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A Redox-active Metal-Organic Macrocycle to Include Organic Dye for Visible-light Photocatalytic Reduction of Carbon Dioxide

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1. 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.[S1] The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXTL version 5.1 software. [S2]

Crystal data for Ni-SSC: $Ni_3C_{75}H_{92}N_{18}O_4S_{12}$, Mr= 1870.52, Triclinic, space group P-1, black block, a = 18.28(2) Å, b = 18.49(2) Å, c = 19.33(2) Å, V = 5250(11) $Å^3$, Z = 2, λ(MoKα) = 0.71073 Å, μ(MoKα)= 0.819 mm^{-1}, T = 220(2)K, 18178 unique reflections [Rint = 0.1686], Final R1[with I > 2σ(I)] = 0.1082, wR2 (all data)= 0.3951. **CCDC NO. 1450384**.

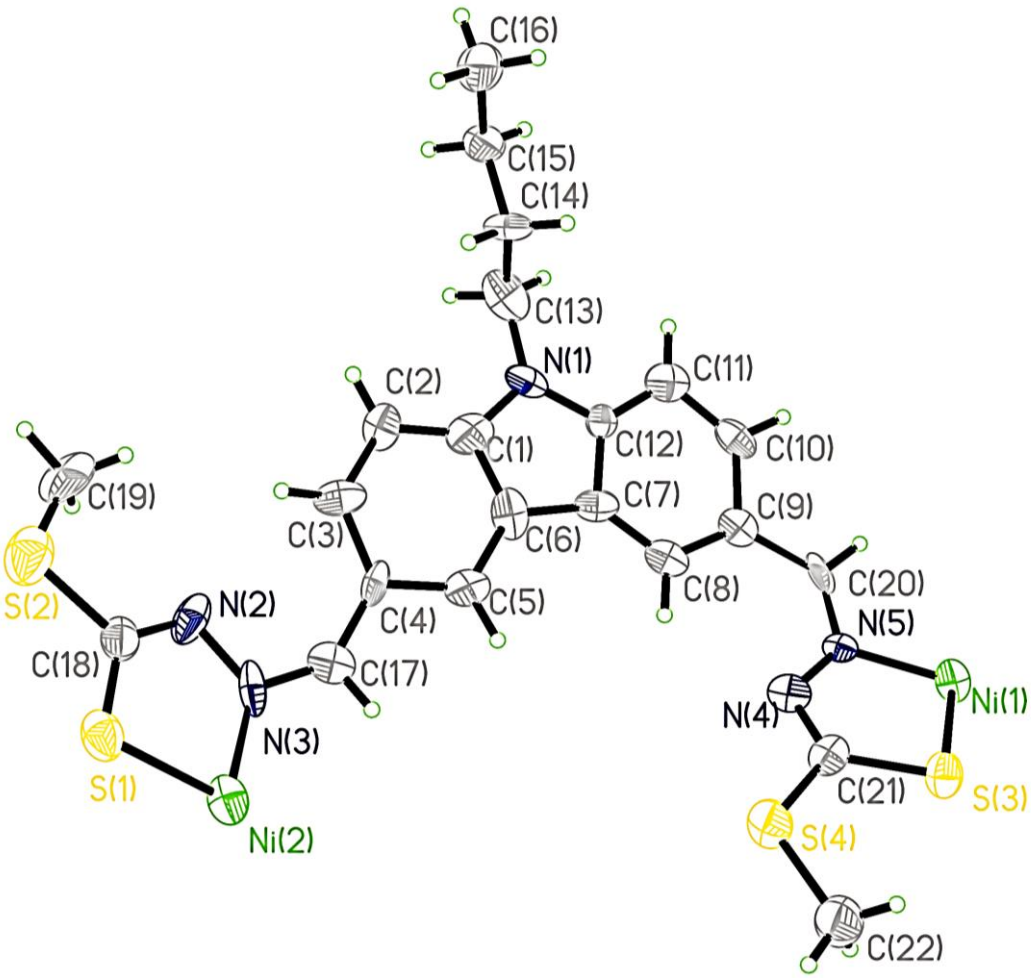

Figure S1. Molecular structure of Ni-**SSC** capsule within an unique asymmetric unit,showing the backbone of the ligands in the complex. Selected bond distances (Å): S(1)-C(18) 1.674(9), S(2)-C(18) 1.794(10), S(2)-C(19) 1.722(10), S(3)-C(21) 1.785(8), S(4)-C(21) 1.744(6), S(4)-C(22) 1.771(11),

