

## **Accepted Article**

Title: Control of Redox Events by Dye Encapsulation Applied to Lightdriven Splitting of Hydrogen Sulfide

Authors: Xu Jing, Yang Yang, Cheng He, Zhiduo Chang, Joost N. H. Reek, and Chunying Duan

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201704327 Angew. Chem. 10.1002/ange.201704327

Link to VoR: http://dx.doi.org/10.1002/anie.201704327 http://dx.doi.org/10.1002/ange.201704327

## WILEY-VCH

#### WILEY-VCH

## Control of Redox Events by Dye Encapsulation Applied to Lightdriven Splitting of Hydrogen Sulfide

Xu Jing<sup>+</sup>, Yang Yang<sup>+</sup>, Cheng He<sup>\*</sup>, Zhiduo Chang, Joost N. H. Reek<sup>\*</sup> and Chunying Duan<sup>\*</sup>

Abstract: Producing solar hydrogen by consuming negative value waste products represents an attractive pathway that presents both economic and environmental benefits. Inspired by the pocket feature of enzymes, a synthetic platform to combine photocatalytic hydrogen evolution with sulfide oxidation in a one-pot process via control over the location of electron transfer steps is reported in this paper. The redox-active coordination vessel Ni-TFT, which exhibits an octahedral pocket, encapsulates an organic dye to pre-organize for photocatalytic proton reduction via an oxidative quenching pathway using the nickel corners as catalysts, generating molecular hydrogen and the oxidized dye. The oxidized dye is displaced by a neutral dye and oxidizes sulfide once outside the pocket to give element sulfur. The overall reaction constitutes hydrogen sulfide splitting, forming molecular hydrogen and elemental sulfur, which is analogous to the water-splitting reaction. The high efficiency, simple separation of hydrogen gas and sulfur solid from the reaction mixture, represent major advantages for potential applications.

Catalytic strategies inspired by natural enzymes that work under ambient conditions have attracted recent interests as they may lead to important future tools for efficient chemical conversions.<sup>[1]</sup> To achieve efficiencies and selectivities similar to that displayed by enzyme, scientists have devised several kind of macrocycles with well-defined pockets, in which chemical transformations can take place.<sup>[2,3]</sup> Reactions performed in such confined spaces can be enhanced reaction rates by the proximity effects, leading to unusual selectivity because of the restricted rotational freedom of substrates in the cage.<sup>[4]</sup> Recently it was demonstrated that confinement effects can be very beneficial if the catalytic active species is only encapsulated during a part of the catalytic cycle.<sup>[5,6]</sup> In view of our interest to develop host-guest systems for photo-catalytic redox reactions,<sup>[7]</sup> as encapsulation of neutral photosensitizers into the hydrophobic pocket of a cage that after photo-induced electron transfer to the redox center may lead to dissociation of the oxidized dye, entails a new strategy to control redox events in solution. Such separation of redox events may avoid unwanted electron transfer and energy transfer processes, and as such it could provide a new synthetic platform to combine photocatalytic hydrogen evolution with substrate oxidation in a one-pot process through control over the location, i.e., inner-

Dr. X. Jing, Prof C. He, Y. Yang, Z. Chang and Prof. C. Duan State Key Laboratory of Fine Chemicals . Dalian University of Technology, Dalian, 116024, China. Dr. X. Jing and Prof. C. Duan Collaborative Innovation Center of Chemical Science and Engineering(Tianjin), Tianjin 300071, China. E-mail:cyduan@dlut.edu.cn Prof J. N. H. Reek Van't Hoff Institute for Molecular Science University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands E-mail:J.N.H.Reek@uva.nl [\*] The two authors contributed equally to this work.

