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

Accepted 00th January 20xx DOI: 10.1039/x0xx00000x

Received 00th January 20xx,

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www.rsc.org/

Published on 21 June 2019. Downloaded on 6/22/2019 3:34:52 AM.

By incorporating 1,2-benzenedithiol as a chelator to construct cobalt dithiolene species, two negatively charged redox-active metal-organic hosts were obtained. By taking advantage of electrostatic interactions, cationic Ru-based photosensitizers were constrained to improve photoinduced electron transfer processes for efficient photocatalytic proton reduction.

Supramolecular approaches have attracted considerable attention with regard to controlling molecular behaviour.^{1,2} In nature, a plethora of mechanisms are harnessed to optimize chemical processes *via* the cumulative influence of many noncovalent bonds, such as hydrophobic interactions, hydrogen bonds and the Coulombic force.^{3,4} Metal-organic architectures constructed by the coordination of metal ions and organic linkers have been considered powerful supramolecular hosts,⁵ in which geometric and electronic characteristics could be embedded within the individual components for recognition, stabilization of reactive intermediates and catalysis with promising supramolecular active sites reminiscent of natural enzymes.⁶⁻⁸

On the other hand, converting solar energy into other forms of energy has initiated interest in fundamental photophysics research for effective chemical transformations.⁹ The efficiency of light energy conversion is always determined by the photoinduced electron transfer (PET) processes and the form of a long-lived charge separation state.¹⁰ The host-guest supramolecular strategy was considered a highly promising way to force close proximity between electron acceptors and the donors to improve the PET processes.^{11,12} With abundant weakly interacting sites on the metal-organic hosts, guests could be caught within the supramolecular hosts in a favourable conformation to form host-guest systems¹³ and avoid unwanted energy transfer processes.¹² photosensitizers plays an important role in the efficient charge and energy transfer processes of photosynthetic systems.¹⁰ Because the metal centres of hosts carry inherent positive charges,⁵ they usually can hardly form host-guest species with metal-based photosensitizers due to Coulombic repulsion. To the best of our knowledge, few negatively charged cages have been reported to date,¹⁴⁻¹⁶ and only one metal-organic cage constructed by Raymond and co-workers can be applied to photocatalytic research via the PET processes.¹⁶ In terms of availability, utilizing electrostatic interactions to construct host-guest species to improve PET processes is a promising approach that has not been reported in the field of light-driven H₂ evolution. In this work, we successfully synthesized two novel negatively charged metal-organic hosts containing CoS₄ cores, which are the first example of the formation of a hostguest system with the star molecule $Ru(bpy)_3^{2+}$ (bpy = 2,2'bipyridine) by electrostatic interactions for application in lightdriven H₂ production. Cobalt dithiolene compounds containing CoS₄ cores are types of artificial hydrogenase mimics that have particularly low overpotentials and display outstanding redox properties.¹⁷ Importantly, the strong coordinating ability of the benzenedithiolate chelator was expected to enhance the stability of hosts and maintain the intrinsic redox potential of cobalt dithiolenes.

The synergistic interaction between redox catalysts and



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 $[\]dagger$ Electronic Supplementary Information (ESI) available: Experimental details, crystal structure and data. CCDC 1916150-1916152. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

Scheme 1 Construction of an Artificial Supramolecular System for Photocatalytic Proton Reduction.

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H₄NAS was synthesized by reducing the reaction product of 1,5-diaminonaphthalene and 2,3-bis(isopropylthio)benzoyl chloride according to the reported literature.¹⁵ The reaction of H₄NAS and Co(BF₄)₂·6H₂O in a DMF solution containing NaOH and NEt₄Cl yielded 68% of the compound Co-NAS. ESI-MS spectrum of Co-NAS exhibited an intense peak at m/z = 548.9222 with isotopic distribution patterns separated by 0.5 Da (Fig. S4.1⁺) and was clearly assignable to the $[Co_2(NAS)_2]^{2-}$ species, indicating the formation of $\mathsf{M}_2\mathsf{L}_2$ species with high stability in solution. Single-crystal structure analysis of Co-NAS revealed that two deprotonated H₄NAS units and two cobalt ions formed a negatively charged quadrangular molecule Co-NAS with an ideal C₂ symmetry via coplanar coordination (Fig. 1a). The average Co-S bond distances of approximately 2.2 Å were in good agreement with the reported for CoS₄, implying that the CoS₄ core retained its original redox activity after modification on the supramolecular hosts. The cobalt ions were located on two parallel edges of the quadrangle with an average distance of 13.2 Å, and the distance between naphthalene groups was approximately 7.7 Å, giving a window of approximately 100 $\mbox{\AA}^2$ and providing potential space to interact with guest molecules.



