

# **Negatively charged metal-organic hosts with cobalt dithiolene species: Improving PET processes for light-driven proton reduction through host-guest electrostatic interaction**

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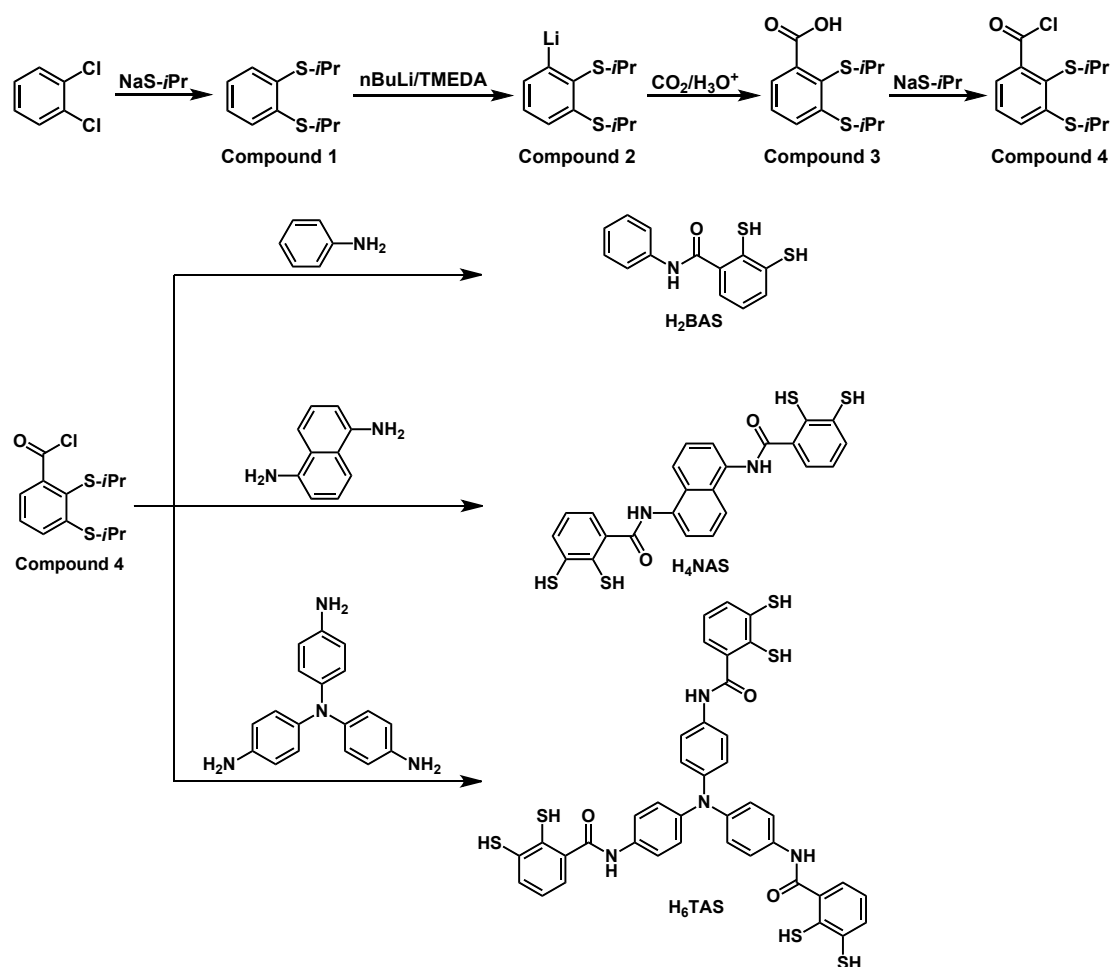
## 1. Experimental Section.

All chemicals were of reagent grade quality obtained from commercial sources. Unless stated otherwise, all operations were carried out under an atmosphere of dry argon using Schlenk and vacuum techniques. Solvents were dried by standard methods and freshly distilled prior to use.  $^1\text{H}$  NMR spectra were measured on a Varian INOVA 400 M spectrometer. ESI mass spectra were carried out on a HPLC-Q-ToF MS spectrometer using methanol as mobile phase. Uv-vis spectra were measured on a HP 8453 spectrometer. The elemental analyses of C, H and N were performed on a Vario EL III elemental analyzer. The solution fluorescent spectra were measured on Edinburgh FS-920. The nanosecond time-resolved transient difference absorption spectra were obtained by using an Edinburgh LP-980 instrument (Edinburgh Instruments, UK). All electrochemical measurements were carried out under argon gas under room temperature performed on a ZAHNER ENNIUM electrochemical workstation with a conventional three-electrode system with a homemade Ag/AgCl electrode as a reference electrode, a platinum silk with 0.5 mm diameter as a counter electrode, and glassy carbon electrode as a working electrode.

For photoinduced hydrogen evolution, each sample was made in a 15 mL flask. Varying amounts of the catalyst, AA and  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  in 1:1:1 DMF/ $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  were added to obtain a total volume of 5.0 mL. The flask was sealed with a septum and protected from air, then degassed by bubbling argon gas for 20 min under atmospheric pressure under room temperature. The pH of this solution was adjusted to a specific pH by adding  $\text{H}_2\text{SO}_4$  or NaOH and measured with a pH meter. After that, the samples were irradiated by a 500 W Xenon lamp. The reaction temperature was 293 K by using a water filter to absorb heat. The generated photoproduct of  $\text{H}_2$  was characterized by GC 7890T instrument analysis using a 5 Å molecular sieve column (0.6 m  $\times$  3 mm), thermal conductivity detector, and argon used as carrier gas. The amount of hydrogen generated was determined by the external standard method. Hydrogen in the resulting solution was not measured and the slight effect of the hydrogen gas generated on the pressure of the flask was neglected for calculation of the volume of hydrogen gas.<sup>S1</sup>

## 2. Preparation and Characterizations.

**Scheme S1** The synthetic route of ligand H<sub>2</sub>BAS, H<sub>4</sub>NAS and H<sub>6</sub>TAS.



Ligand H<sub>2</sub>BAS, H<sub>4</sub>NAS and H<sub>6</sub>TAS were synthesized according to the literature.<sup>S2, S3</sup>

### Synthesis of compound 1:

1,2-Dichlorobenzene (10.72 g, 71.0 mmol) was added dropwise to a suspension of sodium isopropylmercaptane (34.94 g, 356.0 mmol) in DMF (200 mL). The mixture was stirred for 3 days at 100°C and was then cool to ambient temperature. It was then poured into water (500 mL) and extracted with diethyl ether (3 × 100 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. Evaporation of the filtrate and evaporate under vacuum yielded compound 1 as a yellow oil. The crude product was purified by column chromatography (SiO<sub>2</sub>, petrol ether), and the colorless oil compound 1 was obtained. Yield: 13.66 g, 85%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.33 (dd, 2H; ArH), 7.14 (dd, 2H; ArH), 3.48 (m, 2H; SCH), 1.38 (d, 6H; CH<sub>3</sub>), 1.27 (d, 6H; CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz, ppm): δ 137.5, 130.6, 126.3, 36.8, 22.8.

### Synthesis of compound **2**:

A sample of n-butyllithium (8.8 mL of a 2.5 M solution in hexane, 22.0 mmol) was added dropwise to a solution of TMEDA (3.3 mL, 22.0 mmol) and compound **1** (5.0 g, 22.0 mmol) in hexane (200 mL) at 0°C. After 1 h, the ice bath was removed and the stirring was continued under ambient temperature overnight to result in the formation of yellow slurry. The compound **2** was used directly without further purification for the next step reaction.

### Synthesis of compound **3**:

Dry CO<sub>2</sub> was bubbled through a slurry of compound **2** (22.0 mmol) in hexane at 0°C for 2 h. After evaporation of the solvent, the residue was dissolved in water and acidified with hydrochloric acid (37%) to pH 2. The aqueous solution was extracted with diethyl ether (3 × 100 mL) and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>. Volatiles were removed in vacuum and the product was recrystallized from hexane to yield an off-white powder. Yield: 3.39 g, 57%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 12.24 (s, 1H; CO<sub>2</sub>H), 7.66 (dd, 1H; ArH), 7.38 (m, 2H; ArH), 3.54 (m, 2H; SCH), 1.38 (d, 6H; CH<sub>3</sub>), 1.27 (d, 6H; CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz, ppm): δ 171.3, 146.1, 137.8, 129.9, 129.4, 128.8, 126.1, 40.4, 36.1, 22.8, 22.4.

### Synthesis of compound **4**:

Thionyl chloride (1 ml) were added to a solution of compound **3** (1.08 g, 4.0 mmol) in chloroform (10 ml). The reaction mixture was heated under reflux conditions for 3 h, and then the solvent was removed in vacuum. The compound **4** was used directly without further purification for the next step reaction.

### Synthesis of H<sub>2</sub>**BAS** precursor:

Freshly prepared compound **4** was dissolved in THF (20 mL) and this solution was added to a solution of aniline (372.51 mg, 4.0 mmol) and NEt<sub>3</sub> (0.62 mL, 4.0 mmol) in THF (40 mL) at 0°C. Then, the reaction mixture was stirred for 12 h under ambient temperature. Subsequently, insoluble material was removed by filtration and the solvent was removed from the filtrate under vacuum forming orange oil, which was dissolved in ethyl acetate and n-hexane was added slowly to give an off-white powder. Yield: 0.69 g, 50%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 8.87 (s, 1H; NH), 7.63 (m, 3H; ArH), 7.37 (m, 4H; aniline-H), 7.15 (t, *J* = 7.5 Hz, 1H; aniline-H), 3.47 (m, 2H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.40 (d, *J* = 6.7 Hz, 6H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.21 (d, *J* = 6.7 Hz, 6H;

CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz, ppm): δ 165.2, 144.8, 141.3, 137.0, 128.1, 128.0, 127.9, 127.3, 125.1, 123.4, 119.0, 40.2, 35.2, 22.0, 21.7.

