An electron-reservoir Re(I) complex for enhanced efficiency for reduction of CO_2 to CO

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ABSTRACT

Herein we report a highly efficient molecular catalyst of novel Re(I) complex (ReTPS) containing 4,4′-bis (4-(triphenylsilyl)phenyl)-2,2′-bipyridine as a specific ligand. Photophysical studies and density functional theory (DFT) as well as time-dependent DFT (TDDFT) calculations show efficient expansion of π-system by the arylsilyl units, with a minimal electronic effect on the parent Re(I) complex. Electrochemical studies reveal an electron-reservoir characteristic of ReTPS by storing two electrons in the ligand before the Re(I) center is reduced. Faradaic efficiency of 76% and turnover number of 130 were recorded for electrocatalytic and photocatalytic reduction of CO_2, respectively.

1. Introduction

Catalysis is a break-through science for future's sustainable energy, since it turnovers instead of stoichiometrically consuming active materials, and it also lowers the activation energy for chemical reactions [1]. In this regard, catalytic CO_2 to fuel conversion attracted attention ever since the oil crisis of 1970s [2]. A large number of organometallic complexes with transition metals of Re (I), Ru(II), Co(II), Ni(II), Mn(I), and Ir(III) have been used for molecular systems for electrocatalytic [3–7] and photocatalytic [8–10] CO_2 reduction. Among them, Re(I) carbonyl diimine complexes *fac*-Re(I)(N^N)(CO)₃X (where N^N is a neutral diimine ligand and X is a monoanionic halogen ligand) have been widely studied as CO_2 reduction catalysts (CRCs) since the pioneering work of Lehn et al. [11–13] and Meyer et al. [14] in the 1980s. The Re(I) CRCs have high selectivity for CO production both for electrocatalytic [15–25] and photocatalytic [26–33] systems. However, it has been shown that the overall catalytic performance of CO_2 reduction is primarily limited by the fundamental degradation and/or transformation of the Re(I) complexes to catalytically inactive species upon two electron reduction during the catalysis [34]. In this regard, tackling the stability issue of molecular catalysts is the key step

for realizing highly efficient catalytic systems for CO_2 reduction [35–37].

We recently reported a highly efficient and robust Pt(II) H_2-evolving catalyst using electron reservoir approach [38,39]. Molecular electron-reservoirs are compounds, which can store and transfer multiple electrons stoichiometrically and/or catalytically without decomposition. By storing multi-electrons in the specially designed ligand of 4,4′-bis(4-(triphenylsilyl)phenyl)-2,2′-bipyridine, two electron reduction mechanism was facilitated and a very high turnover number (TON) of 510,000 was recorded for H_2 production. Based on such success of electron reservoir approach, we sought to extend it to CO_2 reduction in this work by introducing tetraphenylsilyl (TPS) substituents to the N^N of a Re(I) CRC (Scheme 1). The tetrahedral configuration of four phenyl rings covalently bonded to a silicon atom effectively expands the π-system of N^N, thus provides electron-reservoir character to the Re(I) CRC. The enhanced stability, as well as the improved electrocatalytic and photocatalytic CO_2 reduction activity of TPS-containing molecular Re(I) CRC are examined in this study.
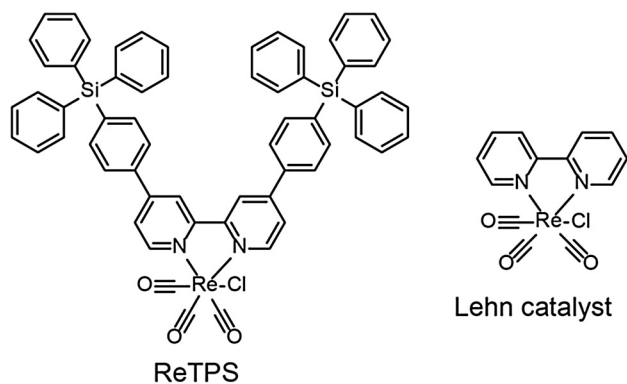
2. Materials and methods

2.1. Synthesis

Commercially available chemicals were used as received. 4-triphenylsilylphenylboronic acid was synthesized as previously described [40,41].

Scheme 1. Chemical structures of ReTPS and Lehn catalyst.

2.1.1. 4,4′-bis(4-(triphenylsilyl)phenyl)-2,2′-bipyridine (TPSbpy)

4,4′-dibromo-2,2′-bipyridine (2.0 g, 6.37 mmol), 4-triphenyl-silylphenylboronic acid (6.1 g, 16.0 mmol), and tetrakis(triphenyl phosphine)palladium(0) (0.37 g, 0.32 mmol) were dissolved in THF (150 mL) and aqueous 2 N Na_2CO_3 solution (75 mL). The mixture was refluxed at 75 °C for 8 h. Then, the crude mixture was poured into brine and washed with EtOAc 3 times (100 mL × 3). The organic layer was collected and dried over $MgSO_4$ and filtered. Then, the filterate was concentrated and chromatographed in silica gel column with n-hexane:EtOAc (4:1 v/v) to give white powder (4.1 g, 4.97 mmol). ^{1}H NMR (300 MHz, CDCl3) δ 8.67–8.66 (m, 4H), 7.71 (d, J = 8.2, 4H), 7.64 (d, J = 8.2, 4H), 7.54–7.51 (m, 14H), 7.50–7.30 (m, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.67, 149.74, 149.21, 139.42, 137.09, 136.40, 135.53, 133.89, 129.77, 127.99, 126.58, 121.70, 119.36.