N(1)-C(1) 1.352(8), N(1)-C(12) 1.367(10), N(1)-C(13) 1.428(13), N(2)-C(18) 1.271(8), N(2)-N(3) 1.387(10), N(3)-C(17) 1.270(7), N(4)-C(21) 1.254(11), N(4)-N(5) 1.305(6), N(5)-C(20) 1.267(9), C(1)-C(6) 1.396(13), C(1)-C(2) 1.427(10), C(2)-C(3) 1.339(9), C(3)-C(4) 1.416(11), C(4)-C(5) 1.441(9), C(4)-C(17) 1.449(8), C(5)-C(6) 1.406(8), C(6)-C(7) 1.464(9), C(7)-C(12) 1.385(10), C(7)-C(8) 1.392(12), C(8)-C(9) 1.364(8), C(9)-C(10) 1.460(11), C(9)-C(20) 1.524(11), C(10)-C(11) 1.434(13), C(11)-C(12) 1.328(8), C(13)-C(14) 1.510(14), C(14)-C(15) 1.457(13), C(15)-C(16) 1.514(16).

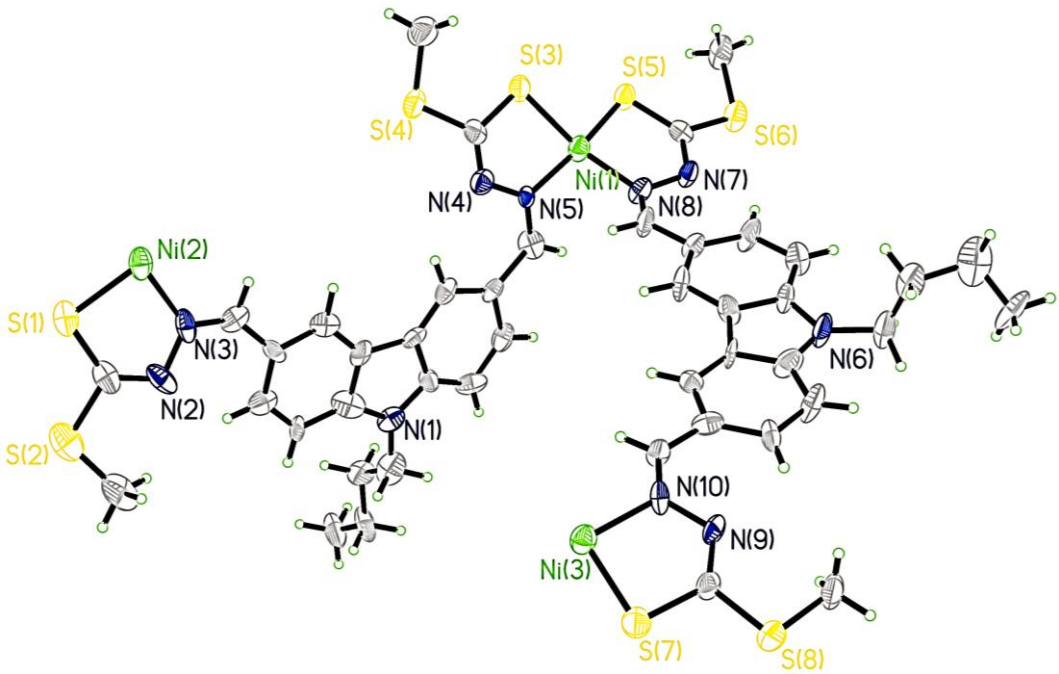

Figure S2. Coordination geometry of the Ni(1) atom in Ni-**SSC**. Selected bond distances (Å) and angles (°): Ni(1)-N(8) 1.892(6), Ni(1)-N(5) 1.907(6), Ni(1)-S(3) 2.140(3), Ni(1)-S(5) 2.141(4); N(8)-Ni(1)-N(5) 99.2(3), N(8)-Ni(1)-S(3) 161.1(2), N(5)-Ni(1)-S(3) 85.30(16), N(8)-Ni(1)-S(5) 88.8(2), N(5)-Ni(1)-S(5) 165.4(2), S(3)-Ni(1)-S(5) 91.09(10).

Crystal data for Ni-MSSC: $NiC_{38}H_{40}N_6S_4$, Mr= 767.71, Orthorhombic, space group P2(1)2(1)2(1), black block, a = 8.454(2) Å, b = 18.860(4) Å, c = 23.003(5) Å, V = 3667.7(15) $Å^3$, Z = 4, λ(MoKα) = 0.71073 Å, μ(MoKα)= 0.794 mm^{-1}, T = 220(2)K, 6452 unique reflections [Rint = 0.0854], Final R1[with I > 2σ(I)] = 0.0556, wR2 (all data)= 0.1268. **CCDC NO. 1450385**.

