Supplementary Material (ESI) for Chemical Communications


**Electronic Supplementary Information**

# Dual modification of a triple-stranded β-helix nanotube with Ru and Re metal complexes to promote photocatalytic reduction of $CO_2$

Norihiko Yokoi, Yuki Miura, Chen-Yuang Huang, Nobuyuki Takatani, Hiroshi Inaba, Tomomi Koshiyama, Shuji Kanamaru, Fumio Arisaka, Yoshihito Watanabe, Susumu Kitagawa, and Takafumi Ueno*

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**Experimental section**

**Physical measurement.** UV-vis spectra were recorded on a SHIMADZU UV-2400PC UV-vis spectrometer. $^{1}$H- and $^{13}$C-NMR spectra were recorded on a NMR A-400 (JEOL). Concentration of ruthenium and rhenium was determined by an inductively coupled plasma (ICP) spectrometer VISTA-PRO (varian). FAB mass spectra were measured on a JMS700 (JEOL). Elemental Analysis was performed on a MT-6 (YANACO). ESI-TOF mass spectra were measured on a LCT (micromass). Circular dichroism spectra were recorded on a JASCO model J-720 spectropolarimeter that was equipped with a JASCO model PTC-348WI Peltiert cooling temperature controller.

**Materials.** Unless otherwise stated, all chemicals were purchased from commercial suppliers and used without further purification. Tetrahydrofuran (THF), acetonitrile ($CH_3CN$), and toluene were distilled from $CaH_2$ under Ar atmosphere and stored with molecular sieves. $Ru(bpy)_2Cl_2{\cdot}2H_2O$,[1] 4-methyl-2,2'-bipyridine,[2] and 4-(2-formylethyl)-4'-methyl-2,2'-bipyridine[3] were prepared according to the literature methods. Cysteine mutants of $[(gp5\beta f)_3]_2$ were prepared by using a Quick Change site-directed mutagenesis kit (Qiagen) DNA sequences of the mutants were determined by an ABI3100 (Applied Biosystems). Expression and purification of the mutants were performed as described in chapter IV of this thesis.

**Synthesis of maleimide derivatives of $Ru^{II}(bpy)_3$ and $Re^{I}(bpy)(CO)_3Cl$.**

**4-(2-hydroxyethyl)-2,2'-bipyridine.** Distilled THF (1.6 ml) and diisopropylamine (1.10 ml, 7.78 mmol) were cooled to –78°C under $N_2$ atmosphere, then a 1.6 M *n*-BuLi

hexane solution (3.90 ml, 6.24 mmol) was added dropwise and the mixture was stirred for 10 min. The mixture was warmed up to 0°C and stirred for 10 min, then cooled down to –78°C and stirred for 15 min. To the mixture was added paraformaldehyde (197 mg, 6.55 mmol) and the mixture was warmed up to 0°C and stirred for 45 min, then the mixture was warmed up to room temperature and stirred for 16 h. To the solution was added a saturated NaCl aqueous solution and a crude product was extracted with $CH_2Cl_2$. The organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure. A crude product was purified by silica gel column chromatography. At first, an elutant was a 1:3 mixture of hexane and ethyl acetate and the eluent was changed to a mixture of an equal amount of methanol and ethyl acetate after the elution of a compound ($R_f$ = 0.39). The product was obtained as brown oil. Yield: 838 mg (82 %). $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.64 (1H, d, *J* = 4.6 Hz), 8.55 (1H, d, *J* = 5.0 Hz), 8.34 (1H, d, *J* = 7.9 Hz), 8.24 (1H, s), 7.83 (1H, t, *J* = 7.7 Hz), 7.31 (1H, t, *J* = 6.5 Hz), 7.18 (1H, d, *J* = 4.9 Hz), 3.95 (2H, t, *J* = 6.3 Hz), 2.94 (2H, t, *J* = 6.3 Hz). Anal. calcd. for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99. Found: C, 70.70; H, 6.03; N, 13.46.

**4-ethylmaleimide-2,2'-bipyridine. (bpy-MI)** 4-(2-Hydroxyethyl)-2,2'-bipyridine (3.50 g, 17.5 mmol), maleimide (2.03 g, 20.9 mmol), triphenylphosphine (5.49 g, 20.9 mmol) were suspended in distilled THF (78 ml) under Ar atmosphere. To the solution was added diisopropylazodicarboxylate (DIAD) (6.87 ml, 34.9 mmol) and the mixture was stirred overnight at room temperature under Ar atmosphere. The mixture was concentrated under reduced pressure and purified by silica gel column chromatography ($\phi$ 5.5cm x 20 cm) with a stepwise gradient of hexane-ethyl acetate from 7:3 to 1:1. The product was obtained as white solid. Yield: 1.43g (32 %). $^1$H NMR (400 MHz,

$CDCl_3$): δ = 8.69 (1H, d, *J* = 4.8 Hz), 8.59 (1H, d, *J* = 4.8 Hz), 8.39 (1H, d, *J* = 8.2 Hz), 8.29 (1H, s), 7.82 (1H, t, *J* = 7.9 Hz), 7.31 (1H, t, *J* = 5.9 Hz), 7.18 (1H, d, *J* = 5.1 Hz), 6.68 (2H, s), 3.86 (2H, t, *J* = 7.6 Hz), 3.01 (2H, t, *J* = 7.6 Hz). $^{13}$C NMR (400 MHz, $CDCl_3$): δ = 170.4, 156.4, 155.9, 149.4, 149.1, 147.8, 136.9, 134.1, 124.0, 123.8, 121.4, 121.2, 38.0, 34.1. Anal. calcd. for $C_{16}H_{13}N_3O_2$: C, 68.81; H, 4.69; N, 15.05. Found: C, 69.08; H, 4.75; N, 14.90. FAB-HR MS: $[C_{16}H_{15}N_3O_2]^+$ calcd: 280.1, found: 280.2.