Fig. 1 Crystal structure of Co–**NAS** (a) and Co–**NAS**/Ru(bpy)₃²⁺ (b) with the cumulative noncovalent bonds shown. (c) The filling pattern of the host and guests. Co cyan, Ru purple, S yellow, N blue, O red, C grey and H white.

As expected, two NEt₄⁺ counter cations were located on both sides of the Co–**NAS** quadrangular plane through hostguest electrostatic interactions (Fig. S3.1⁺). When the photosensitizer ion Ru(bpy)₃²⁺ with two positive charges was added instead of NEt₄⁺, we speculated that Co–**NAS** could bond with Ru(bpy)₃²⁺ in a similar manner to obtain a host-guest complex. Fortunately, the single crystal structure of the Co–**NAS**/Ru(bpy)₃²⁺ complex was obtained, as shown in Fig. 1b and 1c. The negatively charged quadrangular structure was maintained, and the two Ru(bpy)₃²⁺ molecules occupied the positions of NEt₄⁺ through host-guest electrostatic interactions. At the same time, close contacts between the H-atoms of the pyridine ring on the bpy ligand and the oxygen atoms, sulfur atoms and naphthalene nucleus of Co–**NAS** were also observed in the crystal structure (Fig. 1b). The nearest C-H Vie Qar CT-HolinS and C–Η ····π distances were only 2.5 Å: 298 Å? And 3.67Å, respectively, which are typical of hydrogen bonds. These multiple interactions might play an auxiliary role in thermodynamically promoting the binding and maintaining the stability of the host-guest species in peripheral binding manner, which is a special host-guest interaction mode seldom observed.¹⁸ Although Ru(bpy)₃²⁺ is a spherical molecule with a diameter of ca. 11.5 Å, which is larger than the inner window of Co-NAS, electrostatic interactions and hydrogen bonding prompted Co-NAS to capture Ru(bpy)₃²⁺ ions on both sides of its quadrangular window similar to a trap. This peripheral binding mode maintained a distance between Ru(bpy)₃²⁺ and the redox centres of approximately 9.0 Å, and the shortened distance between the electron donors and electron acceptors was beneficial to the subsequent PET processes.



Fig. 2 (a) ITC experiments of Ru(bpy)₃²⁺ upon addition of Co–**NAS** or Co–**TAS** showing the formation of host-guest complex in DMF. (b) Cyclic voltammogram of catalysts (0.1 mM) in DMF containing 0.10 M TBAPF₆. Scan rate: 100 mV/s. (c) H₂ evolution by system containing Ru(bpy)₃²⁺ (0.5 mM) and AA (0.1 M) with various concentration of Co–**NAS**. (d) H₂ evolution by system containing Co–**NAS** (20 μ M), AA (0.1 M) with various concentration of Ru(bpy)₃²⁺.

The modes of interaction between Co-NAS and Ru(bpy)₃²⁺ was further studied by ITC assays and the combined number indicated the presence of $Ru(bpy)_3^{2+}$ triggered the formation of Co-NAS/Ru(bpy)₃²⁺ 1:2 complexes in solution (Fig. 2a).¹⁹ Curve fitting by computer simulation using an "independent" model showed a large Gibbs free energy (ΔG) of $-30.46 \text{ kJ} \cdot \text{mol}^{-1}$ for the Co-NAS/Ru(bpy)₃²⁺ complex, suggesting strong combination between the host Co-NAS and the guest Ru(bpy)₃²⁺ (Fig. S5.9⁺). ¹H NMR titration experiments between Co-NAS and Ru(bpy)₃²⁺ were also executed (Fig. S5.1⁺). The addition of Co-NAS to Ru(bpy)₃²⁺ showed significant upfield shifts in all signals of Ru(bpy)₃²⁺, indicating that Ru(bpy)₃²⁺ combined with Co-NAS to give host-guest species. These results were consistent with the obtained crystal structure.