['] The two authors contributed equally to this work. Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201xxxxxx. space and outer-space of the cavity, respectively.<sup>[7]</sup>

An interesting application of such an approach would be the light-driven splitting of hydrogen sulfide (H2S), as H2S is an abundant chemical feedstock that is collected as a by-product in the oil and gas industry. Whereas hydrogen sulfide itself has little value, after splitting into molecular hydrogen and elemental sulfur, the components have significant economic value. Among the reported decomposition methods, the photochemical splitting of H<sub>2</sub>S by combining sulfide oxidation and proton reduction using solar energy has been postulated as an interesting sustainable strategy.<sup>[8]</sup> However, as sulfide ions always form polysulfides (Sn<sup>2-</sup>) when acting as electron sacrificial reagents<sup>[9]</sup> and both the polysulfide and sulfide can coordinate strongly to a potential transition-metal catalysts, leading to poisoning or decomposition, so far homogeneous catalysts that can split hydrogen sulfide have not been reported. Herein, we report a new strategy in which light-driven proton reduction is combined with sulfide oxidation by separating both redox events in space. We created a nickel-based octahedral pocket that encapsulates fluorescein (FL) as a dye for light-driven hydrogen evolution inside the cavity, whereas the oxidized dye becomes water soluble and performs chemical oxidation outside the pocket (Scheme 1). The overall reaction constitutes hydrogen sulfide splitting, forming elemental sulfur and molecular hydrogen, analogous to watersplitting reaction.



**Scheme 1.** Schematic picture of the approach using a supramolecular system for the encapsulation of an organic dye within the cavity of the polyhedron to combine light-driven hydrogen production with sulfide oxidation by separating both redox events in space.

For the preparation of the new octahedral cage, we used a tritopic ligand, 2,2,2-((nitrilotris(benzene-4,1-diyl))tris-(methanyly lidene))-tris(hydrazinecarbothioamide), H<sub>3</sub>TFT.<sup>[10]</sup> The reaction of Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O with H<sub>3</sub>TFT in DMF solution gave the octahedron Ni-TFT in 40% yield. The coordination of the ligands to the metal ions in the self-assembled structure was confirmed by the splitting and shifting of the resonance signals in the <sup>1</sup>H-NMR spectrum. Specifically, the disappearance of the imine proton C(S)-NH signals at 11.38 ppm and the significant upfield shift of the thiosemicarbazone signals indicate that the bidentate moieties are coordinated to the nickel ions. X-ray structure analysis revealed the formation of Ni<sub>6</sub>L<sub>4</sub> octahedron in the solid state.<sup>[11]</sup> The three rigidly separated NS chelators of each ligand coordinate with three different metal centres, whereas six metal centres occupy the corner positions of the octahedron, each is coordinated in a distorted square planar geometry. The high

coordination ability of sulfur-containing chelators makes the octahedron Ni-TFT very stable, and should therefore allow the photochemical reaction to occur even in the presence of sulfide anions. The octahedral cage possesses ideal  $C_3$  symmetry with one of the four ligands located on the crystallographic  $C_3$  axis. A pseudo-S<sub>4</sub> symmetry is achieved by alternatively arranging the 4 planar ligands onto the eight triangular faces of the octahedron defined by the six metal ions. The M<sub>6</sub>L<sub>4</sub> cage has a similar structure as the palladium octahedron and the nickel octahedron previously reported by Fujita<sup>[12]</sup> and by us.<sup>[13]</sup> The geometry is heavily distorted with an inner volume of approximately 900Å<sup>3</sup>. The separation between the two metal ions coordinated to the same ligand is approximately 14.7 Å, and that between two diagonally opposing metal ions is approximately 20.6 Å. The amine groups in the building blocks that are located within the cavity of the pocket could act as hydrogen-bond acceptors, which together with possible aromatic stacking interactions of the phenyl rings may facility binding of fluorescein molecules (FL) within the pocket of the octahedron.



Figure 1. Structure of the Ni-TFT octahedron cage showing the coordination geometry of the nickel ions and the empty sphere (red ball) from different directions of the octahedron. The nickel, sulfur, nitrogen and carbon atoms have displayed in green, yellow, blue, and grey, respectively.