#### Synthesis of H<sub>2</sub>BAS:

Dry, freshly distilled THF (20 mL) was added to a mixture of precursor (172.8 mg, 0.5 mmol), sodium (69.0 mg, 3.0 mmol) and naphthalene (128.2 mg, 1.0 mmol). The reaction mixture was stirred for 12 h at 25°C. Subsequently, methanol (5 mL) was added to remove unreacted sodium. The solvents were then removed under vacuum. The solid residue was dissolved in degassed water and the resulting solution was washed three times with degassed diethyl ether (3 × 20 mL). The aqueous solution was filtered and HCl (37%) was added dropwise until a white precipitate formed. This precipitate was extracted with ethyl acetate. The organic layer was washed with sat. NaCl aq. and dried over Na<sub>2</sub>SO<sub>4</sub>. The solution was concentrated under reduced pressure to give the product H<sub>2</sub>BAS. Yield: 0.12 g, 90%.

#### Preparation of Co-BAS(Et<sub>4</sub>N)<sub>2</sub>:

A DMF solution (10 mL) of Co(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (183.9 mg, 0.54 mmol) was added with stirring to a DMF solution (20 mL) of H<sub>2</sub>BAS and NaOH (86.4 mg, 2.16 mmol). A deep blue solution developed immediately and it was left to stir overnight. To this solution, NEt<sub>4</sub>Cl (89.5 mg, 0.54 mmol) was added. The solution was allowed to stir under room temperature for 4 h. Then, the solution poured into 200 mL diethyl ether and a blue precipitate formed. Yield: 65%. Elemental analysis calcd for Co(C<sub>13</sub>H<sub>9</sub>NOS<sub>2</sub>)<sub>2</sub>·NC<sub>8</sub>H<sub>20</sub>: H, 5.41; C, 57.69; N, 5.94. Found: H, 5.46; C, 57.28; N, 5.91. ESI-MS: *m/z* = 577.1617 [Co(BAS)]<sup>+</sup>.

#### Synthesis of H<sub>4</sub>NAS precursor:

Freshly prepared compound **4** was dissolved in THF (20 mL) and this solution was added to a solution of 1,5-diaminonaphthalene (284.8 mg, 1.8 mmol) and NEt<sub>3</sub> (0.31 mL, 2.0 mmol) in THF (40 mL) at 0°C. Then, the reaction mixture was stirred for 12 h under ambient temperature. Subsequently, insoluble material was removed by filtration and the solvent was removed from the filtrate under vacuum. The pure product was obtained after washing with diethyl ether. Yield: 1.06 g, 89%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 10.39 (s, 2H; NH), 8.23 (d, *J* = 8.4 Hz, 2H; naphthalene-H), 7.70 (d, *J* = 8.4 Hz, 2H; naphthalene-H), 7.58 (t, *J* = 8.4 Hz, 2H; naphthalene-H), 7.48 (t, *J* = 6.7 Hz, 2H; ArH), 7.37 (dd, *J* = 6.7 Hz, 2.4 Hz, 2H; ArH), 7.19 (dd, *J* = 6.7 Hz, 2.4 Hz, 2H; ArH), 3.60 (m, 4H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.38 (d, *J* = 6.7 Hz, 12H; CH<sub>3</sub>),

1.27 (d,  $J = 6.7$  Hz, 12H; CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz, ppm):  $\delta$  166.8, 146.1, 142.3, 133.4, 129.3, 128.7, 128.5, 127.9, 126.5, 126.2, 120.4, 118.8, 41.4, 36.3, 23.0, 22.7.

#### Synthesis of H<sub>4</sub>NAS:

Dry, freshly distilled THF (20 mL) was added to a mixture of precursor (358.0 mg, 0.54 mmol), sodium (184.0 mg, 8.0 mmol), and naphthalene (346.1 mg, 2.70 mmol). The reaction mixture was stirred for 12 h at 25°C. Subsequently methanol (5 mL) was added to remove unreacted sodium. The solvents were then removed under vacuum. The solid residue was dissolved in degassed water and the resulting solution was washed three times with degassed diethyl ether (3 × 20 mL). The aqueous solution was filtered and HCl (37%) was added dropwise until a white precipitate formed. This precipitate was isolated by filtration and washed with water and diethyl ether. The solid residue was dried under vacuum to give ligand H<sub>4</sub>NAS as off-white powder, which was used directly without further purification for subsequent reaction.

#### Preparation of Co–NAS/(Et<sub>4</sub>N)<sub>2</sub>:

A CH<sub>3</sub>OH solution of Co(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (183.9 mg, 0.54 mmol) was added with stirring to a DMF solution (20 mL) of H<sub>2</sub>NAS and NaOH (86.4 mg, 2.16 mmol). A deep blue solution developed immediately and it was left to stir overnight. To this solution, NEt<sub>4</sub>Cl (89.5 mg, 0.54 mmol) was added, and the solution was allowed to stir under room temperature for 4 h. Then, the solution poured into 200 mL diethyl ether, a blue precipitate formed. The solid was collected and re-dissolved in DMF, dark blue crystals of Co–NAS(Et<sub>4</sub>N)<sub>2</sub> suitable for single crystal X-ray diffraction were obtained by diffusing diethyl ether into the DMF solution. yield: 65%. Elemental analysis calcd for Co<sub>2</sub>(C<sub>24</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub>)<sub>2</sub>·2NC<sub>8</sub>H<sub>20</sub>·2C<sub>3</sub>H<sub>7</sub>NO: H, 5.49; C, 55.83; N, 7.44. Found: H, 5.51; C, 55.67; N, 7.41. ESI-MS:  $m/z = 548.9222$  [Co<sub>2</sub>(NAS)<sub>2</sub>]<sup>2-</sup>.

#### Preparation of Co–NAS/[Ru(bpy)<sub>3</sub>]<sub>2</sub>:

A CH<sub>3</sub>OH solution of Co(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (183.9 mg, 0.54 mmol) was added with stirring to a DMF solution (20 mL) of H<sub>2</sub>NAS and NaOH (86.4 mg, 2.16 mmol). A deep blue solution developed immediately and it was left to stir overnight. Then, the solution poured into 200 mL diethyl ether, a dark blue precipitate formed. The solid was collected and re-dissolved in DMF, to this solution, Ru(bpy)<sub>3</sub>Cl<sub>2</sub> (404.2 mg, 0.54 mmol) was added, and the solution was allowed to stir under room temperature for 4 h, dark green crystals of Co–NAS[Ru(bpy)<sub>3</sub>]<sub>2</sub> suitable for single crystal X-ray diffraction were obtained by diffusing diethyl ether into the DMF solution. Yield:

65%. Elemental analysis calcd for  $\text{Co}_2(\text{C}_{24}\text{H}_{14}\text{N}_2\text{O}_2\text{S}_4)_2 \cdot 2\text{Ru}(\text{C}_{10}\text{H}_8\text{N}_2)_3 \cdot 2\text{Cl} \cdot \text{C}_3\text{H}_7\text{NO}$ : C, 55.96; H, 3.51; N, 9.99; S, 10.77; found: C, 55.88; H, 3.62; N, 10.04; S, 10.75.

Synthesis of  $\text{H}_6\text{TAS}$  precursor:

Freshly prepared compound **4** was dissolved in THF (20 mL) and this solution was added to a solution of 4, 4', 4''-triaminotriphenylamine<sup>S4</sup> (386.2 mg, 1.33 mmol) and  $\text{NEt}_3$  (0.31 mL, 2.0 mmol) in THF (40 mL) at 0°C. Then, the reaction mixture was stirred for 12 h under ambient temperature. Subsequently, insoluble material was removed by filtration and the solvent was removed from the filtrate under vacuum. The pure product was obtained after washing with diethyl ether. Yield: 1.25 g, 90%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  8.85 (s, 3H; NH), 7.62 (dd,  $J = 7.2$  Hz, 1.6 Hz, 3H; ArH), 7.55 (d,  $J = 8.8$  Hz, 6H; triphenylamine-H), 7.36 (m, 6H; ArH), 7.11 (d,  $J = 8.8$  Hz, 6H; triphenylamine-H), 3.60 (m, 6H;  $\text{CH}(\text{CH}_3)_2$ ), 1.36 (d,  $J = 6.7$  Hz, 18H;  $\text{CH}_3$ ), 1.19 (d,  $J = 6.7$  Hz, 18H;  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz, ppm):  $\delta$  166.0, 145.9, 144.3, 142.1, 132.9, 129.1, 128.9, 128.3, 126.3, 124.5, 121.3, 41.3, 36.3, 23.1, 22.7.

Synthesis of  $\text{H}_6\text{TAS}$ :

Dry, freshly distilled THF (20 mL) was added to a mixture of precursor (366.6 mg, 0.35 mmol), sodium (184.0 mg, 8.0 mmol), and naphthalene (337.1 mg, 2.63 mmol). The reaction mixture was stirred for 12 h at 25°C. Subsequently methanol (5 mL) was added to remove unreacted sodium. The solvents were then removed under vacuum. The solid residue was dissolved in degassed water and the resulting solution was washed three times with degassed diethyl ether ( $3 \times 20$  mL). The aqueous solution was filtered and HCl (37%) was added dropwise until a white precipitate formed. This precipitate was isolated by filtration and washed with water and diethyl ether. The solid residue was dried under vacuum to give ligand  $\text{H}_6\text{TAS}$  as yellow powder, which was used directly without further purification for subsequent reaction.

Preparation of  $\text{Co-TAS}/(\text{Et}_4\text{N})_3$ :

A  $\text{CH}_3\text{OH}$  solution of  $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  (183.9 mg, 0.54 mmol) was added with stirring to a DMF solution (20 mL) of  $\text{H}_6\text{TAS}$  and NaOH (86.4 mg, 2.16 mmol). A blue solution developed immediately and it was left to stir overnight. To this solution added  $\text{NEt}_4\text{Cl}$  (89.5 mg, 0.54 mmol), and the solution was allowed to stir under room temperature for 4 h. The solution poured into 200 mL diethyl ether. The solid was collected and re-dissolved in DMF, dark blue crystals of  $\text{Co-TAS}(\text{Et}_4\text{N})_3$  suitable for

single crystal X-ray diffraction were obtained by diffusing diethyl ether into the DMF solution. Yield: 65%. Elemental analysis calcd for  $\text{Co}_3(\text{C}_{39}\text{H}_{24}\text{N}_4\text{O}_3\text{S}_6)_2 \cdot 3\text{NC}_8\text{H}_{20}2\text{C}_3\text{H}_7\text{NO}$ : H, 5.37; C, 56.60; N, 7.95. Found: H, 5.39; C, 56.57; N, 7.78. ESI-MS:  $m/z = 584.9067 [\text{Co}_3(\text{TAS})_2]^{3-}$ .



