

## 两个含双磺酸基团化合物的合成、晶体结构及荧光性质

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**摘要:** 采用缓慢蒸发溶剂法在水中合成了 2 个含双磺酸基的化合物 A-2,5-DSA·(Hphen)<sub>2</sub>·2H<sub>2</sub>O(**1**)和[Co(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·(A-2,5-DSA)·3H<sub>2</sub>O(**2**)(A-2,5-DSA=苯胺-2,5-二磺酸根离子, phen=1,10-邻菲罗啉)。化合物 **1** 中, 相邻的质子化的 1,10-邻菲罗啉反向堆叠在一起, 水分子通过氢键与(Hphen)<sup>+</sup>和苯胺-2,5-二磺酸根离子相连, 形成二维的层状结构。化合物 **2** 中, 钴离子与 2 个 1,10-邻菲罗啉和 2 个水分子配位, 构成[Co(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>阳离子。3 个自由的水分子通过氢键将苯胺-2,5-二磺酸根离子和[Co(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>连接形成三维网状结构。两个化合物中苯胺-2,5-二磺酸根离子均起到平衡电荷的作用。室温下 2 个化合物均具有荧光性质, 其最大发射峰分别在 601 nm 和 441 nm。

**关键词:** 钴离子; 晶体结构; 荧光性质; 合成; 化合物

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## Synthesis, Crystal Structures and Luminescent Properties of Two Compounds Containing Disulfonate Groups

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**Abstract:** The two compounds containing disulfonate groups A-2,5-DSA·(Hphen)<sub>2</sub>·2H<sub>2</sub>O (**1**) and [Co(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·(A-2,5-DSA)·3H<sub>2</sub>O (**2**) (A-2,5-DSA=aniline-2,5-disulfonate anion, phen=1,10-phenanthroline) were synthesized by the slow solvent evaporation method in water. In the compound **1**, the adjacent protonated 1,10-phenanthroline cation (Hphen)<sup>+</sup> reversely stack together. The water molecules connect to the (Hphen)<sup>+</sup> cations and aniline-2,5-disulfonate anions to form two-dimensional layered structure through the hydrogen bonds. In the compound **2**, the cobalt ion coordinates with two 1,10-phenanthroline and two water molecules to generate the [Co(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> cation. The three free water molecules connect to the [Co(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> cations and aniline-2,5-disulfonate anions to form three-dimensional network structure through the hydrogen bonds. In the two compounds, the aniline-2,5-disulfonate anions only balance the charges. The compounds exhibit the luminescence properties with emission maximum at 601 nm and 441 nm at room temperature, respectively. CCDC: 978180, **1**; 978179, **2**.

**Key words:** cobalt ion; crystal structure; luminescent property; synthesis; compound

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## 0 Introduction

In recent years, the synthesis and structure research of the complexes can attract widespread attention of the researchers because of their potential application values in the fields of adsorption-desorption, fluorescence, optical, magnetic and catalytic materials<sup>[1-6]</sup>. Among them, the complexes possessing sulfonate or disulfonate groups were constructed to generate one-dimensional chain, two-dimensional layer and three-dimensional network structures through hydrogen bonds<sup>[7-15]</sup>. Furthermore, these complexes shows various spatial architectures through using the auxiliary ligands containing N-donor such as imidazole, 2,2-bipyridine, 1,10-phenanthroline, and so on. In the efforts to investigate their structures and properties, we have chosen aniline-2,5-disulfonic acid monosodium salt and 1,10-phenanthroline to react with transition metals to generate the compounds containing disulfonate groups. In the past literatures, two such compounds were synthesized by Li's team, which display supramolecular network structures<sup>[16-17]</sup>. Herein, we report the synthesis, structures and luminescent properties of the two-dimensional layered compound A-2,5-DSA  $\cdot$  (Hphen)<sub>2</sub>  $\cdot$  2H<sub>2</sub>O and three-dimensional network compound [Co(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]  $\cdot$  (A-2,5-DSA)  $\cdot$  3H<sub>2</sub>O interlinked by hydrogen bonds.

## 1 Experimental

### 1.1 Material

Co(NO<sub>3</sub>)<sub>2</sub>  $\cdot$  6H<sub>2</sub>O, aniline-2,5-disulfonic acid monosodium salt and 1,10-phenanthroline were of reagent grade and were used without further purification.

