

Supplement information

**Preparation of coordination polymers with  
8-hydroxyquinoline azo benzenesulfonic acid as planar  
multidentate ligand and study of their photochemical and  
photo-stability property**

**Hong-Xia Chen, Feng Zhou, Yong Ma, Xiao-Ping Xu, Jian-Feng Ge, Yong  
Zhang, Qing-Feng Xu<sup>\*</sup>, Jian-Mei Lu<sup>\*</sup>**

*Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical  
Engineering and Materials Science, Soochow University, Suzhou 215123, People's Republic of  
China*

*Key Laboratory of Energy-Saving And Environmental Protection Materials Test & Technical  
Service Center of Jiangsu Province, Soochow University (DuShuHu Campus), 199 Renai Road,  
Suzhou, 215123, China*

\* Corresponding Author. Tel: 0086-512-65880367, Fax: 0086-512-6588-2875.

E-mail address: [lujm@suda.edu.cn](mailto:lujm@suda.edu.cn) (J. Lu), [xuqingfeng@suda.edu.cn](mailto:xuqingfeng@suda.edu.cn) (Q. Xu)

**Table S-1.** UV–vis absorption spectra of **H<sub>2</sub>QBS** and compounds **1-5**.

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**S-10.** <sup>1</sup>H NMR for H<sub>2</sub>QBS.

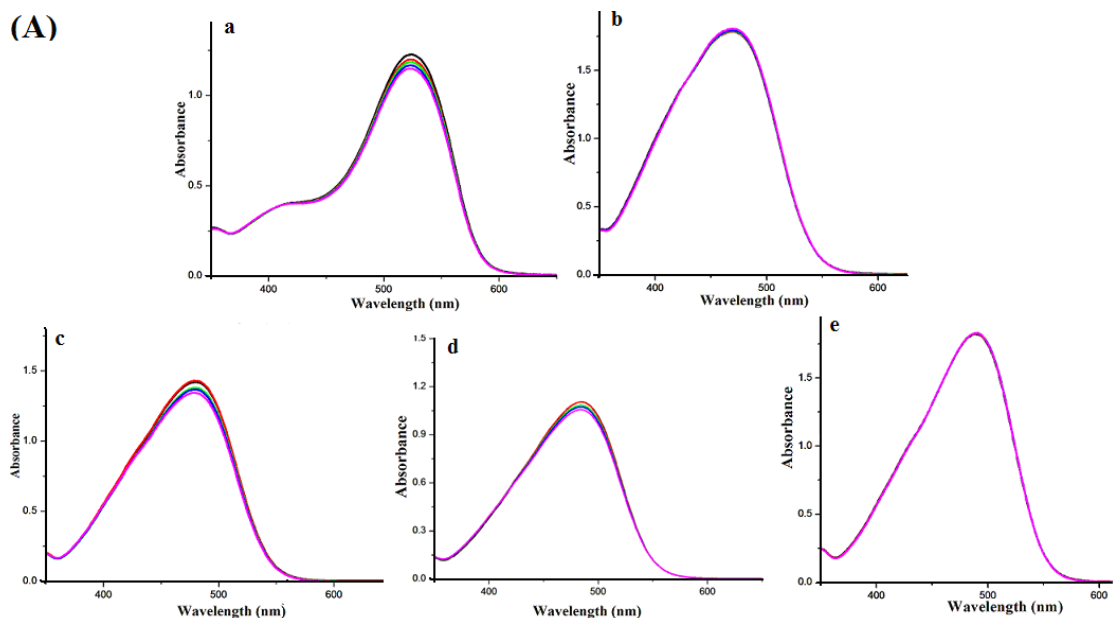
**S-11.** <sup>1</sup>H NMR for compound **1** upon UV ( $\lambda = 254$  nm) irradiation for 0 h (a) and 60 h (b) and 132 h (c), DMSO-d<sub>6</sub> as the solvent)

