# 修饰 NADH 模拟物的金属-有机三元环光催化制氢

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**摘要:**将含有不同还原型烟酰烟腺嘌呤二核苷酸(NADH)活性中心模拟物的有机配体H<sub>2</sub>L<sup>1</sup>和H<sub>2</sub>L<sup>2</sup>与钴离子配位自组装获得2 例具有氧化还原活性且带有正电荷的金属-有机大环Co-L<sup>1</sup>和Co-L<sup>2</sup>。选择阴离子型钌基光敏剂[Ru(dcbpy)<sub>3</sub>]<sup>+</sup>(dcbpy=2,2'-联吡 啶-4,4'-二羧酸)作为光敏中心,金属-有机大环结构作为质子还原催化剂,通过静电作用力将光敏中心封装在其空腔内部以加 速光诱导电子转移(PET)过程,构建了人工光合成体系并应用于光解水制氢研究。相比于未修饰NADH模拟物的金属-有机大 环Co-L<sup>3</sup>以及未修饰NADH模拟物但配位环境相同的单核催化剂Co-L<sup>4</sup>,由Co-L<sup>1</sup>和Co-L<sup>2</sup>构建的金属-有机大环主客体超分子 体系的光催化产氢效率分别提高1.6和6倍,可能是由于NADH活性中心模拟物的引入以及主客体超分子体系的形成有利于 光敏中心与催化中心之间的光致电子转移过程。

关键词:金属-有机大环; NADH模拟物; 主-客体复合物; 光诱导电子转移; 光催化制氢
中图分类号: 0614.81<sup>+</sup>2
文献标识码: A
文章编号: 1001-4861(2021)05-0769-09
DOI: 10.11862/CJIC.2021.092

# Metal-Organic Triangles with NADH Mimics for Photocatalytic Hydrogen Production

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**Abstract:** By incorporating two different reduced nicotinamide adenine dinucleotide (NADH) mimics within the ligand backbone, two positively charged cobalt-based metal-organic triangular hosts Co-L<sup>1</sup> and Co-L<sup>2</sup> (H<sub>2</sub>L<sup>1</sup>=5'-(benzo [d]thiazol-2-yl)- $N'^4$ ,  $N'''''^4$ -bis((E)-pyridin-2-ylmethylene)-[1,1':3',1"-terphenyl]-4,4"-dicarbohydrazide, H<sub>2</sub>L<sup>2</sup>=5'-(benzo[d]imidazol-2-yl)- $N'^4$ ,  $N'''''^4$ -bis((E)-pyridin-2-ylmethylene)-[1,1':3',1"-terphenyl]-4,4"-dicarbohydrazide) have been prepared in high yield and characterized as a redox vehicle for the construction of an artificial photosynthesis (AP) system. By taking advantage of electrostatic interaction to facilitate the formation of host-guest complexes, anionic ruthenium-based photosensitizer [Ru(dcbpy)<sub>3</sub>]<sup>4-</sup> (dcbpy=2,2'-bipyridine-4,4'-dicarboxylic acid) was encapsulated into the suitable cavity of hosts to improve photoinduced electron transfer (PET) processes and to promote photocatalytic hydrogen production. Compared with metal-organic triangular Co-L<sup>3</sup> without NADH mimics (H<sub>2</sub>L<sup>3</sup>=5'-methyl- $N'^4$ ,  $N'''''^4$ -bis((E)-pyridin-2-ylmethylene)-[1,1':3',1"-terphenyl]-4,4"-dicarbohydrazide) and mononuclear catalyst Co-L<sup>4</sup> (HL<sup>4</sup>=(E)-N'-(pyridin-2-ylmethylene)-[1,1':3',1"-terphenyl]-4,4"-dicarbohydrazide) and mononuclear catalyst Co-L<sup>4</sup> (HL<sup>4</sup>=(E)-N'-(pyridin-2-ylmethylene)benzohydrazide) containing the same coordination environment and without NADH mimics, photocatalytic hydrogen production efficiency of the host-guest supramolecular photosynthetic systems could increase 1.6 and 6 times, respectively. The higher catalytic activity is attributed to the formation of host-guest complex between catalyst Co-L<sup>1</sup> and Co-L<sup>2</sup> and photosensitizer [Ru(dcbpy)<sub>3</sub>]<sup>4-</sup> and the introduction of NADH mimics benefiting the PET process between the catalyst and photosensitizer.

Keywords: metal-organic macrocycle; NADH mimic; host-guest complex; photoinduced electron transfer;

photocatalytic hydrogen production

收稿日期:2020-10-28。收修改稿日期:2020-12-28。

国家自然科学基金(No.21890381,21531001)和大连理工大学基本科研业务费(No.DUT20TD101,DUT19ZD102)资助。 \*通信联系人。E-mail:zhaol@dlut.edu.cn

# **0** Introduction

Hydrogen with the high energy density and the minimal environmental pollution was deemed to be ideal candidate for the green energy sources<sup>[1]</sup>. Photocatalytic hydrogen production using light as a clean energy source is one of the most promising processes among various hydrogen production strategies<sup>[2-9]</sup>. To improve the light conversion efficiency is the challenge of photocatalytic hydrogen production, which is usually determined by the photoinduced electron transfer (PET) process and the charge - hole separation state<sup>[10]</sup>. Metalorganic molecular hosts, constructed by the selfassembly of metal ions and organic functional ligands, are the typical model for facilitating the PET process. They have the certain cavity and the specific shape<sup>[11]</sup>, and can encapsulate guest molecules to enforce the proximity between host and guest by electrostatic interaction,  $\pi$  -  $\pi$  interaction and hydrogen bonding, etc.<sup>[12]</sup>, resulting in the PET via a pseudo-intramolecular pathway, where the unwanted electron-transfer processes can be potentially avoided<sup>[13]</sup>. Host-guest supramolecular catalytic synthetic methods that are inspired by natural enzyme prototypes which react under an ambient atmosphere and use benign solvents and clean energy often serve as an ideal model of enzymes in synthetic chemistry<sup>[14-15]</sup>. Therefore, host-guest supramolecular catalytic systems are considered as a strategy for effectively improving the PET process, which can promote the efficiency of photocatalytic hydrogen production<sup>[15-21]</sup>.