### 1.2 Synthesis of the compounds

Synthesis of the compound **1**: Aniline-2,5-disulfonic acid monosodium salt (0.275 g, 1 mmol) and 1,10-phenanthroline (0.198 g, 1 mmol) were added into 20 mL H<sub>2</sub>O and stirred for 2 h to afford a colorless solution. The resulting solution was allowed to stand at ambient temperature for 5 days, yielding colorless block single crystals. Anal. Calcd. for C<sub>30</sub>H<sub>27</sub>N<sub>5</sub>O<sub>8</sub>S<sub>2</sub>: C, 55.41; N, 10.77; H, 4.16. Found: C, 55.53; N, 10.86; H, 4.36%.

Synthesis of the compound **2**: Aniline-2,5-disulfonic acid monosodium salt (0.275 g, 1 mmol), Co(NO<sub>3</sub>)<sub>2</sub>  $\cdot$  6H<sub>2</sub>O (0.291 g, 1 mmol) and 1,10-phenanthroline (0.198 g, 1 mmol) were added into 20 mL H<sub>2</sub>O and stirred for 2 h to afford a colorless solution. The resulting solution was allowed to stand at ambient temperature for 6 days, yielding yellow block single crystals. Anal. Calcd. for C<sub>30</sub>H<sub>31</sub>CoN<sub>5</sub>O<sub>11</sub>S<sub>2</sub>: C, 47.33%; N, 9.20%; H, 4.08%. Found: C, 47.55%; N, 9.38%; H, 4.33%.

### 1.3 Physical measurements

The elemental analyses were performed on a Perkin-Elmer 240C element analyzer. Thermogravimetric analysis experiment was carried out on a TA Q50 unit at a heating rate of 10 °C  $\cdot$  min<sup>-1</sup> under N<sub>2</sub> atmosphere. The luminescence analyses were performed on a Perkin Elmer LS55 fluorescence spectrometer. X-ray single crystal diffraction data were collected at 298(2) K from a single crystal mounted atop a glass fiber with a Bruker Apex-II diffractometer using graphite-monochromated Mo K $\alpha$  ( $\lambda$  = 0.071 073 nm) radiation. The structures were solved by direct methods and refined on  $F^2$  by full-matrix least-squares methods using SHELX-97<sup>[18-20]</sup>. The aniline group in the aniline-2,5-disulfonate anion is disordered. The crystal data and structure refinement are summarized in Table 1. The selected bond lengths and bond angles are listed in Table 2.

CCDC: 978180, **1**; 978179, **2**.

## 2 Results and discussion

### 2.1 Structure description of the compound **1**

The compound **1** crystallizes in the triclinic system with space group  $P\bar{1}$ . The asymmetric unit contains half of aniline-2,5-disulfonate anion, one 1,10-phenanthroline and one water molecules, as shown in Fig.1. The nitrogen atom of 1,10-phenanthroline molecule is protonated by the hydrogen ion. The aniline-2,5-disulfonate anion can just balance the positive charges of the two protonated 1,10-phenanthroline molecules. The planes of 1,10-phenanthroline molecules are parallel in the form of offset face-to-face, showing the  $\pi$ - $\pi$  stacking. The