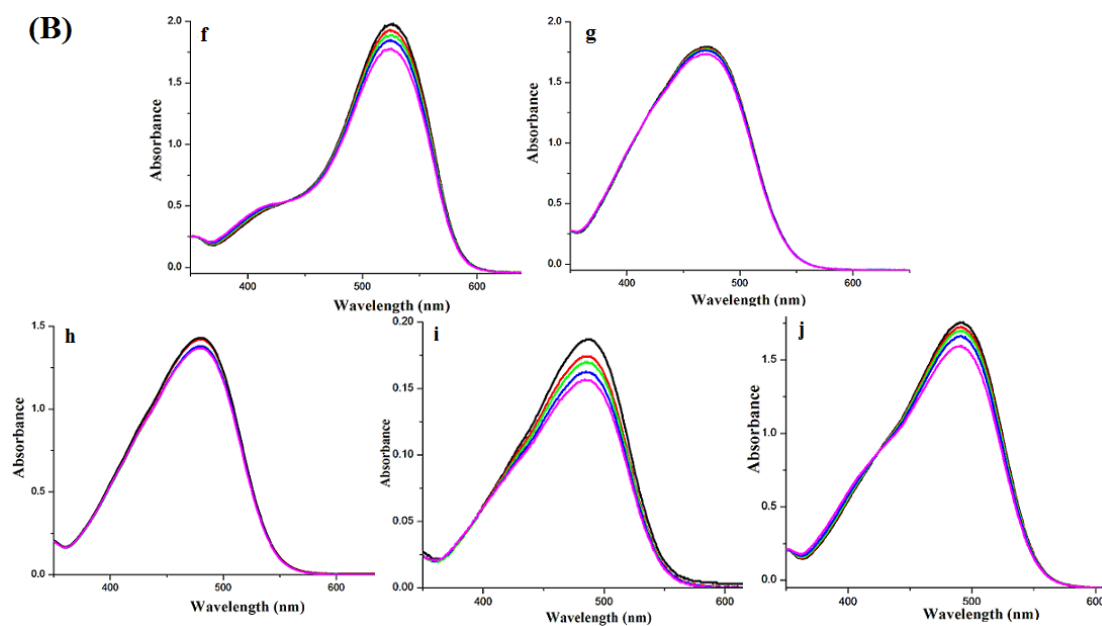
**S-12.** The specific hydrogen bond geometries in the crystal structure of **3** and **5** are also provided in the supplemental information.

Table S-1. UV–VIS absorption spectral about H<sub>2</sub>QBS and compounds 1-5

Compound	Solvent	$\lambda_1$ (nm)	$\lambda_2$ (nm)
H <sub>2</sub> QBS	CH <sub>3</sub> OH	390	~480
H <sub>2</sub> QBS	DMF	396	-
H <sub>2</sub> QBS	DMSO	400	-
1	DMSO	398	526
2	DMSO	398	466
3	DMSO	398	480
4	DMSO	398	487
5	DMSO	398	491

S-2. UV–vis absorption spectral change of compounds 1-5 in DMSO upon irradiation with 365 nm and 450 nm light





**Fig. S-2-1.**(A) UV-vis absorption spectral change of compounds **1-5** in DMSO upon irradiation with 365 nm light (0 min, black; 5min, red, 10 min, green; 20 min, blue; 30 min, purple, a for compound **1**, b for compound **2**, c for compound **3**, d for compound **4** and e for compound **5**,  $c=5\times 10^{-5}\text{M}$  for **1**,  $2.5\times 10^{-5}\text{M}$  for **2**,  $3\times 10^{-5}\text{M}$  for **3**,  $1.5\times 10^{-5}\text{M}$  for **4**,  $3.5\times 10^{-5}\text{M}$  for **5**); (B) UV-vis absorption spectral change of compounds **1-5** in DMSO upon irradiation with 450 nm light (f for compound **1**, g for compound **2**, h for compound **3**, i for compound **4** and j for compound **5**)

### S-3. I<sub>2</sub> absorption procedure of compound **2**

Compound **2** was immersed in solution of I<sub>2</sub> (20 mg) and I<sub>2</sub> (140 mg) in CCl<sub>4</sub> (20 mL) in closed tube for 4h respectively, then filtered. Two powders of **2-1** (dark red) and **2-2** (brown) were washed thoroughly with CCl<sub>4</sub> and Et<sub>2</sub>O for several times till the solution was colorless. The mixture was characterized by SEM-EDS, Raman spectra and TGA.

According to the calculation of PLATON software [1], no residual solvent accessible void in compound **1**, but the proportion of voids in the 2D layer of compound **2** is relatively large (38.9%). Guest molecules such as I<sub>2</sub> may be incorporated between

layers. The crystals of **2** are dried in vacuum for removal of the lattice solvents before the I<sub>2</sub> absorption experiment [2]. Compound **2** was immersed in solution of I<sub>2</sub> (20 mg) and I<sub>2</sub> (140 mg) in CCl<sub>4</sub> (20 mL) in closed tube for 4h respectively, then filtered. Two powders of **2-1** (dark red) and **2-2** (brown) were washed thoroughly with CCl<sub>4</sub> and Et<sub>2</sub>O for several times till the solution was colorless. The mixture was characterized by SEM-EDS, Raman spectra and TGA.

