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

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

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Supporting Information

1. Syntheses and Characterizations.

   General characterization methods and equipment:

   All chemicals were of reagent grade quality obtained from commercial sources and used without further purification.

   $^1$H-NMR spectra and NOESY spectrum were measured on a Varian INOVA 500 M and 100 M spectrometer.

   ESI mass spectra were carried out on a HPLC-Q-Tof MS spectrometer.

   The elemental analyses of C, H and N were performed on a Vario EL III elemental analyzer.

   Uv-vis spectra were measured on a HP 8453 spectrometer. The solution fluorescent spectra were measured on JASCO FP-6500. The solution of fluorescein was prepared in EtOH/H$_2$O 1:1 (v:v), whereas the solution of the Ni$^-$TFT was prepared in DMF.

   Electrochemical measurements were performed on ZAHNER ENNIUM Electrochemical Workstation with a conventional three-electrode system with a homemade Ag/AgCl electrode as a reference electrode, a platinum silk with 0.5 mM diameter as a counter electrode, and glassy carbon electrode as a working electrode. The measurements were performed at room temperature after degassed by nitrogen.

   Preparation of Ni$^-$TFT: H$_3$TFT (54.8 mg, 0.10 mmol) and Ni(CH$_3$COO)$_2$•4H$_2$O (23.8 mg, 0.10 mmol) were dissolved in DMF (5 mL). The solution was stirred for 4 h and cooled to room temperature. Dark red crystals of Ni$^-$TFT were obtained by diffusing diethyl ether into the above-mentioned DMF solution. Yield: approximately 40% (based on the crystals dried in vacuum). Anal. Calc. for C$_{154}$H$_{236}$N$_{58}$Ni$_6$O$_{27}$S$_{12}$: H, 5.85; C, 45.46; N, 19.97; Found: H, 6.05; C 44.99; N 19.71. $^1$H-NMR (DMSO-d$_6$, ppm) 7.96 (s, 3H, CH=N), 7.78 (br, 6H, −NH$_2$), 7.26 (d, 3H, phenyl), 7.17 (d, 3H, phenyl), 6.38 (d, 3H, phenyl), 6.22 (d, 3H, phenyl). ESI–MS,M$^+$: 2535.05.

   Preparation of Ni$^-$DMT: 2-(4-(Dimethylamino)benzylidene)hydrazinecarbothioamide (22.2 mg, 0.1 mmol) and Ni(CH$_3$COO)$_2$•4H$_2$O (23.8 mg, 0.10 mmol) were dissolved in DMF (10 mL) and stirred overnight. Black crystals of Ni$^-$DMT were obtained by diffusing ether into
the above-mentioned DMF solution. Yield: approximately 60% (based on the crystals dried in vacuum). Anal. Calc. for C_{20}H_{26}N_{8}NiS_{2}: H, 5.23; C, 47.92; N, 22.35; Found: H, 5.69; C 48.11; N 21.98. ESI–MS, M^+: 501.12.

Photoinduced hydrogen evolution was performed in a 40 mL flask. Varying amounts of the catalyst, FL and TEA were added to 5.0 mL EtOH/H_{2}O solution (1:1 v/v, pH = 12.6). The flask was degassed by bubbling argon for 20 min under atmospheric pressure at room temperature. Then, the flask was irradiated by a 500 W Xenon lamp at room temperature using a water filter to absorb the heat. The generated photoproduct of H_{2} was characterized by analysis on a GC 7890T instrument using a 5 Å molecular sieve column (0.6 m×3 mm), thermal conductivity detector, and argon as the carrier gas. The amount of hydrogen generated was determined using an external standard. Hydrogen in the resulting solution was not measured, and the slight effect the hydrogen gas generated on the pressure of the flask was neglected for calculation of the volume of hydrogen gas.s1

The photocatalysis of hydrogen sulfide splitting was performed in a 25 mL flask. The catalyst and FL were added in a EtOH/H_{2}O solution (5:1 v/v, pH = 12.6) that contained 0.05 M Na_{2}S, using a 1.0 M HCl solution to adjust the pH. The flask was degassed by bubbling argon for 20 min under atmospheric pressure at room temperature. Then, the flask was irradiated by a 500 W Xenon lamp at room temperature using a water filter to absorb the heat. The generated photoproduct of H_{2} was characterized by a GC 7890T instrument using a 5 Å molecular sieve column (0.6 m × 3 mm). We used hydrogen sulfide gas to form the Na_{2}S solution by bubbling hydrogen sulfide into a 40 mL 0.5 M NaOH aqueous solution to adjust the pH to 12.6. Then, 1 mL of the above-mentioned solution was taken, and 4 mL of ethanol was added to form the reaction solution.
2. Crystallography:

The intensities were collected on a Bruker SMART APEX CCD diffractometer equipped with a graphite-monochromated Mo–Kα (λ = 0.71073 Å) radiation source; the data were acquired using the SMART and SAINT programs. The structures were solved by direct methods and refined on F² by full-matrix least-squares methods using the SHELXTL version 5.1 software.

