Cobalt(II) tris-(2-pyridylmethyl)amine complexes $[\text{Co}(\text{TPA})\text{X}]^+$ bearing coordinating anion ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$ and NCS^-): synthesis and application for carbon dioxide reduction

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Abstract: Four cobalt(II) complexes supported by the tripodal ligand tris-(2-pyridylmethyl)-amine (TPA) and ancillary coordinated anion (X), $[\text{Co}(\text{TPA})\text{X}]^+$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$ and NCS^-) (**1–4**), have been prepared. Magnetic susceptibility measurement and electronic spectroscopy indicate that they are five-coordinated high spin cobalt(II) complexes. The structures of **2–4** have been determined by X-ray crystallography. Reduction of CO_2 to CO has been observed upon irradiation of complexes **1–4** in the presence of *fac*-Ir(ppy)₃ (ppy = C-deprotonated 2-phenylpyridine anion) and under CO_2 atmosphere using blue LEDs. All of these Co complexes were found to be efficient and stable CO_2 reduction catalyst with $\text{TON}(\text{CO}) > 1000$ and CO selectivity $> 90\%$ under 65 hours of irradiation. Among them, $[\text{Co}(\text{TPA})\text{Br}]^+$ showed the best performance in CO_2 reduction with $\text{TON}(\text{CO}) > 1400$ after 65 h. The coordinated anion X played an important role in the photo-catalysis. Density functional theory (DFT) calculation has also been performed to examine the mechanism and role of coordinated anion X in visible-light induced CO_2 reduction.

Keywords: Carbon dioxide reduction, Cobalt tripodal ligands

1. Introduction

The interest on using molecular catalysts for electrochemical and photochemical reduction of carbon dioxide into chemical fuels could be traced back to 1980s [1–5], at which time a lot of research activities on CO_2 reduction were undertaken with objective for finding an alternative energy source to replace the non-renewable fossil fuel. Recently, the elevating atmospheric CO_2 level has piqued the interest of scientists to develop robust and efficient CO_2 reduction catalysts. Yet, molecular catalysts with high efficiency and selectivity for electrochemical and/or photochemical reduction of CO_2 remain scarce in the literature. Although

examples of CO₂ reduction electro-catalysts based on earth-abundant metal ions including that of iron [6,7], nickel [2,8], manganese [9] and cobalt [2,10] are available in literature, the majority of molecular catalysts extensively studied for CO₂ reduction are based on the 2nd and 3rd transition metals such as Ru [11,12], Os [13], Re [14], Rh [15,16] and Ir [16,17].

Compared to electrochemical CO₂ reduction, examples on photochemical CO₂ reduction using molecular catalysts are relatively sparse [18-27]. Photochemical CO₂ reduction involves multi-step reactions and demands the design of highly efficient photo-sensitizer for the generation of strong reductant and robust molecular catalyst for CO₂ activation. In this area, we are interested to develop robust, readily prepared molecular catalysts based on earth-abundant metal for photochemical CO₂ reduction. Chang [29], Bonnin and Robert [30], Lau [31], Beller [32,33] and our group [28] have recently demonstrated visible-light driven reduction of CO₂ to CO using molecular catalysts based on earth-abundant metals.

Despite many activities on CO₂ reduction catalysts with the metal ion supported by macrocyclic ligands [2,25,34,35], metal complexes containing the tetradentate tripodal ligand tris(2-pyridylmethyl)amine (TPA) have not been reported for CO₂ reduction prior to our work on photochemical CO₂ reduction catalyzed by [Co(TPA)Cl]⁺ [28]. It should be noted that transition metal complexes supported by TPA have been receiving much attention in catalysis such as selective oxidation of alkanes [36], atom-transfer radical-polymerization [37], dioxygen activation [38] and water oxidation [39,40]. We have previously reported that [Co(TPA)Cl]Cl is an efficient catalyst for visible-light driven CO₂ reduction with TON > 900 and CO selectivity > 85% over a time period of 70 h in the presence of *fac*-Ir(ppy)₃, abbreviated as Ir(ppy)₃, (ppy = 2-phenylpyridine anion) as photosensitizer [28]. Recently, we have further improved the performance of the photochemical CO₂ reduction with TON > 2400 and CO selectivity > 95% by using a more robust bis-N-heterocyclic carbene Ir(III) complex as photo-sensitizer [41]. As part of our continuous program to understand the reaction mechanism of CO₂ reduction by [Co(TPA)Cl]⁺, we have prepared a series of cobalt complexes coordinated with different anions [Co(TPA)X]⁺ (X = Cl⁻, Br⁻, I⁻, NCS⁻) (**1–4**) and examined the catalytic activity of these complexes towards photochemical CO₂ reduction.