Crystals absorbing I<sub>2</sub> turn brown color and lose their crystallization gradually. Two kinds of powders **2-1** and **2-2** are obtained according to absorbed amount of I<sub>2</sub>. Both are characterized by SEM-EDS, Raman spectrum, XRPD and TGA(See **SI**). The result of SEM-EDS show I element in two samples. The Raman spectra of **2-1** show a typical band at 220 cm<sup>-1</sup>, which indicates free I<sub>2</sub> molecules are occupied in compound [14(b), 15]. But when compound **2** absorbs more I<sub>2</sub> molecules, the intensity of FT-Raman spectrum of compound **2-2** becomes weaken, broaden and blue-shifted [3]. The thermal stability of **2** is surprisingly high and the decomposition temperature is about 480°C, which can be ascribed to the loss of all organics and coordinated solvents [4]. The composition of the residue (48.2%) may be ascribed to the lead salt mixture such as 0.8 PbSO<sub>4</sub> (49.4%, calculated), and 0.2 PbS (39%, calculated according to Pb). The thermal decomposition of **2-1** is characterized by a step (2.9%) from room temperature to 150 °C corresponding to a total of 0.07 I<sub>2</sub> molecules (2.8%, calculated value). After that the compound keeps stable till 450°C, similar with the high stability of compound **2**. The composition of the residue (41.4%) may be compound due to the high decomposition temperature of lead salts such as 0.3 PbSO<sub>4</sub> (48.1%, calculated), and 0.7 PbS (37.9%, calculated according to Pb). The thermal decomposition of **2-2** is different from **2** and **2-1**. The TG curve is characterized by

three steps from room temperature to 800 °C corresponding to a total of solvent molecules of crystallization, all organics and four iodine molecules. The 15.9% residue includes 0.3 PbSO<sub>4</sub> and 0.7 PbS (calculated value is 14.5% for PbS, 18.4% for PbSO<sub>4</sub>) respectively. It may be ascribed to the interaction of Pb and I<sub>2</sub> so that the thermal stability of **2-2** is changed in some degree.

#### S-4. EDS for I<sub>2</sub> in compound **2**

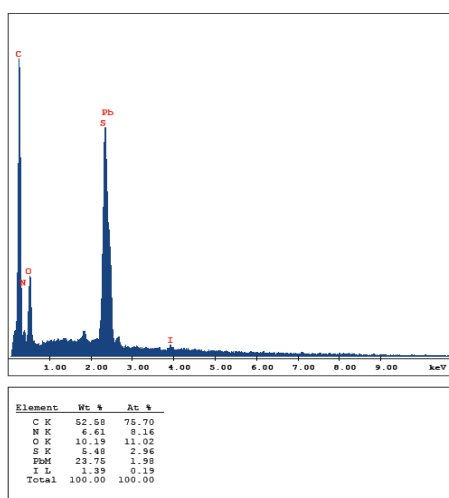


Fig. S-4-1. EDS for compound **2-1**

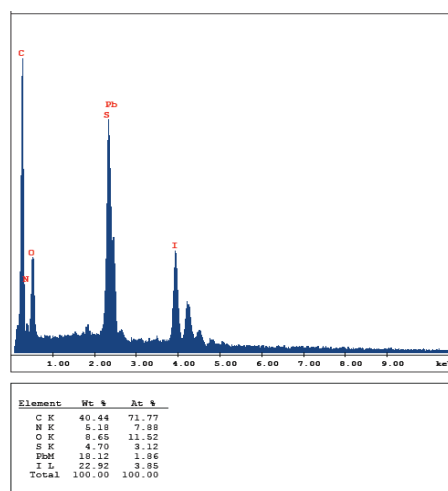
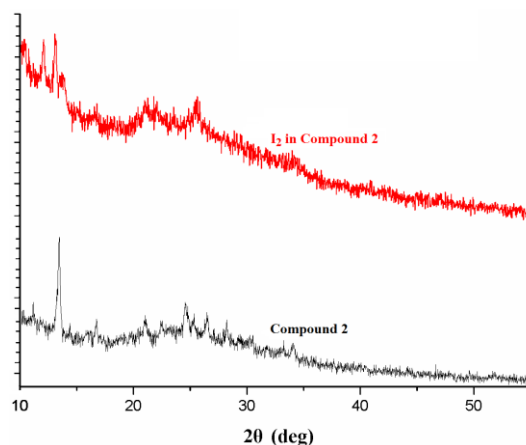