### 3. Single Crystal X-ray Crystallography.

Intensities of single crystals were collected on a Bruker SMART APEX CCD diffractometer equipped with graphite monochromated Mo-K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) using the SMART and SAINT programs.<sup>S5,S6</sup> The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares methods with SHELXTL *version* 5.1 software.<sup>S7</sup>

Crystal data of Co–NAS:  $\text{Co}_2(\text{C}_{24}\text{H}_{14}\text{N}_2\text{O}_2\text{S}_4)_2 \cdot 2\text{NC}_8\text{H}_{20} \cdot 4\text{C}_3\text{H}_7\text{NO} \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ ,  $M = 1702.02$ , Triclinic, space group P-1, black blue rod,  $a = 10.9909(6)$ ,  $b = 12.8403(7)$ ,  $c = 17.7740(9) \text{ \AA}$ ,  $\alpha = 69.3587(13)$ ,  $\beta = 88.5929(14)$ ,  $\gamma = 75.5745(15)$ ,  $V = 2267.8(2) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.246 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 0.606 \text{ mm}^{-1}$ ,  $T = 220(2) \text{ K}$ . 7890 unique reflections [ $R_{\text{int}} = 0.0448$ ]. Final  $R_I$  [with  $I > 2\sigma(I)$ ] = 0.0748,  $wR_2$  (all data) = 0.1992 for the data collected. CCDC number 1916150.

Crystal data of Co–NAS/[Ru(bpy) $_3$ ] $_2$ :  $\text{Co}_2(\text{C}_{24}\text{H}_{14}\text{N}_2\text{O}_2\text{S}_4)_2 \cdot 2\text{Ru}(\text{C}_{10}\text{H}_8\text{N}_2)_3 \cdot 2\text{Cl} \cdot 4\text{C}_3\text{H}_7\text{NO} \cdot 4\text{CH}_3\text{OH} \cdot 6\text{H}_2\text{O}$ ,  $M = 2837.88$ , Triclinic, space group P-1, black green rod,  $a = 13.8188(8)$ ,  $b = 14.0788(9)$ ,  $c = 18.6554(12) \text{ \AA}$ ,  $\alpha = 94.464(2)$ ,  $\beta = 101.089(2)$ ,  $\gamma = 99.865(2)$ ,  $V = 3485.9(4) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.352 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 0.671 \text{ mm}^{-1}$ ,  $T = 200(2) \text{ K}$ . 12095 unique reflections [ $R_{\text{int}} = 0.0762$ ]. Final  $R_I$  [with  $I > 2\sigma(I)$ ] = 0.0910,  $wR_2$  (all data) = 0.2175 for the data collected. CCDC number 1916151.

Crystal data of Co–TAS:  $\text{Co}_3(\text{C}_{39}\text{H}_{24}\text{N}_4\text{O}_3\text{S}_6)_2 \cdot 3\text{NC}_8\text{H}_{20} \cdot 9\text{C}_3\text{H}_7\text{NO} \cdot 2\text{H}_2\text{O}$ ,  $M = 2839.40$ , Triclinic, space group P-1, black blue rod,  $a = 13.8759(13)$ ,  $b = 19.6896(18)$ ,  $c = 28.663(3) \text{ \AA}$ ,  $\alpha = 109.279(3)$ ,  $\beta = 93.004(4)$ ,  $\gamma = 105.142(4)$ ,  $V = 7052.2(11) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.337 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 0.594 \text{ mm}^{-1}$ ,  $T = 199(2) \text{ K}$ . 24545 unique reflections [ $R_{\text{int}} = 0.0484$ ]. Final  $R_I$  [with  $I > 2\sigma(I)$ ] = 0.0827,  $wR_2$  (all data) = 0.2443 for the data collected. CCDC number 1916152.

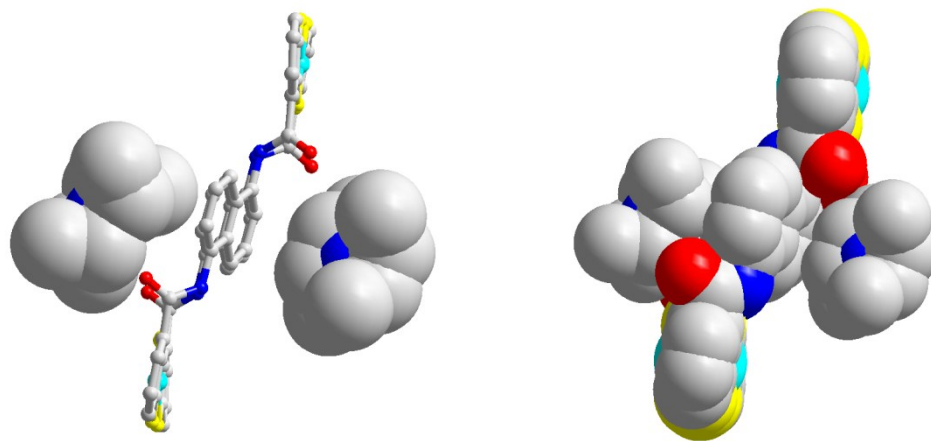
In the structural refinement of Co–NAS, all the non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbones and the solvent DMF and methanol molecules were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. To assist the stability of refinements, the carbon atoms of methylene on each  $\text{Et}_4\text{N}^+$  cation were disordered into two parts with the *s.o.f* of each part being fixed at 0.5.

In the structural refinement of Co–NAS/[Ru(bpy) $_3$ ] $_2$ , all the non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbones,  $\text{Ru}(\text{bpy})_3^{2+}$  and the solvent DMF and methanol molecules were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. One DMF

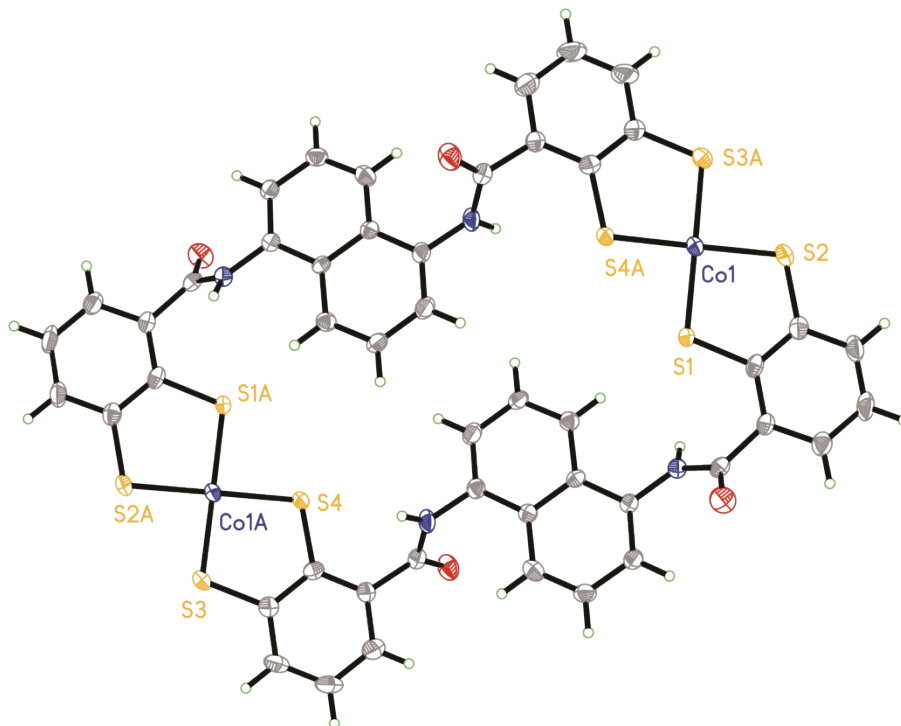
and two methanol molecules were restrained as idealized regular polygons.

In the structural refinement of Co-TAS, all the non-hydrogen atoms in the structure of Co-TAS were refined anisotropically. Hydrogen atoms within the ligand backbones, counter cations and the solvent molecules were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms.

**Figure S3.1** The crystal structure of Co–NAS with  $\text{Et}_4\text{N}^+$  and the filling pattern of the host and guests. The Co, S, N, O, and C are drawn in cyan, yellow, blue, red, white, and grey, respectively.



**Figure S3.2** An ORTEP plot of the molecular tetrahedron Co–NAS, showing 30% probability displacement ellipsoids of non-hydrogen atoms.



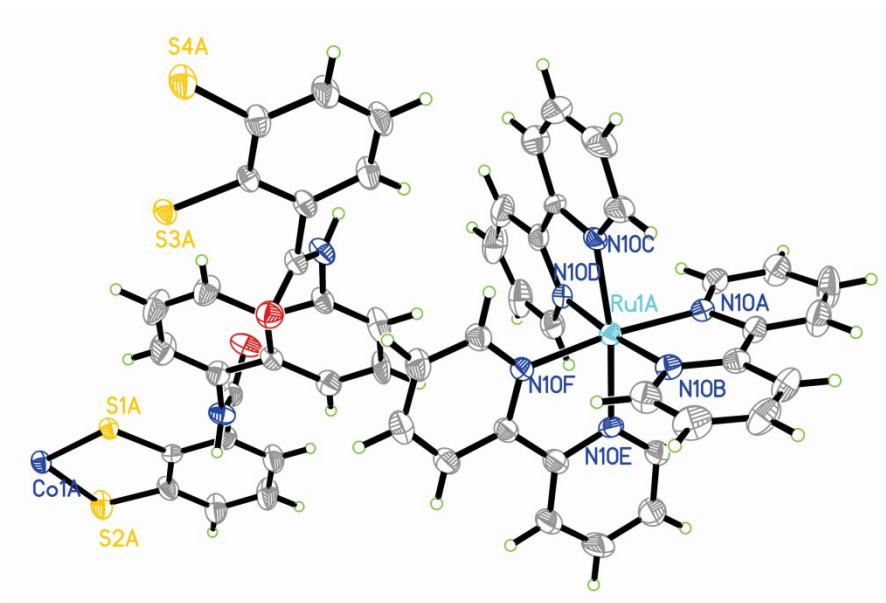
**Table S3.1** Selective bond distance (Å) in Co–NAS.

	bond distance (Å)		bond distance (Å)
Co(1)-S(3)	2.1571(13)	S(2)-C(2)	1.758(5)
Co(1)-S(2)	2.1616(12)	S(3)-C(23)	1.748(5)
Co(1)-S(1)	2.1660(12)	S(3)-Co(1)	2.1571(13)
Co(1)-S(4)	2.1692(12)	S(4)-C(24)	1.758(4)
S(1)-C(1)	1.764(4)	S(4)-Co(1)	2.1692(12)

