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Synthesis of new CO_2-soluble ruthenium(II) and cobalt(II) polypyridine complexes bearing fluorinated alkyl chains and their application to photoreduction of *liq*. CO_2

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ABSTRACT

Eight types of new CO_2-soluble or CO_2-philic ruthenium(II) and cobalt(II) polypyridine complexes, namely, $[M(F84OPh)_3](BArF)_2$, $[M(F44OPh)_3](BArF)_2$, $[M(F62Ph)_3](BArF)_2$, and $[M(F62O)_3](BArF)_2$ (M = Ru or Co, BArF: tetrakis[3,5-bis(trifluoromethyl)phenyl]borate), were prepared from bipyridine derivatives bearing highly fluorinated alkyl chains and applied to the photoreduction of *liq*. CO_2 under a high pressure of 6.8 MPa at 35 °C. All these complexes have higher philicity toward *liq*. CO_2 than the corresponding complexes with PF^{6-} as the counteranion. Using the Ru(II)–Co(II) systems of $[M(F44OPh)_3](BArF)_2$ and $[M(F62O)_3](BArF)_2$, direct photoreduction of CO_2 was achieved without the use of any organic solvent.

1. Introduction

The conversion of solar energy into chemical energy is an important and promising candidate for addressing the problems of fossil fuel depletion and global warming. According to Lehn et al. [1], Ru(II) and Co(II) polypyridine complexes function as photocatalysts for the reduction of CO_2 dissolved in organic solvents. It is expected that supercritical CO_2 (sc-CO_2) or *liq*. CO_2 as solvent and substrate will enhance the reduction efficiency of the photoreaction. However, the original complexes do not dissolve in a nonpolar CO_2 phase, owing to their ionic property. The development and application of "CO_2-soluble" complexes to CO_2 photoreduction are interesting and attractive because considerable improvement in reaction efficiency is expected to be possible and the use of harmful organic solvents can be avoided.

The solubility of polar complexes in sc-CO_2 or *liq*. CO_2 is expected to be enhanced by incorporating "CO_2-philic" ligands, an enhancement that can be achieved by the introduction of fluoroalkyl chains into the parent ligands to enhance their lipophilicity [2–7]. In this paper, we present a preliminary report on the first preparation of CO_2-soluble Ru(II) and Co(II) polypyridine complexes bearing fluorinated alkyl chains and their application to the photoreduction of *liq*. CO_2 under high pressure.

2. Results and discussion

2.1. Synthesis of ligands

Four new ligands, F84OPh, F44OPh, F62Ph, and F62O, were prepared from appropriate 2,2′-bipyridine derivatives and fluoroalkyl chains, as shown in Scheme 1, according to the literature [5–15]: F84OPh and F44OPh were obtained by coupling between 4,4′-bis(*p*-hydroxyphenyl)-2,2′-bipyridine and the corresponding 4-(perfluoroalkyl)butyl tosylates [5–9,11–13,15]. F62Ph was prepared by the Suzuki coupling reaction between 4,4′-dibromo-2,2′-bipyridine and *p*-(2-(perfluorohexyl)ethyl)phenylboronic acid [8–12,16,17]. On the other hand, F62O was synthesized by the substitution reaction between 4,4′-dinitro-2,2′-bipyridine-1,1′-dioxide and potassium 2-(perfluorohexyl)ethoxide followed by subsequent deoxygenation with PBr_3 (Scheme 1) [8–13].

2.2. Synthesis of Ru(II) and Co(II) complexes

The Ru(II) and Co(II) complexes were directly prepared from their corresponding metal chlorides and each of their ligands following a typical procedure. For the synthesis of Ru complexes from F84OPh, F62Ph, and F62O and Co complexes from F84OPh and F62Ph, fluorinated alcohols were necessary to increase the solubility of the ligand, as shown in Scheme 2. To examine the effects of the counteranion on the solubility of the complexes, PF_6^- was exchanged with $BArF^-$ (tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) (Scheme 2) [3,19–24].

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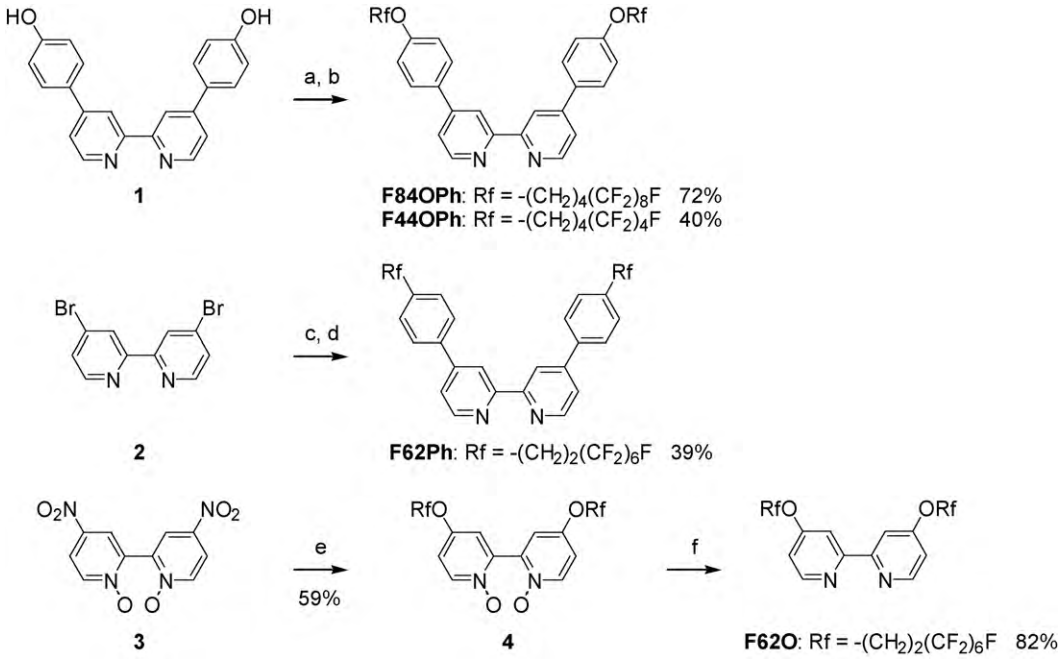