Fig. S-4-2. EDS for compound **2-2**

#### S-5. XRPD for I<sub>2</sub> in compound **2**



S-5-1. XRPD for I<sub>2</sub> in compound **2**

## S-6. FT-Raman I<sub>2</sub> in compound 2

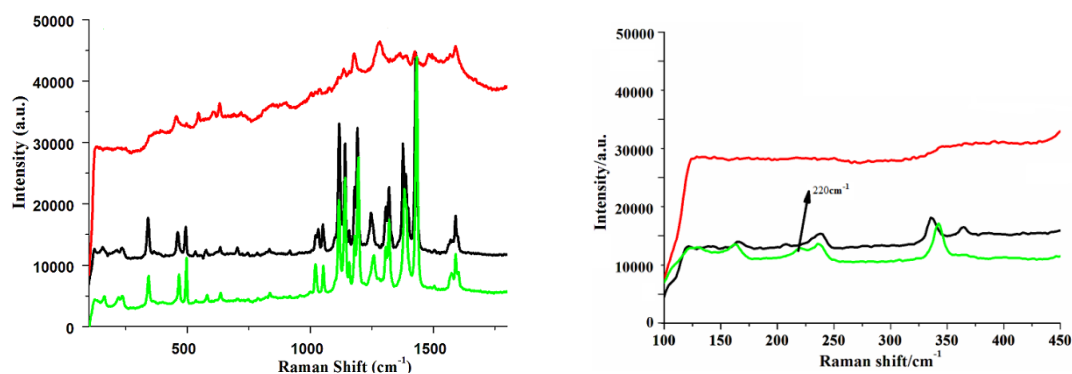


Fig. S-6-1. FT-Raman I<sub>2</sub> in compound 2 (compound 2, black, compound 2-1, green and compound 2-2, red)

## S-7. TGA curve of I<sub>2</sub> in compound 2

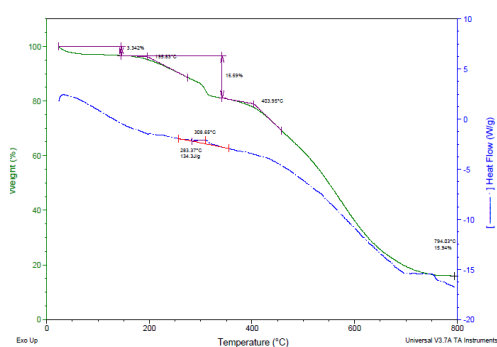


Fig. S-7-1. TGA curve of compound 2-1

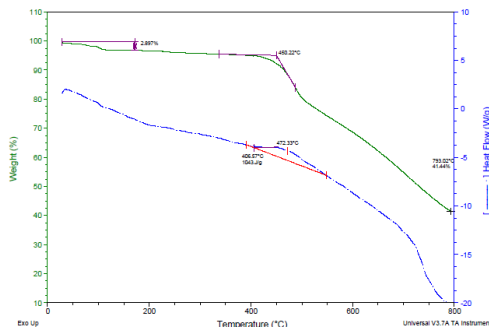


Fig. S-7-2. TGA curve of compound 2-2

## S-8. TGA study

The thermal decomposition of **1** is characterized by a dehydration step (14.4%) from room temperature to 96°C corresponding to a total of three water molecules, including one water molecule of crystallization and two water molecules of coordination, respectively (13.0%, calculated value); the following step (51.2%) from 96 to 586 °C, corresponds to the decomposition of all organics (calculated value, 52.1%); The final residue of **1** is 34.2% at 749.3°C (calculated 34.0%), assigned to Na<sub>2</sub>SO<sub>4</sub>.

For **2**, the thermal stability is surprisingly high and the decomposition temperature is about 480°C, which can be ascribed to the loss of all organics and coordinated solvents. The composition of the residue (48.2%) may be compound due to the high

decomposition temperature of lead salts such as 0.8% PbSO<sub>4</sub> (49.4%, calculated), and 0.2% PbS (39%, calculated according to Pb, with the oxygen atom may be obtained from floating N<sub>2</sub> atmosphere).

The thermal decomposition of **3** shows a slow dehydration step (3.1%) from 25-121 °C, which is probably due to the compound obtained from water solution without further dryness and free water molecule leaves from material surface. The following dehydration step (23%), from 121-485 °C, corresponds to a total of two DMSO molecules of coordination (24.8%, calculated value); the following steps are the decomposition of organic ligands and sulfonate. The final residue of **3** is 14.8% at 967.06 °C (calculated 12.9%), assigned to ZnO.