Crystal data for Ni–TFT: C₁₅₄H₂₃₆N₅₈Ni₆O₂₇S₁₂ [Ni₆(C₂₄N₁₀H₂₁S)₄·18(C₃H₇NO)·4CH₃OH·5H₂O], Mr = 4068.99, Hexagonal, space group R3, dark-red block, a = 22.521(1) Å, c = 47.501(5) Å, V = 20865(3) Å³, Z = 3, Dc= 0.971 g cm⁻³, T = 180(2)K, μ(Mo-Kα) = 0.543 mm⁻¹. [Rₐ = 0.1095]. For 16290 unique reflects, final R₁ [with I >2σ(I)] = 0.0796, wR₂ (all data) = 0.1826, GOOF = 1.030. CCDC NO.1439166.

Crystal data for Ni–DMT: C₂₀H₂₆N₈NiS₂ [Ni(C₁₀H₁₃N₄S)₂], Mr = 501.32, Monoclinic, space group P2₁/c, red block, a = 10.409(1) Å, b = 7.442(1) Å, c = 15.388(1) Å, V = 1139.3(1) Å³, Z = 2, Dc= 1.461 g cm⁻³, T = 296 (2)K, μ(Mo-Kα) = 1.060 mm⁻¹. [Rₐ = 0.0204]. For 2011 unique reflects, final R₁ [with I >2σ(I)] = 0.0329, wR₂ (all data) = 0.0981, GOOF = 1.045. CCDC NO.1439165.

For the refinement of Ni–TFT and Ni–DMT, non-hydrogen atoms were refined anisotropically. Except the solvent water molecules, hydrogen atoms were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. Several bond distances in solvent molecules were restrained as idealized values. Thermal parameters on adjacent atoms of the solvent molecules were restrained to be similar.
Figure S1. Molecular structure of Ni-TFT capsule within an unique asymmetric unit, showing the backbone of the ligand in the complex.

Selected Bond Distances (Å)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(1)-C(1)</td>
<td>1.691(4)</td>
</tr>
<tr>
<td>S(3)-C(21)</td>
<td>1.759(4)</td>
</tr>
<tr>
<td>N(2)-N(3)</td>
<td>1.384(4)</td>
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<tr>
<td>N(3)-C(2)</td>
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<tr>
<td>N(4)-C(11)</td>
<td>1.390(5)</td>
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<tr>
<td>N(5)-N(6)</td>
<td>1.392(4)</td>
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<tr>
<td>N(6)-C(12)</td>
<td>1.321(4)</td>
</tr>
<tr>
<td>N(8)-C(21)</td>
<td>1.301(4)</td>
</tr>
<tr>
<td>N(9)-C(22)</td>
<td>1.317(4)</td>
</tr>
<tr>
<td>N(10)-C(16)</td>
<td>1.397(4)</td>
</tr>
</tbody>
</table>
Figure S2 Coordination geometry of the Ni(1) atom in Ni-TFT. Selected bond distances (Å) and angles (°): Ni(1)-N(3) 1.825(2), Ni(1)-N(6A) 1.986(3), Ni(1)-S(1) 2.1403(12), Ni(1)-S(2A) 2.165(1), N(3)-Ni(1)-N(6A) 98.7(1), N(3)-Ni(1)-S(1) 87.1 (1), N(6A)-Ni(1)-S(1) 163.7(1), N(3)-Ni(1)-S(2A) 166.2(1), N(6A)-Ni(1)-S(2A) 85.8(1), S(1)-Ni(1)-S(2A) 92.1(1). Symmetry Code: A: 1-y, 1+x-y, z.
Figure S3 Coordination geometry of the Ni(2) atom in Ni-TFT. Selected bond distances (Å) and angles (°): Ni(2)-N(13) 1.880(2), Ni(2)-N(9) 1.876(3), Ni(2)-S(4) 2.128(1), Ni(2)-S(3) 2.161(1), N(13)-Ni(2)-N(9) 101.4(1), N(13)-Ni(2)-S(4) 87.3(1), N(9)-Ni(2)-S(4) 165.1(1), N(13)-Ni(2)-S(3) 164.2(1), N(9)-Ni(2)-S(3) 83.4(1), S(4)-Ni(2)-S(3) 91.4(1).
Figure S4 Coordination geometry of the Ni(1) atom in Ni-DMT. Selected bond distances (Å) and angles (°): Ni(1)-S(1) 2.180(1), Ni(1)-N(3) 1.911(2), N(3)-Ni(1)-S(1) 85.4(1), N(3)-Ni(1)-S(1A) 94.5(1); Symmetry Code: A: -x, 1 -y, -z.
3. ESI-MS and NMR Spectral Data