The structure of the Ni-TFT in solution was characterized by ESI-MS analysis, revealing a single charged species (m/z = 2535.05) that corresponds to  $HNi_6(TFT)_4^+$ . To further evaluate the binding of the FL dye in the cage, ten equivalents of FL were added to the cage solution, which was subjected to ESI-MS analysis. A new, intense peak at m/z = 2867.11 was observed in the mass spectrum of that could clearly be attributed to the species  $HNi_6(TFT)_4 \supset FL^+$ . A comparison of experimentally obtained peak with those obtained via the simulation, based on natural isotopic abundance, confirms the formation of this host guest complex. The <sup>1</sup>H-NMR spectrum of FL (0.2 mM) in the presence of Ni-TFT(0.1 mM) of (Figure S6) shows significant upfield shifts of the signals associated with the base-ring protons of the FL, ( $\delta$  = 0.15 ppm in an average), indicating that the FL molecules are encapsulated within the  $\pi$ -electron-rich pocket of the Ni-TFT octahedron.[14]

The binding of **FL** in the Ni–**TFT** cage was also studied by fluorescence. As expected, the Ni–**TFT** cage appeared to be an efficient quencher of the excited state of **FL**(Figure 2b). The addition of 50  $\mu$ M Ni–**TFT** to an EtOH/H<sub>2</sub>O solution of **FL**(10  $\mu$ M) quenches approximately 80% of the emission intensity of FL. The emission (at 525 nm) of an **FL** solution (10  $\mu$ M) containing Ni–**TFT** (50  $\mu$ M) decayed in a clearly exponential fashion with a

luminescence lifetime similar to that of the decay of the emission of **FL** (4.50 ns) (Figure S8). The fact that the emission intensity was quenched but the lifetime of the remaining luminescence is similar to that of the free dyes suggests that the quenching process is due to the formation of the host-guest complex.<sup>[7a]</sup> The titration profile of **FL** (10  $\mu$ M) in the solution was analysed with a Hill plot, and the best fit of the profile indicates the formation of a 1:1 host-guest complex with an association constant of 5.4(± 0.2)×10<sup>4</sup> M<sup>-1</sup> (Figure S10). This forms the basis to perform light-driven redox chemistry within the redox active cage, allowing further reactions with the oxidized dye such as sulifde oxidation. <sup>[15]</sup>

The cyclic voltammogram of Ni–TFT (0.1 mM), recorded in DMF solution, display two reduction waves related to the Ni<sup>II</sup>/Ni<sup>I</sup> and Ni<sup>I</sup>/Ni<sup>0</sup> reduction process around -1.2–1.5 V(vs. Ag/AgCl), respectively. These potentials fall well in the range for proton reduction in aqueous media.<sup>[16]</sup> Indeed, the addition of Et<sub>3</sub>NH<sup>+</sup> (Et<sub>3</sub>N, triethylamine) to the Ni–TFT solution (DMF) leads to a new wave near the redox peak at -1.50 V that increases with increasing acid concentration (Figure 2a), indicating that Ni–TFT acts as an electro-catalyst for proton reduction.



Figure 2. Cyclic voltammograms of Ni–TFT(0.1 mM) containing 0.1 M TBAPF<sub>6</sub> (black line) in the presence of different concentrations of HNEt<sub>3</sub>CI [0.6 mM (green line), 1.2 mM (blue line), 1.8 mM (red line), 2.4 mM (purple line)scan rate: 100 mV/s] (a). Emission spectra of FL (10  $\mu$ M) (black line) upon addition of Ni–TFT up to 50.0  $\mu$ M(b). Light-driven hydrogen evolution of systems containing FL (2.0 mM), and theNi–TFT concentration fixed at 2.0  $\mu$ M (black), 4.0  $\mu$ M (red line)or6.0  $\mu$ M (blue line)andNEt<sub>3</sub> (10% v/v)(fig c), or Na<sub>2</sub>S (0.05 M) solution (fig d) as the electron donor.

