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Control of Redox Events by Dye Encapsulation Applied to Light-Driven Splitting of Hydrogen Sulfide

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Abstract: Solar production of hydrogen by consuming low-value waste products is an attractive pathway that has both economic and environmental benefits. Inspired by the reactive pocket of enzymes, a synthetic platform to combine photocatalytic hydrogen evolution with sulfide oxidation in a one-pot process via control over the location of the electron-transfer steps is developed. The redox-active coordination vessel **Ni-TFT**, which has 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.

Catalytic strategies inspired by natural enzymes that work under ambient conditions have attracted interest as they may lead to important future tools for efficient chemical conversions.^[1] To achieve efficiencies and selectivities similar to those displayed by enzyme, scientists have devised several kind of macrocycles with well-defined pockets, in which chemical transformations can take place.^[2,3] Reactions performed in such confined spaces can have enhanced reaction rates as a result of the proximity effects, leading to unusual selectivity because of the restricted rotational freedom of substrates in the cage.^[4] 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.^[5,6] In view of our interest to develop host-guest systems for photo-catalytic redox reactions,^[7] 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, that is, the inner-space and outer-space of the cavity, respectively.^[7]

An interesting application of such an approach would be the light-driven splitting of hydrogen sulfide (H_2S), as H_2S 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_2S by combining sulfide oxidation and proton reduction using solar energy has been postulated as an interesting sustainable strategy.^[8] However, as the sulfide ions always form polysulfides (S_n^{2-}) when acting as sacrificial reagents^[9] and both the polysulfide and sulfide can coordinate strongly to a potential transition-metal catalyst, 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 water-splitting reaction.

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Scheme 1. Schematic representation of using a supramolecular system for the encapsulation of an organic dye within the cavity of the supramolecular 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(methanylylidene))tris(hydrazinecarbothioamide), H_3TFT .^[10] The reaction of $Ni(CH_3COO)_2 \cdot 4H_2O$ with H_3TFT in DMF solution gave the octahedral 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 1H NMR spectrum. Specifically, the disappearance of the imine proton C(S)-NH signals at $\delta = 11.38$ 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_6L_4 octahedron in the solid state (Figure 1).^[11] The three rigidly separated N,S

Figure 1. Different views of the structure of the Ni-TFT octahedral cage showing the coordination geometry of the nickel ions and the empty sphere (red ball). The Ni green, S yellow, N blue, and C gray.

chelators of each ligand coordinate with three different metal centers, whereas six metal centers 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_4 symmetry is achieved by alternatively arranging the four planar ligands onto the eight triangular faces of the octahedron defined by the six metal ions. The M_6L_4 cage has a similar structure as the palladium octahedron and the nickel octahedron previously reported by Fujita^[12] and by us.^[13] The geometry is heavily distorted with an inner volume of approximately $900 \text{ \AA}^3$. The separation between the two metal ions coordinated to the same ligand is approximately $14.7 \text{ \AA}$, and that between two diagonally opposing metal ions is approximately $20.6 \text{ \AA}$. 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 facilitate binding of fluorescein molecules (FL) within the pocket of the octahedron.

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 $HNi_6(TFT)_4 \cdot FL^+$. 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 1H -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 π -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 $50 \mu\text{M}$ Ni-TFT to an EtOH/ H_2O solution of FL ($10 \mu\text{M}$) quenches approximately 80% of the emission intensity of FL. The emission (at 525 nm) of an FL solution ($10 \mu\text{M}$) containing Ni-TFT ($50 \mu\text{M}$) 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 in the Supporting Information). 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.^[7a] The titration profile of FL ($10 \mu\text{M}$) in the solution was analyzed with a Hill plot, and the best fit of the profile indicates the formation of a 1:1 host-guest complex

Figure 2. a) Cyclic voltammograms of Ni-TFT (0.1 mM) containing 0.1 M TBAPF₆ (black line) in the presence of different concentrations of HNEt₃Cl [0.6 mM (green line), 1.2 mM (blue line), 1.8 mM (red line), 2.4 mM (purple line) scan rate: 100 mVs⁻¹]. b) Emission spectra of FL (10 mM) (black line) upon addition of Ni-TFT up to 50.0 mM. c) Light-driven hydrogen evolution of systems containing FL (2.0 mM), and the Ni-TFT concentration fixed at 2.0 mM (black), 4.0 mM (red line) or 6.0 mM (blue line) and NEt₃ (10% v/v), or d) Na₂S (0.05 M) solution as the electron donor.

with an association constant of $5.4(\pm 0.2) \times 10^4 \text{ M}^{-1}$ (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 sulfide oxidation.^[15]

The cyclic voltammogram of Ni-TFT (0.1 mM), recorded in DMF solution, display two reduction waves related to the $\text{Ni}^{\text{II}}/\text{Ni}^{\text{I}}$ and $\text{Ni}^{\text{I}}/\text{Ni}^0$ 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.^[16] Indeed, the addition of Et_3NH^+ (Et_3N , 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.