The thermal decomposition of **4** is characterized by a dehydration step (24.3%) from room temperature to 469 °C, which is probably due to the compound obtained from water solution without further dryness, one <sup>i</sup>PrOH molecule and one DMSO molecule (25.7%, calculated value); the following step from 469 to 800 °C, corresponds to the decomposition of all organics and sulfate group; the 31.2% residue includes MnSO<sub>4</sub> (calculated value is 29% for MnSO<sub>4</sub>).

The thermal decomposition of **5** is characterized by a dehydration step (3.1%) from room temperature to 134 °C corresponding to a total of two water molecules (3.2%, calculated value); the following step from 134 to 800 °C, corresponds to the decomposition of all organics and sulfate group; The residue (18.6%) is consistent with the calculated value (18.8%), assuming CdSO<sub>4</sub> as the final product.



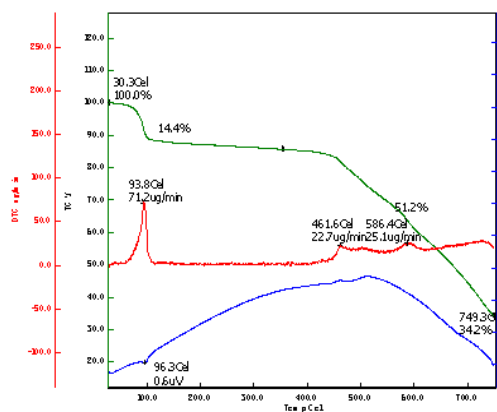


Fig. S-8-1. TGA curve of compound 1

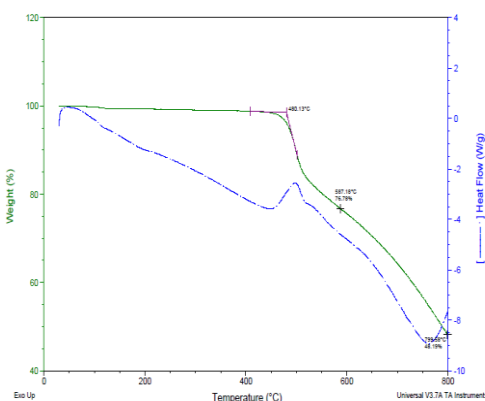


Fig. S-8-2. TGA curve of compound 2

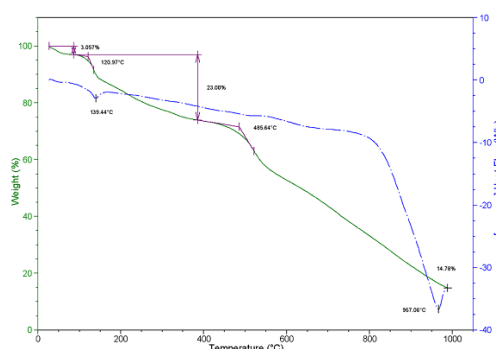


Fig. S-8-3. TGA curve of compound 3

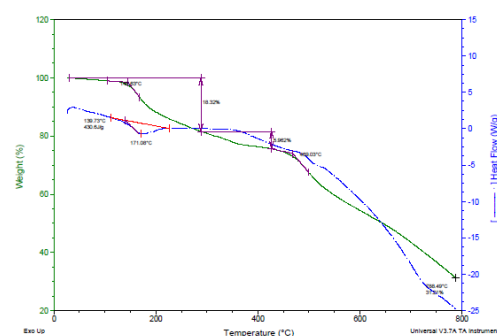


Fig. S-8-4. TGA curve of compound 4

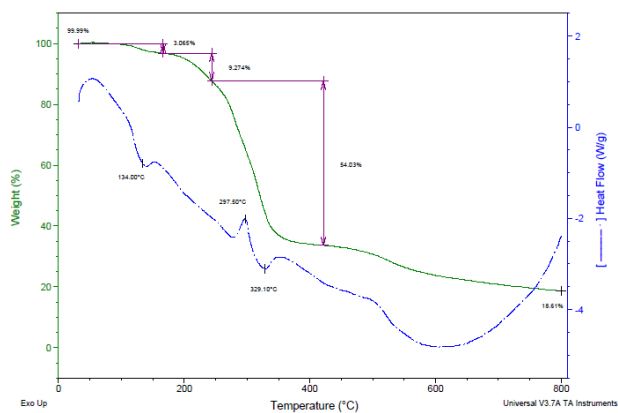


Fig. S-8-5. TGA curve of compound 5

### S-9. XRPD curve of compounds 1-5

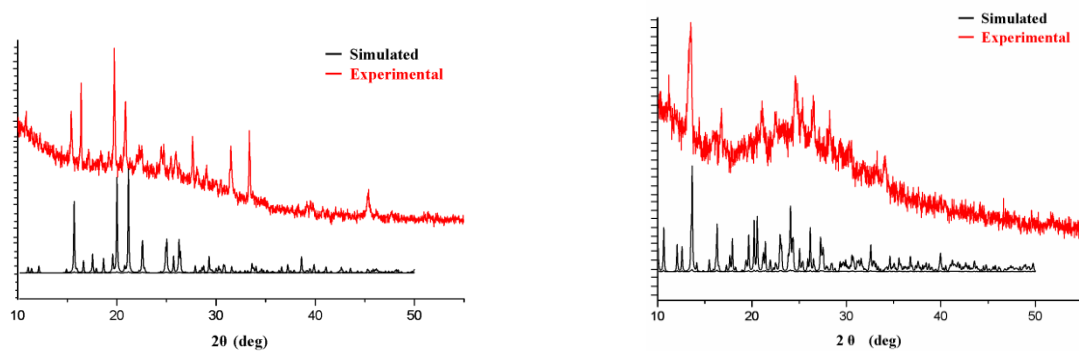


Fig. S-9-1. XRPD for compound 1

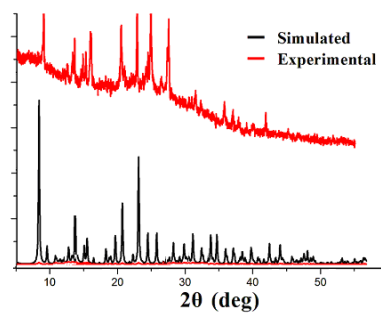