Cyclic voltammograms displayed a pair of reversible redox peaks of the coupled Co^{III}/Co^{II} reduction process at approximately -0.55 V (vs. Ag/AgCl) (Fig. 2b), which was in good agreement with reported cobalt dithiolene species.¹⁷ The

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result indicated that the CoS_4 groups embedded within Co-NAS still maintained redox activity. The PET processes between $Ru(bpy)_3^{2+}$ and Co-NAS were investigated by fluorescence titration (Fig. S5.3⁺). The addition of Co-NAS to a DMF solution containing $Ru(bpy)_3^{2+}$ caused obvious emission quenching following linear Stern-Volmer behavior with a constant of 2.7×10^4 M⁻¹, which was assignable to the photoinduced electron transfer from excited $Ru(bpy)_3^{2+}$ to the CoS_4 cores in Co-NAS, indicating that Co-NAS was capable of being activated directly for proton reduction. In fact, such intense quenching between host and guest enabled effective photoinduced electron transfer *via* a pseudo-intramolecular pathway comparable to that of reported host-guest system.¹²

Hydrogen evolution was carried out in a typical light-driven reduction system containing the catalyst Co-NAS (0.04 mM), the photosensitizer $Ru(bpy)_{3^{2+}}$ (0.5 mM) and the electron donor ascorbic acid (AA, 0.1 M). As shown in Fig. 2c, under the optimized conditions, the volume of H₂ evolution was up to 400 µL in 9 h with an initial turnover frequency (TOF) of approximately 40 h⁻¹. The efficiency is comparable to that of previous relative host-guest systems for the photocatalytic hydrogen production.^{20,21} Under saturated reaction conditions, when the concentrations of $Ru(bpy)_3^{2+}$ and AA were fixed, the initial rate constant of H₂ production exhibited a linear relationship with the concentration of the Co-NAS. When the concentrations of Co-NAS and AA fixed, TOF maintained unchanged with the variation of the concentration of $Ru(bpy)_{3^{2+}}$ (Fig. 2d). We inferred that the increase of catalyst facilitated the formation of host-guest species and the rate of H₂ evolution depend on the concentration of the host-guest complexes $Co-NAS/Ru(bpy)_3^{2+}$ rather than that of $Ru(bpy)_3^{2+}$. Control experiments with either free Ru(bpy)₃²⁺ or Co-NAS produced trace H₂, demonstrating that both species contributed to the PET processes for H_2 production. The fluorescence quenching efficiency of Co-NAS to $Ru(bpy)_3^{2+}$ is significantly higher than that of AA under the reaction conditions (Fig. 3a). From a mechanistic point of view, the tight combination of Co-**NAS** and $Ru(bpy)_3^{2+}$ enhanced the electron transfer from excited Ru(bpy)₃²⁺ to Co-NAS by oxidation quenching processes in a pseudo-intramolecular pathway similar to internal host-guest systems.¹² The reduced Co-NAS could further transfer electrons to protons to complete the H₂ production. To verify PET processes, the transients absorption spectrum of Ru(bpy)₃²⁺ with Co-NAS in the presence of AA was investigated. The appearance of a new absorption peak at approximately 420 nm at 0.8 µs assigned to the absorption maximum of Ru^{III} ion confirmed the occurrence of efficient photoinduced electron transfer processes from the excitedstate $*Ru(bpy)_3^{2+}$ to the Co-**NAS** (Fig. S5.8⁺).²²

To further investigate the potential factors that influence the photocatalytic H₂ evolution, a mononuclear compound, Co–**BAS** (where H₂**BAS** = 2,3-dimercapto-N-phenyl benzamide), resembling a corner of the Co–**NAS** compound was designed and prepared. However, only a trace amount of H₂ was detected after 9 h under the same conditions (0.08 mM Co– **BAS** while ensuring the same concentration of cobalt ions) (Fig. 3d). Obviously, a comparison of the H₂ evolution relativity between Co–**NAS**/Ru(bpy)₃²⁺ and Co–**BAS**/Ru(bpy)₃²⁺ Gystems revealed that the formation of host-guest species through electrostatic interactions is a promising method for improving the PET processes.