Table 1 Crystal data and structure refinement for compounds 1 and 2

Empirical formula	C <sub>30</sub> H <sub>27</sub> N <sub>5</sub> O <sub>8</sub> S <sub>2</sub>	C <sub>30</sub> H <sub>31</sub> CoN <sub>5</sub> O <sub>11</sub> S <sub>2</sub>
Formula weight	649.69	760.65
Temperature / K	298(2)	298(2)
Wavelength / nm	0.071 073	0.071 073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> / nm	0.723 06(8)	0.985 80(8)
<i>b</i> / nm	1.051 97(11)	1.143 49(9)
<i>c</i> / nm	1.075 19(12)	1.443 01(12)
$\alpha$ / (°)	101.632 0(10)	91.591 0(10)
$\beta$ / (°)	103.527(2)	90.310 0(10)
$\gamma$ / (°)	108.366(2)	102.472(2)
Volume / nm <sup>3</sup>	0.720 26(14)	1.587 5(2)
<i>Z</i>	1	2
<i>D<sub>c</sub></i> / (g·cm <sup>-3</sup> )	1.498	1.591
Absorption coefficient / mm <sup>-1</sup>	0.248	0.743
<i>F</i> (000)	338	786
Crystal size / mm	0.21×0.17×0.12	0.13×0.10×0.06
Theta range for data collection / (°)	3.05 to 25.02	2.56 to 25.02
Limiting indices	$-8 \leq h \leq 8, -12 \leq k \leq 12, -12 \leq l \leq 8$	$-11 \leq h \leq 11, -10 \leq k \leq 13, -16 \leq l \leq 17$
Reflections collected / unique	3 598 / 2 505 ( <i>R</i> <sub>int</sub> =0.029 3)	8 147 / 5 519 ( <i>R</i> <sub>int</sub> =0.077 9)
Completeness to $\theta=25.02^\circ$ / %	98.40	98.40
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.970 9 and 0.949 8	0.956 8 and 0.909 6
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	2 505 / 0 / 208	5 519 / 0 / 442
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.037	1.003
Final <i>R</i> indices [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> =0.059 6, <i>wR</i> <sub>2</sub> =0.121 1	<i>R</i> <sub>1</sub> =0.073 2, <i>wR</i> <sub>2</sub> =0.108 4
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> =0.091 8, <i>wR</i> <sub>2</sub> =0.131 6	<i>R</i> <sub>1</sub> =0.166 2, <i>wR</i> <sub>2</sub> =0.125 9
Largest diff. peak and hole / (e·nm <sup>-3</sup> )	253 and -289	357 and -348

Table 2 Selected bond lengths (nm) and bond angles (°) for compounds 1 and 2

Compound 1					
N(1)-C(1)	0.134 4(6)	N(2)-C(4)	0.132 0(5)	N(3)-C(13)	0.132 5(5)
N(2)-C(8)	0.136 8(4)	N(3)-C(9)	0.136 0(4)	O(1)-S(1)	0.143 9(2)
C(1)-C(2)-S(1)	119.8(3)	O(1)-S(1)-O(2)	113.23(17)	N(1)-C(1)-C(2)	120.4(4)
C(3)-C(2)-S(1)	120.0(3)	O(1)-S(1)-O(3)	112.62(17)	N(1)-C(1)-C(3) <sup>i</sup>	122.1(4)
C(4)-N(2)-C(8)	122.2(3)	O(1)-S(1)-C(2)	106.21(16)	N(2)-C(8)-C(7)	118.7(3)
C(4)-N(2)-H(2)	118.9	O(2)-S(1)-C(2)	106.17(16)	N(2)-C(4)-C(5)	121.2(4)
C(8)-N(2)-H(2)	118.9	O(3)-S(1)-O(2)	112.03(17)		
C(13)-N(3)-C(9)	116.0(4)	O(3)-S(1)-C(2)	105.89(16)		
Compound 2					
Co(1)-N(1)	0.211 3(5)	Co(1)-N(3)	0.215 9(6)	Co(1)-O(7)	0.209 8(5)
Co(1)-N(2)	0.212 9(6)	Co(1)-N(4)	0.211 1(5)	Co(1)-O(8)	0.204 3(4)