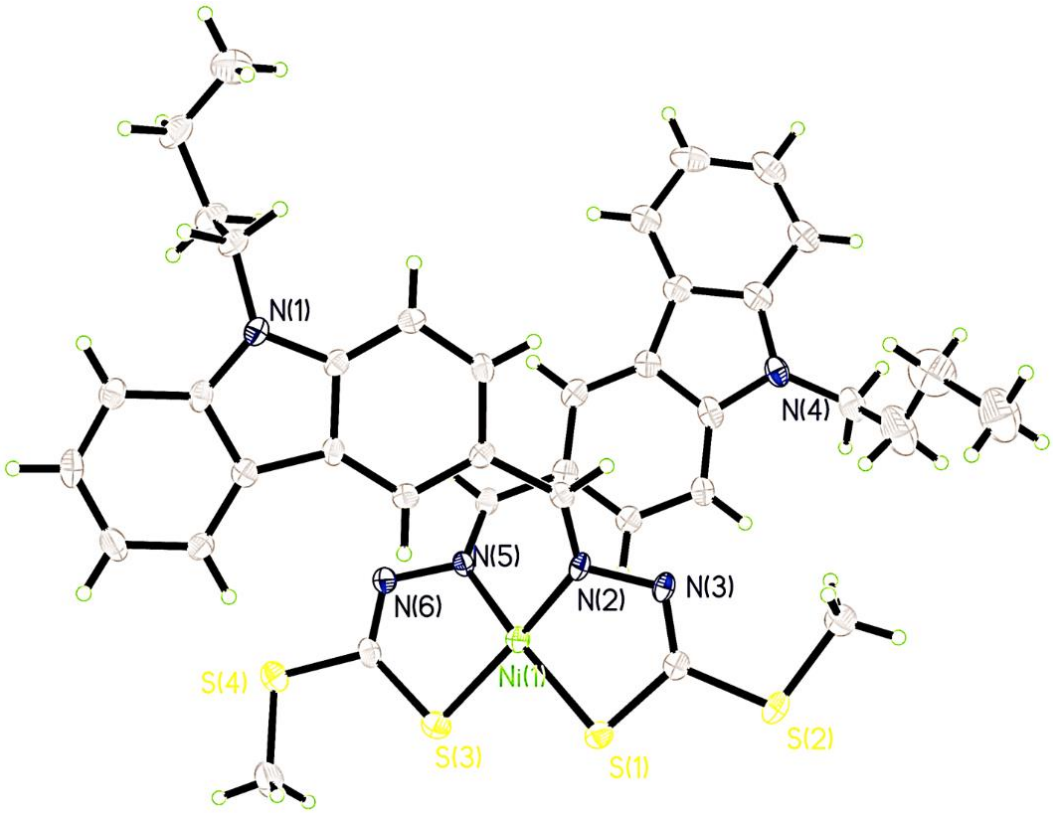

Figure S3. Coordination geometry of the Ni(1) atom in Ni-**MSSC**. Selected bond distances (Å) and angles (°): Ni(1)-N(2) 1.911(4), Ni(1)-N(5) 1.922(4), Ni(1)-S(3) 2.1580(16), Ni(1)-S(1) 2.1658(15); N(2)-Ni(1)-N(5) 98.91(18), N(2)-Ni(1)-S(3) 165.82(14), N(5)-Ni(1)-S(3) 86.58(13), N(2)-Ni(1)-S(1) 86.66(13), N(5)-Ni(1)-S(1) 164.31(14), S(3)-Ni(1)-S(1) 91.48(6).

2. Data for Spectral Titrations