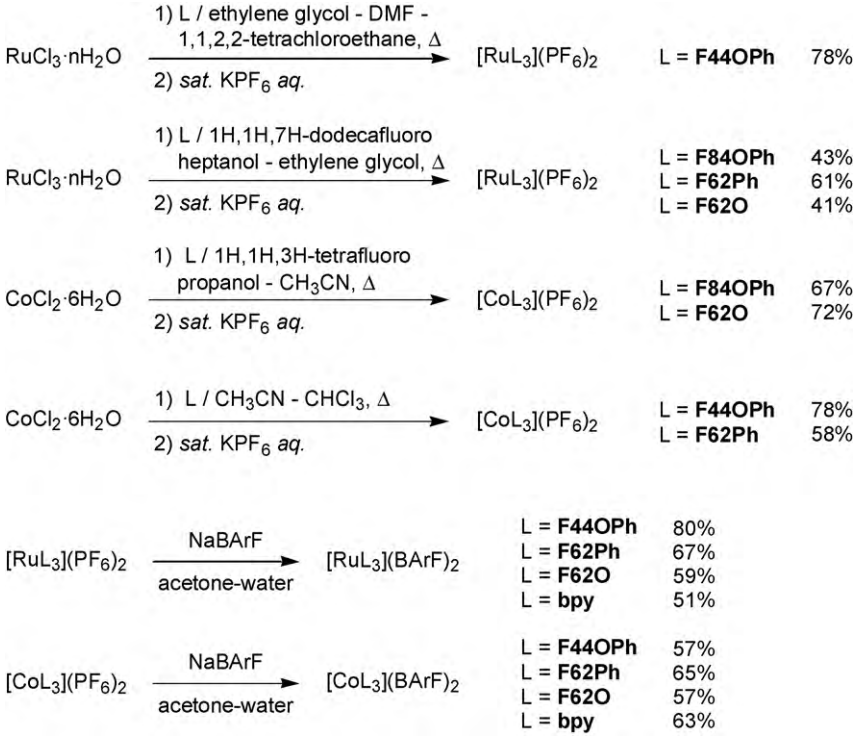
Scheme 1. Synthesis of 2,2′-bipyridine derivatives bearing fluorinated alkyl chains. (a) NaH, dry DMF, 50 °C, 1 h; (b) $F(CF_2)_8(CH_2)_4OTs$ or $F(CF_2)_4(CH_2)_4OTs$, 50 °C, 6–15.5 h; (c) cat. $Pd(PPh_3)_4$, dry toluene, r.t., 1 h; (d) *p*-(2-(perfluorohexyl)ethyl)phenylboronic acid, 4 N KOH *aq.*, 80 °C, 20 h; (e) $F(CF_2)_6(CH_2)_2OK$, 100 °C, 32 h; and (f) PBr_3, dry $CHCl_3$, reflux, 3 h.

All complexes were soluble in fluorinated alcohols as expected. Interestingly, they were also soluble in common aprotic polar solvents, such as DMF, CH_3CN, and acetone, as seen in Scheme 2 and also have enough solubilities in chloroform to be characterized by ^1H NMR.

As $[M(F84OPh)_3](PF_6)_2$ is less soluble than others, its solubilities were examined for MeOH, DMF, CH_3CN, and THF. The solubilities of $[Ru(F84OPh)_3](PF_6)_2$ were 0.4 mg/100 mg (DMF), 0.2 mg/100 ml (CH_3CN), and 0.4 mg/100 ml (THF) and those of $[Co(F84OPh)_3](PF_6)_2$ were 0.25 mg/100 mg (DMF), 0.25 mg/100 ml (CH_3CN) and 0.4 mg/100 ml (THF). However they seemed to decompose gradually in THF and both complexes were insoluble in MeOH.

2.3. Solution behavior of metal complexes in sc-CO_2

At present, the solubility of metal complexes in sc-CO_2 cannot be quantitatively measured. Therefore, we attempted to qualitatively examine the solution behavior of Ru(II) and Co(II) complexes



Scheme 2. Preparation of Ru(II) and Co(II) complexes.

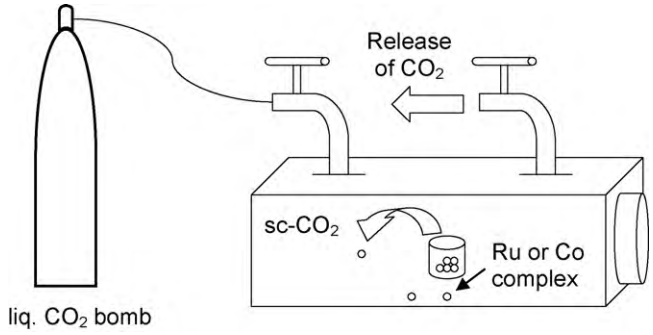


Fig. 1. Experimental setup to study the solution behavior of the metal complexes in sc-CO_2.

using a high-pressure reaction vessel (Fig. 1). The experimental procedure is as follows: a sample bottle containing a Ru(II) or Co(II) complex (3–4 mg) was set in the reaction vessel and *liq*. CO_2 was introduced into the vessel (~10 ml). The complex was steeped in sc-CO_2 at 50 °C under high pressure (~9.4–10.1 MPa). After about 1 h, sc-CO_2 was slowly released as gaseous CO_2 and the change in the appearance of each complex was visually observed.

Figs. 2 and 3, respectively, show the results of solution experiments on Ru(II) and Co(II) complexes with the new ligands, that is, $[ML_3](PF_6)_2$ and $[ML_3](BArF)_2$, in sc-CO_2. $[M(F62O)_3](PF_6)_2$ showed signs of dissolution, while $[Ru(F44OPh)_3](PF_6)_2$ seemed soluble to a lesser extent; other complexes did not exhibit any changes, and thus were considered to be insoluble. It seems that the introduction of a fluorinated alkoxy group increases solubility, whereas introduction of an aromatic structure decreases solubility.