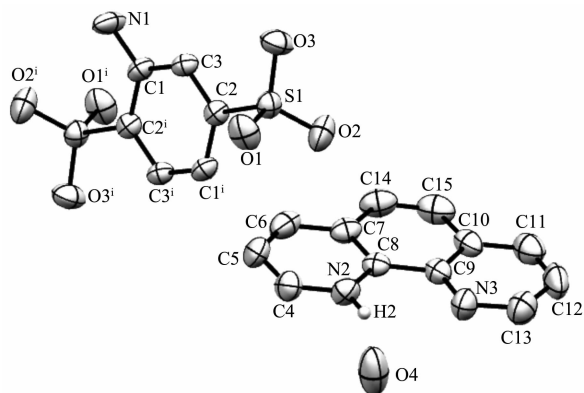
Continued Table 2

O(8)-Co(1)-O(7)	85.81(18)	O(8)-Co(1)-N(1)	93.5(2)	N(1)-Co(1)-N(3)	91.1(2)
O(7)-Co(1)-N(1)	94.07(19)	O(8)-Co(1)-N(2)	171.7(2)	N(2)-Co(1)-N(3)	96.5(2)
O(7)-Co(1)-N(2)	91.5(2)	O(8)-Co(1)-N(3)	86.7(2)	N(4)-Co(1)-N(1)	164.4(2)
O(7)-Co(1)-N(3)	171.2(2)	O(8)-Co(1)-N(4)	96.57(19)	N(4)-Co(1)-N(2)	91.6(2)
O(7)-Co(1)-N(4)	98.5(2)	N(1)-Co(1)-N(2)	78.8(2)	N(4)-Co(1)-N(3)	77.7(2)

Symmetry transformation used to generate equivalent atoms for compound **1**:  $^i -x+1, -y+2, -z$ .

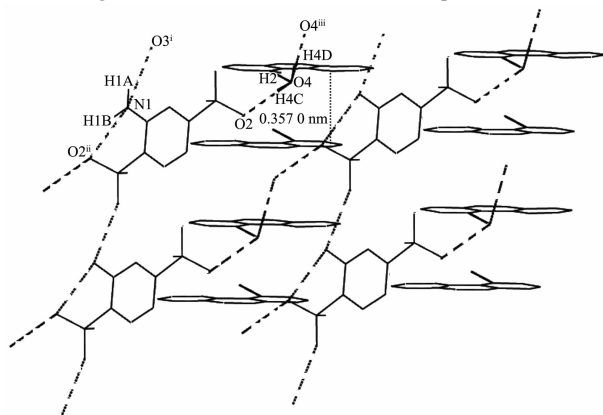
distances between the adjacent 1,10-phenanthroline molecules are 0.357 0 nm, which is similar with the values reported in the other literatures.

The hydrogen bonds can be seen between the water molecules, between the water molecule and sulfonic group, and between water molecule and the protonated nitrogen atom (N2) of 1,10-phenanthroline molecule, which include O4-H4D $\cdots$ O4 $^{iii}$ , O4-H4C $\cdots$ O2 $^{ii}$  and N2-H2 $\cdots$ O4(Symmetry code:  $^{ii} x, y-1, z$ ;  $^{iii} -x,$



Ellipsoids are shown at 50% probability level. Symmetry code:  $^i -x+1, -y+2, -z$

Fig.1 Molecular structure of the compound **1**



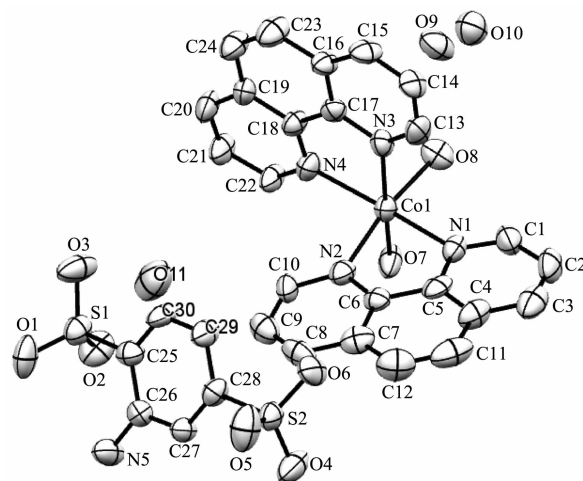
Symmetry code:  $^i x+1, y, z$ ;  $^{ii} x, y-1, z$ ;  $^{iii} -x, -y, -z+1$

Fig.2 A view of the two-dimensional layer structure of the compound **1** with the hydrogen bonds along the  $b$  axis

$-y, -z+1$ ). The aniline group can form hydrogen bonds with adjacent sulfonic groups, including N1-H1A $\cdots$ O3 $^i$  (Symmetry code:  $^i x+1, y, z$ ) and N1-H1B $\cdots$ O2. A view of the two-dimensional layer structure of the compound **1** along the  $b$  axis with the hydrogen bonds is shown in Fig.2. Moreover, the protonated 1,10-phenanthroline molecules and the alkaline aniline group can play important roles in the formation of the structure. The hydrogen-bonding details of the compound **1** are listed in Table 3.