2.1 ESI-MS

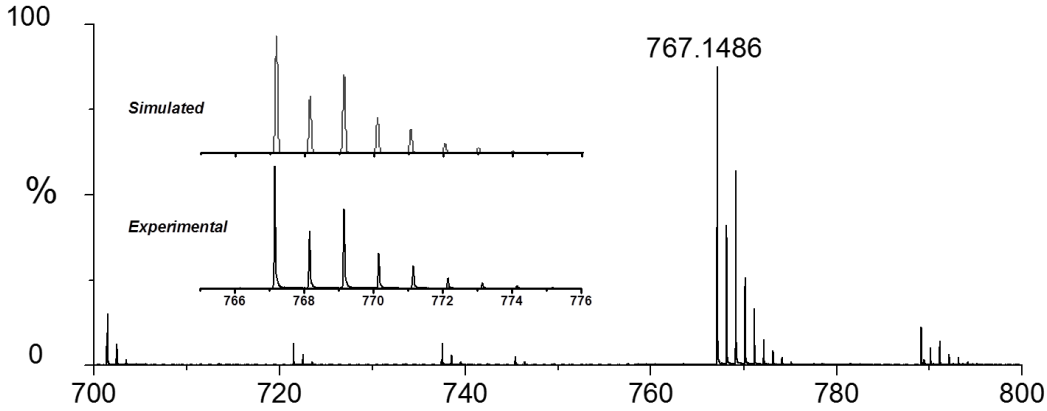

Figure S4. ESI-MS of Ni-**MSSC** in a DMF/CH_3OH solution

Peak number	value	Specie Assigned
1	767.15	[Ni (**MSSC**)$_2$H]$^+$

2.2 UV-vis absorption spectra

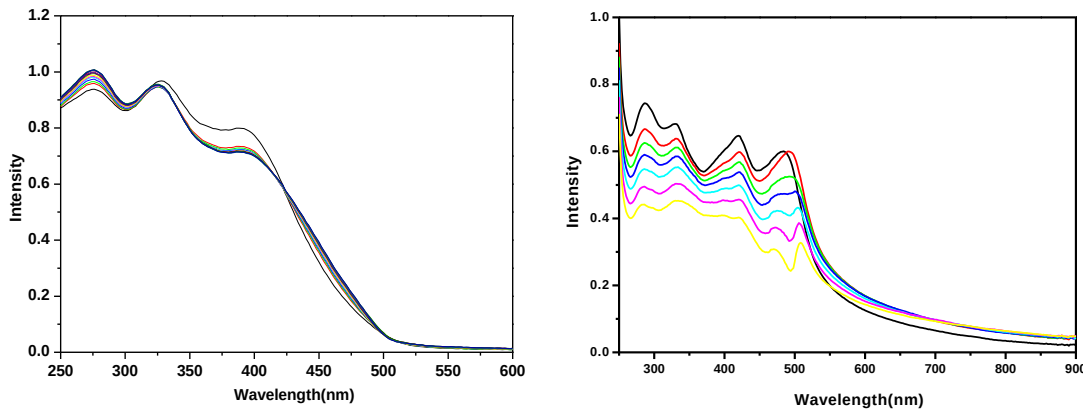

Figure S5. Family of the different UV-vis absorption spectra of fluorescein in CH_3CN/H_2O (1:1, pH = 11.0) upon addition of Ni-**SSC** (left picture) and Ni-**MSSC** (right picture).