To investigate the effect of counterions, the anion was exchanged with $BArF^-$ containing 24 fluorine atoms. As clearly shown in Fig. 3, $[M(F62Ph)_3](BArF)_2$, $[M(F44OPh)_3](BArF)_2$, and $[M(F62O)_3](BArF)_2$ (M = Ru and Co) were more soluble than their corresponding complexes with PF_6^-. In addition, the solubility of the Ru complexes was higher than that of the Co complexes. On the other hand, $[M(bpy)_3](BArF)_2$ compounds were insoluble. These results indicate that both the ligand and the counteranion must be CO_2-philic to solubilize the Ru(II) and Co(II) complexes in sc-CO_2. It was shown that $[M(F62O)_3](BArF)_2$ (M = Ru and Co) compounds are the most soluble in sc-CO_2 and that $[M(F44OPh)_3](BArF)_2$ compounds are highly CO_2-philic.

2.4. Absorption and emission spectra of Ru(II) complexes

Fig. 4 shows the absorption spectra of the Ru(II) complexes. $[Ru(F62O)_3](PF_6)_2$ exhibits a molar extinction coefficient ε comparable to that of $Ru(bpy)_3Cl_2$. On the other hand, $[Ru(F84OPh)_3](PF_6)_2$, $[Ru(F44OPh)_3](PF_6)_2$, and $[Ru(F62Ph)_3](PF_6)_2$ have higher ε values in the visible region than $Ru(bpy)_3Cl_2$ and $[Ru(F62O)_3](PF_6)_2$. These results are attributable to the introduction of phenyl groups at the 4,4′-positions of 2,2′-bipyridine.

The emission spectra of all investigated Ru(II) complexes are shown in Fig. 5. $[Ru(F62O)_3](PF_6)_2$ shows a markedly low emission intensity that was comparable with that of $Ru(bpy)_3Cl_2$. It is thought that excitation energy was lost through nonradiative deactivation by thermal vibration of the fluoroalkoxy groups directly attached to the 2,2′-bipyridine structure. On the other hand, the emission intensity of $[Ru(F84OPh)_3](PF_6)_2$, $[Ru(F44OPh)_3](PF_6)_2$, and $[Ru(F62Ph)_3](PF_6)_2$ was higher than that of $Ru(bpy)_3Cl_2$. This increase is due to the effects of the phenyl groups, which increase ε and prevent deactivation by thermal motion of the flexible fluoroalkyl chains.

2.5. Photoreduction of CO_2 under high pressure

New CO_2-philic and sc-CO_2-soluble Ru(II) and Co(II) complexes, namely, $[M(F44OPh)_3](BArF)_2$ and $[M(F62O)_3](BArF)_2$ (M = Ru and Co), were applied to CO_2 photoreduction experiments in *liq*. CO_2 and a DMF–CO_2 mixture under high pressure. The results are summarized in Table 1, and the appearance of the reaction mixtures in the vessel is shown in Fig. 6. For the $[M(F44OPh)_3](BArF)_2$ system in *liq*. CO_2 (Entry 1), the production of CO and H_2 was detected but the TN_{CO} was about one-fifth of that in DMF–CO_2 (Entry 2). It was observed that a small amount of the complexes dissolved in *liq*. CO_2; however, most of the complexes remained at the bottom of the vessel (Fig. 6a), while all complexes dissolved in DMF–CO_2. On the other hand, $[M(F62O)_3](BArF)_2$ in *liq*. CO_2 showed the same TN_{CO} as that in DMF–CO_2 (Entries 3 and 4) because all the complexes

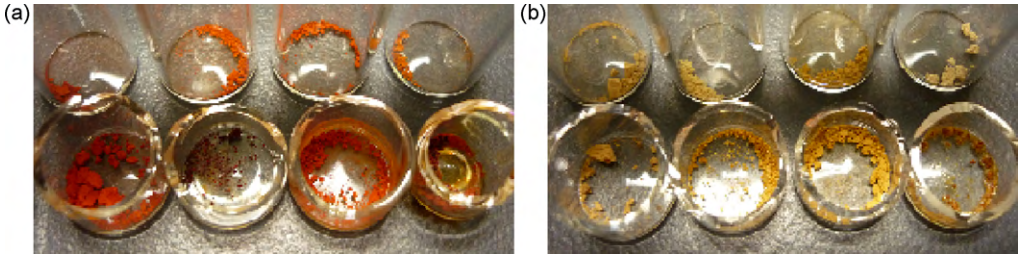


Fig. 2. Solution experiments of Ru (a) and Co complexes (b) in sc-CO_2.
From the left: $[M(F84OPh)_3](PF_6)_2$, $[M(F62Ph)_3](PF_6)_2$, $[M(F44OPh)_3](PF_6)_2$, and $[M(F62O)_3](PF_6)_2$ (M = Ru (a) or Co (b)) were shown. The complexes in bottles in the back row and those in cut-bottles in the front were before sc-CO_2 and after sc-CO_2 exposure, respectively.

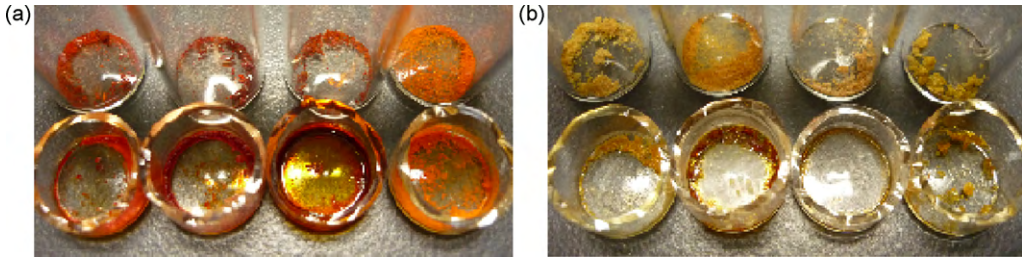


Fig. 3. Solution experiments of Ru (a) and Co complexes (b) in sc-CO_2. From the left, $[M(F62Ph)_3](BArF)_2$, $[M(F44OPh)_3](BArF)_2$, $[M(F62O)_3](BArF)_2$, and $[M(bpy)_3](BArF)_2$ (M = Ru (a) or Co (b)) were shown. The complexes in bottles in the back row and those in cut-bottles in the front were before sc-CO_2 and after sc-CO_2 exposure, respectively.