2. Experimental section

All chemical reagents were of analytical grade. CoCl₂·6H₂O was purchased from Junsei Chem Co., Ltd. CoBr·nH₂O and NaClO₄ were obtained from Acros. Anhydrous CoI₂ was obtained from Strem. Co(SCN)₂ was obtained from Meryer (Shanghai) Chemical Technology Co., Ltd. Tris(2-pyridylmethyl)amine (TPA) and *fac*-Ir(ppy)₃ were synthesized according to literature methods [42,43]. High-resolution electrospray mass spectra (ESI-MS) were recorded using a PE SCIEX Q Star/pulsar mass spectrometer. UV-Vis spectra were measured using Hewlett Packard 8453 Photo-diode Array UV-Visible spectrophotometer. Cyclic voltammetry was performed using a CHI potentiostat electrochemical analyzer 600C. A conventional three electrode system was employed. A glassy carbon electrode (surface area = 0.2 cm²) was used as the working electrode, a Pt wire as the auxiliary electrode, and an Ag/AgNO₃ (0.1 M) electrode

as reference electrode. [$^{14}\text{Bu}_4\text{N}$] PF_6 was recrystallized three times from absolute ethanol and dried in oven before used. The electrolyte solution, 0.1 M [$^{14}\text{Bu}_4\text{N}$] PF_6 in CH_3CN , was purged with Ar or CO_2 (purity $\geq 99.8\%$, Hong Kong Oxygen and Acetylene Co., Ltd.) for 15 min prior to each experiment. Elemental analyses were performed with Elementar vario MICRO select CHNS instrument. Calibration compound used: sulfanilamide (5 mg). Room temperature magnetic data were collected on a Guoy Balance (Sherwood Scientific, Cambridge, UK). Diamagnetic contribution was estimated based on the equation $\chi_D = (-\text{MW}/2) \times 10^{-6} \text{ emu mol}^{-1}$ [44].

2.1. Syntheses

The $[\text{Co}(\text{TPA})\text{X}]^+$ ($\text{X} = \text{Br}^-$, I^- , NCS^-) complexes were prepared according to the procedure reported for $[\text{Co}(\text{TPA})\text{Cl}]\text{Cl}$ [28], except that cobalt(II) salt $\text{CoBr} \cdot n\text{H}_2\text{O}$, CoI_2 , or $\text{Co}(\text{SCN})_2$ was used instead of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. $[\text{Co}(\text{TPA})\text{X}]\text{ClO}_4$ ($\text{X} = \text{Cl}^-$, Br^- , NCS^-) was obtained by addition of NaClO_4 to the reaction mixture.

General procedure: cobalt(II) salt (0.2 mmol) was added to tris(2-pyridylmethylamine) (TPA) (0.204 mmol) in MeOH or THF (8 mL). The mixture was stirred at room temperature for 2 h under argon, which was concentrated to ca. 2 mL. Diethyl ether was added and the resulting precipitate was dried in vacuo. Crystals for X-ray crystal structure determination were obtained from dichloromethane solutions layered with diethyl ether. A similar procedure was employed for the preparation of complexes with perchlorate as counter ion with NaClO_4 (0.4 mmol) added to the reaction mixture after 2 h.

$[\text{Co}(\text{TPA})\text{Cl}]\text{ClO}_4$ (**1**), green solid, 70% yield. High-resolution ESI-MS for $[\text{M}^+]$: calcd.: 384.0052, found: 384.0518. Anal. Calc. for $\text{C}_{18}\text{H}_{18}\text{O}_4\text{N}_4\text{Cl}_2\text{Co}$: C, 44.62; H, 3.72; N, 11.58. Found: C, 44.67; H, 3.71; N, 11.45. UV-Vis (CH_3CN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) = 263 (9132), 487 (215), 616 (130), 637(sh)(150). Magnetic measurement: μ_{eff} (298 K) = 4.51 μ_B .