On the other hand, most enzymatic redox reaction processes often require the assistance of coenzymes, such as reduced nicotinamide adenine dinucleotide (NADH), which plays an important role in the reduction-oxidation metabolism for the electron transfer<sup>[22-24]</sup>. Therefore, the easy preparation NADH mimics as the proton and electron carriers are widely applied to a variety of catalytic chemical transformations<sup>[25]</sup>. Among them, benzothiazole and benzoimidazole are described as two important models for the NADH mimics and exhibit potentially important electron donor ability<sup>[26-28]</sup>. We envisioned that the incorporation of the benzothiazole or benzoimidazole groups into the metalorganic molecular hosts as the proton and electron carriers should be a powerful approach to mimic the activity of these enzymes for further promoting PET process.

The host-guest supramolecular systems constructed by metal-organic macrocycles combined opposite charged photosensitizer have been applied in the field of hydrogen production and obtained satisfactory achievement<sup>[16,18]</sup>. To the best of our knowledge, few metal-organic macrocycles with NADH mimics for photocatalytic hydrogen production have been reported to date<sup>[29-30]</sup>. In this work, we successfully prepared two positively charged metal-organic hosts containing NADH mimics (Scheme 1), which have the PET via pseudo-intramolecular pathway by proximity between the redox site and anionic photosensitizer [Ru(dcbpy)<sub>3</sub>]<sup>4–</sup> (dcbpy=2, 2'-bipyridine-4, 4'-dicarboxylic acid) encapsulated in the pocket, and additionally make NADH mimics as the proton and electron carriers that could



Scheme 1 Structures of ligands  $H_2L^1$ ,  $H_2L^2$  and  $H_2L^3$ 

further accelerate the electron transfer to improve hydrogen production efficiency (Scheme 2)<sup>[30]</sup>. In addition, ONN tridentate coordinated units not only were efficient building blocks that could be used to fix the orientation of ligands coordinated to a transition-metal center at an angle of exactly 90° to endow the high stability of the metal-organic hosts<sup>[31-32]</sup>, but also could insure sufficiently redox potential for proton reduction<sup>[30,33]</sup>. Therefore, they were expected to be good candidates for photocatalytic hydrogen production.



Scheme 2 Procedure for preparation of molecular triangular hosts and construction of artificial host-guest supramolecular systems for photocatalytic hydrogen production

## **1** Experimental

#### 1.1 Materials and instruments

All the chemicals and solvents were of reagent grade quality obtained from commercial sources and used without further purification. The elemental analyses of C, H and N were performed on a Vario EL III elemental analyzer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were collected on a Bruker 400 M spectrometer. ESI mass spectra were obtained from an HPLC-Q-Tof mass spectrometer using acetonitrile as the mobile phase. UV -Vis spectra were collected on an HP 8453 spectrometer. The solution fluorescent spectra were measured on Edinburgh FS-920.

Electrochemical measurements were performed with a ZAHNER ZENNIUM electrochemical workstation with a conventional three-electrode system with a custom-designed 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. Cyclic voltammograms (CVs) with the solution concentrations were 0.1 mmol·L<sup>-1</sup> for the cobalt-based compounds and 0.1 mol·L<sup>-1</sup> (<sup>a</sup>Bu<sub>4</sub>N)PF<sub>6</sub> for the supporting electrolyte. Electrodes were polished on a MD-Nap polishing pad. The measurements were performed at room temperature after the system had been degassed with argon.

In a typical experiment, photoinduced hydrogen evolution was made in a 20.0 mL flask. Varying amounts of the hosts, [Ru(dcbpy)<sub>3</sub>]<sup>4-</sup> and ascorbic acid (H<sub>2</sub>A) in CH<sub>3</sub>CN/H<sub>2</sub>O (1:1, V/V) were added to obtain a total volume of 5.0 mL. The flask was sealed with a septum, degassed by bubbling argon for 15 minutes under atmospheric pressure at room temperature. The pH of this solution was adjusted to a specific pH value by adding H<sub>2</sub>SO<sub>4</sub> or NaOH and measured with a pH meter. After that, the samples were irradiated by a 500 W Xenon Lamp, the reaction temperature was 298 K by using a water filter to absorb heat. The generated photoproduct of H<sub>2</sub> was characterized using a GC 7890T gas chromatograph equipped with a 0.5 nm molecular sieve column (0.6 m×3.0 mm) and a thermal conductivity detector; argon was used as the 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.