**Table S3.2** Selective bond angle (°) in Co–NAS.

	bond angle (°)		bond angle (°)
S(3)-Co(1)-S(2)	88.30(5)	C(24)-S(4)-Co(1)	105.12(16)
S(3)-Co(1)-S(1)	176.22(6)	C(6)-C(1)-S(1)	122.2(3)
S(2)-Co(1)-S(1)	91.42(5)	C(2)-C(1)-S(1)	117.8(3)
S(3)-Co(1)-S(4)	91.73(5)	C(1)-C(2)-S(2)	119.9(3)
S(2)-Co(1)-S(4)	177.17(6)	C(3)-C(2)-S(2)	120.5(4)
S(1)-Co(1)-S(4)	88.73(4)	C(22)-C(23)-S(3)	120.0(4)
C(1)-S(1)-Co(1)	105.68(16)	C(24)-C(23)-S(3)	119.4(4)
C(2)-S(2)-Co(1)	105.07(16)	C(19)-C(24)-S(4)	123.0(4)
C(23)-S(3)-Co(1)	105.30(17)	C(23)-C(24)-S(4)	118.4(3)

**Figure S3.3** An ORTEP plot of the molecular tetrahedron Co–NAS[Ru(bpy)<sub>3</sub>]<sub>2</sub>, showing 30% probability displacement ellipsoids of non-hydrogen atoms.



**Table S3.3** Selective bond distance (Å) in Co–NAS[Ru(bpy)<sub>3</sub>]<sub>2</sub>.

	bond distance (Å)		bond distance (Å)
Co(1)-S(1)	2.1560(18)	S(4)-C(23)	1.748(8)
Co(1)-S(4)	2.158(2)	S(4)-Co(1)	2.158(2)
Co(1)-S(3)	2.1637(19)	Ru(1)-N(102)	2.051(6)
Co(1)-S(2)	2.165(2)	Ru(1)-N(103)	2.053(6)
S(1)-C(1)	1.745(7)	Ru(1)-N(101)	2.054(5)
S(2)-C(2)	1.766(8)	Ru(1)-N(106)	2.057(5)
S(3)-C(24)	1.750(6)	Ru(1)-N(104)	2.060(6)
S(3)-Co(1)	2.1637(19)	Ru(1)-N(105)	2.061(5)



**Table S3.4** Selective bond angle (°) in Co–NAS[Ru(bpy)<sub>3</sub>]<sub>2</sub>.

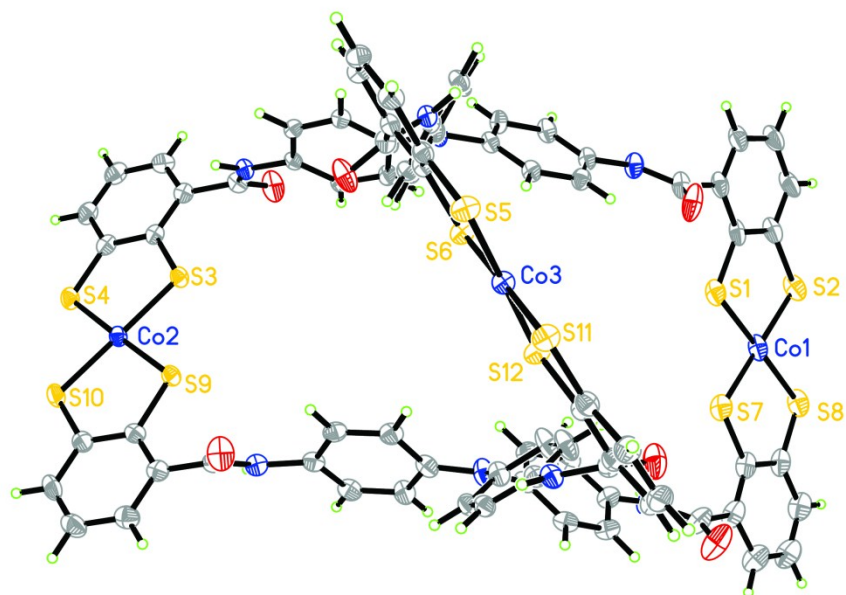
	bond angle (°)		bond angle (°)
S(1)-Co(1)-S(4)	171.27(10)	N(103)-Ru(1)-N(106)	94.5(2)
S(1)-Co(1)-S(3)	87.40(7)	N(101)-Ru(1)-N(106)	172.9(2)
S(4)-Co(1)-S(3)	91.46(8)	N(102)-Ru(1)-N(104)	174.6(2)
S(1)-Co(1)-S(2)	91.31(7)	N(103)-Ru(1)-N(104)	78.8(2)
S(4)-Co(1)-S(2)	90.60(8)	N(101)-Ru(1)-N(104)	97.1(2)
S(3)-Co(1)-S(2)	174.60(10)	N(106)-Ru(1)-N(104)	88.8(2)
C(1)-S(1)-Co(1)	105.8(2)	N(102)-Ru(1)-N(105)	88.4(2)
C(2)-S(2)-Co(1)	104.9(3)	N(103)-Ru(1)-N(105)	171.2(2)
C(24)-S(3)-Co(1)	105.3(2)	N(101)-Ru(1)-N(105)	96.6(2)
C(23)-S(4)-Co(1)	105.0(3)	N(106)-Ru(1)-N(105)	78.9(2)
C(7)-N(1)-C(8)	121.4(6)	N(104)-Ru(1)-N(105)	95.2(2)
C(18)-N(2)-C(17)	121.9(6)	C(101)-N(101)-C(105)	117.9(6)
C(2)-C(1)-C(6)	119.4(6)	C(101)-N(101)-Ru(1)	126.2(5)
C(2)-C(1)-S(1)	118.9(5)	C(105)-N(101)-Ru(1)	115.9(4)
C(6)-C(1)-S(1)	121.6(5)	C(110)-N(102)-C(106)	118.5(6)
C(1)-C(2)-C(3)	120.2(7)	C(110)-N(102)-Ru(1)	125.4(5)
C(1)-C(2)-S(2)	119.0(6)	C(106)-N(102)-Ru(1)	116.1(4)
C(3)-C(2)-S(2)	120.8(6)	C(111)-N(103)-C(115)	119.3(6)
N(102)-Ru(1)-N(103)	98.1(2)	C(111)-N(103)-Ru(1)	125.9(5)
N(102)-Ru(1)-N(101)	78.4(2)	C(115)-N(103)-Ru(1)	114.7(5)
N(103)-Ru(1)-N(101)	90.5(2)	C(120)-N(104)-C(116)	117.8(7)
N(102)-Ru(1)-N(106)	95.9(2)	C(120)-N(104)-Ru(1)	126.8(5)

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	bond angle (°)		bond angle (°)
C(116)-N(104)-Ru(1)	115.4(5)	N(103)-C(111)-C(112)	120.0(9)
C(121)-N(105)-C(125)	118.8(6)	N(103)-C(115)-C(114)	120.9(8)
C(121)-N(105)-Ru(1)	126.3(5)	N(103)-C(115)-C(116)	115.2(6)
C(125)-N(105)-Ru(1)	114.8(5)	N(104)-C(116)-C(117)	120.7(8)
C(130)-N(106)-C(126)	117.9(6)	N(104)-C(116)-C(115)	115.1(6)
C(130)-N(106)-Ru(1)	126.5(5)	N(104)-C(120)-C(119)	123.6(9)
C(126)-N(106)-Ru(1)	115.6(5)	N(105)-C(121)-C(122)	123.2(7)
N(101)-C(101)-C(102)	122.3(7)	N(105)-C(125)-C(124)	120.7(7)
N(101)-C(105)-C(104)	121.5(7)	N(105)-C(125)-C(126)	115.1(6)
N(101)-C(105)-C(106)	114.2(6)	N(106)-C(126)-C(127)	121.4(7)
N(102)-C(106)-C(107)	122.3(7)	N(106)-C(126)-C(125)	115.3(6)
N(102)-C(106)-C(105)	115.3(6)	N(106)-C(130)-C(129)	123.5(7)
N(102)-C(110)-C(109)	121.1(8)		

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**Figure S3.4** An ORTEP plot of the molecular tetrahedron Co-TAS, showing 30% probability displacement ellipsoids of non-hydrogen atoms.



**Table S3.5** Selective bond distance (Å) in Co–TAS.

	bond distance (Å)		bond distance (Å)
Co(1)-S(7)	2.154(2)	S(1)-C(101)	1.738(7)
Co(1)-S(2)	2.164(2)	S(2)-C(102)	1.762(7)
Co(1)-S(1)	2.1665(18)	S(3)-C(126)	1.762(5)
Co(1)-S(8)	2.1671(18)	S(4)-C(125)	1.757(6)
Co(2)-S(9)	2.1607(15)	S(5)-C(139)	1.760(5)
Co(2)-S(10)	2.1618(17)	S(6)-C(138)	1.757(5)
Co(2)-S(3)	2.1655(15)	S(7)-C(201)	1.755(7)
Co(2)-S(4)	2.1667(16)	S(8)-C(202)	1.751(8)
Co(3)-S(12)	2.1662(15)	S(9)-C(226)	1.755(6)
Co(3)-S(11)	2.1663(15)	S(10)-C(225)	1.756(6)
Co(3)-S(5)	2.1692(14)	S(11)-C(239)	1.754(5)
Co(3)-S(6)	2.1694(15)	S(12)-C(238)	1.756(6)