2.3 Time-dependence of Fluorescein

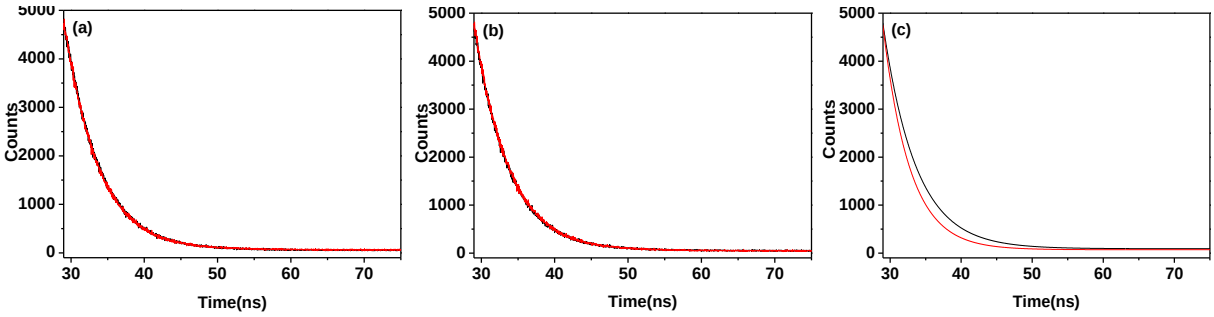

Figure S6. Time-dependence of Fluorescein (black line) and of the fluorescein upon addition of Ni-**SSC** (a), Ni-**MSSC** (b) and **TEA** (c) in CH_3CN/H_2O (1:1, pH =11.0) (red line in each figure). The intensity was recorded at 520 nm with excitation at 472.6 nm.

2.4 Luminescent Titrations

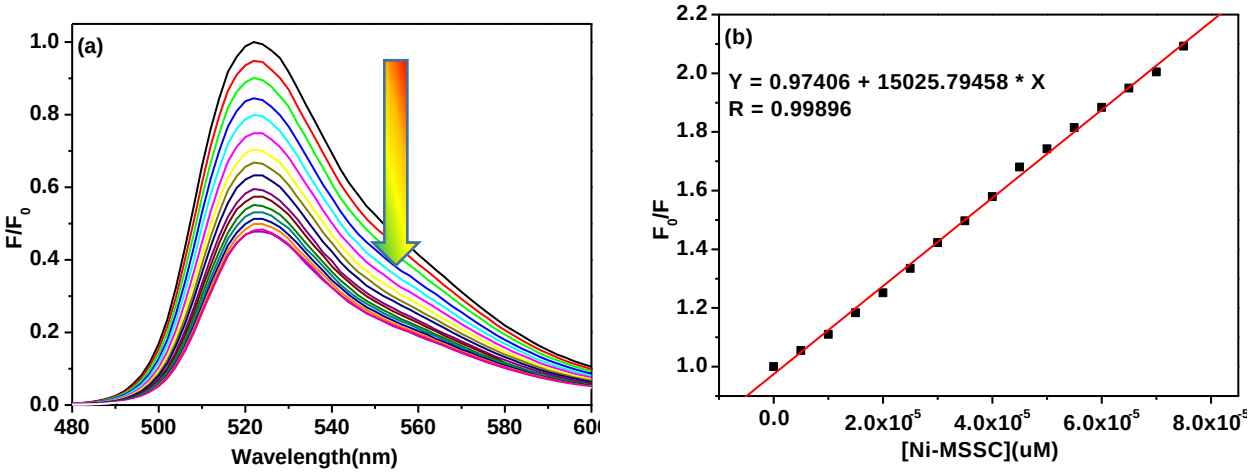

Figure S7. (a) Family of luminescence spectra of fluorescein upon the addition of Ni-**MSSC** in CH_3CN/H_2O solution, excited at 470 nm; (b) The Stern-Volmer Fitting of the titration curve. Fluorescence intensity were recorded at 520nm, excited at 470 nm.