#### **1.2** Syntheses of $H_2L^1$ , $H_2L^2$ and $H_2L^3$

#### 1.2.1 Synthesis of $H_2L^1$

5'-(benzo[d]thiazol-2-yl)-[1,1':3',1"-terphenyl]-4, 4"-dicarbohydrazide (0.48 g, 1.0 mmol) was added to an ethanol solution (25.0 mL) containing 2-pyridylaldehyde (0.24 g, 2.2 mmol). After 5 drops of acetic acid was added, the mixture was heated at 90 °C under magnetic stirring for 12 h. The white solid was collected by filtration, washed with ethanol and dried in vacuum. Yield: 91%. Anal. Calcd. for C<sub>39</sub>H<sub>27</sub>N<sub>7</sub>O<sub>2</sub>S(%): H, 4.14; C, 71.22; N, 14.91. Found(%): H, 4.16; C, 71.34; N, 14.82. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 12.18 (s, 2H), 8.64 (d, 2H), 8.55 (s, 2H), 8.43 (d, 2H), 8.29 (s, 1H), 8.22 (d, 2H), 8.19~8.08 (m, 8H), 8.02 (d, 2H), 7.89 (t, 2H), 7.61 (t, 1H), 7.52 (t, 1H), 7.44 (t, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>): δ 167.24, 163.38, 153.97, 153.77, 150.05, 148.66, 142.84, 141.67, 137.40, 135.22, 134.98, 133.11, 129.04, 127.89, 127.33, 126.32, 125.68, 124.93, 123.59, 122.95, 120.43. ESI-MS Calcd. for  $C_{39}H_{27}N_7O_2S$ : 657.19, Found m/z: 658.20 [M+H]<sup>+</sup>, 680.50 [M+Na]<sup>+</sup>.

#### 1.2.2 Synthesis of $H_2L^2$

The synthesis was same as that of  $H_2L^1$  except that 5' - (1H-benzo[d]imidazol-2-yl) - [1,1':3',1''-terphenyl]-4,4"-dicarbohydrazide (0.46 g, 1.0 mmol) was used to replace 5'-(benzo[d]thiazol-2-yl)-[1,1':3',1"-terphenyl]-4,4"-dicarbohydrazide. Yield: 91%. Anal. Calcd. for C<sub>39</sub>H<sub>28</sub>N<sub>8</sub>O<sub>2</sub>(%): H, 4.41; C, 73.11; N, 17.49. Found (%): H, 4.43; C, 73.01; N, 17.44. <sup>1</sup>H NMR (400 MHz, DMSO - d<sub>6</sub>): δ 14.71 (s, 1H), 13.19 (s, 1H), 12.19 (s, 1H), 8.96 (d, 1H), 8.65 (d, 3H), 8.56 (s, 1H), 8.32~ 8.06 (m, 10H), 8.03 (d, 1H), 7.97~7.83 (m, 2H), 7.83~ 7.69 (m, 2H), 7.70~7.57 (m, 2H), 7.51~7.39 (m, 1H), 7.34~7.20 (m, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>):  $\delta$ 163.47, 153.78, 152.45, 151.25, 150.01, 148.79, 148.67, 144.26, 143.20, 141.11, 139.17, 137.34, 135.52, 132.95, 132.70, 132.15, 129.01, 128.47, 128.19, 127.66, 127.12, 125.28, 125.08, 124.89, 123.35, 122.39, 120.44, 119.51, 111.95. ESI-MS Calcd. for C<sub>39</sub>H<sub>28</sub>N<sub>8</sub>O<sub>2</sub>: 640.23, Found *m/z*: 641.20 [M+H]<sup>+</sup>, 663.30 [M+Na]<sup>+</sup>.

#### 1.2.3 Synthesis of $H_2L^3$

The synthesis was same as that of  $H_2L^1$  except that 5'-methyl-[1,1':3',1"-terphenyl]-4,4"-dicarbohydrazide (0.36 g, 1.0 mmol) was used to replace 5'-(benzo[d] thiazol-2-yl)-[1,1':3',1"-terphenyl]-4,4"-dicarbohydrazide. Yield: 93%. Anal. Calcd. for  $C_{33}H_{26}N_6O_2(\%)$ : H, 4.87; C, 73.59; N, 15.60. Found(%): H, 4.90; C, 73.44; N, 15.51. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  12.13 (s, 2H), 8.64 (d, 2H), 8.53 (s, 2H), 8.10~7.88 (m, 13H), 7.64 (s, 2H), 7.44 (t, 2H), 2.51 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO -d<sub>6</sub>):  $\delta$  163.50, 153.79, 150.00, 148.55, 143.91, 140.34, 139.65, 137.33, 132.47, 128.87, 127.95, 127.50, 124.87, 123.31, 120.41, 21.62. ESI - MS Calcd. for C<sub>33</sub>H<sub>26</sub>N<sub>6</sub>O<sub>2</sub>: 538.21, Found *m/z*: 539.30 [M+H]<sup>+</sup>, 561.30 [M+Na]<sup>+</sup>. 1.3 Syntheses of Co-L<sup>1</sup>, Co-L<sup>2</sup>, Co-L<sup>3</sup> and Co-L<sup>4</sup>

Co-L<sup>1</sup>: H<sub>2</sub>L<sup>1</sup> (65.70 mg, 0.1 mmol) and Co(NO<sub>3</sub>)<sub>2</sub>· 6H<sub>2</sub>O (29.10 mg, 0.1 mmol) were dissolved in CHCl<sub>3</sub>/ CH<sub>3</sub>OH (20.0 mL, 1: 1, V/V) to give a brown solution. After addition of NaClO<sub>4</sub> (36.70 mg, 0.3 mmol), brown precipitates were isolated and dried under vacuum. Yield: 50%. Anal. Calcd. for Co<sub>3</sub>C<sub>117</sub>H<sub>81</sub>N<sub>21</sub>O<sub>30</sub>S<sub>3</sub>Cl<sub>6</sub>(%): H, 2.97; C, 51.16; N, 10.71. Found(%): H, 2.98; C,

Co- $L^2$ : The synthesis was same as that of Co- $L^1$  except that  $H_2L^2$  (64.10 mg, 0.1 mmol) was used to replace  $H_2L^1$ . Yield: 53%. Anal. Calcd. for Co<sub>3</sub>C<sub>117</sub>H<sub>84</sub>N<sub>24</sub>O<sub>30</sub>Cl<sub>6</sub>(%): H, 3.14; C, 52.13; N, 12.47. Found(%): H, 3.16; C, 52.09; N, 12.42. ESI-HRMS *m/z*: [Co<sub>3</sub>( $L^2$ )<sub>3</sub>]<sup>3+</sup>, 697.485 5.