After the electrochemical proton reduction reaction was established, we first investigated the photo-chemical proton reduction reaction. The irradiation of a solution containing FL (2.0 mM), Ni-TFT (4.0  $\mu$ M), and NEt<sub>3</sub> (10% v/v) in H<sub>2</sub>O/EtOH (1:1 v/v) solution resulted in the hydrogen generation at pH=11.0-13.0 (Figure S13) as determined by GC, and the most efficient hydrogen production was achieved at pH≈12.6. Control experiments revealed that the absence of any of the individual components led to the failure for produce hydrogen, indicating that all three species are essential for hydrogen generation. In addition, in the absence of light no hydrogen was formed either. When the concentrations of FL(2.0 mM) and NEt<sub>3</sub> (10% volume) were fixed, the volume of hydrogen produced as a function of the concentration of Ni–TFT (between 2.0  $\mu$ M and 6.0  $\mu$ M) was linear. The initial turnover frequency was 1250 mole of hydrogen per mole of catalyst per hour, and the turnover number reached

25,000 per mole of Ni–**TFT**, which is the largest value reported to date for related system with **FL** as photosensitizer. <sup>[17]</sup>

The superiority of the host-guest system over other relevant systems is attributed to the pre-organization effect of the **FL** in the pocket, allowing a direct photo-induced electron transfer (PET) process from the excited state **FI**<sup>\*</sup> to the redox catalyst. The new pathway *via* oxidative quenching is thereby facilitated leading to direct reduction of the catalytic active sites and the oxidized dye guest **FL**<sup>\*</sup>.<sup>[6]</sup> When all species are free in solution, the pathway *via* reductive quenching, i.e. the quenching of the excited state **FI**<sup>\*</sup> by the electron donor that is present in excess to form unstable **FL**<sup>-</sup> radical anions, is predominant.<sup>[18]</sup> As such, the preorganization leads to prolonged lifetime of the system and this new synthetic platform allows in principle the combination of photocatalytic hydrogen evolution with substrate oxidation via the oxidized dye in a one-pot process.

In analogy to water splitting reaction,<sup>[19]</sup> the splitting of  $H_2S$  to produce both molecular hydrogen and elemental sulfur consists of two half reactions: proton reduction and sulfide oxidation. We anticipated that this would particularly interesting for the current system. The coupling of photochemical reduction of protons that occurs via oxidative quenching of the dye to generate molecular hydrogen with a chemical reaction that the oxidized photosensitizer that oxidizes sulphide to elemental sulfur will lead to the overall reaction of the hydrogen sulfide splitting.<sup>[20]</sup>



**Figure 3.**(a) Pictures showing the reaction mixture solution before irradiation (top) and after after irradiation (bottom); (b)XRD pattern of the yellowish powerand (c)a picture of the collected powder.

In a simple model reaction, H<sub>2</sub>S gas was bubbled into a H<sub>2</sub>O/EtOH (1:5 v/v) solution containing FL (2.0 mM) and NaOH (0.1 M) to adjust the pH value to12.6, a pH value that is most efficient for hydrogen production for the aforementioned FL/Ni-TFT/NEt<sub>3</sub> system, leading to a concentration of S<sup>2-</sup> of *ca*. 0.05 M. The resulting solution was then used for hydrogen production under irradiation after addition of the Ni-TFT octahedron. As shown in Figure 4a, the bright yellow solution turned turbid yellow with yellowish power and hydrogen gas formed after 24 hours of irradiation. A yellowish solid formed after further bubbling H<sub>2</sub>S gas to adjust the pH value to 8.0, which is required for the precipitation of elemental sulphur.<sup>[21]</sup> Powder X-ray diffraction of the yellowish solid (ca. 1 mg) that was separated through filtration indexed to a-S that matches well with spectra of commercial elemental sulfur. When the concentration of FL was fixed at 2.0 mM, the volume of the hydrogen produced as a function of Ni–**TFT** concentration (between 2.0  $\mu$ M and 6.0  $\mu$ M) was linear, just as found in the proton reduction reaction with

artificial reductant  $\text{Et}_3N$ , and the calculated turnover number reached 2600 per mole of catalyst.