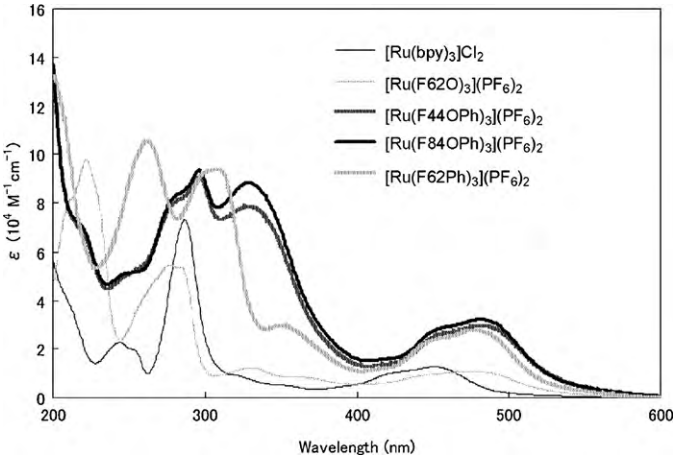


Fig. 4. Absorption spectra of $Ru(bpy)_3Cl_2$, $[Ru(F44OPh)_3](PF_6)_2$, $[Ru(F62O)_3](PF_6)_2$, $[Ru(F62Ph)_3](PF_6)_2$, and $[Ru(F84OPh)_3](PF_6)_2$ (2×10^{-5} M) in degassed and N_2 saturated CH_3CN at room temperature.

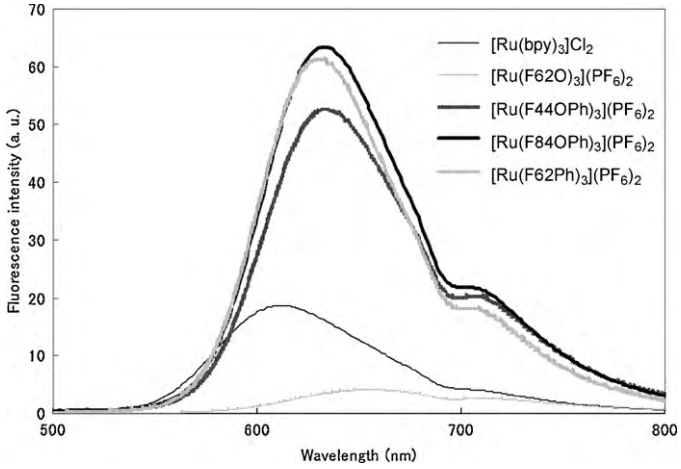


Fig. 5. Emission spectra of $Ru(bpy)_3Cl_2$, $[Ru(F44OPh)_3](PF_6)_2$, $[Ru(F62O)_3](PF_6)_2$, $[Ru(F62Ph)_3](PF_6)_2$ and $[Ru(F84OPh)_3](PF_6)_2$ (2×10^{-5} M) in degassed and N_2 saturated CH_3CN at room temperature. The excitation wavelength is 450 nm.

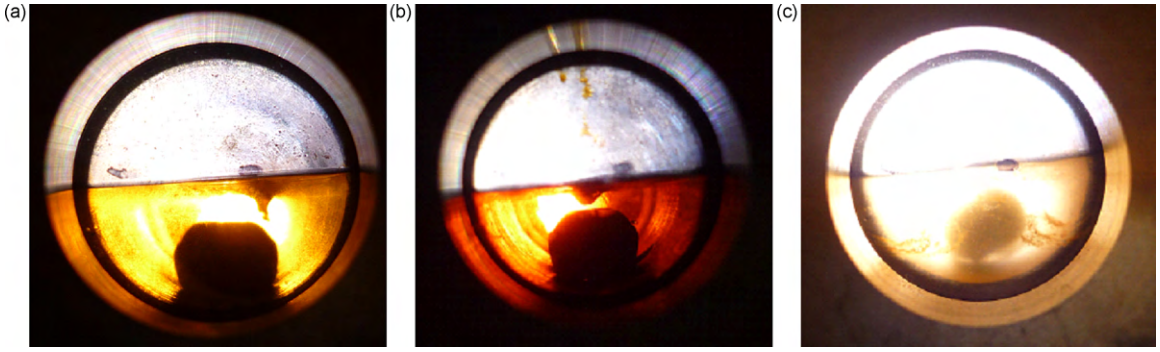


Fig. 6. Photos of the photoreduction systems of *liq*. CO_2 in the high-pressure reaction vessel. (a) $[Ru(F44OPh)_3](BArF)_2$ and $[Co(F44OPh)_3](BArF)_2$ system at 35 °C and 6.8 MPa, (b) $[Ru(F62O)_3](BArF)_2$ and $[Co(F62O)_3](BArF)_2$ system at 35 °C and 6.8 MPa, and (c) $[Ru(F62O)_3](PF_6)_2$ and $[Ru(F62O)_3](PF_6)_2$ system at 25 °C and 5.6 MPa.

dissolved in *liq*. CO_2 (Fig. 6b). For $[M(F62O)_3](PF_6)_2$, however, no CO or H_2 was detected (Entry 5) because only small amounts of the complexes dissolved in sc-CO_2 (Fig. 6c), which was due to PF_6^-, as mentioned above. The modification of both the ligand and counteranion of the complexes resulted in high solubility and high CO production for $[M(F62O)_3](BArF)_2$ (M = Ru and Co). The lower TN_{CO} of the $[M(F62O)_3](BArF)_2$ system than that of the $[M(F44OPh)_3](BArF)_2$ system in DMF–CO_2 (Entry 2 vs Entry 4) is due to the lower absorption and emission properties of the former system, which arises from the aliphatic side chain of F62O, as mentioned above.

Table 1
CO_2-photoreduction using sc-CO_2 soluble and CO_2-philic Ru(II) and Co(II) complexes under high pressure.