Fig. 3 (a) Emission spectra of Ru(bpy)₃²⁺ (10 μ M) upon the addition of catalysts (40 μ M) and AA (0.1 M). (b) Emission spectra of Ru(bpy)₃²⁺ (10 μ M) upon addition of 40 mM Et₄NCI (black line), 40 μ M Co–**TAS** (red line) and both 40 μ M Co–**TAS** and 40 mM Et₄NCI (blue line). The spectra show the recovery of emission in the presence of Et₄NCI. (c) H₂ evolution by system containing Ru(bpy)₃²⁺ (0.5 mM), AA (0.1 M) with various concentration of Co–**TAS**. (d) H₂ evolution by system containing Ru(bpy)₃²⁺ (0.5 mM), AA (0.1 M) and catalysts (Co–**NAS**: 0.04 mM, Co–**TAS**: 0.04 mM, CO–**TAS**

At the same time, a triangular prism with three CoS₄ cores was prepared to sufficiently elucidate the role of peripheral binding by electrostatic interactions in PET processes. Singlecrystal Co-TAS was obtained by vapour diffusion of diethyl ether into a DMF solution of H_6 TAS (4,4',4"-tri(2,3-dimercapto benzamido)triphenylamine) and Co(BF₄)₂·6H₂O containing NaOH and NEt₄Cl with a yield of 48%. The ESI-MS spectrum of Co-**TAS** in DMF exhibited an intense peak at m/z = 584.9067with the exact isotopic distribution fingerprint of the species [Co₃(TAS)₂]³⁻ (Fig. S4.2). Single-crystal analysis of Co-TAS revealed a pseudo- C_3 symmetric M_2L_3 triangular prism constructed by two ligands on the top and bottom faces of the triangular prism defined by three cobalt ions located on its three edges (Fig. 4). The three separate dithiolene chelators of each ligand were coordinated to three different metal centres, while each metal cenre coordinated to two dithiolene chelators from two deprotonated ligands via the same coplanar mode as Co-NAS. The separation of Co-Co on the edges was approximately 7.4 Å. Two triangular faces kept a height of approximately 8.5 Å, producing a potential space between each two edges for the recognition of guest molecules. As shown in Fig. 4a, three Et₄N⁺ counter cations Et₄N⁺ were evenly distributed at the opening windows of Co-TAS in exactly the same way as Co-NAS, which indicated that $Ru(bpy)_{3}^{2+}$ could replace Et_4N^+ to form a Co-NAS/ $Ru(bpy)_{3^{2+}}$ complex for light-driven proton reduction.

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Although we did not obtain direct evidence from the singlecrystal structure of Co–**TAS** together with $Ru(bpy)_3^{2+}$, the mode of interaction between them was confirmed by ITC assays and provided insight into the thermodynamics of host-guest species. Microcalorimetric titration of host-guest complexation verified the inclusion number of 3 with a ΔG of -33.26 kJ·mol⁻¹ for the Co-TAS/Ru(bpy) $_{3}^{2+}$ complex (Fig. 1a). The quenching constant of 1.8×10^4 M⁻¹ was slightly weaker than that of the $Co-NAS/Ru(bpy)_{3}^{2+}$ complex (Fig. S5.4⁺). The redox potential of Co-TAS was -0.55 V, similar to that of Co-NAS (Fig. 2a). Irradiation of a solution containing Co-TAS (0.04 mM), Ru(bpy)₃²⁺ (0.5 mM) and AA (0.1 M) gave 350 μ L of H₂ (Fig. 3c). The results suggested that Co-TAS was able to combine Ru(bpy)₃²⁺ with the assistance of electrostatic interactions for light-driven proton reduction in a pseudo-intramolecular pathway.



Fig. 4 (a) Crystal structure of Co–**TAS** with three Et_AN^+ inlaving on the window. (b) Crystal structure of Co-TAS. (c) The filling pattern of the host and guests. Co cyan, Ru purple, S vellow, N blue, O red, C grev and H white.

To validate whether the PET processes in photoinduced H₂ production either occurred by a pseudo-intramolecular pathway or just proceeded through an intermolecular pathway, an inhibition experiment was performed. The addition of nonlight-absorbing species Et₄NCl efficiently recovered the emission of both the Co-NAS/Ru(bpy)₃²⁺ and Co-TAS/ $Ru(bpy)_{3}^{2+}$ systems (Fig 3b and S5.6⁺), indicated that Et₄NCl could act as an inhibitor to extrude $Ru(bpy)_{3^{2+}}$ out of the window of hosts. As shown in Fig. 3d, when Et₄NCl was added to aforementioned two reaction systems, the volume of the H_2 produced was only 40% and 25% of the original value under the same experimental conditions for Co-NAS and Co-TAS, respectively. The exhibited inhibition behaviours in photocatalytic proton reduction suggested that the combination of host and guest through electrostatic interactions played an important role in photoinduced electron transfer processes for efficient H₂ evolution.