Control experiments revealed that molecular hydrogen and elemental sulfur did not form in the absence of the catalyst or when the reaction was carried out in the dark. Similar to the proton reduction reaction, the pre-organization of the dye with Ni–TFT cage leads to a direct photo-induced electron transfer from the excited state  $FL^*$  to the redox catalyst (oxidative quenching), reducing the nickel complexes of the vessel, expelling the oxidized dye  $FL^+$  from the cage.<sup>[22]</sup> The reduced redox vessel reduces protons to produce molecular hydrogen. The oxidized  $FL^+$  species further oxidizes sulfide in the bulk solution to generate solid sulphur. The cage system with FI will undergo the next cycle of photo excitation required for proton reduction catalysis.



Figure 4. Molecular structure with the atomic-numbering scheme of Ni-DMT.

To confirm the importance of the cage, control experiments were performed using mono-nuclear compound Ni-DMT, which was synthesized by reacting Ni(CH<sub>3</sub>COO)<sub>2</sub>•4H<sub>2</sub>O with the ligand HDMT.<sup>[23]</sup> The crystal structure (Figure 4) exhibited that the ligand environment around nickel in Ni-DMT is similar to those of the Ni-TFT cage. To a solution containing 2 mM of FL, 0.05 M of Na<sub>2</sub>S that generated by the same procedure as previously indicated, and 24 µM Ni-DMT, that ensured the same concentration of the nickel ions, only 0.32 mL hydrogen was generated and no yellow precipitate was observed, under the same reaction conditions. Luminescence titrations of FL (10 µM) quenched about 38% of the emission upon the addition of up to 0.024 mM Ni-DMT and gave the quenching constant (Ksv) about 1530M<sup>-1</sup>. With the consideration of the much larger concentration of Na<sub>2</sub>S (0.05 M) under catalysis conditions, reduction quenching by Na2S that gives the reduced organic dye FL<sup>-</sup> is the dominant process, the sulfide ions formed polysulfides  $S_n^{2}$  and no element sulfur was obtained under these conditions.

To further confirm the role of the cage and pre-organization effect, a classic inhibition experiment was carried out by adding a non-reactive quest, glucosamine (GLA), that competes for the binding pocket with the dye.<sup>[13]</sup> The addition of **GLA** (2.0 mM) quenched the photocatalytic H<sub>2</sub>S splitting of the FI(2.0 mM)/Ni-TFT(4.0 µM)/Na<sub>2</sub>S(0.05 M) reaction mixture, 0.32 mL hydrogen gas was generated and no yellow precipitate was observed. Notably, the addition of the same amount GLA into the FI (2.0 mM)/Ni-DMT(24.0 µM)/Na<sub>2</sub>S(0.05 M) didn't change the reaction outcome of this experiment. The competitive inhibition behaviour of the supramolecular system confirmed the relevance of encapsulation of the organic dye for the overall reaction. These experiments show the importance of the pre-organization of the FI and the catalysts in the Ni-TFT cage leading to high local concentration of the catalyst-dye complex their by facilitating the oxidative guenching pathway.

