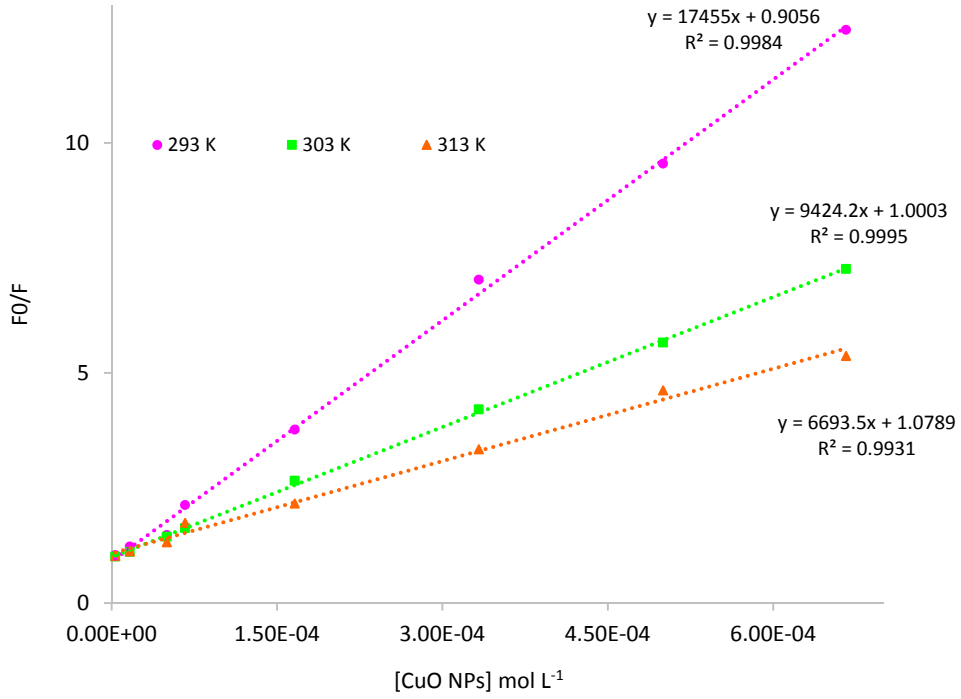

Figure S5.2. Plot of the intensities of the fluorescence spectra vs the concentration of CuO NPs. Slopes of the curves at 293, 303 and 313K are Stern–Volmer constants (K_{SV}) at the cited temperatures.

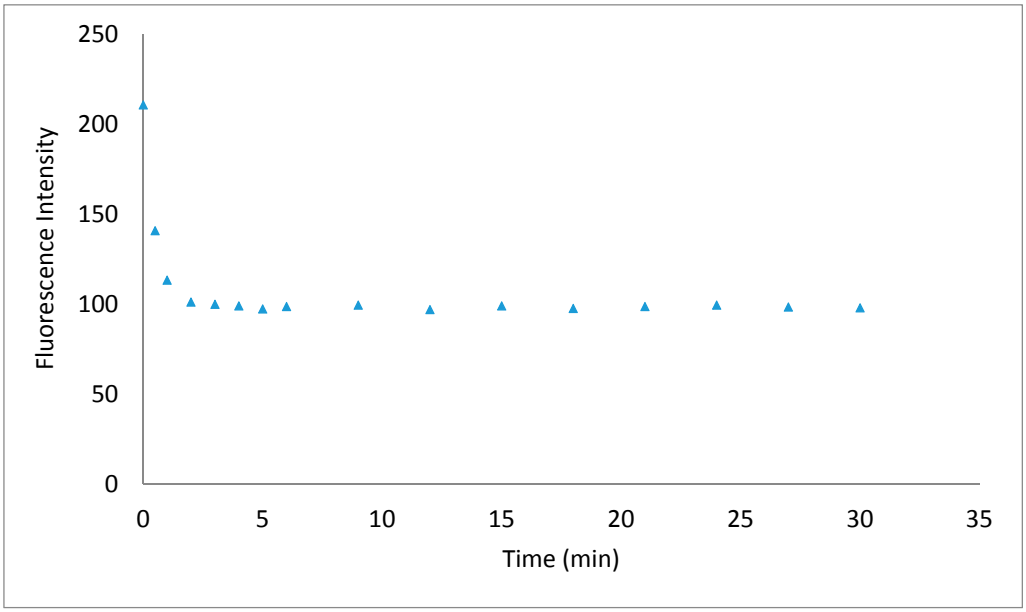

Figure S6. Plot of the intensity fluorescence vs time elapsed after the addition of CuO NPs (0.1 mL, 100 μM) to H_2SB (1 mL, 100 μM).

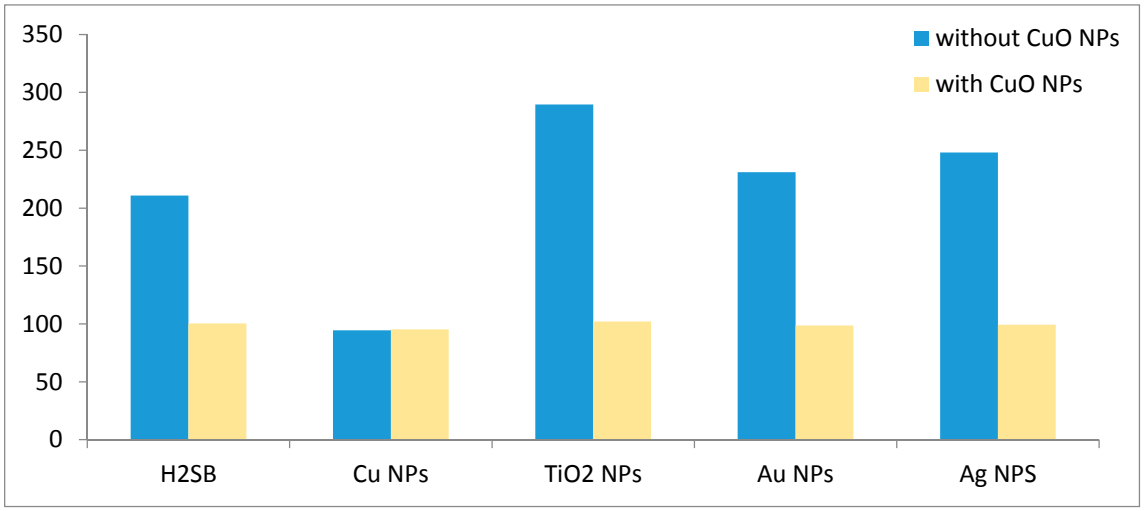

Figure S7. Fluorescence responses of H_2SB (1.0 mL, 100 μM) toward a suspension of CuO NPs (0.1 mL, 100 μM) in the presence of TiO_2, Cu, Ag and Au NPs (0.1 mL, 100 μM). All experiments were performed in ethanol-water in 80:20 v/v (pH about 7.0) under λ_{ex} = 390 nm.