$[\text{Co}(\text{TPA})\text{Br}]\text{ClO}_4$ (**2**), blue solid, 70% yield. High-resolution ESI-MS for $[\text{M}^+]$, calcd.: 428.0047, found: 428.0040. Anal. Calc. for $\text{C}_{18}\text{H}_{18}\text{O}_4\text{N}_4\text{BrClCo}$: C, 40.87; H, 3.41; N, 10.6; Found: C, 40.82; H, 3.45; N, 10.5. UV-Vis (CH_3CN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) = 263 (7765), 501(172), 613(200). Magnetic measurement: μ_{eff} (298 K) = 4.33 μ_B .

$[\text{Co}(\text{TPA})\text{I}]\text{I}$ (**3**), blue solid, 80% yield. High-resolution ESI-MS for $[\text{M}^+]$, calcd.: 475.9908, found: 475.9903. Anal. Calc. for $\text{C}_{18}\text{H}_{18}\text{N}_4\text{I}_2\text{Co}$: C, 35.82; H, 2.99; N, 9.29. Found: C, 35.97; H, 3.09; N, 9.19 %. UV-Vis (CH_3CN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) = 247 (19335), 515(170), 611(281). Magnetic measurement: μ_{eff} (298 K) = 4.25 μ_B .

$[\text{Co}(\text{TPA})(\text{NCS}-\kappa\text{N})]\text{ClO}_4$ (**4**), green solid, 55% yield. High-resolution ESI-MS for $[\text{M}^+]$, calcd.: 407.0615, found: 407.0611 (M^+). Anal. Calc. for $\text{C}_{19}\text{H}_{18}\text{O}_4\text{N}_5\text{ClSCo} \cdot \text{CH}_2\text{Cl}_2$: C, 40.57; H, 3.38; N, 11.83, S, 5.41. Found: C, 40.99; H, 3.40; N, 11.96, S 5.46 %. UV-Vis (CH_3CN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) = 261 (8157), 328 (1993), 476 (172), 606 (296). Magnetic measurement: μ_{eff} (298 K) = 4.18 μ_B .

2.2. X-ray crystallography

X-Ray diffraction data were collected on Bruker X8 Proteum or Bruker D8-Venutre diffractometer. The crystal was kept at 294 K or 100 K in the course of data collection. The diffraction images were interpreted and diffraction intensities were integrated by using the SAINT program. Multi-scan SADABS was applied for absorption correction. By using Olex2 [45], the structure was solved with the ShelXS [46] structure solution program using direct methods and refined with the XL [45] refinement package using least-squares minimization. The positions of the hydrogen atoms were calculated on the basis of the riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and these positions participated in the calculation of the final R_{indices} . In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically.

2.3. Computational details

All the computations were performed by using Gaussian 09 package [47]. The molecular structures were optimized using the M06L functional [48]. Frequency calculations at the same level were carried out to corroborate all of the stationary points as minima and to compute free energies. The 6-31G* Pople basis set [49] was employed for all the atoms except for Co and I atom with effective core potential (ECP) type of basis set LANL2DZ [50]. The solvent effect was included by the single point calculations for all the optimized gas-phase structures with self-consistent reactions field (SCRF) based on the polarizable continuum model (PCM) [51] and the solvent was acetonitrile which was also the solvent used in the experiments. The functional of M06 [52] was applied in the single point calculations to compute energy; 6-311+G* basis set [53] was applied on all the atoms except for Co and I atom with the Hay-Wadt relativistic effective core potentials (RECPs) LANL2TZ(f) [54].