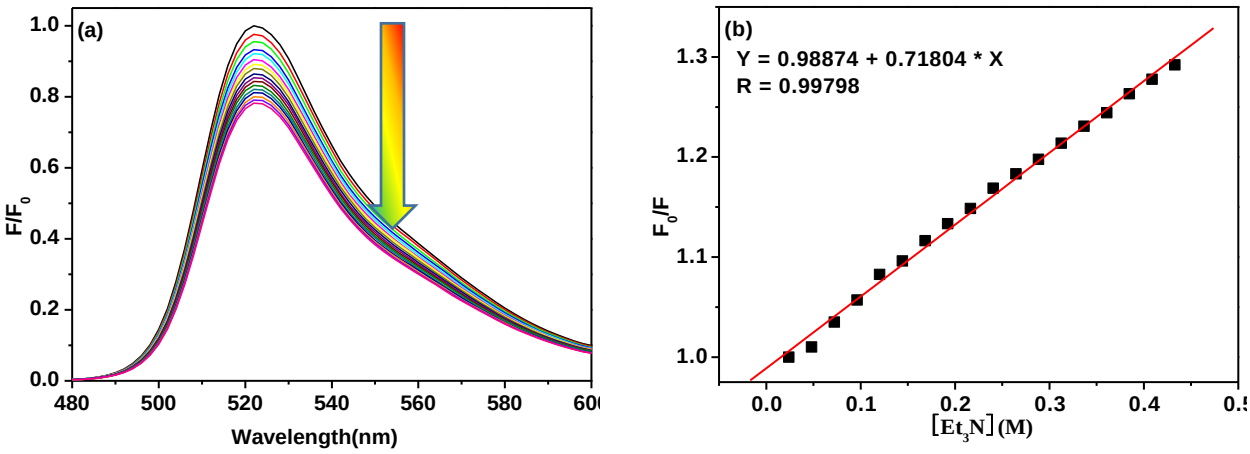

Figure S8. (a) Family of luminescence spectra of fluorescein upon the addition of TEA in CH_3CN/H_2O solution, excited at 470 nm; (b) The Stern-Volmer Fitting of the titration curve. Fluorescence intensity were recorded at 520nm, excited at 470 nm.