In view of practical applications the current process is also interesting as the hydrogen and solid sulfer can be collected in separate steps. An example of a potential semi-contineous

process of the splitting procedure is shown in Figure 5b.<sup>[24]</sup> H<sub>2</sub>S is bubbled into the reactor (first reactor) generating a pH at which elemental sulfur precipitates and can be isolated (second reactor), after which the NaOH solution can be added to generate the proper Na<sub>2</sub>S concentration. In the final reactor the **FL** photo-sensitizer and the Ni–**TFT** catalyst can produce molecular hydrogen via direct light irradiation which can be easily separated from solution. The remaining solution can be transferred to the first reactor to adjust the pH value with H<sub>2</sub>S gas for the formation of precipitates of elemental sulfur from the solution, and the next cycle is started. If needed, additional photosensitizer (and sometimes a small amount of catalyst) can be added to maintain the efficiency of the recyclable systems.



**Figure 5**. (a) Turnover number of hydrogen( per Ni atom, cyan bars) and sulphur(per Ni atom, pink bars)produced of systems containing FL(2.0 mM)/ Na<sub>2</sub>S (0.05 M) with Ni–TFT(4.0  $\mu$ M) and Ni–DMT (24  $\mu$ M) in the absence and presence of **GLA** (2.0 mM). (b) Schematic picture of the recyclability of the system via continuous bubbling of H<sub>2</sub>S gas and the addition of a dyes to obtain molecular hydrogen and elemental sulfur under irradiation.

In summary, a new synthetic platform to combine the photocatalytic hydrogen evolution and sulfide oxidation in a one-pot procedure was developed *via* control the host-guest location of the redox events. The encapsulation of organic dye within the pocket of the redox active vessel modified photocatalytic proton reduction in the inner space of the pocket to get the molecular hydrogen and oxidized dye. The oxidized dye gets out of the pocket *via* equilibrium-controlled host-guest interaction and causes sulfide oxidation outside the cavity to give element sulfur, further completing the overall formation of molecular hydrogen and elemental sulfur, analogous to the water-splitting reaction. The simple separation of the molecular hydrogen and elemental sulphur from solution makes this system interesting compared to other photocatalytic systems. It provides an easy implementation for potential practical applications in the chemical industry.

**Acknowledgements** This study was supported by NSFC (21421005, 21531001 and 21501041) and CPSF (No. 2016 M 590195).

Keywords: Metal-organic Vessel •Hydrogen sulphide splitting
Photocatalytic hydrogen generation• Supramolecular catalysis

- a) M. Hoarau, C. Hureau, E. Gras, P. Faller, *Coord. Chem. Rev.* 2016, 308, 445–459; b) K. J. Young, B. J. Brennan, R. Tagore, and G. W. Brudvig, *Acc. Chem. Res.*2015, 48, 567–574; c)T. Hisatomi, J. Kubota, K. Domen, *Chem. Soc. Rev.*, 2014, 43, 7520–7535.d) M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis, *Chem. Rev.* 2010, *110*, 6446–6446;
- For reviews see : a) S. H. A. M. Leenders, R. Gramage-Doria, B. de Bruin, and J. N. H. Reek, *Chem. Soc. Rev.*, **2015**, *44*, 433–48; b) M. Raynal, P. Ballester, A. Vidal-Ferran, P.W.N.M. van Leeuwen, *Chem. Soc. Rev.*, **2014**, *43*, 1734-87; c) M. Yoshizawa, J. K. Klosterman, M. Fujita, *Angew. Chem. Int. Ed.*, **2009**, *48*, 3418–3438; d) T. R. Cook, V. Vajpayee, M. H. Lee, P. J. Stang, K. W. Chi, *Acc. Chem. Res.* **2013**, *46*, 2464–2474; e) M. D. Ward,P. R. Raithby, *Chem. Soc. Rev.* **2013**, *42*, 1619–1636. f) J. Meeuwissen, J. N. H. Reek, *Nat. Chem.* **2010**, *2*, 615.