In summary, we reported two new negatively charged metal-organic hosts containing redox active cobalt dithiolenes and both of them were devoted to developing a new strategy for the construction of host-guest system by electrostatic interactions to accelerate the light driven H_2 generation. Cobalt dithiolene species have not only suitable potential for the H₂ evolution reaction but also special coordination modes hosts and enhance their stability. The host guest species with the photosensitizer Ru(bpy)₃²⁺ and the supermolecular redox hosts assembled by peripheral binding way were first characterized by single-crystal diffraction. The experiments indicated that the host-guest system obtained through electrostatic interaction was a promising platform for improving the PET processes from an excited-state photosensitizer to the redox sites and provided a new reference for other fields, such as biosensing and conduction.

This work was supported by the National Natural Science Foundation of China (No: 21531001 and 21820102001) and the Fundamental Research Funds for the Central Universities (DUT18LK53 and DUT19ZD102).

Conflicts of interest

There are no conflicts to declare.

Notes and references

- 1 C. J. Brown, F. D. Toste, R. G. Bergman and K. N. Raymond, Chem. Rev., 2015, 115, 3012.
- 2 X. Jing, C. He, L. Zhao and C. Duan, Acc. Chem. Res., 2019, 52, 100.
- 3 K. Drauz and H. Waldmann, Enzyme Catalysis in Organic Synthesis, Wiley-VCH, Weinheim, 2002.
- D. Voet and J. G. Voet, Biochemistry, Wiley, New York, 2004. 4
- T. R. Cook and P. J. Stang, Chem. Rev., 2015, 115, 7001. 5
- 6 Y. Ueda, H. Ito, D. Fujita and M. Fujita, J. Am. Chem. Soc., 2017. 139. 6090.
- 7 P. Mal, B. Breiner, K. Rissanen and J. R. Nitschke, Science, 2009, 324, 1697.
- W. Cullen, A. J. Metherell, A. B. Wragg, C. G. P. Taylor, N. H. 8 Williams and M. D. Ward, J. Am. Chem. Soc., 2018, 140, 2821.
- 9 S. Berardi, S. Drouet and A. Llobet, Chem. Soc. Rev., 2014, 43, 7501.
- 10 P. D. Frischmann, K. Mahata and F. Würthner, Chem. Soc. Rev., 2013, 42, 1847.
- 11 A. M. Kluwera, M. Lutzb, P. W. N. M. van Leeuwena and J. N. H. Reek., Proc. Natl. Acad. Sci. U.S.A., 2009, 106, 10460.
- 12 X. Jing, C. He, Y. Yang and C. Duan, J. Am. Chem. Soc., 2015, 137. 3967.
- 13 L. J. Jongkind, X. Caumes, A. P. T. Hartendorp and J. N. H. Reek, Acc. Chem. Res., 2018, 51, 2115.
- 14 I. M. Müller, D. Möller and C. A. Schalley, Angew. Chem. Int. Ed., 2005, 44, 480.
- 15 B. Birkmann, R. Fröhlich and F. E. Hahn, Chem. Eur. J., 2009, 15, 9325.
- 16 D. M. Dalton, F. D. Toste, R. G. Bergman and K. N. Raymond, J. Am. Chem. Soc., 2015, 137, 10128.
- 17 W. R. McNamara, Z. Han, P. L. Holland and R. Eisenberg, J. Am. Chem. Soc., 2011, 133, 15368.
- 18 V. McKee, J. Nelsonbc and R. M. Town, Chem. Soc. Rev., 2003, 32, 309.
- 19 J. Demers and A. Mittermaieri, J. Am. Chem. Soc., 2009, 131, 4355.
- 20 C. He, J. Wang, L. Zhao, T. Liu, J. Zhang and C. Duan, Chem. Common., 2013, 49, 627.
- 21 L. Yang, X. Jing, C. He, Z. Chang and C. Duan, Chem. Eur. J., 2016, **22**, 18107.
- 22 D. Thiruppathi, P. Karuppasamy, M. Ganesan, V. K. Sivasubramanian, T. Rajendran and S. Rajahopal, J. Photochem. Photobiol. A, 2014, 295, 70.

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