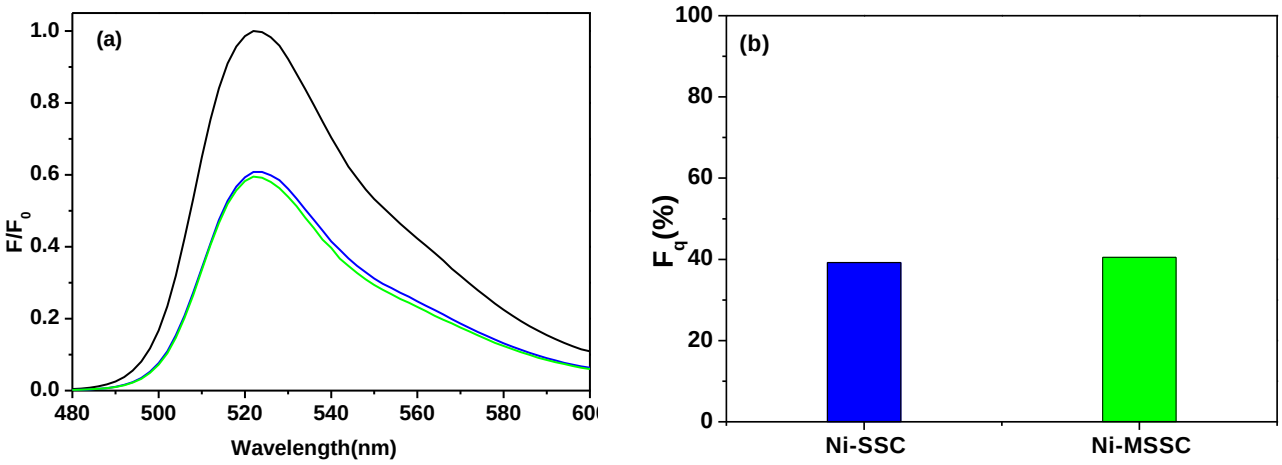

Figure S9. (a) Normalized fluorescence of **Fl** (10 μM, black line) in a CH_3CN/H_2O solution (1:1, pH = 11.0) and of the aforementioned solution upon addition of Ni-**SSC** (15 μM, blue line) and Ni-**MSSC** (45 μM, green line); (b) The amount of fluorescence quenching with Ni-**SSC** (15 μM, blue bar) and Ni-**MSSC** (45 μM, green bar), respectively. Fluorescence intensity were recorded at 520nm, excited at 470 nm.

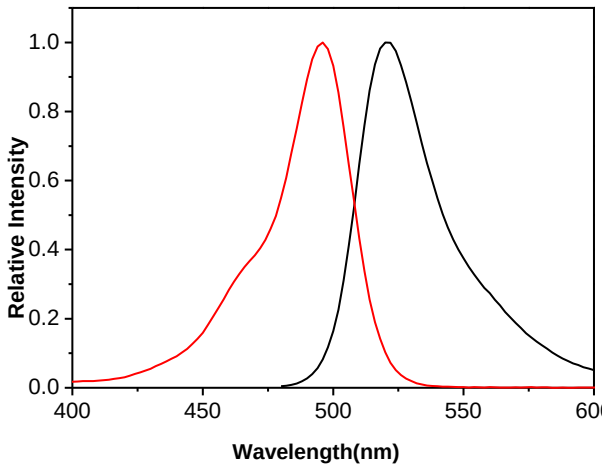

Figure S10. Normalized absorption (red line) and emission spectra (black line) of **Fl**, excited at 470 nm.

2.5 Electrochemistry Titrations

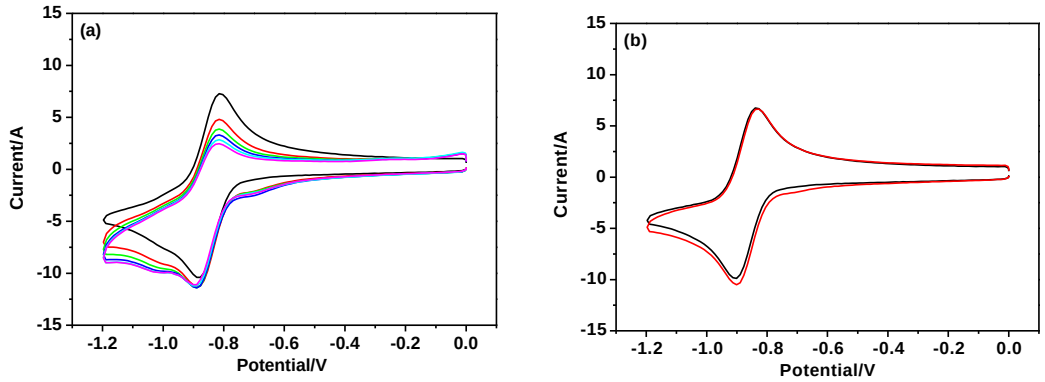

Figure S11. (a) Cyclic voltammogram of 1.0 mM Ni-**MSSC** (black line) upon addition of **Et_3NH^+** with different concentration; (b) upon exposure CO_2 up to saturation (red line). Scan Rate: 100 mV/s.