**Table S3.6** Selective bond angle (°) in Co–TAS.

	bond angle (°)		bond angle (°)
S(7)-Co(1)-S(2)	177.01(7)	C(139)-S(5)-Co(3)	104.97(16)
S(7)-Co(1)-S(1)	86.34(7)	C(138)-S(6)-Co(3)	105.62(17)
S(2)-Co(1)-S(1)	91.76(8)	C(201)-S(7)-Co(1)	105.1(2)
S(7)-Co(1)-S(8)	91.83(8)	C(202)-S(8)-Co(1)	104.9(2)
S(2)-Co(1)-S(8)	90.05(7)	C(226)-S(9)-Co(2)	105.36(19)
S(1)-Co(1)-S(8)	178.13(9)	C(225)-S(10)-Co(2)	104.7(2)
S(9)-Co(2)-S(10)	91.78(6)	C(239)-S(11)-Co(3)	105.47(19)
S(9)-Co(2)-S(3)	86.72(5)	C(238)-S(12)-Co(3)	105.08(18)
S(10)-Co(2)-S(3)	177.17(7)	C(102)-C(101)-S(1)	119.1(5)
S(9)-Co(2)-S(4)	177.36(7)	C(106)-C(101)-S(1)	121.8(5)
S(10)-Co(2)-S(4)	89.85(6)	C(103)-C(102)-S(2)	120.7(5)
S(3)-Co(2)-S(4)	91.73(6)	C(101)-C(102)-S(2)	119.2(5)
S(12)-Co(3)-S(11)	91.40(6)	C(124)-C(125)-S(4)	120.8(5)
S(12)-Co(3)-S(5)	178.90(6)	C(126)-C(125)-S(4)	119.1(4)
S(11)-Co(3)-S(5)	87.80(5)	C(121)-C(126)-S(3)	121.7(4)
S(12)-Co(3)-S(6)	89.45(6)	C(125)-C(126)-S(3)	118.8(4)
S(11)-Co(3)-S(6)	178.91(6)	C(137)-C(138)-S(6)	121.4(4)
S(5)-Co(3)-S(6)	91.34(5)	C(139)-C(138)-S(6)	118.4(4)
C(101)-S(1)-Co(1)	105.3(2)	C(138)-C(139)-S(5)	119.6(4)
C(102)-S(2)-Co(1)	104.5(2)	C(134)-C(139)-S(5)	121.2(4)
C(126)-S(3)-Co(2)	105.15(19)	C(202)-C(201)-S(7)	119.1(6)
C(125)-S(4)-Co(2)	105.13(18)	C(206)-C(201)-S(7)	121.0(5)

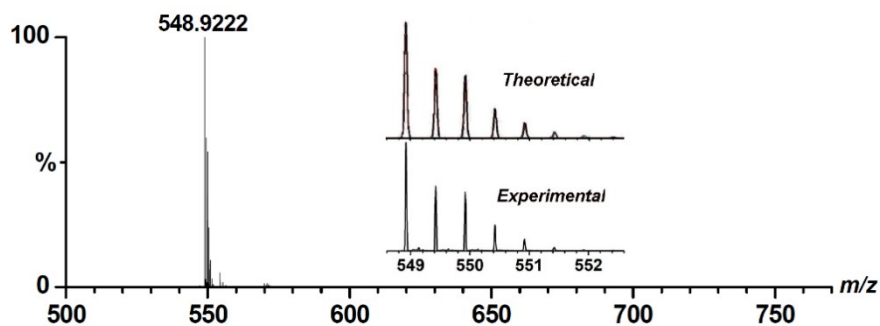
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	bond angle (°)		bond angle (°)
C(203)-C(202)-S(8)	120.8(5)	C(225)-C(226)-S(9)	118.4(4)
C(201)-C(202)-S(8)	119.0(5)	C(239)-C(238)-S(12)	119.3(4)
C(224)-C(225)-S(10)	121.3(5)	C(237)-C(238)-S(12)	121.0(4)
C(226)-C(225)-S(10)	119.8(4)	C(238)-C(239)-S(11)	118.6(4)
C(221)-C(226)-S(9)	121.3(4)	C(234)-C(239)-S(11)	122.0(4)

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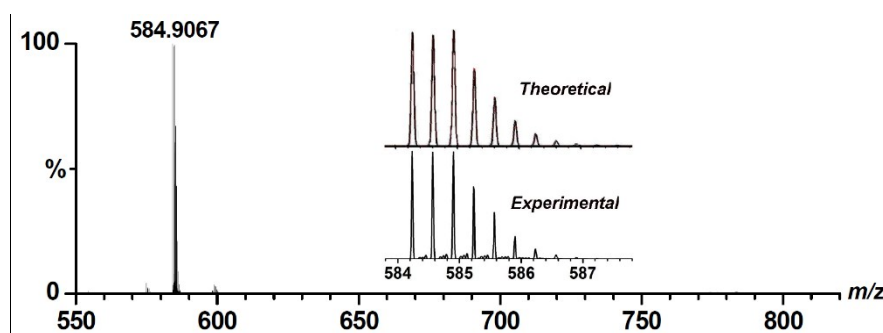
#### 4. ESI-MS Spectra.

**Figure S4.1.** ESI-MS spectrum of Co–NAS (0.10 mM) in DMF solution. The insert shows the measured and simulated isotopic patterns at  $m/z = 548.9222$ .



Peak	Value of m/z	Specie assigned
1	548.9222	$[\text{Co}_2(\text{NAS})_2]^{2-}$

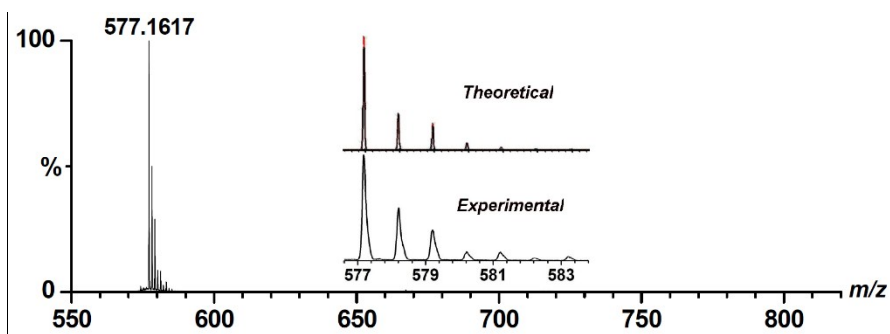
**Figure S4.2.** ESI-MS spectra of Co-TAS (0.10 mM) in DMF solution. The insert shows the measured and simulated isotopic patterns at  $m/z = 584.9067$ .



Peak	Value of $m/z$	Specie assigned
1	584.9067	$[\text{Co}_3(\text{TAS})_2]^{3-}$



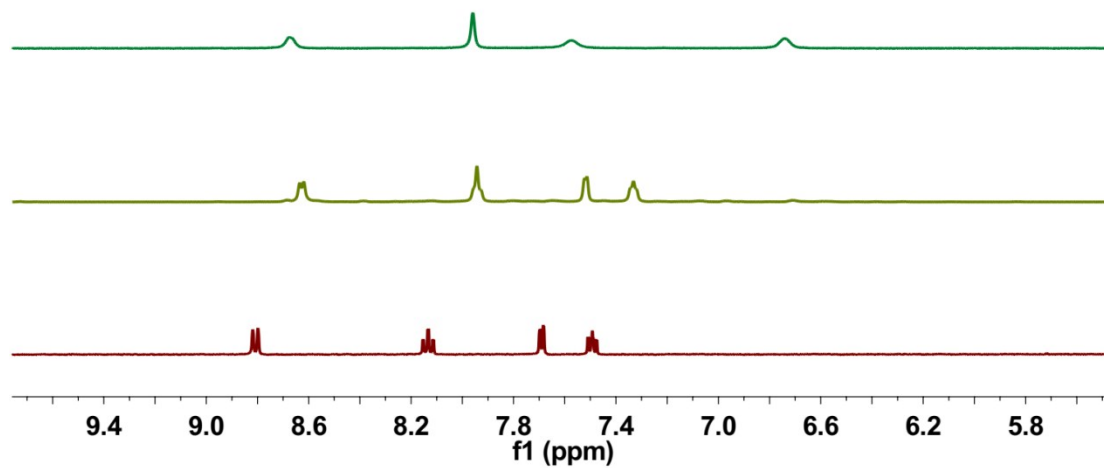
**Figure S4.3.** ESI-MS spectra of Co-BAS (0.10 mM) in DMF solution. The insert shows the measured and simulated isotopic patterns at  $m/z = 577.1617$ .



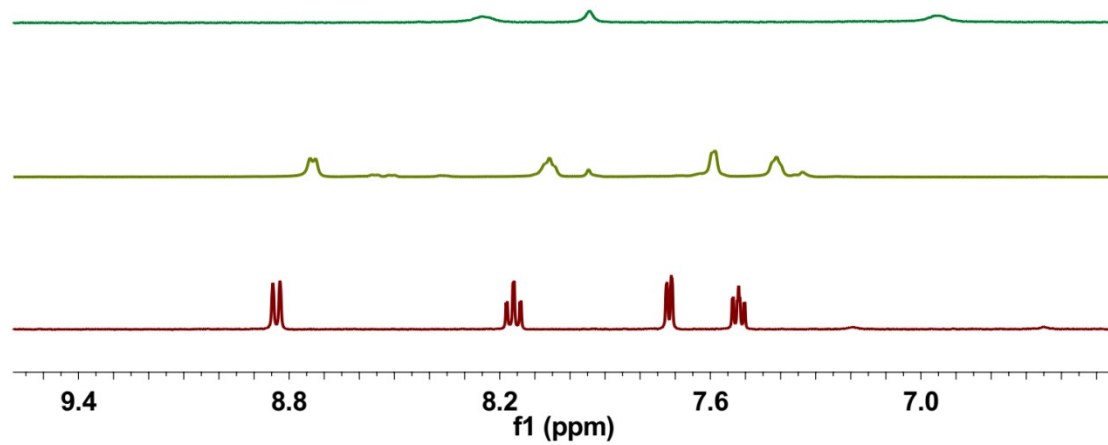
Peak	Value of $m/z$	Specie assigned
1	577.1617	$[\text{Co}(\text{BAS})_2]^-$

## 5. Data for Spectral Titrations.

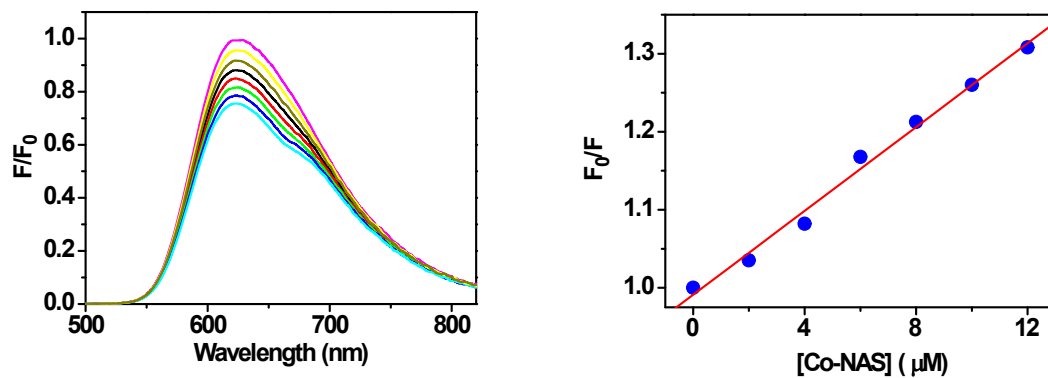
**Figure S5.1.**  $^1\text{H}$  NMR spectra (aromatic region) of free Co-NAS (0.1 mM) (a), free  $\text{Ru}(\text{bpy})_3^{2+}$  (0.1 mM) (c) and of  $\text{Ru}(\text{bpy})_3^{2+}$  (0.2 mM) and Co-NAS (0.1 mM) (b) in  $d_6$ -DMSO.