Entry	Ligand	Counteranion	Solvents	Temp. (°C)	Pressure (MPa)	TN[a] CO	TN[a] H_2
1	F44OPh	BArF	CO_2[c]	35	6.8	6.0	1.2
2	F44OPh	BArF	DMF–CO_2[b]	50	7.3	27.1	3.3
3	F62O	BArF	CO_2[c]	35	6.8	17.7	1.8
4	F62O	BArF	DMF–CO_2[b]	50	6.6	15.6	0.5
5	F62O	PF_6	CO_2[c]	25	5.6	–	–

Reaction conditions: Ru complex, 2.5 μmol; Co complex, 2.5 μmol; light, Xe lamp (400–750 nm: HOYA L39, HA50); reaction time, 48 h.
[a] Turnover number (TN) refers to the mol of CO or H_2 generated per mol of the Co complex.
[b] *Liq*. CO_2 (5 ml), trietanolamine (1 ml), DMF (4 ml).
[c] *Liq*. CO_2 (8 ml), triethylamine (2 ml).

3. Conclusion

Four 2,2′-bipyridine derivatives with highly fluorinated side chains were synthesized and their Ru(II) and Co(II) complexes were prepared. The CO_2-soluble or CO_2-philic Ru(II) and Co(II) complexes $[M(F62O)_3](BArF)_2$ and $[M(F44OPh)_3](BArF)_2$ were synthesized with new 2,2′-bipyridines bearing fluorinated alkyl chains, namely, F62O and F44OPh. The solubilities of these complexes were enhanced in combination with a highly fluorinated counteranion, $BArF^-$. Applying the new Ru(II) and Co(II) complexes, we successfully realized CO_2 photoreduction in sc-CO_2 without the use of any other organic solvent.

4. Experimental

4.1. General

Dry solvents used in the reactions were freshly distilled from appropriate drying agents before use. Chemicals used were obtained from commercial suppliers and used without further purifications including fluorinated compounds from Daikin Industries, Ltd. All compounds were characterized by ^1H NMR (Bruker AC-300P or AVANCE500) and ESI–MS (Mariner). IR spectra were recorded on and a JASCO FT/IR 400. UV–vis and emission spectra of the complexes were recorded as an acetonitrile solution on a JASCO V-550 and a JASCO V-750, respectively.

4.2. Synthesis of the ligands

4.2.1. Synthesis of 4,4′-bis(p-(4-(perfluorooctyl)butoxy)phenyl))-2,2′-bipyridine (F84OPh)

Under nitrogen, 4,4′-bis(*p*-hydroxyphenyl)-2,2′-bipyridine **1** (50.0 mg, 0.147 mmol) was suspended in dry DMF (6 ml) and stirred at 80 °C. After adding large excess amount of NaH (51.1 mg, 1.28 mmol) and stirring for 1 h, 4-(perfluorooctyl)butyl *p*-toluenesulfonate (301 mg, 0.466 mmol) was added. The suspension was stirred for 15.5 h. After cooling to r.t., the precipitate was filtered through a 0.45-μm membrane filter and washed with a large amount of H_2O, methanol and chloroform to obtain a gray solid in 72% (137 mg, 0.106 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.84 (d, J = 6.54 Hz, 2H; 6-Py-*H* and 6′-Py-*H*), 8.71 (s, 2H; 3-Py-*H* and 3′-Py-*H*), 8.35 (d, J = 6.54 Hz, 2H; 5-Py-*H* and 5′-Py-*H*), 7.93 (d, J = 9.09 Hz, 4H; Ar-*H*), 7.15 (d, J = 9.09 Hz, 4H; Ar-*H*), 4.17 (t, J = 5.82 Hz, 4H; Ar-OCH_2), 2.08–2.23 (m, 4H; CF_2CH_2, 4H), 1.82–1.93 (m, 8H; $ArOCH_2CH_2CH_2$); IR (KBr): 1592, 1205, 1041 cm^{-1}; mp 226.2–227.1 °C.

4.2.2. Synthesis of 4,4′-bis(p-(4-(perfluorobutyl)butoxy)phenyl)-2,2′-bipyridine (F44OPh)

Under nitrogen, 4,4′-bis(*p*-hydroxyphenyl)-2,2′-bipyridine **1** (251 mg, 0.737 mmol) was suspended in dry DMF (40 ml) and stirred at 60 °C for 30 min. After adding large excess amount of NaH (258 mg, 6.45 mmol) and stirring for 10 min, 4-(perfluorobutyl)butyl *p*-toluenesulfonate (879 mg, 1.97 mmol) was added and the suspension was stirred for 5 h. After cooling to r.t., the mixture was concentrated, suspended in water and extracted with chloroform (50 ml × 4). The organic layer was dried with *anhyd*. Na_2SO_4 and concentrated. The residue was filtered again and washed with large amount of water and small amount of hexane to obtain brownish white solid. The residue was purified by recrystallization from ethanol/water (v/v, 10/1) to obtain white solid in 40% (263 mg, 0.296 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.71 (d, J = 5.14 Hz, 2H; 6-Py-*H* and 6′-Py-*H*), 8.69 (d, J = 1.60 Hz, 2H; 3-Py-*H* and 3′-Py-*H*), 7.75 (d, J = 8.63 Hz, 4H; Ar-*H*), 7.52 (dd, J_1 = 5.14 Hz, J_2 = 1.60 Hz, 2H; 5-Py-*H* and 5′-Py-*H*), 7.01 (d, J = 8.63 Hz, 4H; Ar-*H*), 4.07 (t, J = 5.70 Hz, 4H; OCH_3), 2.09–2.30 (m, 4H; CF_2CH_2), 1.78–2.00 (m, 8H, OCH_2CH_2 CH_2); IR (KBr): 1592, 1237, 1040 cm^{-1}; mp 139.0–141.8 °C.

