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COMMUNICATION

A robust and efficient cobalt molecular catalyst for CO₂ reduction

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Visible–light driven CO₂ reduction is considered to be a sustainable energy source. However, earth–abundant molecular catalysts with high efficiency and robustness towards solar-driven CO₂ reduction are limited. Herein, we report a cobalt complex supported by a tetradentate tripodal ligand which demonstrates catalytic solar–driven CO₂ reduction with TON(CO) > 900 over 70 h in the presence of a photosensitizer.

Driven by the depletion of fossil fuels and the deterioration of the environment, there is a surging demand on the development of renewable and sustainable energy sources. In this regard, solar energy is considered as one of the most viable renewable energy sources for powering our planet.¹ Being an intermittent energy source, solar energy has to be captured and stored in the form of electrical or chemical energy. Solar splitting of water into hydrogen and oxygen is considered as one of the most promising approaches for solar-to-fuel conversion.² Solar–driven carbon dioxide reduction into chemical fuels and chemical feedstocks are even more appealing because this can remediate its high concentration level in the atmosphere. In addition, CO₂ reduction provides a channel for recycling of the C1 building block from atmospheric CO₂. Yet, solar-driven photochemical CO₂ reduction is a longstanding unsolved problem, due to the high stability of CO₂.³

Over the past few decades, potent molecular catalysts that could photochemically reduce CO₂ are sparse in literature.⁴ Most of them are the 2nd and 3rd row transition metal ion-based molecular systems, with Re(bpy)(CO)₃X (bpy=bipyridine, X=halide), Ir(tpy)(ppy)Cl (tpy= 2,2':6',2'-terpyridine, ppy= 2,2'-phenylpyridine anion) and some multinuclear Re–Ru complexes being the prototypes.⁵ However, considering the scarcity and the price of these 2nd and 3rd row transition metals, large scale solar-to-fuel conversion from these systems is not feasible. Thus, there is an increasing demand on the development of visible light–driven CO₂ reduction catalysts

based on earth–abundant transition metal ions. Recently, Chang, Bonin and Robert reported two efficient visible–light driven CO₂ reduction molecular catalysts based on nickel and iron complexes supported by tetradentate ligands.⁶ Among many tetradentate ligands, we are particularly interested in the tetradentate tripodal ligands TPA (TPA = tris(2-pyridylmethyl)amine) for its strong chelating effect.⁷ Indeed, transition metal complexes supported by TPA have received considerable attention for selective oxidation of alkanes and dioxygen activation.⁸ Very recently, Thapper *et al.* reported a water oxidation catalyst based on the TPA supported dinuclear cobalt system [(TPA)Co(μ–OH)(μ–O₂)Co(TPA)](ClO₄)₃.⁹ Herein, we report a highly robust and efficient CO₂ reduction catalyst based on a cobalt–TPA system.

[Co^{II}(TPA)Cl][Cl] (**1**) is prepared in high yield (70%) by mixing CoCl₂·6H₂O with TPA.¹⁰ Instead of a six-coordinated Co^{II} complex, we isolated a five-coordinated cobalt complex with trigonal bipyramidal (TBP) geometry based on X-ray crystallographic analysis (Fig. 1 inset). ¹H NMR and UV-vis spectroscopies also support the TBP structure of **1** in solution state (Fig S1 and S2). Electrochemical studies of **1** in 0.1 M [(*n*-Bu)₄N][PF₆] in dry CH₃CN indicated two irreversible reduction peaks at –1.94 and –2.30 vs Fc⁺⁰ at 100 mVs^{–1} (Fig. 1) which are assigned as Co^{III/I} and Co^{I/0} reduction respectively. The Co^{III/I} reduction of **1** is unexpectedly more negative compared with other cobalt complexes supported by similar ligand scaffold.¹¹ This negative reduction potential may be crucial for an effective CO₂ reduction catalyst. It is reported that Co^{III/I} reduction peak should be more negative than –1.65 V vs Fc⁺⁰ for a reasonable CO₂ binding with metal complexes.¹² An electrocatalytic current at Co^{III/I} reduction potential is observed under CO₂ atmosphere, revealing that **1** is an electrocatalyst for CO₂ reduction (Fig. 1) The negative Co^{III/I} reduction potential together with no precatalytic current before the onset of the electrocatalytic current for CO₂ reduction, prompted us to use **1** as precatalyst for visible–light driven photochemical reduction of CO₂ to CO.