Figure S5. ESI–MS spectra of Ni–TFT in a methanol/acetonitrile solution (top picture) and in the presence of FL in the aforementioned solution (bottom picture). The inserts show the measured and simulated isotopic patterns at $m/z = 2535.05$ (top) and $m/z = 2867.11$ (bottom), respectively.
Figure S6 \(^1\)H NMR spectra of fluorescein (a), Ni–TFT in the presence of fluorescein (b) and Ni–TFT (c) in DMSO-\(\text{d}_6\).
Figure S7 Partial NOESY spectrum of the Ni–TFT (0.1 mM) and FI (1mM) mixture in DMSO-d$_6$. 
Figure S8 (a) Family of the differentiate Uv-vis absorption spectra (ΔΔ = A(Ni−TFT+FL)-A(Ni−TFT)) of fluorescein (0.1 mM, black line) in EtOH/H_2O (1:1, pH = 12.6) upon addition of 50μM (red line) and 100 μM (blue line) Ni−TFT, respectively. (b) Time–dependence of the Fluorescein (10μM) (red line) and of the fluorescein (10 μM) upon addition of Ni−TFT (50 μM) (black line) in EtOH/H_2O (1:1, pH = 12.6). The intensity was recorded at 525 nm with the excitation at 470 nm.
Figure S9(a) Family of fluorescence of fluorescein (10 μM, black line) in EtOH/H₂O (1:1, pH = 12.6) upon addition of Ni–TFT up to 8.0 μM, respectively; (b) The titration curve of aforementioned system upon addition of Ni–TFT up to 8.0 μM and the Hill plot of the titration curve of fluorescein upon addition of Ni–TFT showing the associate constant.
$F_0$ is the original intensity of the emission, which is 1.0 for the normalized data.

$F_L$ is the final intensity of the emission, which is about 0.0 for the calculated value.

$n$ is the mole equiv of the Ni–TFT added to the solution of the fluorescein solution

$F$ is the measured intensity of the emission data.

**Figure S10**  the Hill plot of the titration curve of fluorescein upon addition of Ni–TFT showing the associate constant.
Figure S11 Family of fluorescence of fluorescein (10 μM, black line) in EtOH/H₂O (1:1, pH = 12.6) upon addition of Ni-DMT, respectively.
Figure S12  Family of fluorescence of fluorescein (10 μ M, black line) in EtOH/H₂O (1:1, pH = 12.6) upon addition of Na₂S, respectively.
Figure S13 Light-driven hydrogen evolution of the systems containing FL (2.0 mM), NEt₃ (10% v/v), and Ni-TFT in an EtOH/H₂O solution (1:1 in volume) at different pH values for 10 h.
**Figure S14** XRD pattern of the yellowish powder (top). The standard XRD pattern of α-sulfur powder (down).
Figure S15 Cyclic voltammograms of Ni–TFT(0.1 mM) containing 0.1 M TBAPF₆ (black line) at different scan rate: 100 mV/s, 150 mV/s, 200 mV/s, 250 mV/s, 300 mV/s.

Figure S16 Cyclic voltammograms of Ni–TFT(0.1 mM) containing 0.1 M TBAPF₆ (black line) scan rate of 100 mV/s
Figure S17  Cyclic voltammograms of Ni–DMT (0.1 mM) containing 0.1 M TBAPF₆, scan rate of 100 mV/s
References:


(S2) SMART, Data collection software (version 5.629) (Bruker AXS Inc., Madison, WI, 2003).

(S3) SAINT, Data reduction software (version 6.45) (Bruker AXS Inc., Madison, WI, 2003).

(S4) Sheldrick, G. M. SHELXTL97, Program for Crystal Structure Solution (University of Göttingen: Göttingen, Germany, 1997).