51.05; N, 10.66. ESI-HRMS m/z:  $[Co_3(L^1)_3]^{3+}$ , 714.450 7.

Co-L<sup>3</sup>: The synthesis was same as that of Co-L<sup>1</sup> except that H<sub>2</sub>L<sup>3</sup> (53.90 mg, 0.1 mmol) was used to replace H<sub>2</sub>L<sup>1</sup>. Yield: 60%. Anal. Calcd. for Co<sub>3</sub>C<sub>99</sub>H<sub>78</sub>N<sub>18</sub>O<sub>30</sub>Cl<sub>6</sub>(%): H, 3.29; C, 49.77; N, 10.55. Found(%): H, 3.30; C, 49.96; N, 10.52. ESI-HRMS *m/z*:  $[Co_3(L^3)_3]^{2+}$ , 893.195 9;  $[Co_3(L^3)_3 \cdot ClO_4^{--}]^{2+}$ , 942.670 4.

Co-L<sup>4</sup> (HL<sup>4</sup>=N'-(pyridin-2-ylmethylene)benzohydrazide): Benzohydrazide (136.20 mg, 1.0 mmol), 2 pyridylaldehyde (117.80 mg, 1.1 mmol) and Co(ClO<sub>4</sub>) ·  $6H_2O$  (182.90 mg, 0.5 mmol) were mixed in ethanol (25.0 mL) and heated to 90 °C for 12 hours. After the reaction mixture was allowed to cool down to 25 °C, Co-L<sup>4</sup> was precipitated as a brown solid, which was collected by filtration, washed with ethanol and dried in vacuum. Yield: 60%. Anal. Calcd. for CoC<sub>26</sub>H<sub>22</sub>N<sub>6</sub>O<sub>10</sub>Cl<sub>2</sub> (%): H, 3.13; C, 44.09; N, 11.86. Found(%): H, 3.15; C, 43.98; N, 11.78. ESI-HRMS m/z: [Co(L<sup>4</sup>)<sub>2</sub>]<sup>+</sup>, 507.107 2.

#### 2 Results and discussion

# 2.1 ESI-HRMS spectra of metal-organic triangles ESI-HRMS spectra analysis exhibited the expect-

ed isotopic patterns of  $[Co_3(\mathbf{L}^1)_3]^{3+}$  species at m/z= 714.450 7 for Co- $\mathbf{L}^1$  (Fig. 1a), of  $[Co_3(\mathbf{L}^2)_3]^{3+}$  species at m/z=697.485 5 for Co- $\mathbf{L}^2$  (Fig. 1b), of  $[Co_3(\mathbf{L}^3)_3]^{2+}$  and  $[Co_3(\mathbf{L}^3)_3 \cdot ClO_4^{--}]^{2+}$  species at m/z=893.195 9 and

942.670 4 for Co- $L^3$  (Fig. 1c), respectively, reflecting the formation of three isostructural cobalt-based  $M_3L_3$ triangle species and the substantial stability of molecular triangles Co- $L^1$ , Co- $L^2$  and Co- $L^3$  in solution<sup>[34-35]</sup>.



Inset: measured and simulated isotopic patterns at m/z=714.450 7, 697.485 5, 893.195 9 and 942.670 4, respectively Fig.1 ESI-HRMS spectra of triangles Co-L<sup>1</sup> (0.5 mmol·L<sup>-1</sup>), Co-L<sup>2</sup> (0.5 mmol·L<sup>-1</sup>) and Co-L<sup>3</sup> (0.5 mmol·L<sup>-1</sup>)

in DMF/CH<sub>3</sub>CN (1:1, V/V)

#### 2.2 CV of metal-organic triangles

CV of Co-L<sup>1</sup> (0.1 mmol·L<sup>-1</sup> recorded in DMF showed the coupled Co<sup>II</sup>/Co<sup>1</sup> and Co<sup>III</sup>/Co<sup>II</sup> reduction processes at approximately -1.21 and -0.82 V (vs Ag/ AgCl), respectively (Fig.2)<sup>[36]</sup>, which is similar to the potential of reported cobalt-based cage<sup>[13]</sup>, while the potentials of Co-L<sup>2</sup> and Co-L<sup>3</sup> are similar to Co-L<sup>1</sup> (Fig.2). The Co<sup>II</sup>/Co<sup>I</sup> potential falls well within the range of that of proton reduction in aqueous media<sup>[37]</sup>, indicating that three metal-organic triangles in its reduced state are capable of directly reducing protons.