4.2.3. Synthesis of 4,4′-bis(p-(2-perfluorohexyl)ethylphenyl)-2,2′-bipyridine (F62Ph) [18]

Under nitrogen, $Pd(PPh_3)_4$ (256 mg, 0.222 mmol, 12 mol%) was added to the solution of 4,4′-dibromo-2,2′-bipyridine **2** (580 mg, 1.85 mmol) in dry toluene (100 ml). After stirring for 1 h, *p*-(2-(perfluorohexyl)ethyl)phenylboronic acid (1.90 g, 4.06 mmol) and 4 N KOH *aq*. (9.2 ml, 36.8 mmol) were added and the mixture was stirred at 80 °C. After stirring for 20 h, the mixture was cooled to r.t. and 1 N Na_2CO_3 *aq*. (15.0 ml) and NH_3 *aq*. (8.0 ml) were added to the mixture. The precipitate was filtered and washed with large amount of acetone and the filtrate was concentrated. Water was added and the mixture was extracted with chloroform (50 ml × 3). The organic layer was dried with *anhyd*. Na_2SO_4 and concentrated again. The residue was purified by silica gel column chromatography (chloroform to ethyl acetate) and alumina column chromatography with chloroform to obtain a white solid in 39% (720 mg, 0.720 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.75 (dd, J_1 = 5.15 Hz, J_2 = 0.75 Hz, 2H; 6-Py-*H* and 6′-Py-*H*), 8.72 (dd, J_1 = 1.83, J_2 = 0.75 Hz, 2H; 3-Py-*H* and 3′-Py-*H*), 7.76 (d, J = 8.45 Hz, 4H; Ar-*H*), 7.55 (dd, J_1 = 5.15 Hz, J_2 = 1.83 Hz, 2H; 5-Py-*H* and 5′-Py-*H*), 7.37 (d, J = 8.45 Hz, 4H; Ar-*H*), 2.98–3.03 (m, 4H; ArCH_2), 2.35–2.53 (m, 4H, $ArCH_2CH_2$); IR (KBr): 1592, 1221 cm^{-1}; mp 152.3–153.9 °C.

4.2.4. Synthesis of 4,4′-bis[2-(perfluorohexyl)ethoxy]-2,2′-bipyridine-1,1′-dioxide (**4**) [13]

Potassium metal (261 mg, 6.68 mmol) was cut into small pieces and immediately added to the solution of 2-(perfluorohexyl)ethanol (6.0 ml, 27.7 mmol) in diethyl ether (6.0 ml) under nitrogen atmosphere. The mixture was stirred at r.t. for several hours until potassium dissolved completely. 4,4′-Dinitro-2,2′-bipyridine-1,1′-dioxide **3** (600 mg, 2.16 mmol) was added to the solution and diethyl ether was removed by distillation, then the suspension was stirred at 100 °C for 32 h. The mixture was cooled to r.t., acidified to pH 4 by *conc*. HCl *aq*. and concentrated under vacuum. Large amount of chloroform was added to the residue and the suspension was sonicated several times to dissolve the brownish yellow solid. Insoluble precipitate was removed by filtration and the filtrate was concentrated. The residue was sonicated three times in hexane (30 ml), then the suspension was filtered again to obtain yellow powder (1.17 g, 1.28 mmol, 59%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 (d, J = 7.26 Hz, 2H; 6-*H* and 6′-*H*), 7.48 (d, J = 3.62 Hz, 2H; 3-*H* and 3′-*H*), 6.93 (dd, J_1 = 7.26 Hz, J_2 = 3.62 Hz, 2H; 5-*H* and 5′-*H*), 4.34 (t, J = 6.44 Hz, 4H; OCH_2), 2.58–2.74 (m, 4H; OCH_2CH_2); IR (KBr): 1202, 1015 cm^{-1}; mp 157.3–160.3 °C.

4.2.5. Synthesis of 4,4′-bis(2-(perfluorohexyl)ethoxy)-2,2′-bipyridine (F62O) [10]

Phosphorus tribromide (0.7 ml, 6.64 mmol) was added to the suspension of 4,4′-bis[2-(perfluorohexyl)ethoxy]-2,2′-bipyridine-1,1′-dioxide **4** (1.10 g, 1.21 mmol) in dry chloroform (50 ml). After refluxing for 3 h, the suspension was cooled in a water bath, basified with 6 N NaOH *aq*. and extracted with chloroform (80 ml × 4). The organic layer was combined, dried with *anhyd*. Na_2SO_4, and concentrated. The residue was sonicated in ethyl acetate and the suspension was filtered to obtain white solid in 82% (878 mg, 1.00 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.66 (d, J = 6.27 Hz, 2H; 6-Py-*H* and 6′-Py-*H*), 8.63 (s, 2H; 3-Py-*H* and 3′-Py-*H*), 7.18 (d, J = 6.27 Hz, 2H; 5-Py-*H* and 5′-Py-*H*), 4.74 (t, J = 5.88 Hz, 4H; OCH_2), 2.71–2.85 (m, 4H; OCH_2CH_2); IR (KBr): 1587, 1242, 1036 cm^{-1}; mp 189.3–191.4 °C.

4.3. Preparation of Ru(II) and Co(II) complexes [19,25,26]

4.3.1. Ru(4,4′-bis(p-(4-(perfluorooctyl)butoxy)phenyl)-2,2′-bipyridine)$_3$(PF_6)$_2$ [Ru(F84OPh)$_3$](PF_6)$_2$

Under nitrogen, $RuCl_3 \cdot nH_2O$ (5.0 mg, 22.9 μmol as n = 3) and 4,4′-bis(*p*-(4-(perfluorooctyl)butoxy)phenyl)-2,2′-bipyridine F84OPh (109 mg, 84.6 μmol) were reacted in a mixture of degassed ethylene glycol (2 ml) and degassed 1H,1H,7H-dodecafluoroheptanol (6 ml) at 150 °C for 21 h. All solvents were removed under vacuum to obtain dark-red solid. The residue was purified by molecular sieve type chromatography (Sephadex LH-20) using MeOH/acetone (v/v, 1/1) and the counteranion was exchanged by adding *sat*. KPF_6 *aq*. The precipitate was filtered through a 0.45-μm membrane filter to obtain red solid (41.9 mg, 9.84 μmol, 43%). ESI–MS: m/z = 1984 (100%, $[M\text{-}2(PF_6)]^{2+}$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.49 (br, 6H; 3-Py-*H* and 3′-Py-*H*), 7.91 (d, J = 6.00 Hz, 6H; 6-Py-*H* and 6′-Py-*H*), 7.69 (d, J_1 = 6.00 Hz, J_2 = 1.50 Hz, 6H; 5-Py-*H* and 5′-Py-*H*), 7.76 (d, J = 8.50 Hz, 12H; Ar-*H*), 7.04 (d, J = 8.50 Hz, 12H; Ar-*H*), 4.07 (t, J = 6.00 Hz, 12H; Ar-OCH_2), 2.10–2.26 (m, 12H; CF_2CH_2, 4H), 1.79–1.98 (m, 24H; $ArOCH_2CH_2CH_2$); IR (KBr): 1604, 1208, 851 cm^{-1}; mp 284.4–287.1 °C.