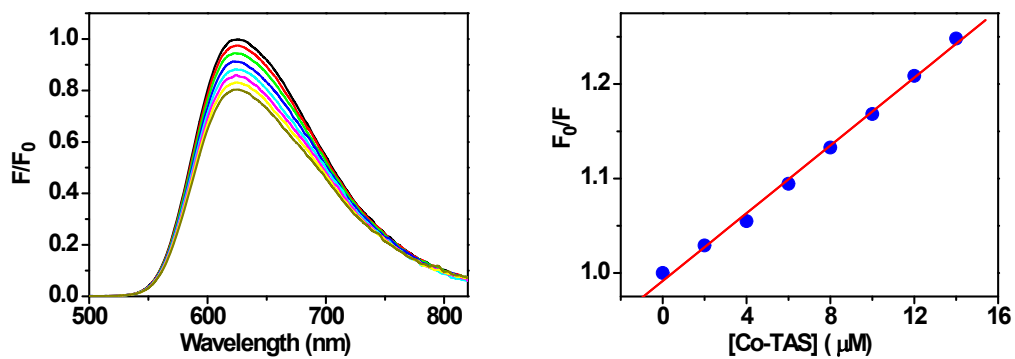
**Figure S5.2.**  $^1\text{H}$  NMR spectra (aromatic region) of free Co-TAS (0.1 mM) (a), free  $\text{Ru}(\text{bpy})_3^{2+}$  (0.1 mM) (c) and of  $\text{Ru}(\text{bpy})_3^{2+}$  (0.3 mM) and Co-TAS (0.1 mM) (b) in  $d_6$ -DMSO.



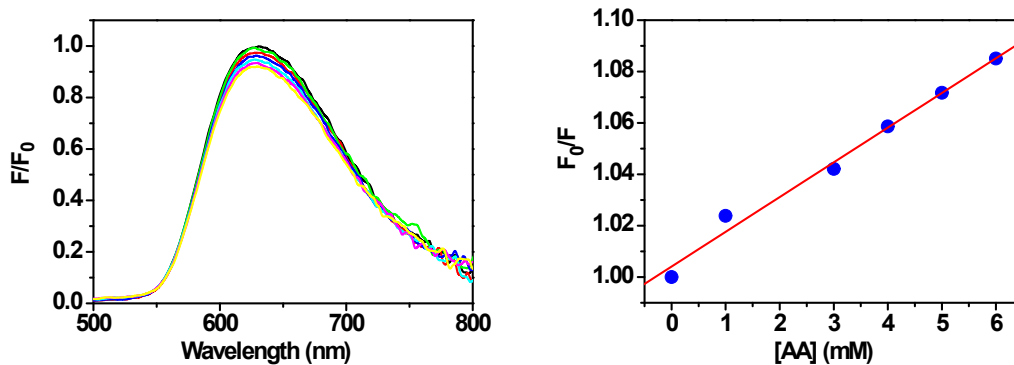
**Figure S5.3.** (Left) Family of luminescence spectra of  $\text{Ru}(\text{bpy})_3^{2+}$  ( $50 \mu\text{M}$ ) in  $\text{DMF}/\text{CH}_3\text{CN}/\text{H}_2\text{O} = 1:1:1$  solution at pH 4.15 upon the addition of Co-NAS. (Right) The Stern-Volmer Fitting of the titration curve. Fluorescence intensity was recorded at 618 nm, excited at 460 nm.



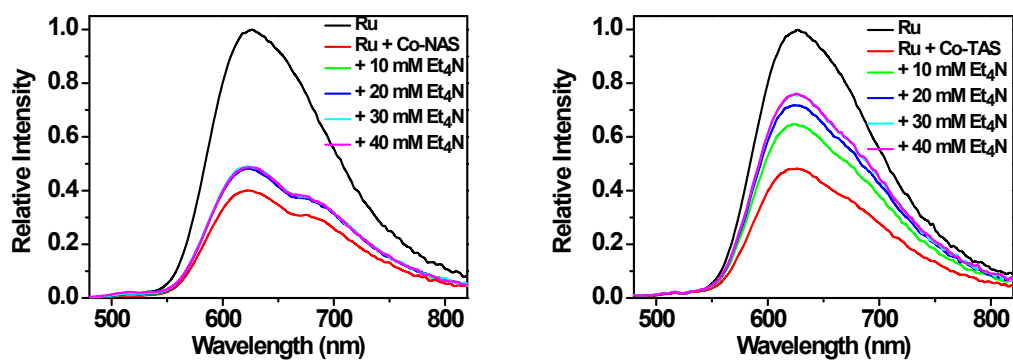
**Figure S5.4.** (Left) Family of luminescence spectra of  $\text{Ru}(\text{bpy})_3^{2+}$  ( $50 \mu\text{M}$ ) in  $\text{DMF}/\text{CH}_3\text{CN}/\text{H}_2\text{O} = 1:1:1$  solution at pH 4.15 upon the addition of Co-TAS. (Right) The Stern-Volmer Fitting of the titration curve. Fluorescence intensity was recorded at 618 nm, excited at 460 nm.



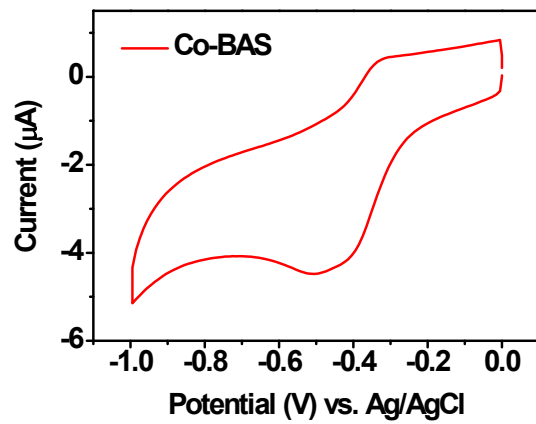
**Figure S5.5.** (Left) Family of luminescence spectra of  $\text{Ru}(\text{bpy})_3^{2+}$  ( $50 \mu\text{M}$ ) in  $\text{DMF}/\text{CH}_3\text{CN}/\text{H}_2\text{O} = 1:1:1$  solution at pH 4.15 upon the addition of **AA**. (Right) The Stern-Volmer Fitting of the titration curve. Fluorescence intensity was recorded at 618 nm, excited at 460 nm.



**Figure S5.6.** Family of luminescence spectra of 50  $\mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$  with 40.0  $\mu\text{M}$  Co-NAS (left)/Co-TAS (right) in  $\text{DMF}/\text{CH}_3\text{CN}/\text{H}_2\text{O} = 1:1:1$  solution at pH 4.15 upon the addition of  $\text{Et}_4\text{NCl}$ . Fluorescence was excited at 460 nm.