## 2.2 Structure description of the compound **2**

The compound **2** crystallizes in triclinic system with space group  $P\bar{1}$ . The Co(II) is six-coordinated, which is coordinated with two 1,10-phenanthroline ligands and two water molecules to form  $[\text{Co}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$  cation. The four nitrogen atoms (N1, N2, N3 and N4) are in the equatorial basal plane, and two oxygen atoms are at the axial position. The aniline-2,5-disulfonate anion uncoordinates with the cobalt ion, just balances the charges, as shown in Fig.3. The asymmetric unit also contains three free water molecules. The Co-N distances are in the range of 0.211 1(5)



Ellipsoids are shown at 50% probability level

Fig.3 Molecular structure of the compound **2**

Table 3 Hydrogen bond lengths and bond angles for the compounds **1** and **2**

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
Compound <b>1</b>				
N1-H1A...O3 <sup>i</sup>	0.086 0	0.213 8	0.293 7	154.34
N1-H1B...O2	0.086 0	0.226 2	0.287 9	128.68
N2-H2...O4	0.086 0	0.193 8	0.274 8	156.45
O4-H4C...O2 <sup>ii</sup>	0.085 0	0.199 9	0.283 9	169.37
O4-H4D...O4 <sup>iii</sup>	0.085 0	0.210 4	0.294 5	170.03
Compound <b>2</b>				
N5-H5B...O1	0.086 0	0.240 0	0.297 3	124.46
O7-H7C...O4 <sup>i</sup>	0.085 0	0.191 0	0.275 8	174.77
O7-H7D...O6 <sup>ii</sup>	0.085 0	0.191 6	0.276 3	174.39
O8-H8C...O9	0.085 0	0.183 9	0.267 2	166.39
O8-H8D...O1 <sup>iii</sup>	0.085 0	0.201 3	0.284 7	166.38
O9-H9C...O10 <sup>iv</sup>	0.085 0	0.194 2	0.278 9	173.81
O9-H9D...O10 <sup>v</sup>	0.085 0	0.190 0	0.274 7	174.01
O10-H10C...O3 <sup>v</sup>	0.085 0	0.189 6	0.274 4	175.50
O10-H10D...O11 <sup>vi</sup>	0.085 0	0.189 2	0.274 1	176.18
O11-H11C...O2	0.085 0	0.192 5	0.277 4	177.09
O11-H11D...O5 <sup>ii</sup>	0.085 0	0.206 2	0.291 2	177.74

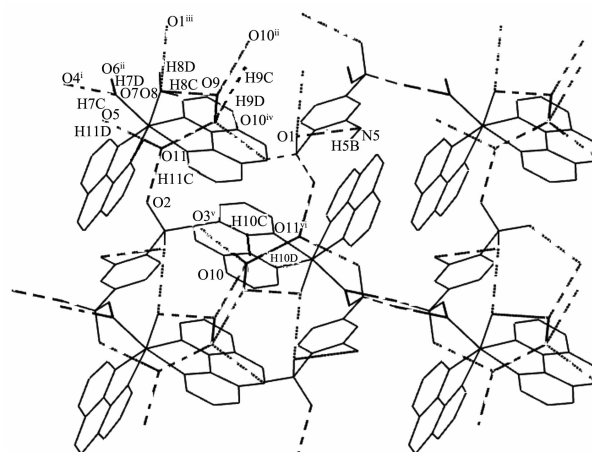
Symmetry code for compound **1**: <sup>i</sup> $x+1, y, z$ ; <sup>ii</sup> $x, y-1, z$ ; <sup>iii</sup> $-x, -y, -z+1$ . Symmetry code for compound **2**: <sup>i</sup> $-x+1, -y+1, -z+2$ ;

<sup>ii</sup> $x+1, y, z$ ; <sup>iii</sup> $x+1, y+1, z$ ; <sup>iv</sup> $-x+1, -y+2, -z+1$ ; <sup>v</sup> $x, y+1, z$ ; <sup>vi</sup> $-x+1, -y+1, -z+1$ .

nm to 0.215 9 (6) nm. The Co-O distances are between 0.204 3(4) nm and 0.209 8(5) nm. The angles of *cis* N-Co(1)-O are between 86.7(2)° and 171.7(2)°.