4.3.2. Co(4,4′-bis(p-(4-(perfluorooctyl)butoxy)phenyl)-2,2′-bipyridine)$_3$(PF_6)$_2$ [Co(F84OPh)$_3$](PF_6)$_2$

Under nitrogen, $CoCl_2 \cdot 6H_2O$ (24.6 mg, 103 μmol) was dissolved in a mixture of degassed acetonitrile (8 ml) and 1H,1H,3H-tetrafluoropropanol (17 ml) at r.t. After the mixture became clear blue solution, 4,4′-bis(*p*-(4-perfluorooctyl)butoxyphenyl)-2,2′-

bipyridine F84OPh (400 mg, 310 μmol) was added and stirred at 110 °C for 5 h. Filtration through a 0.45-μm membrane filter was performed to remove unreacted F84OPh, then the solvents were removed under reduced pressure to obtain brownish-yellow solid. The residue was purified by molecular sieve type chromatography (Sephadex LH-20) using MeOH/acetone (v/v, 1/1) and the counteranion was exchanged by adding *sat.* KPF_6 *aq.* The precipitate was filtered through a 0.45-μm membrane filter to obtain yellow solid (289 mg, 68.6 μmol, 67%). ESI–MS: m/z = 1962 (100%, $[M\text{-}2(PF_6)]^{2+}$), 1308 (10%, $[M\text{-}2(PF_6)]^{3+}$); IR (KBr): 1604, 1205, 845 cm^{-1}; mp 199.2–201.8 °C.

4.3.3. *Ru(4,4′-bis(p-(4-(perfluorobutyl)butoxy)phenyl)-2,2′-bipyridine)$_3$(PF$_6$)$_2$ [Ru(F44OPh)$_3$](PF$_6$)$_2$*

Under nitrogen, $RuCl_3{\cdot}nH_2O$ (8.2 mg, 37.6 μmol as n = 3) and 4,4′-bis(*p*-(4-perfluorobutyl)butoxyphenyl)-2,2′-bipyridine F44OPh (100 mg, 113 μmol) were reacted in a mixture of degassed ethylene glycol (4 ml), degassed DMF (4 ml) and degassed 1,1,2,2-tetrachloroethane (2 ml) at 140 °C for 20 h. All solvents were removed under vacuum to obtain wine red solid. The residue was purified by molecular sieve type chromatography (Sephadex LH-20) using MeOH/acetonitrile (v/v, 1/1) and the counteranion was exchanged by adding *sat.* KPF_6 *aq.* The precipitate was filtered through a 0.45-μm membrane filter to obtain red solid (89.3 mg, 29.2 μmol, 78%). ESI–MS: m/z = 1383 (100%, $[M\text{-}2(PF_6)]^{2+}$); ^1H NMR (500 MHz, $CDCl_3$): δ 8.49 (br, 6H; 3-Py-*H* and 3′-Py-*H*), 7.91 (d, J = 6.00 Hz, 6H; 6-Py-*H* and 6′-Py-*H*), 7.76 (d, J = 9.00 Hz, 12H; Ar-*H*), 7.70 (dd, J_1 = 6.00 Hz, J_2 = 2.00 Hz, 6H; 5-Py-*H* and 5′-Py-*H*), 7.04 (d, J = 9.00 Hz, 12H; Ar-*H*), 4.07 (t, J = 5.75 Hz, 12H; OCH_3), 2.10–2.29 (m, 12H; CF_2CH_2), 1.79–2.00 (m, 24H, $OCH_2CH_2\,CH_2$); IR (KBr): 1604, 1237, 843 cm^{-1}; mp 271.1–274.3 °C.

4.3.4. *Co(4,4′-bis(p-(4-(perfluorobutyl)butoxyphenyl)-2,2′-bipyridine)$_3$(PF$_6$)$_2$ [Co(F44OPh)$_3$](PF$_6$)$_2$*

Under nitrogen, $CoCl_2{\cdot}6H_2O$ (5.3 mg, 22.3 μmol) was dissolved in a mixture of degassed acetonitrile (1 ml) and degassed chloroform (4 ml) at r.t. After the mixture became clear blue solution, 4,4′-bis(*p*-(4-perfluorobutyl)butoxyphenyl)-2,2′-bipyridine F44OPh (60.9 mg, 68.5 μmol) was added and stirred at 70 °C for 5 h. All solvents were removed under reduced pressure to obtain yellow solid. The residue was purified by molecular sieve type chromatography (Sephadex LH-20) using MeOH/acetonitrile (v/v, 1/1) and the counteranion was exchanged by adding *sat.* KPF_6 *aq.* The precipitate was filtered through a 0.45-μm membrane filter to obtain yellow solid (52.2 mg, 17.3 μmol, 78%). ESI–MS: m/z = 1362 (100%, $[M\text{-}2(PF_6)]^{2+}$), 1308 (20%, $[M\text{-}2(PF_6)]^{3+}$); IR (KBr): 1603, 1236, 843 cm^{-1}; mp 244.7–248.7 °C.

4.3.5. *Ru(4,4′-bis(p-(2-(perfluorohexyl)ethyl)phenyl)-2,2′-bipyridine)$_3$(PF$_6$)$_2$ [Ru(F62Ph)$_3$](PF$_6$)$_2$*

Under nitrogen, $RuCl_3{\cdot}nH_2O$ (8.4 mg, 32.1 μmol as n = 3) and 4,4′-bis(*p*-(2-(perfluorohexyl)ethyl)phenyl)-2,2′-bipyridine F62Ph (100 mg, 100 μmol) were reacted in a mixture of degassed ethylene glycol (5 ml) and degassed 1H,1H,7H-dodecafluoroheptanol (5 ml) at 150 °C for 16 h. Dark orange suspension gradually became clear red solution, and all solvents were removed under vacuum to obtain red solid. The residue was purified by molecular sieve type chromatography (Sephadex LH-20) using MeOH/acetone (v/v, 1/1) and the counteranion was exchanged by adding *sat.* KPF_6 *aq.* The precipitate was filtered through a 0.45-μm membrane filter to obtain orange solid (67.0 mg, 19.7 μmol, 61%). ESI–MS: m/z = (100%, 1549 $[M\text{-}2(PF_6)]^{2+}$); ^1H NMR (300 MHz, $CDCl_3$): δ 8.53 (br, 6H; 3-Py-*H* and 3′-Py-*H*), 7.99 (d, J = 6.00 Hz, 6H; 6-Py-*H* and 6′-Py-*H*), 7.71–7.82 (m, 18H; 5-Py-*H* and 5′-Py-*H* and Ar-*H*), 7.41 (d, J = 8.40 Hz, 12H; Ar-*H*), 2.92–3.09 (m, 12H; $ArCH_2$), 2.30–2.57 (m, 12H, $ArCH_2CH_2$); IR (KBr): 1611, 1200, 841 cm^{-1}; mp 238.0–240.7 °C.