2.4. Photocatalytic CO₂ reduction

The conditions for photocatalytic CO₂ reduction using cobalt catalyst have been reported previously [28]. A mixture of cobalt catalyst (5 μ M) and Ir(ppy)₃ (0.4 mM) in a 4 mL of CH₃CN/TEA (4:1, v/v; TEA = triethylamine) mixture was purged with CO₂ (purity $\geq$ 99.8%) for 10 min, and 250 μ L CH₄ was injected to the reaction mixture prior to the irradiation using blue LEDs (centered at 460 nm). All of the reaction mixtures and LEDs were cooled by aluminum blocks, PC cooling fans, and compressed air. Gas sample (200 μ L) was drawn from the headspace of the tube and injected to GC-TCD for measurement. Photolysis products were analyzed using the Agilent 7890A gas chromatographic system equipped with a thermal conductivity detector (TCD) and a HP-Plot 5 Å column with Ar as the carrier gas. The oven temperature was held at 40 °C; inlet and detector temperature were set at 80 °C and 150 °C respectively. A multi-point calibration curve was established separately for CO ($R^2 = 0.9997$), H₂ ($R^2 = 0.9997$) and CH₄ ($R^2 = 0.9977$).

3. Results and discussion

All the [Co(TPA)X]⁺ complexes were prepared in moderate to good yields by the reactions of cobalt(II) salts with TPA. The [Co(TPA)X]⁺ (X = Cl⁻, Br⁻, NCS⁻- κ N) complexes

were isolated as ClO_4^- salt because of their better crystal quality for X-ray crystallographic analysis and non-hygroscopic nature. Attempts were made to prepare ClO_4^- salt of $[\text{Co}(\text{TPA})\text{I}]^+$ but complete metathesis of ClO_4^- with I^- was found to be difficult in our hands. Hence, $[\text{Co}(\text{TPA})\text{I}]\text{I}$ (**3**) was prepared and used for the present study. Magnetic susceptibility measurements revealed that complexes **1–4** are high spin with μ_{eff} of 4.51, 4.33, 4.25 and 4.18 μ_{B} , respectively. Crystals of **2–4** suitable for X-ray crystal structure determinations were obtained by layering of diethyl ether onto CH_2Cl_2 solutions. The structures of **2–4** are isomorphous to that of $[\text{Co}(\text{TPA})\text{Cl}]^+$, adopting a distorted trigonal bipyramidal geometry (Fig. 1). The Co(II)-N (amine) distances of these complexes are virtually identical, being 2.194 Å (avg.), 2.195 Å (avg.) and 2.198(2) Å for **2**, **3**, and **4**, respectively. These bond distances are similar to that of $[\text{Co}(\text{TPA})\text{Cl}]^+$ (2.2 Å, avg.) [28] and literature reported Co-N distances involving high spin cobalt(II) ion (Table 1) [55]. The Co(II)-N(pyridyl) distances of **2** (2.067 Å, avg.) and **3** (2.068 Å, avg.) are comparable with that of $[\text{Co}(\text{TPA})\text{Cl}]^+$ (2.062 Å, avg.) but are slightly longer than that of **4** (2.058 Å, avg.). In general, longer Co(II)-N(pyridyl) distances are observed in the presence of bulky coordinated anion.

Fig. 1. Structures of **2** (30% probability ellipsoids), **3** and **4** (50% probability ellipsoids). Hydrogen atoms, counter ions and solvent molecules have been removed for clarity.

Table 1

Selected bond distances (Å) and angles (°) for **2–4**.

2*			
Co1-N1	2.191(3)	Co2-N5	2.197(2)
Co1-N2	2.070(2)	Co2-N6	2.059(2)
Co1-N3	2.075(2)	Co2-N7	2.066(3)
Co1-N4	2.061(3)	Co2-N8	2.081(3)
Co1-Br1	2.4268(5)	Co1-Br2	2.4300(5)