In this regards, *fac*-Ir(ppy)₃, abbreviated as Ir(ppy)₃, was chosen as the photosensitizer for the present studies for its absorption in the visible–light region and large negative excited state redox potential ($E_{1/2}[\text{Ir}(\text{ppy})_3^+/\text{Ir}(\text{ppy})_3^*] = -2.17 \text{ V vs Fc}^{+/0}$, CH₃CN, Fig S3 and Table S1). Indeed, Ir(ppy)₃ was used in combination with nickel and iron catalysts for visible–light driven photochemical reduction of CO₂.⁶ Catalytic performance of **1** (5 μM) and Ir(ppy)₃ (0.4 mM) in a 4 mL CO₂-saturated CH₃CN/TEA (4:1, v/v; TEA = triethylamine) irradiated under blue LEDs (centered at 460 nm) is showed in Fig 2. Photolysis products H₂ and CO were identified and quantified using GC–TCD equipped with molecular sieve column. The amount of H₂ and CO was determined using CH₄ as the internal standard.¹³ Ion chromatographic analysis revealed that no formic acid was produced in the reactions (see supporting information). Maximum CO production turnover frequency (TOF) of 50 h⁻¹ was observed during the first 8 hours. Remarkably, the fast CO production rate could be resumed by addition of fresh Ir(ppy)₃ (Fig. S4). *Based on results of three parallel reaction runs, averaged turnover numbers (TON) of 953 and CO selectivity of 85 % were achieved after 70 h. To the best of our knowledge, it is the first homogeneous visible–light driven CO₂ reduction molecular catalyst with TON > 900 based on 5 μM cobalt catalyst.* Despite the CO selectivity in the present system could not reach 100 %, the CO/H₂ mixture could be converted to liquid hydrocarbon using Fischer Tropsch process¹⁴.

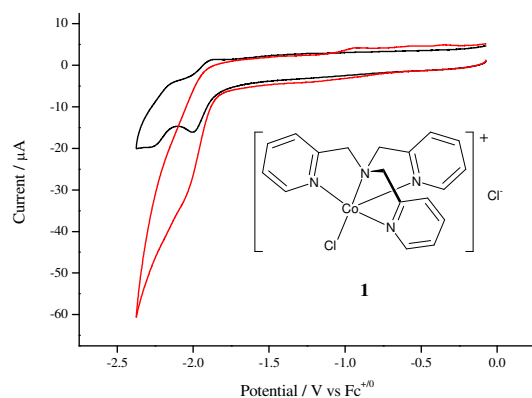


Fig 1. Cyclic voltammograms of **1** in 0.1 M [(n-Bu)₄N][PF₆]/CH₃CN solution under Ar (black) and CO₂ (red) atmosphere using a glassy carbon disk electrode at a scan rate of 100 mV s⁻¹. The inset shows the structure of **1**.

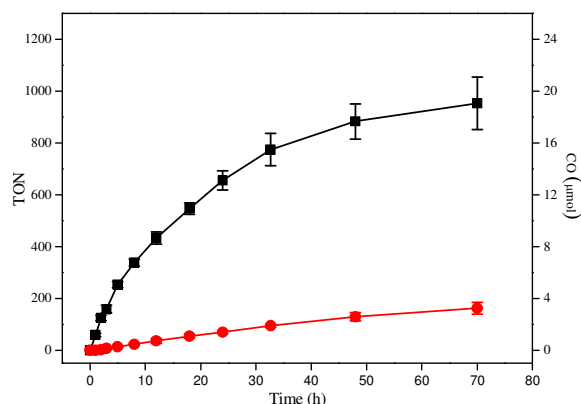


Fig 2. Photocatalytic production of CO (black square) and H₂ (red circle) in the presence of 5 μM **1**, 0.4 mM Ir(ppy)₃ in a CO₂-saturated CH₃CN/TEA(4:1, v/v) solution based on the averaged results of three parallel reaction runs.