Scan rate: 100 mV · s<sup>-1</sup>

# 2.3 Supramolecular complex formation between [Ru(dcbpy)<sub>3</sub>]<sup>4-</sup> and Co-L<sup>1</sup>

To localize the PET process and the hydrogen production reaction inside the pocket, the anionic [Ru(dcbpy)<sub>3</sub>]<sup>4-</sup> was selected as an ideal photosensitizer not only because of its appropriate size and excellent photophysical properties, but also due to its four negative charges that could be encapsulated by the cationic host by electrostatic interaction<sup>[16]</sup>. The host-guest binding behavior was investigated by fluorescence spectra. Fluorescence titration results revealed that the triangle  $Co-L^1$  is an efficient quencher of the excited state of  $[\operatorname{Ru}(\operatorname{dcbpy})_3]^{4-}$ . The addition of Co-L<sup>1</sup> (10.0  $\mu$ mol·L<sup>-1</sup>) into a CH<sub>3</sub>CN/H<sub>2</sub>O solution (1:1, V/V, pH=5.75) containing  $[Ru(dcbpy)_3]^{4-}$  (10.0  $\mu$ mol·L<sup>-1</sup>) quenched approximately 30% of the emission intensity of  $[Ru(dcbpy)_3]^{4-}$  (Fig. 3a). The best fitting of the titration profile suggested a 1:1 host-guest behavior with an association constant ( $K_{ass}$ ) of 5.36×10<sup>5</sup> L·mol<sup>-1</sup> (Fig. S1, Supporting information). Meanwhile, Co-L<sup>1</sup> did not lead to any obvious changes in the absorption spectra of [Ru(dcbpy)<sub>3</sub>]<sup>4-</sup> under the same conditions (Fig. 3b), sug-

gesting that the quenching process was likely a classical PET from the excited state \*[Ru(dcbpy)<sub>3</sub>]<sup>4-</sup> to the redox catalyst  $\text{Co-}L^{1[38]}$ , and that  $\text{Co-}L^1$  was capable of being activated directly for proton reduction. Importantly, the emission of a CH<sub>3</sub>CN/H<sub>2</sub>O (1:1, V/V, pH=5.75) solution containing  $[Ru(dcbpy)_3]^{4-}$  (10.0  $\mu$ mol·L<sup>-1</sup>) and Co -  $L^1$  (20.0  $\mu$ mol ·  $L^{-1}$ ) was exponentially decaying at 622 nm with a lifetime of 0.804 µs (Fig. 3c), which is basically the same as that of a pure  $[Ru(dcbpy)_3]^{4-}$ solution (0.805  $\mu$ s, Fig.S6). The results showed that the  $Co-L^{1}/[Ru(dcbpy)_{3}]^{4-}$ host-guest complexes and [Ru(dcbpy)<sub>3</sub>]<sup>4-</sup> species itself with its fluorescent lifetime being maintained apparently coexist in the titration mixture. The fact that the decay behavior approximates well to a typical exponential function suggests that the complex species does not affect the fluorescence emission of [Ru(dcbpy)<sub>3</sub>]<sup>4-</sup>. The encapsulation of  $[Ru(dcbpy)_3]^{4-}$  inside the pocket of Co-L<sup>1</sup> likely promotes the PET process via a pseudo-intramolecular pathway<sup>[39]</sup>, where the unwanted electron-transfer processes could potentially be avoided.



Fig.3 (a) Emission quenching of  $[\text{Ru}(\text{dcbpy})_3]^{4-}$  (10.0 µmol·L<sup>-1</sup>) upon the addition of hosts (10.0 µmol·L<sup>-1</sup>) in CH<sub>3</sub>CN/H<sub>2</sub>O (1:1, *V/V*, pH=5.75); (b) Family of differentiate UV-Vis absorption spectra of  $[\text{Ru}(\text{dcbpy})_3]^{4-}$  (10.0 µmol·L<sup>-1</sup>) in CH<sub>3</sub>CN/H<sub>2</sub>O (1:1, *V/V*, pH=5.75) upon addition of Co-L<sup>1</sup> (5.0 and 10.0 µmol·L<sup>-1</sup>); (c) Fluorescence decay curves of  $[\text{Ru}(\text{dcbpy})_3]^{4-}$  (10.0 µmol·L<sup>-1</sup>) upon addition of Co-L<sup>1</sup> (20.0 µmol·L<sup>-1</sup>) in CH<sub>3</sub>CN/H<sub>2</sub>O (1:1, *V/V*) at pH=5.75, and the intensity was recorded at 622 nm with the excitation at 405 nm