N2-Co1-N1	77.47(10)	N6-Co2-N5	77.43(9)
N3-Co1-N1	78.12(10)	N7-Co2-N5	77.16(9)
N4-Co1-N1	77.28(10)	N8-Co2-N5	77.28(9)
N4-Co1-N2	119.60(9)	N6-Co2-N7	118.17(10)
N2-Co1-N3	115.36(10)	N6-Co2-N8	113.52(9)
N4-Co1-N3	111.59(10)	N7-Co2-N8	114.19(10)
N1-Co1-Br1	177.82(7)	N5-Co2-Br2	178.72(7)
N2-Co1-Br1	100.56(8)	N6-Co2-Br2	103.02(7)
N3-Co1-Br1	102.03(8)	N7-Co2-Br2	103.59(6)
N4-Co1-Br1	104.60(8)	N8-Co2-Br2	101.45(7)
3*			
Co1-N1	2.073(7)	Co1A-N1A	2.080(7)
Co1-N2	2.066(6)	Co1A-N2A	2.067(6)
Co1-N3	2.057(7)	Co1A-N3A	2.067(7)
Co1-N4	2.203(6)	Co1A-N4A	2.187(7)
Co1-I1	2.6503(12)	Co1A-I1A	2.6288(12)
N1-Co1-N4	77.4(3)	N1A-Co1A-N4A	77.3(3)
N1-Co1-I1	100.6(2)	N1A-Co1A-I1A	100.62(19)
N2-Co1-N1	115.6(3)	N2A-Co1A-N1A	117.7(2)
N2-Co1-N4	77.2(2)	N2A-Co1A-N3A	111.6(3)
N2-Co1-I1	103.96(17)	N2A-Co1A-N4A	77.4(2)
N3-Co1-N1	113.6(3)	N2A-Co1A-I1A	105.60(18)
N3-Co1-N2	116.5(2)	N3A-Co1A-N1A	117.4(3)
N3-Co1-N4	77.0(3)	N3A-Co1A-N4A	78.3(3)
N3-Co1-I1	103.76(19)	N3A-Co1A-I1A	100.8(2)
N4-Co1-I1	178.01(18)	N4A-Co1A-I1A	176.91(18)
4			
Co1-N1	2.062(2)	N1-Co1-N4	77.99(8)
Co1-N2	2.061(2)	N2-Co1-N1	116.03(9)
Co1-N3	2.051(2)	N2-Co1-N4	78.01(8)
Co1-N4	2.198(2)	N3-Co1-N1	110.02(9)
Co1-N5	1.996(2)	N3-Co1-N2	121.04(9)
		N3-Co1-N4	77.67(8)
		N5-Co1-N1	103.64(9)
		N5-Co1-N2	100.56(9)
		N5-Co1-N3	102.30(9)
		N5-Co1-N4	178.22(9)

* Each asymmetric unit contains two crystallographic independent molecules.

UV-visible absorption spectra of **1–4** were recorded in CH₃CN (Fig. 2). Each complex exhibits two distinct absorption bands, corresponding to d-d transitions, in the region of 450–700 nm with molar absorptivity < 300 M⁻¹ cm⁻¹. This indicates that complexes **1–4** are present as five-coordinated species in acetonitrile [56]. A blue shift in the absorption peak maximum of the 1st d-d transition band from **3** to **2**, **1**, and **4** (λ_{max} = 476 nm (**4**), 487 nm (**1**), 501 nm (**2**) and 515

nm (**3**)) is in accordance with the position of ligand X in the spectro-electrochemical series ($X = \text{NCS}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$).

Fig. 2. UV-visible absorption spectra of **1–4** in CH_3CN at $2 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3$ at room temperature.

Electrochemical properties of **1–4** under argon and carbon dioxide atmosphere were investigated using cyclic voltammetry (CV) in 0.1 M $[\text{nBu}_4\text{N}]\text{PF}_6$ CH_3CN solutions, and representative cyclic voltammograms are shown in Fig. 3. The reduction peaks are irreversible for all of the complexes. Complex **1** shows its first reduction wave with E_{pc} at -1.96 V whereas the first E_{pc} was observed at -1.83, -1.72, and -1.76 V for **2–4** respectively. Interestingly, although the first reduction E_{pc} values for complexes **1–4** span from -1.96 to -1.72 V vs $\text{Fc}^{+/0}$, significant discharge of current for all these complexes under CO_2 atmosphere was observed at ~ -2.04 V. A suggestion is that $[\text{Co}^{\text{I}}\text{-CO}_2]$ adduct is formed at the first E_{pc} [57] while a second electron transfer at ~ -2.04 V results in the reduction of coordinated CO_2 [58].

Fig. 3. Cyclic voltammograms of **1** (a), **2** (b), **3** (c) and **4** (d) in 0.1 M [n Bu₄N]PF₆ CH₃CN solutions under Ar (black) and CO₂ (red) atmosphere using a glassy carbon disk electrode at a scan rate of 100 mV s⁻¹.