We also studied the effects of other experimental parameters on the CO production in our system. The amount of CO production increases with the concentration of **1**, indicating that **1** is the catalyst for CO₂ reduction (Table S2). However, as in the case of Chang and co-workers,⁶ no linear dependence between CO production and the concentration of **1** was observed. It was also noted that for a 50 μM **1** in CO₂-saturated CH₃CN/TEA (4 mL, 4:1, v/v) solution, the amount of CO produced increased with the concentration of Ir(ppy)₃ at low Ir(ppy)₃ concentration (0.025–0.1 mM), and leveled off when the concentration of Ir(ppy)₃ was beyond 0.3 mM, meaning that less amount of Ir(ppy)₃ could be used for CO production (Table S3, Fig S5).

Control experiments revealed all components are necessary for CO production (Table 1). No CO was produced if the solution was bubbled with Ar (entry 4). We also run the reaction using other cobalt complexes e.g. [Co(dmgH)₂(py)Cl] and Co(acac)₃ (entry 7 and 8) and [Ru(bpy)₃]²⁺ as the photosensitizer (entry 9), and the fact that no or trace amount of CO was produced indicated the uniqueness of **1** and Ir(ppy)₃. A mercury poison test was also conducted, and the lack of change in catalytic activity revealed that the formation of the photolysis products were not due to the presence of metals (entry 6).

Table 1. Control experiments for photochemical CO₂ reduction.

Entry	Photosensitizer	Catalyst	CO (μmol)*
1	Ir(ppy) ₃	-	0
2	-	1	0
3	Ir(ppy) ₃	1	<0.1 (no TEA)
4	Ir(ppy) ₃	1	0 (Ar is used)
5	Ir(ppy) ₃	1	41.5
6	Ir(ppy) ₃	1	37.2 (Hg added) ^a
7	Ir(ppy) ₃	Co(dmgH) ₂ (py)Cl	0
8	Ir(ppy) ₃	Co(acac) ₃	3.1
9	[Ru(bpy) ₃][PF ₆] ₂	1	0

*Typical reaction condition: 0.4 mM photosensitizer, 50 μM catalyst in a 4 mL CO₂-saturated CH₃CN/TEA (4:1,v/v) irradiated under blue LEDs for 24 h; a: 0.8 mL Hg is added to reaction. dmgH = dimethylglyoximate and py = pyridine, acac = acetylacetonate; bpy = 2,2'-bipyridine

To study the mechanism of our system, we measured the quenching rate of [Ir(ppy)₃]^{*} in the presence of TEA and **1**. The bimolecular quenching rate constant k_q was determined using Stern-Volmer equation (equation 1)¹⁵

$$\tau_0/\tau = 1 + k_q \tau_0 [Q] \quad (1)$$

where τ_0 and τ are the lifetimes of the excited state in the absence and presence of quencher Q respectively.

Both **1** and TEA follow good Stern-Volmer behaviour (Fig 3 and Fig S6). The measured quenching rate constants for **1** and TEA are $5.29 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ and $4.14 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ respectively. Despite TEA following a good Stern-Volmer behaviour, reductive quenching of [Ir(ppy)₃]^{*} is not feasible from thermodynamic consideration ($E_{1/2}[\text{Ir}(\text{ppy})_3^+/\text{Ir}(\text{ppy})_3^*] = +0.31 \text{ V vs SCE}$),¹⁶ Hence, direct oxidative quenching of Ir(ppy)₃ by **1** is more favourable in our photocatalytic system.