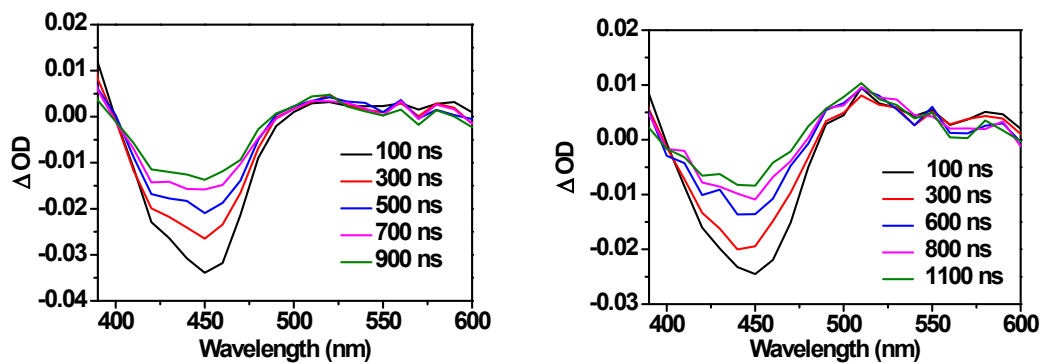


**Figure S5.7.** Cyclic voltammogram of 0.1 mM Co-BAS in DMF containing 0.10 M TBAPF<sub>6</sub>. Scan Rate: 100 mV/s.



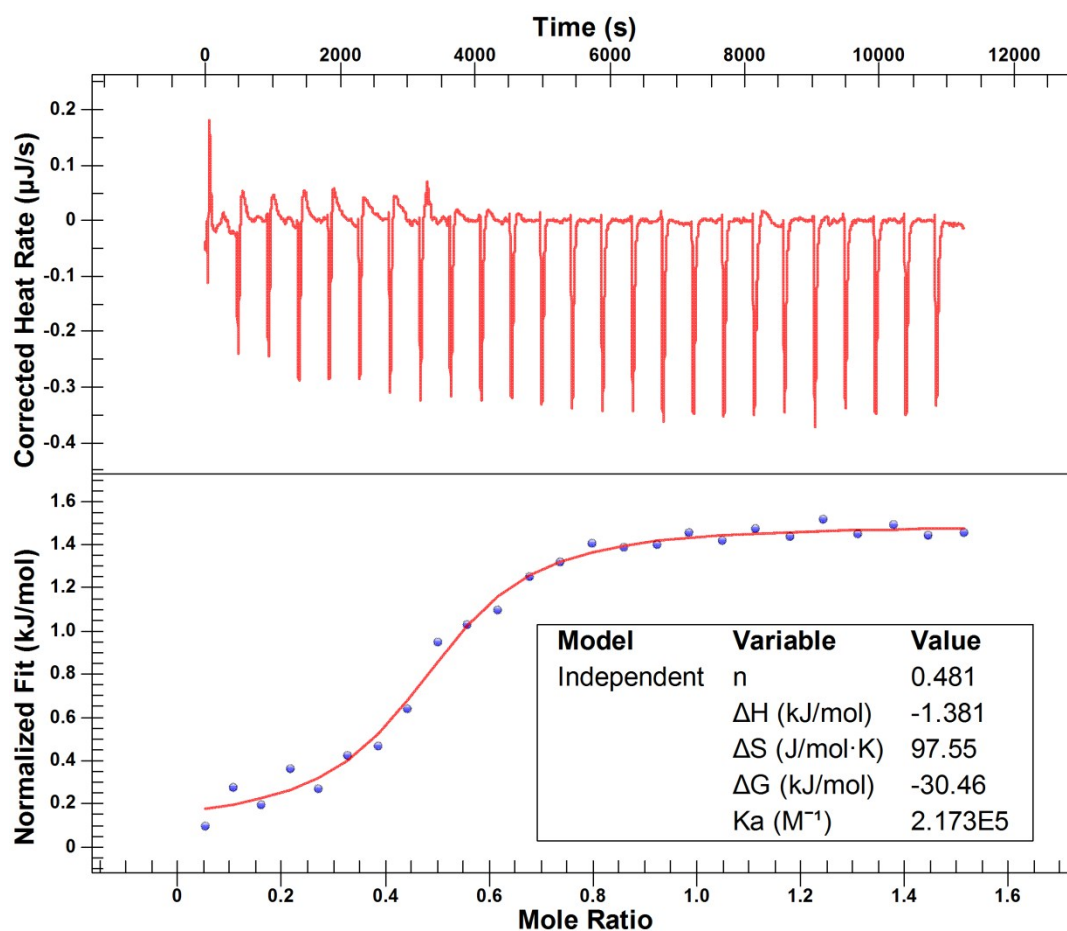


**Figure S5.8.** Transient absorption spectra of Ru(bpy)<sub>3</sub><sup>2+\*</sup> (Left) and in the presence of AA (0.1 M) and Co-NAS (40.0 μM) (Right) in DMF/CH<sub>3</sub>CN/H<sub>2</sub>O = 1:1:1 solution at 298 K after the laser flash under Ar.



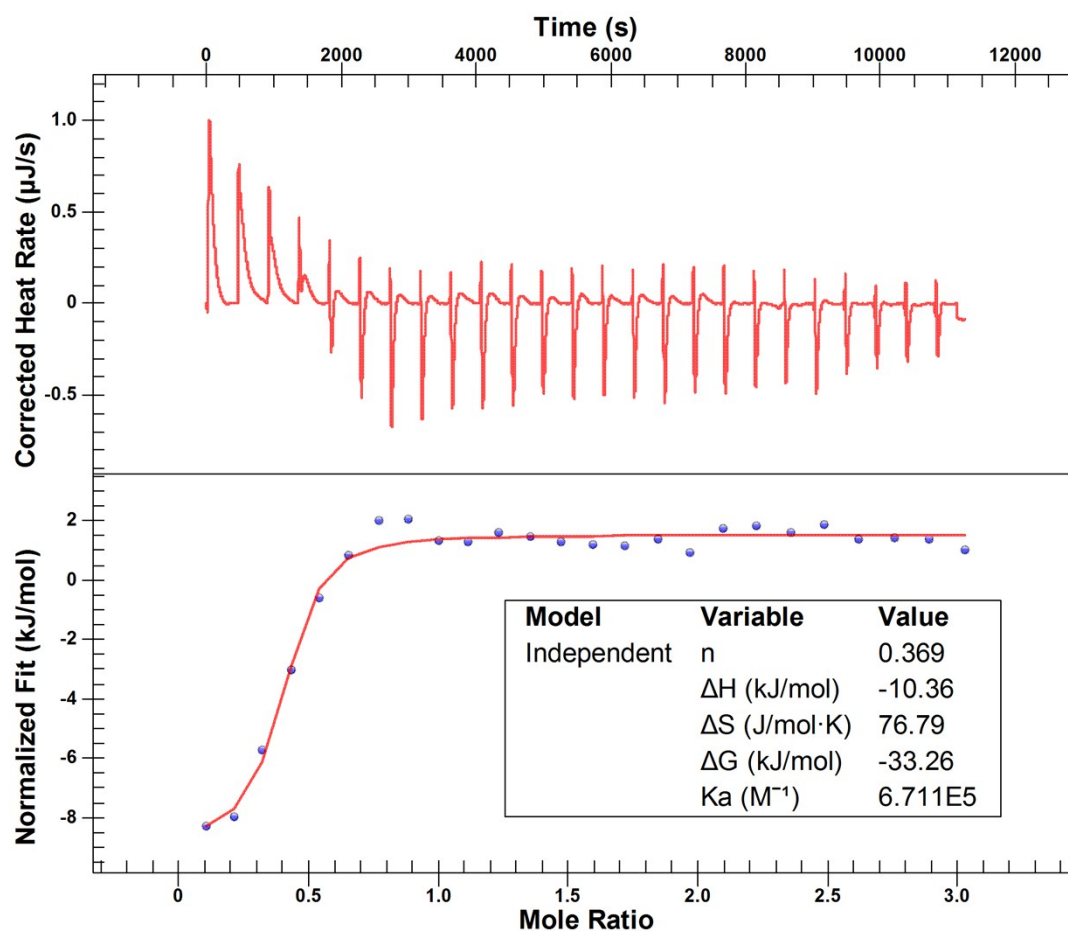
**Figure S5.9.** The ITC experiments were performed by an isothermal titration microcalorimeter under atmospheric pressure and at 25.0 °C, giving the association constants ( $K$ ) and the thermodynamic parameters. A solution of host in a 0.25 mL syringe was sequentially injected with stirring at 250 rpm into a solution of guest in the sample cell (1.30 mL volume). All the thermodynamic parameters reported in this work were obtained by using the ‘independent’ model.

Microcalorimetric titration of Co–NAS with  $\text{Ru}(\text{bpy})_3^{2+}$  in DMF solution at 298.15 K. (Top) Raw data for sequential 25 injections (10  $\mu\text{L}$  per injection) of Co–NAS solution (1.0 mM) injecting into  $\text{Ru}(\text{bpy})_3^{2+}$  solution (0.2 mM). (Bottom) Apparent reaction heat obtained from the integration of calorimetric traces.



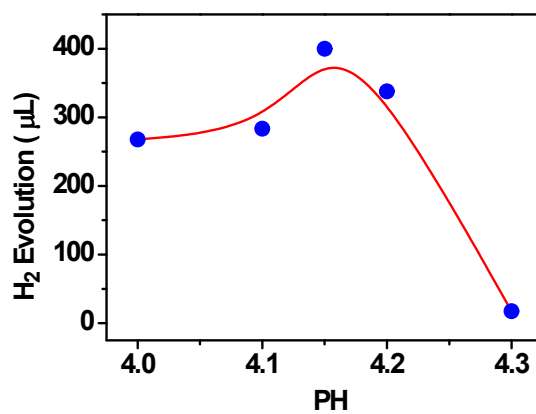
**Figure S5.10.** The ITC experiments were performed by an isothermal titration microcalorimeter under atmospheric pressure and at 25.0 °C, giving the association constants (K) and the thermodynamic parameters. A solution of host in a 0.25 mL syringe was sequentially injected with stirring at 250 rpm into a solution of guest in the sample cell (1.30 mL volume). All the thermodynamic parameters reported in this work were obtained by using the ‘independent’ model.

Microcalorimetric titration of Co-TAS with Ru(bpy)<sub>3</sub><sup>2+</sup> in DMF solution at 298.15 K. (Top) Raw data for sequential 25 injections (10 μL per injection) of Co-TAS solution (1.0 mM) injecting into Ru(bpy)<sub>3</sub><sup>2+</sup> solution (0.1 mM). (Bottom) Apparent reaction heat obtained from the integration of calorimetric traces.

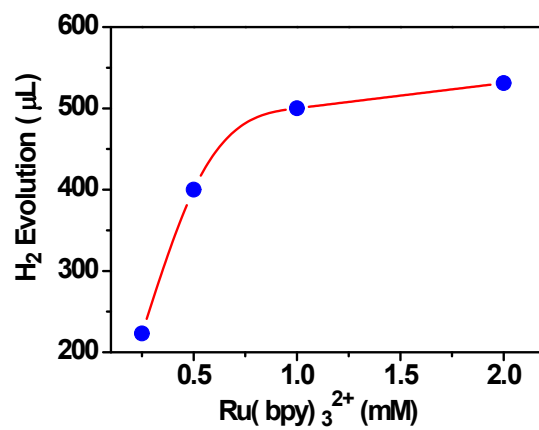


## 6. Data Relative to Hydrogen Production.

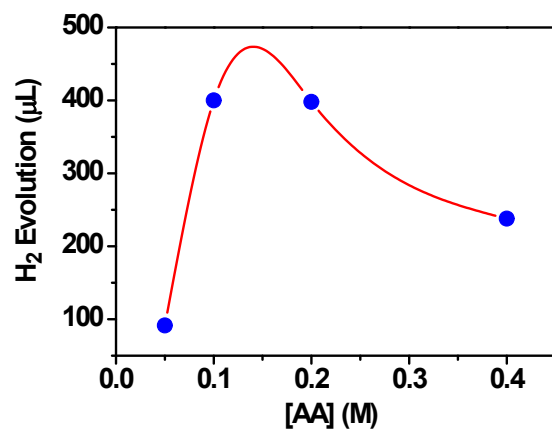
**Figure S6.1.** Photocatalytic hydrogen evolution in 1:1:1 DMF/CH<sub>3</sub>CN/H<sub>2</sub>O of the systems containing Co-NAS (40.0 μM), Ru(bpy)<sub>3</sub><sup>2+</sup> (0.5 mM) and AA (0.1 M) at different pH value.