The hydrogen bond N5-H5B...O1 can be seen between the aniline group and the sulfonate group. The hydrogen atoms (H7C, H7D, H8C and H8D) in the coordinated water molecules form hydrogen-bondings with the O1, O4 and O6 atoms of the sulfonate groups, including O7-H7C...O4<sup>i</sup>, O7-H7D...O6<sup>ii</sup> and O8-H8D...O1<sup>iii</sup> (Symmetry code: <sup>i</sup> $-x+1, -y+1, -z+2$ ; <sup>ii</sup> $x+1, y, z$ ; <sup>iii</sup> $x+1, y+1, z$ ), with O9 atom of the uncoordinated water molecule, including O8-H8C...O9. The hydrogen bonds can be formed between the uncoordinated water molecules, including O9-H9D...O10<sup>iv</sup>, O9-H9C...O10<sup>v</sup>, O10-H10D...O11<sup>vi</sup> (Symmetry code: <sup>ii</sup> $x+1, y, z$ ; <sup>iv</sup> $-x+1, -y+2, -z+1$ ; <sup>vi</sup> $-x+1, -y+1, -z+1$ ), between the uncoordinated water molecules and the sulfonate groups, including O10-H10C...O3<sup>v</sup>, O11-H11C...O2 and O11-H11D...O5<sup>ii</sup> (Symmetry code: <sup>ii</sup> $x+1, y, z$ ; <sup>v</sup> $x, y+1, z$ ). Consequently, [Co(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>, aniline-2,5-disulfonate anion and the uncoordinated water molecules are interlinked by

the hydrogen bonds, respectively. A view of the network structure of the compound **2** along the *b* axis with the hydrogen bonds is shown in Fig.4. The hydrogen bonds can extend to form the three-dimensional structure. The hydrogen bonds play an important role in stabilizing the crystal structure. The hydrogen-bonding details of the compound **2** are listed



Symmetry code: <sup>i</sup> $-x+1, -y+1, -z+2$ ; <sup>ii</sup> $x+1, y, z$ ; <sup>iii</sup> $x+1, y+1, z$ ; <sup>iv</sup> $-x+1, -y+2, -z+1$ ; <sup>v</sup> $x, y+1, z$ ; <sup>vi</sup> $-x+1, -y+1, -z+1$

Fig.4 A view of the network structure of the compound **2** with the hydrogen bonds along the *b* axis

in Table 3.

### 2.3 Thermo-gravimetric analysis

The thermal gravimetric analysis was carried out to characterize the thermal stability of the compound **2**. The experiment was performed under the flowing nitrogen gas with a heating rate of  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ , the TGA curve of the compound is shown in Fig.5. The weight-loss step of 12.0% (Calcd. 11.8%) below  $181\text{ }^{\circ}\text{C}$  was attributed to the release of the two coordinated and three uncoordinated water molecules. And then a slow weightlessness between  $181\text{ }^{\circ}\text{C}$  and  $400\text{ }^{\circ}\text{C}$  was attributed to the partial decomposition of aniline-2,5-disulfonate anion. The weight-loss step observed between  $400\text{ }^{\circ}\text{C}$  and  $535\text{ }^{\circ}\text{C}$  was attributed to the decomposition of the remainder aniline-2,5-disulfonate anion. The weight of the remainder gradually makes a loss in the temperature range of  $535\text{ }^{\circ}\text{C}$  to  $820\text{ }^{\circ}\text{C}$ .