4.3.6. *Co(4,4′-bis(p-(2-(perfluorohexyl)ethyl)phenyl)-2,2′-bipyridine)$_3$(PF$_6$)$_2$ [Co(F62Ph)$_3$](PF$_6$)$_2$*

Under nitrogen, $CoCl_2{\cdot}6H_2O$ (12.3 mg, 51.7 μmol) was dissolved in a mixture of degassed acetonitrile (10 ml) and degassed chloroform (10 ml) at r.t. After the mixture became clear blue solution, 4,4′-bis(*p*-(2-perfluorohexyl)ethylphenyl)-2,2′-bipyridine F62Ph (180 mg, 180 μmol) was added and refluxed for 5 h. All solvents were removed under reduced pressure to obtain yellow solid. The residue was purified by molecular sieve type chromatography (Sephadex LH-20) using MeOH/acetone (v/v, 1/1) and the counteranion was exchanged by adding *sat.* KPF_6 *aq.* The precipitate was filtered through a 0.45-μm membrane filter to obtain beige solid (101 mg, 30.1 μmol, 58%). ESI–MS: m/z = 1528 (100%, $[M\text{-}2(PF_6)]^{2+}$); IR (KBr): 1611, 1199, 845 cm^{-1}; mp 198.0–201.1 °C.

4.3.7. *Ru(4,4′-bis(2-(perfluorohexyl)ethoxy)-2,2′-bipyridine)$_3$(PF$_6$)$_2$ [Ru(F62O)$_3$](PF$_6$)$_2$*

Under nitrogen, $RuCl_3{\cdot}nH_2O$ (10.0 mg, 45.8 μmol as n = 3) and 4,4′-bis(2-(perfluorohexyl)ethoxy)-2,2′-bipyridine F62O (150 mg, 170 μmol) were reacted in a mixture of ethylene glycol (6 ml) and 1H,1H,7H-dodecafluoroheptanol (5 ml) 150 °C for 16 h. Dark orange suspension gradually became clear red solution. All solvents were removed under vacuum to obtain red solid. The residue was purified by molecular sieve type chromatography (Sephadex LH-20) using MeOH/acetone (v/v, 1/1) and the counteranion was exchanged by adding *sat.* KPF_6 *aq.* The precipitate was filtered through a 0.45-μm membrane filter to obtain orange solid (57.0 mg, 18.8 μmol, 41%). ESI–MS: m/z = 881 (100%, $[F62O + H]^+$), 1371 (40%, $[M\text{-}2(PF_6)]^{2+}$); ^1H NMR (500 MHz, $CDCl_3$): δ 8.50 (d, J = 5.75 Hz, 6H; 3-Py-*H* and 3′-Py-*H*), 8.00 (d, J = 2.50 Hz, 6H; 6-Py-*H* and 6′-Py-*H*), 6.87 (dd, J_1 = 5.75 Hz, J_2 = 2.50 Hz 6H; 5-Py-*H* and 5′-Py-*H*), 4.46 (t, J = 6.50 Hz, 12H; OCH_2), 2.61–2.78 (m, 12H; OCH_2CH_2); IR (KBr): 1618, 1235, 843 cm^{-1}; mp 267.2–272.1 °C.

4.3.8. *Co(4,4′-bis(2-(perfluorohexyl)ethoxy)-2,2′-bipyridine)$_3$(PF$_6$)$_2$ [Co(F62O)$_3$](PF$_6$)$_2$*

Under nitrogen, $CoCl_2{\cdot}6H_2O$ (12.3 mg, 51.7 μmol) was dissolved in a mixture of degassed acetonitrile (1 ml) and degassed chloroform (1 ml) at r.t. After the mixture became clear blue solution, 4,4′-bis(2-(perfluorohexyl)ethoxy)-2,2′-bipyridine F62O (208 mg, 236 μmol) and 1H,1H,3H-tetrafluoropropanol (2 ml) were added and refluxed for 5 h. Blue solution gradually became yellow and all solvents were removed under reduced pressure to obtain yellow solid. The residue was purified by molecular sieve type chromatography (Sephadex LH-20) using MeOH/acetone (v/v, 1/1) and the counteranion was exchanged by adding *sat.* KPF_6 *aq.* The precipitate was filtered through a 0.45-μm membrane filter to obtain beige solid (110 mg, 37.0 μmol, 72%). ESI–MS: m/z = 1350 (100%, $[M\text{-}2(PF_6)]^{2+}$), 900 (80%, $[M\text{-}2(PF_6)]^{3+}$), 1423 (30%, $[M\text{-}(PF_6)]^{2+}$); IR (KBr): 1617, 1237, 839 cm^{-1}; mp 240.0–243.9 °C.

4.4. Procedure of solution behavior study of Ru(II) and Co(II) complexes in sc-CO_2

Solution behavior of new complexes in sc-CO_2 was investigated according to the following procedure (Fig. 1).

1. The high-pressure vessel was completely replaced with CO_2.
2. Under CO_2 stream, a sample bottle containing Ru or Co complex (3–4 mg) was set in a vessel and the vessel was closed tightly.
3. *Liq.* CO_2 (10 ml) was introduced and the temperature was raised to 50 °C to change *liq.* CO_2 into sc-CO_2.
4. After 1 h, the vessel was cooled to r.t. and sc-CO_2 was released as gaseous CO_2.
5. The change of complex was examined by sight.

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