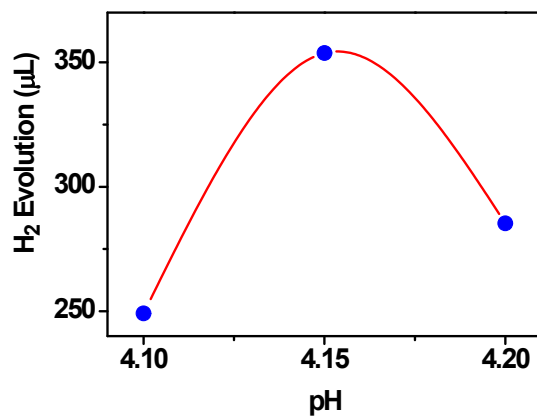
**Figure S6.2.** Photocatalytic hydrogen evolution in 1:1:1 DMF/CH<sub>3</sub>CN/H<sub>2</sub>O of the systems containing Co-NAS (40.0 μM), and AA (0.1 M) at pH 4.15 with various Ru(bpy)<sub>3</sub><sup>2+</sup> concentration.



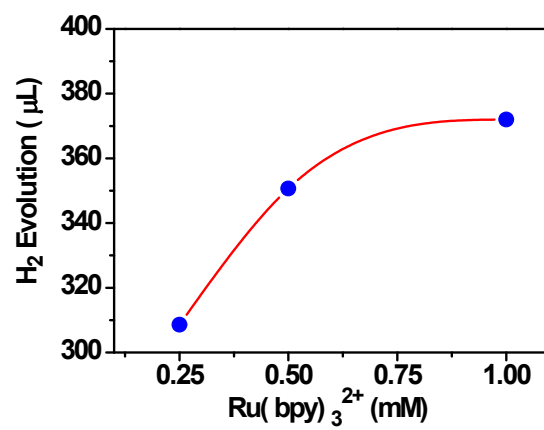
**Figure S6.3.** Photocatalytic hydrogen evolution in 1:1:1 DMF/CH<sub>3</sub>CN/H<sub>2</sub>O of the systems containing Co-NAS (40.0 μM), and Ru(bpy)<sub>3</sub><sup>2+</sup> (0.5 mM) at pH 4.15 with various AA concentration.



**Figure S6.4.** Photocatalytic hydrogen evolution in 1:1:1 DMF/CH<sub>3</sub>CN/H<sub>2</sub>O of the systems containing Co-TAS (40.0 μM), Ru(bpy)<sub>3</sub><sup>2+</sup> (0.5 mM) and AA (0.1 M) at different pH value.

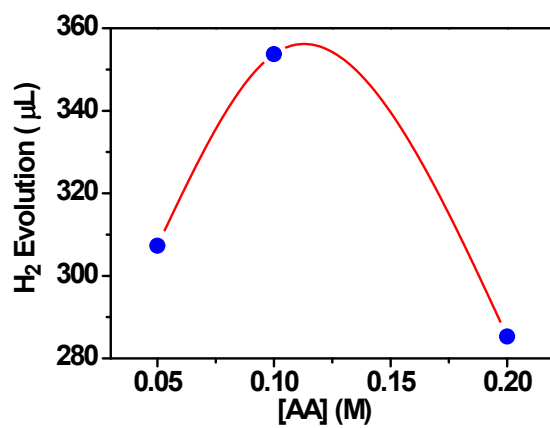


**Figure S6.5.** Photocatalytic hydrogen evolution in 1:1:1 DMF/CH<sub>3</sub>CN/H<sub>2</sub>O of the systems containing Co-TAS (40.0 μM), and AA (0.1 M) at pH 4.15 with various Ru(bpy)<sub>3</sub><sup>2+</sup> concentration.

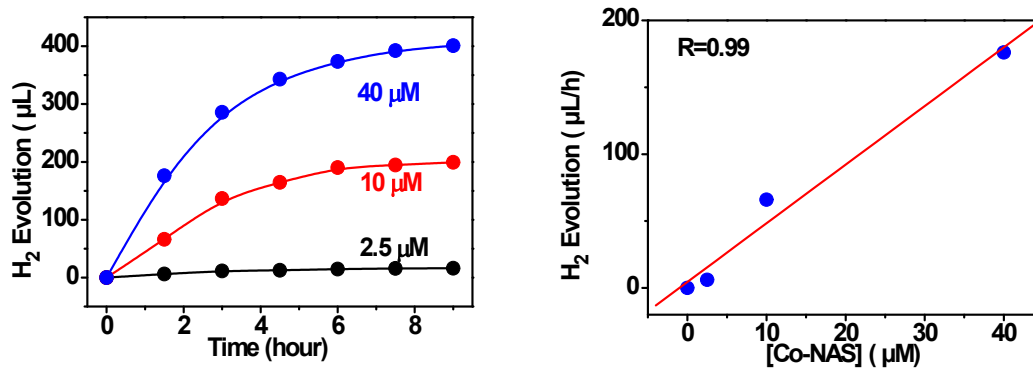




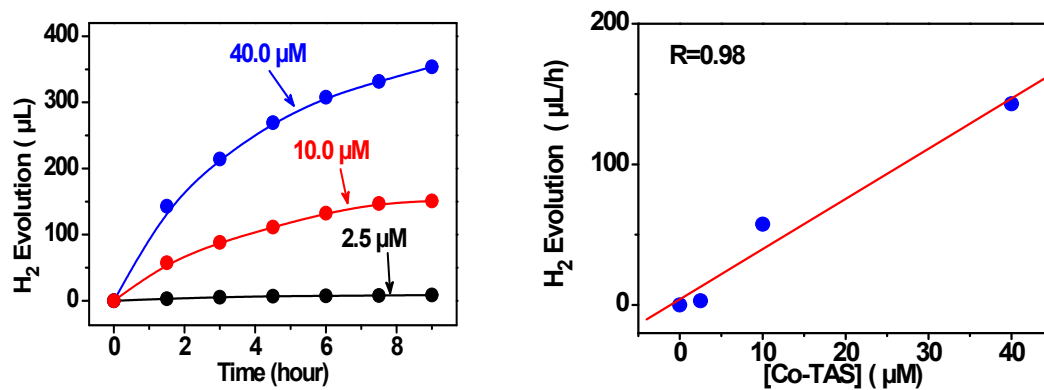
**Figure S6.6.** Photocatalytic hydrogen evolution in 1:1:1 DMF/CH<sub>3</sub>CN/H<sub>2</sub>O of the systems containing Co-TAS (40.0 μM), and Ru(bpy)<sub>3</sub><sup>2+</sup> (0.5 mM) at pH 4.15 with various AA concentration.



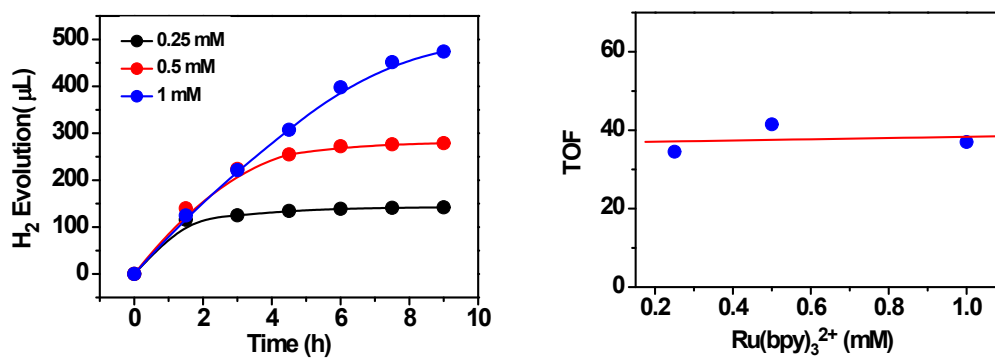
**Figure S6.7.** (Left) Rate of hydrogen evolution in 1:1:1 DMF/CH<sub>3</sub>CN/H<sub>2</sub>O at pH 4.15 with 0.5 mM Ru(bpy)<sub>3</sub><sup>2+</sup>, 0.1 M AA and various Co-NAS concentration. (Right) The initial rate of H<sub>2</sub> evolution vs. concentration of Co-NAS.



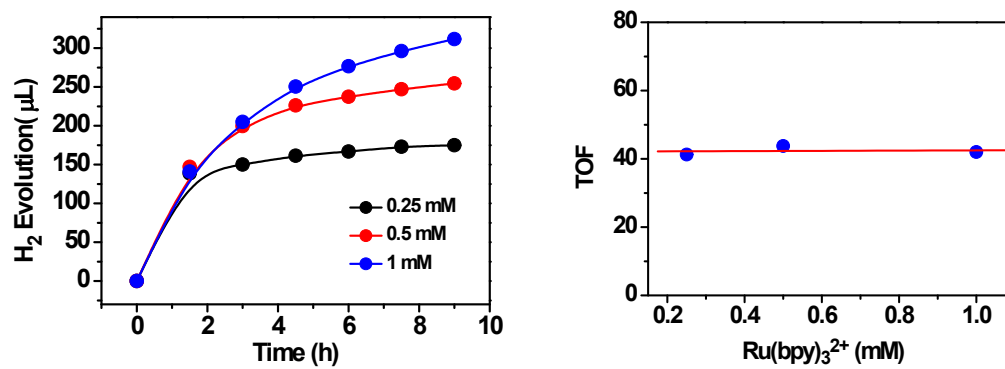
**Figure S6.8.** (Left) Rate of hydrogen evolution in 1:1:1 DMF/CH<sub>3</sub>CN/H<sub>2</sub>O at pH 4.15 with 0.5 mM Ru(bpy)<sub>3</sub><sup>2+</sup>, 0.1 M AA and various Co-TAS concentration. (Right) The initial rate of H<sub>2</sub> evolution vs. concentration of Co-TAS.



**Figure S6.9.** (Left) Hydrogen evolution in 1:1:1 DMF/CH<sub>3</sub>CN/H<sub>2</sub>O at pH 4.15 with various Ru(bpy)<sub>3</sub><sup>2+</sup> concentration, 0.1 M AA and 2×10<sup>-5</sup> M Co-NAS. (Right) The initial TOF of H<sub>2</sub> evolution vs. concentration of Ru(bpy)<sub>3</sub><sup>2+</sup>.



**Figure S6.10.** (Left) Hydrogen evolution in 1:1:1 DMF/CH<sub>3</sub>CN/H<sub>2</sub>O at pH 4.15 with various Ru(bpy)<sub>3</sub><sup>2+</sup> concentration, 0.1 M AA and 2×10<sup>-5</sup> M Co-TAS. (Right) The initial TOF of H<sub>2</sub> evolution vs. concentration of Ru(bpy)<sub>3</sub><sup>2+</sup>.



## 7. References.

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