- [3] a) P. Thordarson, E. J. A. Bijsterveld, A. E. Rowan, and R. J. M. Nolte, *Nature*, **2003**, *424*, 915–8; b) Z. J. Wang, K. N. Clary, R. G. Bergman, K. N. Raymond, F. D. Toste, *Nature Chem.* **2013**, *5*, 100–103; c) M. Schulze, V.Kunz, P. D.Frischmann, F. Würthner, *Nat. Chem.* **2016**, *8*, 576–583; e) a) V. Bocokić, A. Kalkan, M. Lutz, A. L. Spek, D. T. Gryko, and J. N. H. Reek, *Nat. Commun.*, **2013**, *4*, 2670.
- [4] a) M. Yoshizawa, M. Tamura and M. Fujita, *Science*, **2006**, *312*, 251-254; b) M. J. Wiester, P. A. Ulmann, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2011**, *50*, 114–137 b) Y. Kohyama, T. Murase, M. Fujita, *J. Am. Chem.* Soc. **2014**, *136*, 2966–2969;
- [5] M. Kaphan, M. D. Levin, R. G. Bergman, K. N. Raymond, F. D. Toste, *Science* 2015, 350, 1235-1238.
- [6] a) M. Frank, J. Ahrens, I. Bejenke, M. Krick, D. Schwarzer, G. H. Clever, *J. Am. Chem. Soc.* 2016, *138*, 8279–8287; b) D. M. Dalton, S. R. Ellis, E. M. Nichols, R. A. Mathies, F. D. Toste, R. G. Bergman, K. N. Raymond, *J. Am. Chem. Soc.* 2015, *137*, 10128–10131; c) M. Porel, C. H. Chuang, C. Burda, V. Ramamurthy, *J. Am.Chem. Soc.* 2012, *134*, 14718–14721.
- [7] a) X. Jing, C. He, Y. Yang, C. Y. Duan, J. Am. Chem. Soc. 2015, 137,3967–3974; b) L. Yang, C. He, X. Liu, J. Zhang, H. Sun,Huimin Guo, Chem. Eur. J. 2016, 22, 5253–5260; c) A.M. Kluwer, R. Kapre, F. Hartl, M. Lutz, A. L. Spek, A.M. Brouwer, P. W. N. M van Leeuwen, J. N. H. Reek PNAS, 2009, 26, 10460.
- [8] a) Z. Lei, W. You, M. Liu, G. Zhou, T. Takata, M. Hara, K. Domen, C. Li, *Chem. Commun.* **2003**, 2142–2144; b) S. V. Tambwekar, M. Subrahmanyam, *Int. J. Hydrogen Energy* **1997**, *22*, 959–965; c) W. G. Ma, J. F. Han, W. Yu, D. Yang, H. Wang, X. Zong, C. Li, *ACS Catal.* **2016**, *6*, 6198–6206.
- [9] a) F. Bedoya-Lora, A. Hankin, G. H. Kelsall, *Electrochem. Commun.* **2016**, 68, 19-22; b) X. Zong, J. Han, B. Seger, H. Chen, G. Lu, C. Li, L. Wang. *Angew. Chem. Int. Ed.* **2014**, 53, 4399–4403; c) J. Zaman, A. Chakma, *Fuel Process. Technol.* **1995**, *41*, 159–198.
- [10] T. Mallegol, S. Gmouh, M. Meziane, M. Blanchard-Desce, O. Mongin, Synthesis, 2005, 11, 1771–1774.
- [11] Data for Ni-**TFT** C<sub>154</sub>H<sub>236</sub>N<sub>58</sub>N<sub>16</sub>O<sub>27</sub>S<sub>12</sub>, Mr = 4068.99, Hexagonal, space group *R*3, dark-red block, *a* = 22.521(1) Å, *c* = 47.501(5) Å, *V* =20865(3) Å<sup>3</sup>, Z = 3, Dc= 0.971 g cm<sup>-3</sup>, *T* = 180(2)K,  $\mu$ (Mo-K $\alpha$ ) = 0.543mm<sup>-1</sup>. [*R*<sub>int</sub>= 0.1095]. For 16290 unique reflects, final *R*<sub>1</sub>[with I >2 $\sigma$ (I)] =0.0796, wR<sub>2</sub> (all data) = 0.1826, GOOF = 1.030. CCDC No. 1439166.