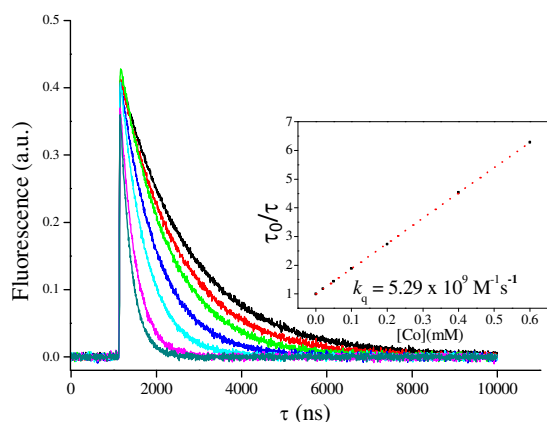
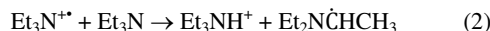


Fig 3. Fluorescence spectra of 20 μM $\text{Ir}(\text{ppy})_3$ CH_3CN solution in the absence (black), 20 μM (red), 50 μM (green), 100 μM (blue), 200 μM (cyan), 400 μM (magenta) and 600 μM (deep cyan) of **1**. The inset shows the linear plot ($R^2 = 0.9999$) of ratio of $\text{Ir}(\text{ppy})_3$ excited state lifetime at 514 nm versus **1** according to Stern-Volmer equation.

Based on our studies and the mechanistic studies on transition metal complexes catalyzed CO_2 reduction reported in literature,^{3-4,6} it is likely that the photochemical CO_2 reduction begins with the oxidative quenching of $[\text{Ir}(\text{ppy})_3]^*$ by **1**, generating a Co^{I} species. Further reduction of Co^{I} to Co^0 by $[\text{Ir}(\text{ppy})_3]^*$ is excluded according to the electrochemical studies of **1** (E_{pc} of $\text{Co}^{\text{I}/0}$ of -2.3 V vs $E_{1/2}$ ($[\text{Ir}(\text{ppy})_3]^*/[\text{Ir}(\text{ppy})_3]^+$ of -2.17 V vs $\text{Fc}^{+/0}$). Co^{I} then binds with CO_2 to form a $[\text{Co}-\text{CO}_2]^+$ species followed by another 1 electron reduction, liberating CO and Co^{II} for CO_2 reduction.³ The catalytic cycle is completed via the reduction of the oxidized $[\text{Ir}(\text{ppy})_3]^+$ with TEA as sacrificial donor.⁶ The oxidized TEA⁺ radical reacts with other TEA, forming a protonated TEA i.e. TEAH⁺ which acts as a proton source to protonate the Co^{I} to form $\text{Co}^{\text{III}}-\text{H}$ (equation 2).¹⁷ Hydrogen can be produced from protonation of $\text{Co}^{\text{III}}-\text{H}^{17}$ or the $\text{Co}^{\text{III}}-\text{H}$ is further reduced and then protonated to give hydrogen.^{2,18} Thus, an alternative sacrificial donor may be considered in order to maintain the high selectivity of CO/H_2 production over prolonged period.



In conclusion, we reported a potent molecular catalyst **1** based on earth-abundant transition metal ions for visible-light driven CO_2 reduction with $\text{TON}(\text{CO}) > 900$ over 70 h and CO selectivity of 85%. **1** is considered to provide an insight for practical solar-to-fuel conversion considering that i) the performance of **1** in CO production is highly efficient when compared with the nickel ($\text{TON}(\text{CO}) = 1500$, 0.2 μM , 7h) and iron ($\text{TON}(\text{CO}) = 140$, 2 μM , 55h) CO_2 reduction catalysts which are reported as one of the best molecular catalysts based on earth-abundant transition metal ions, and ii) the supporting ligand TPA is easy to synthesize and also commercially available in a bargain value. We believe that the present studies would provide a new direction on the development of catalysts for high efficiency and practical solar-to-fuel conversion.

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Notes and references

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 Electronic Supplementary Information (ESI) and crystallographic data of **1** in CIF Format (CCDC 1044164) is available. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

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