2.1.2. Re(TPSbpy)(CO)₃Cl (ReTPS)

Rhenium(I) pentacarbonyl chloride (300 mg, 0.83 mmol) and TPSbpy (750 mg, 0.91 mmol) were dissolved in PhMe (25 mL). The mixture was refluxed at 110 °C overnight under argon atmosphere. After cooling to room temperature, PhMe was evaporated in vacuo. The crude mixture was dissolved in acetone and poured into water. The resulting precipitate was collected by filtration and dried in vacuo. The filtrate was collected and chromatographed in silica gel column with n-hexane:EtOAc (1:1 v/v) to give orange powder (430 mg, 0.38 mmol). ^{1}H NMR (300 MHz, CDCl3) δ 9.07 (d, J = 5.8 Hz, 2H), 8.37 (s, 2H), 7.78 (d, J = 8.1 Hz, 4H), 7.69 (d, J = 7.9 Hz, 6H), 7.64–7.53 (m, 12H), 7.53–7.30 (m, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.33, 189.86, 156.30, 153.48, 151.65, 138.60, 137.71, 136.82, 136.54, 133.53, 130.17, 128.30, 126.73, 124.95, 121.25. HRMS-FAB+: calculated for M^+: 1130.2131; found: 1130.2140. Elemental analysis calculated for $C_{61}H_{44}ClN_2O_3ReSi_2$: C 64.79, H 3.92, N 2.48; found: C 64.90, H 3.96, N 2.47.

2.1.3. Re(bpy)(CO)₃Cl (Lehn catalyst)

Rhenium(I) pentacarbonyl chloride (300 mg, 0.83 mmol) and 2,2′-bipyridine (130 mg, 0.83 mmol) were dissolved in PhMe (15 mL). The mixture was refluxed at 110 °C overnight under argon atmosphere. After cooling to room temperature, the crude mixture was poured into diethyl ether and the bright yellow precipitate was collected by filtration and dried in vacuo (320 mg, 0.69 mmol). ^{1}H NMR (300 MHz, CDCl3) δ 9.08 (d, J = 5.1 Hz, 2H), 8.20 (d, J = 7.9 Hz, 2H), 8.08 (t, J = 7.9 Hz, 2H), 7.56 (t, J = 6.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.23, 189.60, 155.86, 153.50, 127.37, 123.24. HRMS-FAB+: calculated for M^+: 461.9772; found: 461.9778. Elemental analysis calculated for $C_{13}H_8ClN_2O_3Re$: C 33.81, H 1.75, N 6.07; found: C 33.86, H 1.74, N 6.06.

2.2. Photophysical characterization

Absorption spectra were recorded on a Perkin Elmer Lambda 1050 from 250 to 600 nm. Steady-state photoluminescence (PL) spectra were obtained on a PTI FluorescenceMaster spectrofluorometer in the range of 400–800 nm.

2.3. Computational details

Ground state geometry of the Re(I) CRCs were computed using the B3LYP level of density functional theory (DFT) [42,43], in which the 6-31G** basis set was adopted for C, H, N, Cl, and Si atoms, while the "double-ζ" quality LanL2DZ basis set consisting of Hay and Wadt's effective core potentials [44,45] was employed for Re atom. Time-dependent DFT (TDDFT) [46] was employed to calculate 50 singlet and 50 triplet excitations using the same level of theory while 6-311G** basis set was applied for C, H, N, Cl, and Si atoms and LanL2DZ basis set was employed for Re atom. The solvent effects were included for all calculations by applying the integral equation formalism for the polarizable continuum model (IEF-PCM) [47] with N,N-dimethylformamide (DMF) as a solvent. All calculations were carried out using Gaussian 09 [48].

2.4. Electrochemical experiments

Cyclic voltammetric and electrocatalytic experiments were carried out with a Jaissle Potentiostat/Galvanostat 1030 PC.T. in a one-compartment cell using three-electrode assemblies including a platinum wire working electrode, a platinum plate counter electrode, and a pseudo Ag/AgCl reference electrode. Cyclic voltammetry measurements were carried out after N_2 or CO_2 saturation of 1 mM Re(I) complexes in DMF/MeCN 1:1 v/v solution with 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) as a supporting electrolyte. The scan rate was 50 mV/s. Electrocatalytic CO_2 reduction experiments were performed by applying constant potential to the same samples after CO_2 saturation. Potentials reported were obtained by calibrating the pseudo reference electrode vs. ferrocene as an external standard.

2.5. Photocatalytic CO_2 reduction

Photocatalytic CO_2 reduction system was prepared by adding 50 μM Re(I) CRC in 5 mL DMF/TEOA 5:1 v/v into 20 mL air-tight vial. The sample vial was CO_2-bubbled for 15 min. Then the vial was irradiated with a halogen lamp (Philips GU 5.3 50W, 12V 36D) with a water filter to remove IR (Fig. S4). The spectra of the halogen lamp in visible region with and without water filter are described in Fig. S5. To maintain the irradiation light intensity during the photolysis, the halogen lamp was driven in constant current mode. The sample position was adjusted for the light intensity of ca. 50 mW/cm^2.

2.6. Catalytic product analysis

The headspace gas (2 mL) was collected using a luer lock-type air-tight syringe and analyzed by gas chromatography (Thermo Scientific Trace GC ULTRA) equipped with a thermal conductivity detector (TCD) to perform product analysis. The amount of CO and H_2 produced within the vial was calculated with the integrated area of each signals calibrated by external standards. No production of H_2 was observed for all samples.