After the electrochemical proton reduction reaction was established, we first investigated the photochemical proton reduction reaction. The irradiation of a solution containing FL (2.0 mM), Ni-TFT (4.0 μM), and NEt_3 (10% v/v) in $\text{H}_2\text{O}/\text{EtOH}$ (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_3 (10% volume) were fixed, the volume of hydrogen produced as a function of the concentration of Ni-TFT (between 2.0 μM and 6.0 μM) 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.^[17]

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 FL^* 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^+ .^[6] When all species are free in solution, the pathway via reductive quenching, that is, the quenching of the excited state FL^* by the electron donor that is present in excess to form unstable $\text{FL}^{\cdot-}$ radical anions, is predominant.^[18] 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,^[19] 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 photo-sensitizer that

oxidizes sulfide to elemental sulfur will lead to the overall reaction of the hydrogen sulfide splitting.^[20]

In a simple model reaction, H_2S gas was bubbled into a $\text{H}_2\text{O}/\text{EtOH}$ (1:5 v/v) solution containing FL (2.0 mM) and NaOH (0.1M) to adjust the pH value to 12.6, a pH value that is most efficient for hydrogen production for the aforementioned FL/Ni-TFT/ NEt_3 system, leading to a concentration of S^{2-} of ca. 0.05 M. The resulting solution was then used for

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

hydrogen production under irradiation after addition of the Ni-TFT octahedron. As shown in Figure 3a, the bright yellow solution turned turbid yellow with yellowish powder and hydrogen gas formed after 24 h of irradiation. A yellowish solid formed after further bubbling H_2S gas to adjust the pH value to 8.0, which is required for the precipitation of elemental sulfur.^[21] Powder X-ray diffraction of the yellowish solid (ca. 1 mg) that was separated through filtration indexed to α -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 μM and 6.0 μM) was linear, just as found in the proton reduction reaction with artificial reductant Et_3N , and the calculated turnover number (TON) 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.^[22] The reduced redox vessel reduces protons to produce molecular hydrogen. The oxidized FL^+ species further oxidizes sulfide in the bulk solution to generate solid sulfur. The cage system with FL will undergo the next cycle of photo excitation required for proton reduction catalysis.

To confirm the importance of the cage, control experiments were performed using mono-nuclear compound Ni-DMT, which was synthesized by reacting Ni(CH_3COO) $_2$ ·4H $_2$ O with the ligand HDMT.^[23] The crystal structure (Figure 4) showed that the ligand environment

Figure 4. Molecular structure of Ni-DMT. Ni light blue, N dark blue, S yellow.

around nickel in Ni-DMT is similar to that of the Ni-TFT cage. To a solution containing 2 mM of FL, 0.05 M of Na $_2$ 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 (K_{sv}) about 1530 M $^{-1}$. With the consideration of the much larger concentration of Na $_2$ S (0.05 M) under catalysis conditions, reduction quenching by Na $_2$ S that gives the reduced organic dye FL $^-$ 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 guest, glucosamine (GLA), that competes for the binding pocket with the dye.^[13] The addition of GLA (2.0 mM) quenched the photocatalytic H $_2$ S splitting of the FL (2.0 mM)/Ni-TFT (4.0 μM)/Na $_2$ 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 FL (2.0 mM)/Ni-DMT (24.0 μM)/Na $_2$ S (0.05 M) did not change the reaction outcome of this experiment. The competitive inhibition behavior 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 FL and the catalysts in the Ni-TFT cage leading to high local concentration of the catalyst-dye complex their by facilitating the oxidative quenching pathway.

In view of practical applications the current process is also interesting as the hydrogen and solid sulfur can be collected in separate steps. An example of a potential semi-continuous process of the splitting procedure is shown in Figure 5b.^[24] H $_2$ 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 $_2$ S concentration. In the final

Figure 5. a) Turnover number of hydrogen (per Ni atom, cyan bars) and sulfur (per Ni atom, pink bars) produced of systems containing FL (2.0 mM)/Na $_2$ S (0.05 M) with Ni-TFT (4.0 μM) and Ni-DMT (24 μM) in the absence and presence of GLA (2.0 mM). b) Schematic representation of the recycling of the system via continuous bubbling of H $_2$ S gas and the addition of dyes to obtain molecular hydrogen and elemental sulfur under irradiation.