# 2.4 Catalytic behaviour of the metal-organic triangles in $H_2$ evolution

Photocatalytic hydrogen production was carried out in a solution containing the catalyst Co- $L^1$ , the photosensitizer [Ru(dcbpy)<sub>3</sub>]<sup>4-</sup> and the electron donor H<sub>2</sub>A. Under the optimized conditions, the volume of hydrogen reached 472 µL after 24 hours irradiation with an initial turnover frequency (TOF) of approximately 84  $h^{-1}$  (Fig.4a), which was comparable to those of previously reported relative host-guest systems for photocatalytic hydrogen production<sup>[18,40]</sup>. Control experiments indicated that Co-L<sup>1</sup>, [Ru(dcbpy)<sub>3</sub>]<sup>4-</sup> and H<sub>2</sub>A are three necessities for photocatalytic hydrogen production. Obviously, hydrogen could hardly be produced without light. Under saturated reaction conditions, when the concentrations of [Ru(dcbpy)<sub>3</sub>]<sup>4-</sup> and H<sub>2</sub>A were determined in high concentration, the initial rate of hydrogen production was linearly related to the  $Co-L^1$  concentration ranging from 1.0 to 2.5 µmol·L<sup>-1</sup> and exhibited pseudo-zero-order kinetics of hydrogen production (Fig. 4b and S18). And when the concentrations of  $Co-L^1$  and  $H_2A$  were determined, the initial hydrogen production TOF did not change with the concentration of  $[Ru(dcbpy)_3]^{4-}$  (Fig. 4c and S19). However, when the concentration of  $[Ru(dcbpy)_3]^{4-}$  exceeded a certain value, the hydrogen production decreaseed with the increase of the [Ru(dcbpy)<sub>3</sub>]<sup>4-</sup> after 12 hours of irradiation. (Fig. S17). We inferred that too much photosensitizer free in the system leading the aggregation-caused quenching would be detrimental to the light absorption and electron transfer of the host-guest complex<sup>[41-42]</sup>. Therefore, the results confirmed that the rate of hydrogen production is only related to the concentration of [Ru(dcbpy)<sub>3</sub>]<sup>4-</sup> encapsulated inside the pocket of host Co-L<sup>1</sup>. Another isostructural cobalt-based redox-active host  $Co - L^2$  containing benzoimidazole backbone possessed the similar redox potential and host-guest characteristic with that of  $\text{Co-}L^1$  (Fig.2, S2, S7, S11). Under the same optimized conditions, the volume of hydrogen generated by Co-L<sup>2</sup> was 513 µL after 24 hours irradiation (Fig. 4a), showing the similar redox activity with  $Co-L^1$ .

To investigate the potential factors of NADH mimics on the triangles that influence the photocatalytic hydrogen production, triangle Co- $L^3$  without NADH mimics was designed and prepared. Ligand  $H_2L^3$  was synthesized by the Schiff base reaction of 2-formylpyridine with the corresponding hydrazide in EtOH. Compound Co-L<sup>3</sup> was considered as an ideal reference compound not only because of its same structural features with Co-L<sup>1</sup> and Co-L<sup>2</sup>, but also based on the fact that it exhibited the similar redox potential and host-guest characteristic (Fig. 2, S3, S8, S12). Under the same conditions, the volume of hydrogen generated by Co-L<sup>3</sup> was 320  $\mu$ L after 24 hours irradiation (Fig. 4a), which was only approximately 65% of those of Co-L<sup>1</sup> and Co-L<sup>2</sup>. We inferred that the incorporation of NADH mimics as the proton and electron carriers likely made the cobalt corners of the triangles more easily capture electrons from the photosensitizer for further improving photocatalytic hydrogen production efficiency<sup>[26-28,43-44]</sup>.

From a mechanistic viewpoint, the encapsulation of one guest molecule  $[Ru(dcbpy)_3]^{4-}$  inside the pocket of the host first enforces the proximity between the cobalt-based redox catalytic site and the photosensitizer  $[Ru(dcbpy)_3]^{4-}$  by the electrostatic interaction. This host-guest supramolecular system then allows a direct PET process from the excited state  $*[Ru(dcbpy)_3]^{4-}$  to the redox catalyst via a powerful pseudo-intramolecular pathway to avoid unwanted electron transfer<sup>[45]</sup>. Together with the ability to transfer electrons and protons of the NADH mimics, host-guest supramolecular systems further promote efficiency for photocatalytic hydrogen production.

To investigate the role of the host-guest encapsulation in the photocatalytic hydrogen production within



Fig.4 (a) Hydrogen production by systems containing  $[\operatorname{Ru}(\operatorname{dcbpy})_3]^{4-}$  (0.25 mmol·L<sup>-1</sup>) and H<sub>2</sub>A (0.2 mol·L<sup>-1</sup>) with Co-L<sup>1</sup> (2.5 µmol·L<sup>-1</sup>), Co-L<sup>2</sup> (2.5 µmol·L<sup>-1</sup>), Co-L<sup>3</sup> (2.5 µmol·L<sup>-1</sup>) and Co-L<sup>4</sup> (7.5 µmol·L<sup>-1</sup>); (b) Hydrogen production by systems containing  $[\operatorname{Ru}(\operatorname{dcbpy})_3]^{4-}$  (0.25 mmol·L<sup>-1</sup>) and H<sub>2</sub>A (0.2 mol·L<sup>-1</sup>) with various concentrations of Co-L<sup>1</sup>; (c) Hydrogen production by systems containing Co-L<sup>1</sup> (2.5 µmol·L<sup>-1</sup>), H<sub>2</sub>A (0.2 mol·L<sup>-1</sup>) with various concentrations of  $[\operatorname{Ru}(\operatorname{dcbpy})_3]^{4-}$ 