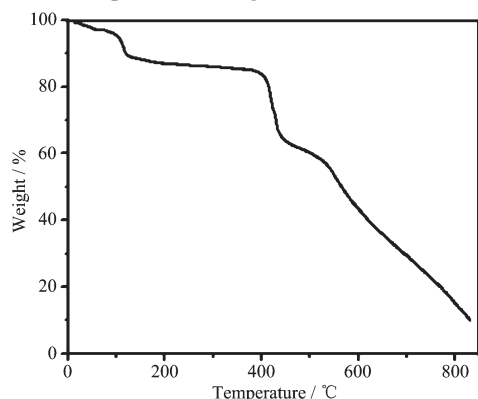


Fig.5 TGA curve of the compound **2**

### 2.4 Luminescent properties

The solid-state fluorescent spectra of aniline-2,5-disulfonic acid monosodium salt, the compounds **1** and **2** at room temperature are depicted in Fig.6. It can be observed that the compound **1** displays the fluorescent emission band is at  $601\text{ nm}$  upon an excitation at  $315\text{ nm}$  and the compound **2** shows a strong emission peak at  $441\text{ nm}$ , when excited at  $315\text{ nm}$ . The main emission peaks of the aniline-2,5-disulfonic acid monosodium salt and 1,10-phenanthroline are at  $392\text{ nm}$  and  $380\text{ nm}$ , respectively. The emission band of the compound **1** happens a large red shift phenomenon and the fluorescence intensity decreases, and the emission peak of the compound **2** happens red shift and the fluorescence intensity

becomes stronger, comparing the aniline-2,5-disulfonic acid monosodium salt and 1,10-phenanthroline. Obviously, the reasons of our fluorescence emissions are different from those reported in the literatures<sup>[16-17]</sup>, where the fluorescence emission peaks of the complexes can be assigned to intra-ligand  $\pi-\pi^*$  charge transfer of 1,10-phenanthroline molecules. In our research, the  $\pi-\pi$  stacking interactions between the 1,10-phenanthroline molecules and the coordination of the 1,10-phenanthroline to the cobalt ion play important roles in the fluorescence emission. For compound **1**, the  $\pi-\pi$  stacking interactions between the 1,10-phenanthroline molecules can mainly cause the fluorescence emission, moreover, it also depend on the transitions between the energy levels of aniline groups, where the narrow transitions of the vibration energy levels can cause the broad absorption band. For compound **2**, the cobalt ion has empty  $4f$  electronic orbits and  $3d$  orbits is not full of electrons, and the 1,10-phenanthroline molecule has delocalized electrons. The coordination of the 1,10-phenanthroline ligands to the cobalt ion causes the ligand-to-metal charge transfer, which is the main reason of the fluorescence emission. Furthermore, the deprotonation of sulfonic acid group and the transitions between the energy levels of sulfonate anion and 1,10-phenanthroline also contribute to the fluorescence emission.

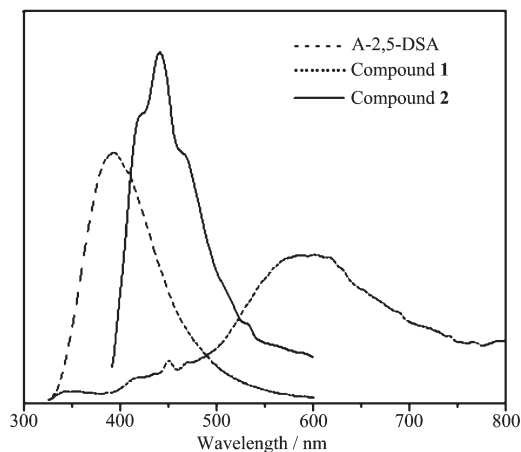


Fig.6 Solid-state emission spectra of the aniline-2,5-disulfonic acid monosodium salt, compounds **1** and **2** at room temperature



### 3 Conclusion

In summary, the two compounds A-2,5-DSA · (Hphen)<sub>2</sub> · 2H<sub>2</sub>O and [Co(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] · (A-2,5-DSA) · 3H<sub>2</sub>O were synthesized in water by the slow solvent evaporation method. For the compound **1**, the protonated 1,10-phenanthroline molecules in the opposite direction stack together in the form of face-to-face. The water molecules connect to the (Hphen)<sup>+</sup> cations and aniline-2,5-disulfonate anions to form the two-dimensional layer structure by the hydrogen bonds. For the compound **2**, the three uncoordinated water molecules connect to the [Co(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> cations and aniline-2,5-disulfonate anions to form the three-dimensional network structure through the hydrogen bonds. The fluorescence spectra of the compounds show that the emission peaks all have red shift, compared with the fluorescence spectra of the aniline-2,5-disulfonic acid monosodium salt and 1,10-phenanthroline.

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