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 $_2$ 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.

In summary, a new synthetic platform to combine the photo-catalytic 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 give molecular hydrogen and oxidized dye. The oxidized dye leaves the pocket via equilibrium-controlled host-guest interaction and causes sulfide oxidation outside the cavity to give element sulfur, 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 sulfur from solution makes this system interesting compared to other photocatalytic systems. It provides an easy implementation for potential practical applications in the chemical industry.

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Conflict of interest

The authors declare no conflict of interest.

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- [1] 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, 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.
- [2] For Reviews see: a) S. H. A. M. Leenders, R. Gramage-Doria, B. de Bruin, J. N. H. Reek, *Chem. Soc. Rev.* **2015**, *44*, 433–448; b) M. Raynal, P. Ballester, A. Vidal-Ferran, P. W. N. M. van Leeuwen, *Chem. Soc. Rev.* **2014**, *43*, 1734–1787; c) M. Yoshizawa, J. K. Klosterman, M. Fujita, *Angew. Chem. Int. Ed.* **2009**, *48*, 3418–3438; *Angew. Chem.* **2009**, *121*, 3470–3490; 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, R. J. M. Nolte, *Nature* **2003**, *424*, 915–918; b) Z. J. Wang, K. N. Clary, R. G. Bergman, K. N. Raymond, F. D. Toste, *Nat. Chem.* **2013**, *5*, 100–103; c) M. Schulze, V. Kunz, P. D. Frischmann, F. Würthner, *Nat. Chem.* **2016**, *8*, 576–583; d) V. Bocokić, A. Kalkan, M. Lutz, A. L. Spek, D. T. Gryko, J. N. H. Reek, *Nat. Commun.* **2013**, *4*, 2670.
- [4] a) M. Yoshizawa, M. Tamura, 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; *Angew. Chem.* **2011**, *123*, 118–142; c) 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, H. 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, *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 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; *Angew. Chem.* **2014**, *126*, 4488–4492; 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**, 1771–1774.
- [11] Data for Ni-TFT $\text{C}_{154}\text{H}_{236}\text{N}_{58}\text{Ni}_6\text{O}_{27}\text{S}_{12}$, $M_r = 4068.99$, Hexagonal, space group $R\bar{3}$, dark-red block, $a = 22.521(1)$, $c = 47.501(5)$ Å, $V = 20865(3)$ Å³, $Z = 3$, $\rho_{\text{calcd}} = 0.971$ g cm⁻³, $T = 180(2)$ K, $\mu(\text{Mo-K}\alpha) = 0.543$ mm⁻¹. [$R_{\text{int}} = 0.1095$]. For 16290 unique reflects, final R_1 [with $I > 2\sigma(I)$] = 0.0796, wR_2 (all data) = 0.1826, GOOF = 1.030. CCDC 1439166 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
- [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; *Angew. Chem.* **2008**, *120*, 891–895.
- [14] S. M. Biros, R. M. Yeh, K. N. Raymond, *Angew. Chem. Int. Ed.* **2008**, *47*, 6062–6064; *Angew. Chem.* **2008**, *120*, 6151–6153.
- [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. L. Holland, 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; *Angew. Chem.* **2012**, *124*, 1699–1702.
- [19] S. Fukuzumi, T. Kishi, H. Kotani, Y.-M. Lee, W. Nam, *Nat. Chem.* **2011**, *3*, 38–41.
- [20] a) “Conversion of hydrogen sulfide to sulfur and hydrogen”: M. A. Plummer, P. M. Beazley, United States Patent, NO. 4592905, **1986**; 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*, 5407–5454.
- [23] S. Chandra, S. Goel, S. D. Dwivedi, *Int. J. Appl. Biol. Pharm. Technol.* **2012**, *3*, 149–159; Data for Ni-DMT: $\text{C}_{20}\text{H}_{26}\text{N}_3\text{NiS}_2$, $M_r = 501.32$, Mono-clinic, space group $P2_1/c$, $a = 10.409(1)$, $b = 7.442(1)$, $c = 15.388(1)$ Å, $V = 1139.3(1)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.461$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 1.060$ mm⁻¹. [$R_{\text{int}} = 0.0204$]. For 2011 unique reflects, final R_1 [with $I > 2\sigma(I)$] = 0.0329, wR_2 (all data) = 0.0981, GOOF = 1.045. CCDC 1439165 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
- [24] H. Huang, Y. Yu, K. H. Chung, *Energy Fuels* **2009**, *23*, 4420–4425.

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