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the cavity of the host, a mononuclear compound  $\text{Co-}L^4$ was designed and prepared for further comparison (Fig. S13). Co -  $L^4$  had the same coordination environment with aforementioned three hosts and a redox potential of -1.11 V (vs Ag/AgCl) (Fig.S14). Fluorescence spectrum indicated that PET displayed in a normal bimolecular manner between Co-L<sup>4</sup> and  $[Ru(dcbpy)_3]^{4-}$  (Fig.S4, S9, S10). As expected, under the same conditions, irradiation of a solution containing Co- $L^4$  (7.50  $\mu$ mol· $L^{-1}$ ),  $[\operatorname{Ru}(\operatorname{dcbpy})_3]^{4-}$  (0.25 mmol·L<sup>-1</sup>) and H<sub>2</sub>A (0.2 mol·L<sup>-1</sup>) gave 76 µL after 24 hours (Fig.4a), which was only approximately 15% of those of  $\text{Co}-\text{L}^1$  and  $\text{Co}-\text{L}^2$ . Meanwhile, an unreactive species,  $[Fe(dcbpy)_3]^{4-}$ , that has a same structure with [Ru(dcbpy)<sub>3</sub>]<sup>4-</sup> was selected as inhibitor to be added into our reaction systems<sup>[46-47]</sup>. It is worth noting that due to the [Fe(dcbpy)<sub>3</sub>]<sup>4-</sup> did not quench the emission of the [Ru(dcbpy)<sub>3</sub>]<sup>4-</sup>, the addition of  $[Fe(dcbpy)_3]^{4-}$  (0.10 mmol·L<sup>-1</sup>) in to a solution of the  $[Ru(dcbpy)_3]^{4-}$  (10.0 µmol·L<sup>-1</sup>) and the Co-L<sup>1</sup> (30.0  $\mu$ mol·L<sup>-1</sup>) resulted in an emission recovery of the same band (Fig. 5a). Such a recovery of the emission of [Ru(dcbpy)<sub>3</sub>]<sup>4-</sup> was also indicative for the substitution of encapsulated [Ru(dcbpy)<sub>3</sub>]<sup>4-</sup> molecules in the pocket of the molecular triangle  $\text{Co} - L^1$ . Under the same conditions, the volumes of hydrogen produced were only 22.5%, 7.8% and 11.9% of the original system in the present of  $[Fe(dcbpy)_3]^{4-}$  (2.5 mmol·L<sup>-1</sup>) for Co - L<sup>1</sup>,  $Co-L^2$  and  $Co-L^3$ , respectively (Fig.5b). However, when the addition of  $[Fe(dcbpy)_3]^{4-}$  into a solution containing  $Co-L^4$  and  $[Ru(dcbpy)_3]^{4-}$ , the volume of the produced hydrogen did not obviously change and no fluorescence emission recovery was observed (Fig. 5b and S10). These results further confirmed the advantage of the functionalized host-guest systems on this photocatalytic reaction.



Fig.5 (a) Fluorescence spectra of [Ru(dcbpy)<sub>3</sub>]<sup>4-</sup> (10.0 μmol·L<sup>-1</sup>) in CH<sub>3</sub>CN/H<sub>2</sub>O (1:1, *V/V*, pH=5.75) upon addition of Co-L<sup>1</sup> (30.0 μmol·L<sup>-1</sup>) showing the recovery of emission in the presence of [Fe(dcbpy)<sub>3</sub>]<sup>4-</sup> (0.1 mmol·L<sup>-1</sup>);
(b) Hydrogen production by systems containing [Ru(dcbpy)<sub>3</sub>]<sup>4-</sup> (0.25 mmol·L<sup>-1</sup>), H<sub>2</sub>A (0.2 mol·L<sup>-1</sup>) and the hosts (2.5 μmol·L<sup>-1</sup>) after 24 hours of irradiation, and the cyan bars and magenta show the absence and presence of [Fe(dcbpy)<sub>3</sub>]<sup>4-</sup>

#### **3** Conclusions

In summary, we reported two positively charged cobalt-based metal-organic triangles containing NADH mimics. The experiments indicate that the host-guest complexes obtained by the electrostatic interaction accelerate PET processes via a powerful pseudointramolecular pathway. Simultaneously, the incorporation of NADH mimics further improves photocatalytic hydrogen production efficiency. This promising supramolecular platform provides a new inspiration to develop new strategies toward expanding application of the coenzyme mimics.

Supporting information is available at http://www.wjhxxb.cn

#### **References:**

- [1] Zhou C, Shi R, Waterhouse G I N, Zhang T R. Coord. Chem. Rev., 2020,419:213399
- [2] Ran J R, Zhang J, Yu J G, Jaroniec M, Qiao S Z. Chem. Soc. Rev., 2014,43:7787-7812
- [3] Li X, Yu J G, Jaroniec M. Chem. Soc. Rev., 2016,45:2603-2636
- [4] Wu K, Hou Y J, Lu Y L, Fan Y Z, Fan Y N, Yu H J, Li K, Pan M, Su C Y. Chem. Eur. J., 2019,25:11903-11909

- [5] Xiao T X, Zhong W W, Zhou L, Xu L X, Sun X Q, Elmes R B P, Hu X Y, Wang L Y. Chin. Chem. Lett., 2019,30:31-36
- [6] Li X, Yu J G, Low J X, Fang Y P, Xiao J, Chen X B. J. Mater. Chem. A, 2015,3:2485-2534
- [7] Xie A, Pan Z H, Yu M, Luo G G, Sun D. Chin. Chem. Lett., 2019,30: 225-228
- [8] 吴浅耶,张晨曦,孙康,江海龙.化学学报,2020,78:688-694
   WU Q Y, ZHANG C X, SUN K, JIANG H L. Acta Chim. Sinica, 2020, 78:688-694
- [9] Pan Y T, Qian Y Y, Zheng X S, Chu S Q, Yang Y J, Ding C M, Wang X, Yu S H, Jiang H L. Natl. Sci. Rev., 2021,8(1):nwaa224
- [10]Frischmann P D, Mahata K, Würthner F. Chem. Soc. Rev., 2013,42: 1847-1870
- [11]Pan M, Wu K, Zhang J H, Su C Y. Coord. Chem. Rev., 2020,378:333-349
- [12]Lehn J M. Supramolecular Chemistry: Concepts and Perspectives. Weinheim: Wiley-VCH, 1995:2-6
- [13]Jing X, He C, Yang Y, Duan C Y. J. Am. Chem. Soc., 2015,137:3967 -3974
- [14]Brown C J, Toste F D, Bergman R G, Raymond K N. Chem. Rev., 2015,115:3012-3035
- [15]He C, Wang J, Zhao L, Liu T, Zhang J, Duan C Y. Chem. Commun., 2013.49:627-629
- [16]Yang L, He C, Liu X, Zhang J, Sun H, Guo H M. Chem. Eur. J., 2016,22:5253-5260
- [17]Nurttila S S, Becker R, Hessels J, Woutersen S, Reek J N H. Chem. Eur. J., 2018,24:16395-16406
- [18]Cai J K, Zhao L, Wei J W, He C, Long S R, Duan C Y. Chem. Commun., 2019,55:8524-8527
- [19]杨林林, 景旭, 何成, 段春迎. 无机化学学报, **2017,33**(6):913-922 YANG L L, JING X, HE C, DUAN C Y. *Chinese J. Inorg. Chem.*, **2017,33**(6):913-922
- [20]李和川, 李明凤, 何成, 段春迎. 无机化学学报, **2018,34**(1):11-19 LI H C, LI M F, HE C, DUAN C Y. *Chinese J. Inorg. Chem.*, **2018**, **34**(1):11-19
- [21]张文言,杨阳,黄慧琳,景旭,段春迎. 无机化学学报, 2020,36(10): 1988-1996