The findings from cyclic voltammetry and bulk electrolysis on **1** [59] indicated that **1–4** are potent electro-catalysts for CO₂ reduction; in this work, only photochemical reduction of CO₂ using these complexes as catalysts was focused because of our interest in visible-light driven CO₂ reduction. The performance of **1–4** in visible-light induced CO₂ reduction was evaluated using the same reaction conditions reported in our previous work, *i.e.* irradiating cobalt complex (5 μM) and Ir(ppy)₃ (0.4 mM) in 4 mL CO₂-saturated CH₃CN/TEA solution (4:1, v/v; TEA = triethylamine) using blue LEDs as light source (Fig. 4) [28,41]. The products, H₂ and CO, were identified and quantified using a GC-TCD equipped with a molecular sieve column. Similar to our previous finding on [Co(TPA)Cl]⁺, *all complexes showed initial TOF of ~ 10 min⁻¹, TON(CO) > 1000, CO selectivity > 90% over a 65 h time of irradiation, and the TON (CO) of 1 was comparable to that of [Co(TPA)Cl]Cl*. Therefore, complexes **1–4** may follow the same CO₂ reduction reaction mechanism as [Co(TPA)Cl]Cl [28,41,62] (see the Supporting Information). Interestingly, among these four complexes, **1** was the least active catalyst with TON(CO) > 1000, followed by **3** with TON(CO) > 1200 and **4** with TON > 1300. Complex **2** was found to show the best performance towards the photochemical CO₂ reduction with TON(CO) *i.e.* > 1400 over 65 h. This finding is suggestive of different deactivation steps of the photochemical reaction

catalyzed by complexes **1–4**, respectively, and *lends support to the coordinated anion to play discernible effect(s) in the catalytic cycle of CO₂ reduction*. The effect(s) of coordinated anion X could involve a multitude of factors such as stability of [Co(TPA)X]⁺ catalyst, effect on the deactivation step(s) of the photo-catalytic cycle, and activation of CO₂ upon coordination to cobalt center. Nevertheless, further investigation is needed to understand the role of the coordinated anion in the photocatalytic CO₂ reduction. In literature, Ott and Thapper reported the importance of chloride ligand in affecting the mechanisms of iron complexes in water oxidation [60,61]. Herein, density functional theory (DFT) calculations were performed in order to shed insight into the role of the coordinated anion X in the mechanism of CO₂ reduction. The effect of coordinated anion X upon the deactivation steps of the photo-catalytic CO₂ reduction is beyond the scope of the present calculations described in the following section.

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

The reaction pathway of CO₂ reduction catalyzed by [Co(TPA)Cl]⁺ was previously examined [62]. Similar calculation methodologies were employed here to calculate the reaction pathways of **2–4**. Consistent with their magnetic susceptibility values, complexes **1–4** all have quartet states as their ground states. Triplet ground states become the ground states upon one electron reduction (the calculated Co^{II/I} reduction potential for **1–4** are listed in Table 2, left column) with their respective reduction intermediates denoted as **1-IntA**, **2-IntA**, **3-IntA**, and **4-IntA**. The calculated reduction potentials are comparable with each other, since the reduced 1e⁻ is localized on the cobalt center and the TPA ligand (Fig. 5), and the X ion does not appear to show much effect on the spin density distributions on the Co^I intermediate.

The subsequent CO₂ binding and protonation processes after the reduction of [Co(TPA)X]⁺ are depicted in Scheme 1. The CO₂ bindings are all slightly energetically exothermic, and for **4-IntA** with NCS⁻ ligand, it has almost no energy change, as there is no change in the trigonal bipyramidal structure. After the protonation process, the coordination around the Co center becomes octahedral, and singlet ground states for all **IntC** species are obtained after charge transfer. The protonation process for **4-IntC** is slightly energetically favorable by -1.1 kcal mol⁻¹, while for **1-IntC**, **2-IntC**, and **3-IntC**, they are endothermic with free energy of 1.5, 3.0, and 9.3 kcal mol⁻¹, respectively (Scheme 1). Despite the very similar bond lengths between cobalt center and the carbon atom from COOH group, the distances between the H atom from COOH group and the ancillary ligand X in the intermediates are 2.15, 2.30, 2.70 and 1.88 Å, respectively (Fig. 6). Apparently, the closer the distance between H atom and ligand X, the more feasible the protonation process is. Therefore, the ancillary ligand X could exert influence on the protonation process by modulating the hydrogen bonding interaction.