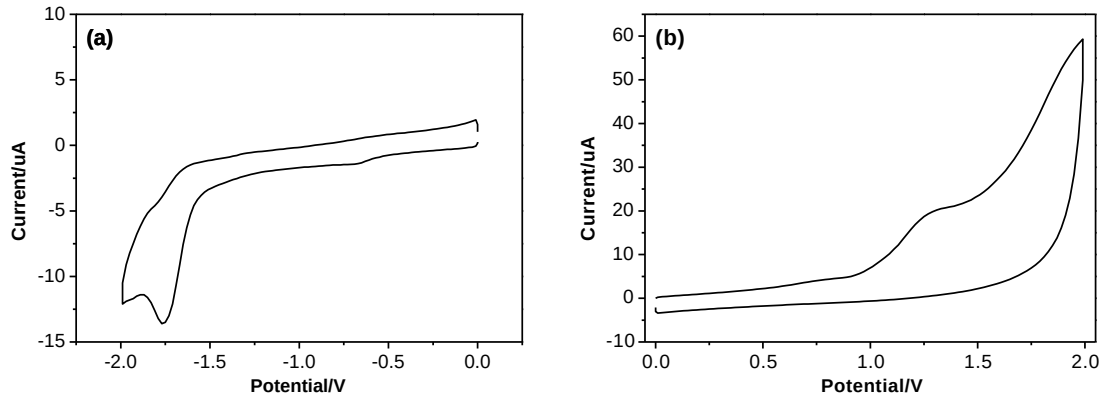

Figure S12. Cyclic voltammogram of 1.0 mM ligand **SSC** (a) and 1.0 mM **Fl** (b). Scan Rate: 100 mV/s.

3. Data Relative to Hydrogen Production and Reduction of Carbon Dioxide

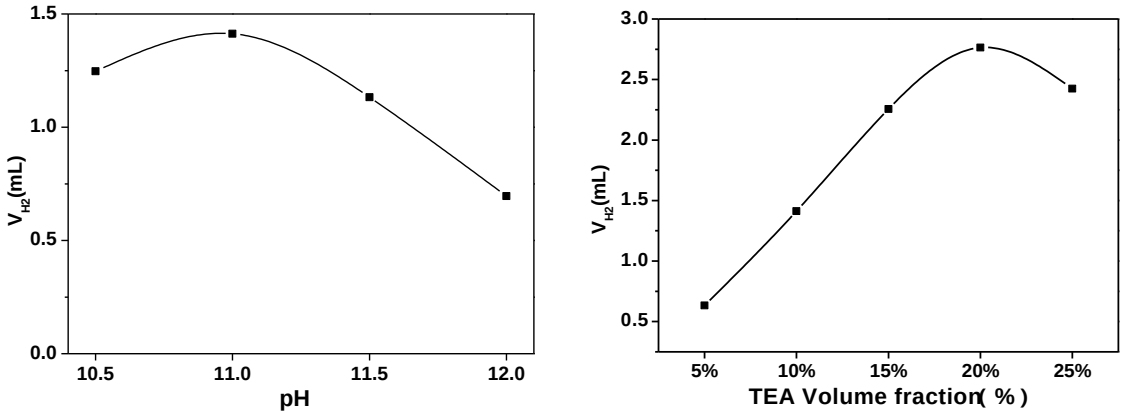

Figure S13. Left picture: Light-driven hydrogen evolution of the systems containing **Fl** (4.0 mM), NEt_3 (10%, v/v), and 10 μM Ni-**SSC** in an CH_3CN/H_2O solution (1:1) with different pH at 10.5, 11.0, 11.5, 12.0; Right one: Light-driven hydrogen evolution of the systems containing **Fl** (4.0 mM) and 10 μM Ni-**SSC** in an CH_3CN/H_2O solution (1:1) at pH =11.0 with different various **TEA** concentration.

4. References

[S1] SMART Data collection software, version 5.629; Bruker AXS Inc.: Madison, WI, 2003. SAINT Data reduction software, version 6.45; Bruker AXS Inc.: Madison, WI, 2003.

[S2] G. M. Sheldrick, SHELXTL V5.1, Software Reference Manual, Bruker, AXS, Inc.: Madison, WI, 1997.