ZHANG W Y, YANG Y, HUANG H L, JING X, DUAN C Y. *Chinese* J. Inorg. Chem., **2020**,**36**(10):1988-1996

- [22]Yadav R K, Oh G H, Park N J, Kumar A, Kong K J, Baeg J O. J. Am. Chem. Soc., 2014,136:16728-16731
- [23]Sun Z T, Lonsdale R, Ilie A, Li G Y, Zhou J H, Reetz M T. ACS Catal., 2016,6:1598-1605
- [24]Litman Z C, Wang Y J, Zhao H M, Hartwig J F. Nature, 2018,560: 355-359

[25]McSkimming A, Colbran S B. Chem. Soc. Rev., 2013, 42:5439-5488

- [26]Feng Y S, Yang C Y, Huang Q, Xu H J. Tetrahedron, 2012,68:5053-5059
- [27]Zhu C, Saito K, Yamanaka M, Akiyama T. Acc. Chem. Res., 2015,48: 388-398
- [28]Gao S, Huang S, Duan Q, Hou J H, Jiang D Y, Liang Q C, Zhao J X. Int. J. Hydrogen Energy, 2014,39:10434-10444
- [29]Zhao L, Wei J W, Lu J H, He C, Duan C Y. Angew. Chem. Int. Ed., 2017,56:8692-8696
- [30]Zhao L, Wang J, Wu P Y, He C, Guo X Y, Duan C Y. Sci. Rep., 2017, 7:14347
- [31]Wei J W, Zhao L, He C, Zheng S J, Reek J N H, Duan C Y. J. Am. Chem. Soc., 2019,141:12707-12716
- [32]Zhao L, Cai J K, Li Y N, Wei J W, Duan C Y. Nat. Commun., 2020, 11:2903
- [33]Zhao L, Wei J W, Zhang J, He C, Duan C Y. Angew. Chem. Int. Ed., 2017,56:15284-15288
- [34]Zhao L, Wei J W, Zhang F L, He C, Zheng S J, Duan C Y. RSC Adv., 2017,7:48989-48993
- [35]Zhou J, Zhang Y Z, Yu G C, Crawley M R, Fulong C R P, Friedman A E, Sengupta S, Sun J F, Li Q, Huang F H, Cook T R. J. Am. Chem. Soc., 2018,140:7730-7736
- [36]Baffert C, Artero V, Fontecave M. Inorg. Chem., 2007,46:1817-1824
- [37]Artero V, Chavarot-Kerlidou M, Fontecave M. Angew. Chem. Int. Ed., 2011,50:7238-7266
- [38]Jiang P J, Guo Z J. Coord. Chem. Rev., 2004,248:205-229
- [39]Nelissen H F M, Kercher M, De Cola L, Feiters M C, Nolte R J M. Chem. Eur. J., 2002,8:5407-5414
- [40]Zheng S J, Zhao L, Wei J W, He C, Liu G Z, Duan C Y. Inorg. Chem. Commun., 2019.109:107558
- [41]Mei J, Leung N L C, Kwok R T K, Lam J W Y, Tang B Z. Chem. Rev., 2015,115:11718-11940
- [42]Wu K, Li K, Chen S, Hou Y J, Lu Y L, Wang J S, Wei M J, Pan M, Su C Y. Angew. Chem. Int. Ed., 2020,59:2639-2643
- [43]Odella E, Wadsworth B L, Mora S J, Goings J J, Huynh M T, Gust D, Moore T A, Moore G F, Hammes - Schiffer S, Moore A L. J. Am. Chem. Soc., 2019,141:14057-14061
- [44]Ranjeesh K C, Illathvalappil R, Veer S D, Peter J, Wakchaure V C, Goudappagouda, Raj K V, Kurungot S, Babu S S. J. Am. Chem. Soc., 2019,141:14950-14954
- [45]Dong J F, Wang M, Zhang P, Yang S Q, Liu J Y, Li X Q, Sun L C. J. Phys. Chem. C, 2011,115:15089-15096
- [46]Zhang S Q, Han L, Li L N, Cheng J, Yuan D Q, Luo J H. Cryst. Growth Des., 2013,13:5466-5472
- [47]Elliott C M, Caramori S, Bignozzi C A. Langmuir, 2005,21:3022-3027