The reduction potentials calculated for **1-IntC** to **4-IntC** are listed in Table 2. Their comparable reduction potentials are suggestive of similar catalytic efficiency. This is in accordance to the data presented in Fig. 4. As depicted in the Fig. 4, the initial turnover frequencies judging from the slopes of the plot of TON versus time for the first several hours of the photochemical reaction were similar for complexes **2–4**. For the reduced intermediates **1-IntD** to **4-IntD**, the strength of hydrogen bond still makes a difference to their second protonation process. Intermediates with stronger hydrogen bond, such as **1-IntD** and **4-IntD**, are less feasible to attract the second proton and break the C-O bond compared with analogues **2-IntD** and **3-IntD** as the COOH groups in **1-IntD** and **4-IntD** are more stabilized by the ancillary ligand Cl⁻ and NCS⁻ (Fig. 6). Once the C-O bond in COOH group is broken, the ground state of the complexes becomes quartet again. Similar energies are observed for the subsequent dissociations of H₂O and CO from the cobalt species depicted in Scheme 2. The trigonal bipyramidal coordination geometry of cobalt complex is restored via the extrusion of CO from the coordination sphere.

Table 2
Reduction potentials for complexes **1–4**.

X	Reduction reaction (L = TPA) (vs. Fc ⁺ /Fc in CH ₃ CN)	
	[CoLX] ⁺ + e ⁻ → [CoLX] ⁰	[Co(COOH)LX] ⁺ + e ⁻ → [Co(COOH)LX] ⁰
Cl ⁻	-2.07	-0.63
Br ⁻	-2.07	-0.67
I ⁻	-1.93	-0.57
NCS ⁻	-2.03	-0.74

Fig. 5. Spin-density difference plots for the reduction intermediate of (a) **1-IntA**, (b) **2-IntA**, (c) **3-IntA**, and (d) **4-IntA**, respectively. The blue surface corresponds to an excess of α -electron density, and the green surface corresponds to an excess of β -electron density.

Scheme 1. Computed free energy surface for CO₂ binding and protonation on intermediates of (a) **1-IntA**, (b) **2-IntA**, (c) **3-IntA**, and (d) **4-IntA**, respectively. Hydrogen atoms in the TPA ligand are removed for clarity.

Fig. 6. Optimized structures of (a) **1-IntC**, (b) **2-IntC**, (c) **3-IntC**, and (d) **4-IntC**, respectively, with selected structural parameters (bond length in Å).

Scheme 2. Free energy profiles for the second protonation process of (a) **1-IntD**, (b) **2-IntD**, (c) **3-IntD**, and (d) **4-IntD**, respectively, leading to the breakage of the C–O bond and the release of H₂O and CO.

4. Conclusion

We have prepared a series of [Co(TPA)X]⁺ complexes (X = Cl⁻, Br⁻, I⁻, and NCS⁻) (**1–4**), which have been characterized by various spectroscopic means. Three of them have their structures determined by X-ray crystallography. Photocatalytic CO₂ reduction using [Co(TPA)X]⁺ in combination with Ir(ppy)₃ revealed that these complexes are robust and potent

CO₂ reduction catalysts with initial TOF of 10 min⁻¹, TON(CO) > 1000 and CO selectivity > 90% over an irradiation time period of 65 h. More importantly, the coordinated anion plays a discernible effect on the performance of the Co catalyst towards photocatalytic CO₂ reduction, with TON(CO) > 1500, 1300, 1200 and 1000 for Br⁻, NCS⁻, I⁻ and Cl⁻ respectively. DFT calculation suggested that different anions can have influence on the stability of [Co-COOH] intermediate. DFT calculation also revealed that facile CO liberation from Co-TPA is attributed to the driving force for the restoration of Co-TPA to the trigonal bipyramidal geometry.

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Appendix A. Supplementary data

CCDC 1487737, 1487733 and 1487734 contain the supplementary crystallographic data for **2–4**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at

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