Fig. S-9-2. XRPD for compound 2

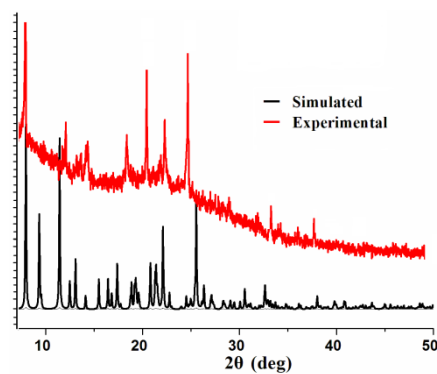


Fig. S-9-3. XRPD for compound 3

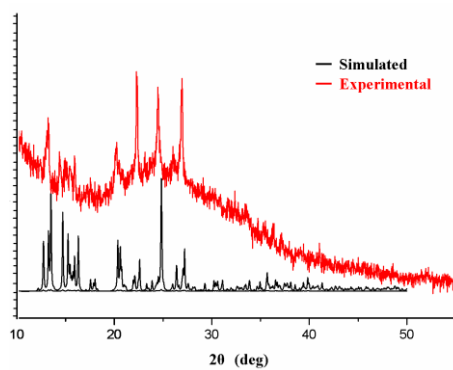


Fig. S-9-4. XRPD for compound 4

Fig. S-9-5. XRPD for compound 5

## S-10. <sup>1</sup>H NMR for H<sub>2</sub>QBS

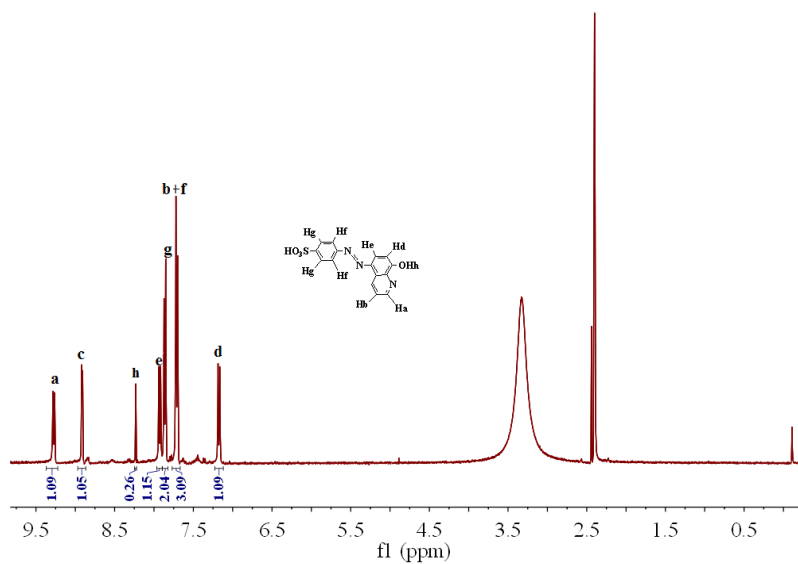


Fig. S-10-1. <sup>1</sup>H NMR for H<sub>2</sub>QBS in DMSO-d<sub>6</sub> (c=7.6×10<sup>-2</sup> mol/L)

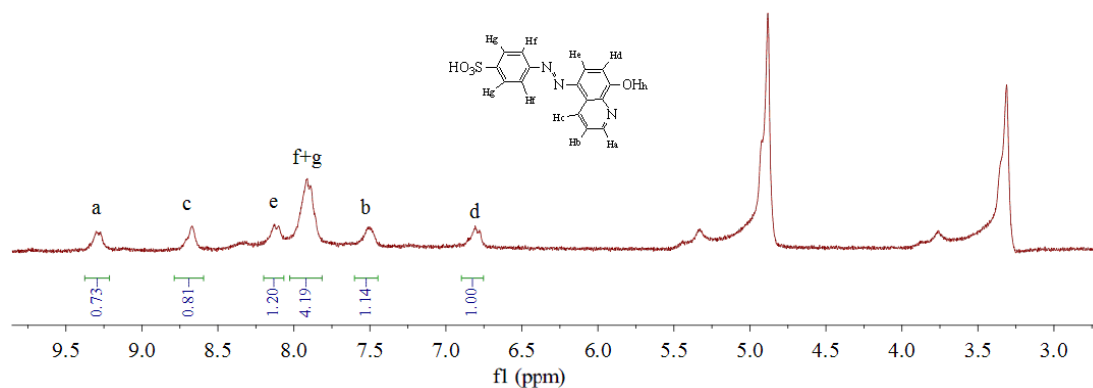


Fig. S-10-2.  $^1\text{H}$  NMR for  $\text{H}_2\text{QBS}$  in  $\text{CD}_3\text{OD}$  ( $c=7.6\times 10^{-2}$  mol/L)

S-11.  $^1\text{H}$  NMR for compound 1 upon UV( $\lambda=254$  nm) irradiation for 0 h (a) and 60 h (b) and 132 h (c), DMSO-d<sub>6</sub> as the solvent)