- [12] M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi, K. Ogura, *Nature*. **1995**, 378, 469–471.
- [13] C. He, Z. Lin, Z. He, C. Y. Duan, C. H. Xu, Z. M. Wang, C. H. Yan, Angew. Chem. Int. Ed. 2008, 47, 877-881.
- [14] S. M. Biros, R. M. Yeh, K. N. Raymond, Angew. Chem. Int. Ed. 2008, 47, 6062–6064.
- [15] B. Ginovska-Pangovska, A. Dutta, M. L. Reback, J. C. Linehan, W. J. Shaw, Acc. Chem. Res. 2014, 47, 2621–2630.
- [16] A. L. Cour, M. Findeisen, A. Hazell, R. Hazell, G. Zdobinsky, J. Chem. Soc. Dalton Trans., 1997, 121–128
- [17] Z. Han, L. Shen, W. W. Brennessel, P. LHolland, R. Eisenberg, J. Am. Chem. Soc.2013, 135, 14659–14669.
- [18] Z. Han, W. R. McNamara, M. S. Eum, P. L. Holland, R. Eisenberg, Angew. Chem. Int. Ed. 2012, 51, 1667–1670
- [19] S. Fukuzumi, T. Kishi , H. Kotani, Y.-M. Lee, W. Nam, Nat. Chem. 2011, 3, 38–41.
- a) M. A. Plummer, P. M. Beazley, Conversion of hydrogen sulfide to sulfur and hydrogen. *United States Patent*. **1986**, NO. 4592905; .b) H.
   Shiina, M. Oya, K. Yamashita, A. Miyoshi, H. Matsui. *J. Phys. Chem.* **1996**, *100*, 2136–2140.
- [21] K. Petrov, S. Srinivasan, Int. J. Hydrogen Energy, 1996, 21,163-169.
- [22] H. F. M. Nelissen, M. Kercher, L. De Cola, M. C. Feiters, R. J. M. Nolte. Chem. Eur. J. 2002, 8, 5407–54
- [23] S. Chandra, S. Goel, S. D. Dwivedi, *Int. J. Appl. Bio. & Pharm. Tech.* **2012**, *3*, 149-159. Data for Ni-**DMT**: C<sub>20</sub>H<sub>26</sub>N<sub>8</sub>NiS<sub>2</sub>, Mr = 501.32, Monoclinic, space group *P*<sub>21</sub>/c, *a* = 10.409(1) Å, *b* = 7.442(1) Å, *c* =15.388(1) Å, *V* = 1139.3(1) Å<sup>3</sup>, Z = 2, Dc = 1.461 g cm<sup>-3</sup>,  $\mu$ (Mo-Kα) = 1.060 mm<sup>-1</sup>. [*R*<sub>int</sub>= 0.0204]. For 2011 unique reflects, final*R*<sub>1</sub> [with I >2σ(I)] = 0.0329, wR<sub>2</sub>(all data) = 0.0981, GOOF = 1.045.CCDC No. 1439165.
- [24] H. Huang, Y. Yu, K. H. Chung, Energy Fuels. 2009, 23, 4420–4425.

#### WILEY-VCH

# COMMUNICATION

#### **Entry for the Table of Contents**

#### COMMUNICATION

#### Text for Table of Contents

A supramolecular cage that allows to combine a photocatalytic hydrogen evolution with sulfide oxidation in a one-pot process was developed, by preorganization of the dye controlling the crucial electron transfer steps. The overall lloop constitutes hydrogen sulfide splitting, forming molecular hydrogen and elemental sulfur, which is analogous to the water-splitting reaction.