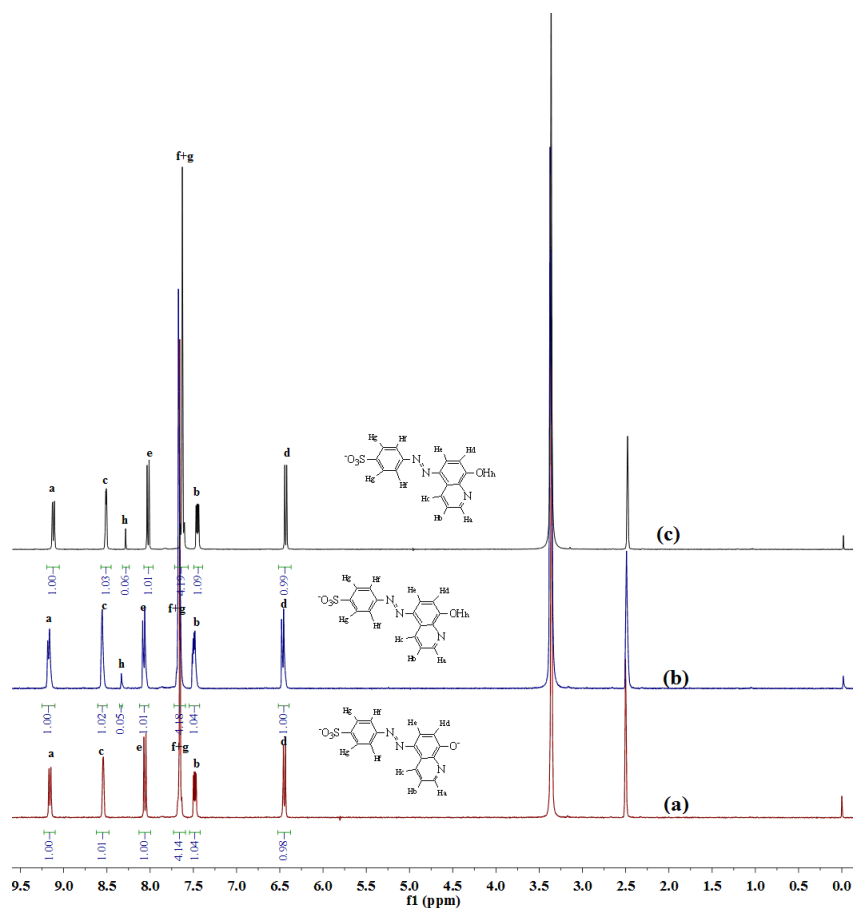


Fig. S-11-1.  $^1\text{H}$  NMR for compound 1 upon UV( $\lambda = 254$  nm) irradiation ( $c = 4.9\times 10^{-2}$  mol/L)

## S-12. Hydrogen bond geometries in the crystal structure of **3** and **5**

### S-12-1. Hydrogen bond geometries in the crystal structure of **3**

Compound	D-H...A	H...A(Å)	D...A(Å)	D-H...A(°)
<b>3</b>	C(17)-H(17A)...O(7)#5	2.53	3.429(17)	153.5
	C(17)-H(17A)...O(7')#5	2.50	3.440(15)	164.5

Symmetry transformations used to generate equivalent atoms for **3**: #1 -x+2, -y+1, -z #2 -x+1, -y+1, -z #3 -x+1, y-1/2, -z+1/2 #4 x+1, y-1, z #5 x+1, y, z

### S-12-2. Hydrogen bond geometries in the crystal structure of **5**

Compound	D-H...A	H...A(Å)	D...A(Å)	D-H...A(°)
<b>5</b>	O(14)-H(14B)...O(2)	2.41(6)	2.960(5)	125(6)
	O(14)-H(14B)...O(8)	2.27(5)	2.908(6)	135(7)
	O(14)-H(14A)...O(3)	1.89(3)	2.685(5)	165(9)
	O(13)-H(13B)...O(1)	1.88(2)	2.680(6)	165(7)
	O(13)-H(13A)...O(3)	2.49(5)	3.012(6)	122(5)
	O(11)-H(11B)...O(8)	2.61(6)	3.024(6)	113(5)
	O(11)-H(11B)...O(2)	2.110(17)	2.916(6)	169(6)
	O(11)-H(11A)...N(1)	2.53(2)	3.318(7)	165(6)
	O(10)-H(10B)...O(7)	2.239(16)	3.045(5)	169(6)
	O(10)-H(10A)...O(5)	1.91(2)	2.706(5)	163(6)

Symmetry transformations used to generate equivalent atoms for **5**: #1 x-1, y-1, z #2 x+1, y+1, z.

## References

- [1] A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2001.
- [2] (a) B. F. Abrahams, M. Moylan, S. D. Orchard, R. Robson, *Angew. Chem.*, 2003, **115**, 1892; *Angew. Chem. Int. Ed.*, 2003, **42**, 1848; (b) J. P. Lang, Q. F. Xu, R. X. Yuan, and B. F. Abrahams, *Angew. Chem. Int. Ed.*, 2004, **43**, 4741.
- [3] (a) P. D. Boyle, J. Christie, T. Dyer, S. M. Godfrey, I. R. Howson, C. McArthur, B. Omar, R. G. Pritchard and G. R. Williams, *J. Chem. Soc., Dalton Trans.*, 2000, 3106; (b) J. Janczak, Y. M.

Idemori, *Inorg. Chem.*, 2002, **41**, 5059; (c) W. Holzer, W. F. Murphy and H. J. Bernstein, *J. Chem. Phys.*, 1970, **52**, 399; (d) W. Dzwolak, *Biochemistry.*, 2007, **46**, 1568.

[4] (a) Z. H. Jiang, H. B. Song and H. G. Wang, *Dalton Trans.*, 2006, 665. (b) R. B. Fu, S. C. Xiang, S. M. Hu, L. S. Wang, Y. M. Li, X. H. Huang and X. T. Wu, *Chem. Commun.*, 2005, 5292; (c) S. Mishra, E. Jeanneau, S. Daniele, G. Ledoux, and Prak. N. Swamy, *Inorg. Chem.*, 2008, 47, 9333; (d) D. F. Sun, S. Q. Ma, Y. X. Ke, T. M. Petersen and H. C. Zhou, *Chem. Commun.*, 2005, 2663.