**$Ru(bpy)_2(bpy\text{-}MI)(ClO_4)_2$. (Ru-MI).** An anhydrous ethanol solution (13.5 ml) of bpy-MI (72.8 mg, 0.261 mmol) and $Ru(bpy)_2Cl_2\cdot 2H_2O$ (65.5 mg, 0.126 mmol) was refluxed for 2 h under Ar atmosphere. After cooling, to the solution was added an aqueous solution of $NaClO_4$ (20 M, 25.8 μl, 0.261 mmol) and the mixture was stored at room temperature for 6 h (**Caution**: perchlorate is explosive and must be handled with care). A red solid was collected by filtration and dried in air, and then dissolved in acetone (2 ml). To the solution was added diethyl ether (45 ml) and the product was obtained as red solid and collected by centrifugation. Yield: 30.8 mg (36 %). $^1$H NMR (400MHz, DMSO-$d_6$): δ = 8.84 (5H, d, *J* = 8.0 Hz), 8.77 (1H, s), 8.17 (5H, t, *J* = 8.1 Hz), 7.78–7.69 (4H, m), 7.63–7.48 (7H, m), 7.41 (1H, d, *J* = 5.9 Hz), 6.96 (2H, s), 3.78 (2H, t, *J* = 5.9 Hz), 3.01 (2H, t, *J* = 6.4 Hz). Anal. Calcd for $C_{36}H_{33}Cl_2N_7O_{12}Ru$: C, 46.64; H, 3.59; N, 10.57. Found C, 46.88; H, 3.39; N, 10.32. FAB MS-LR: calcd. For $[M\text{-}ClO_4]^+$ m/z 693.1; found: 693.1.

**$Re(bpy\text{-}MI)(CO)_3Cl$. (Re-MI)** A distilled toluene solution (29 ml) of bpy-MI (422 mg, 1.51 mmol) and $Re(CO)_5Cl$ (544 mg, 1.50 mmol) was refluxed for 2 h with stirring under Ar atmosphere. The product was obtained as yellow precipitate and washed with diethyl ether. Yield: 750 mg (86%). $^1$H NMR (400 MHz, DMSO-$d_6$): δ = 9.03 (1H, d, *J* = 5.3 Hz), 8.90 (1H, d, *J* = 5.7 Hz), 8.80 (1H, d, *J* = 8.3 Hz), 8.74 (1H, s), 8.38

(1H, t, *J* = 8.2 Hz), 7.78 (1H, t, *J* = 6.8 Hz), 7.65 (1H, d, *J* = 5.8 Hz), 7.04 (2H, s), 3.87 (2H, t, *J* = 6.8 Hz), 3.11 (2H, t, *J* = 6.6 Hz). ESI TOF-MS ($CH_3CN$): calcd. for $[M-Cl]^+$ *m/z* 550.04; found: 550.04.

**Synthesis of succinimidyl ester derivatives of $Ru^{II}(bpy)_3$ and $Re^{I}(bpy)CO_3Cl$.**

**4-(2-carboxylethyl)-4'-methyl-2,2'-bipyridine.** The product was prepared according with a previous method[4] with some modification. To an acetone solution (13 ml) of 4-(2-formylethyl)-4'-methyl-2,2'-bipyridine (794 mg, 3.51 mmol) was added powder $KMnO_4$ (279.0 mg, 1.77 mmol) and the mixture was stirred at room temperature for 5 min. To the mixture was added $KMnO_4$ (277 mg, 1.76 mmol) and stirred for 2 h, and then was added 2-propanol (8 ml) and stirred overnight. The solvent was concentrated under reduced pressure and a crude product was suspended in $H_2O$ (4.4 ml). The mixture was heated to 90ºC for 1 h and brown precipitate was removed by filtration. The filtrate was concentrated under reduced pressure and the pH of the solution was adjusted to 3.6 by the addition of 1N HCl. The product was obtained as white precipitate. Yield: 539.1mg(63%). $^1$H NMR (DMSO-$d_6$, 270 MHz): δ = 12.2(1H, s), 8.56(1H, d, *J* = 5.1 Hz), 8.54(1H, d, *J* = 5.0 Hz), 8.26(1H, s), 8.23(1H, s), 7.33(1H, d, *J* = 4.9 Hz), 7.28(1H, d, *J* = 5.2 Hz), 2.94(2H, t, *J* = 6.6 Hz), 2.65(2H, t, *J* = 6.6 Hz), 2.42(3H, s). FAB MS-LR (Glycerol): calcd. for $[M+H]^+$ m/z 243.3; found 243.2.

**$Ru(bpy)_2$(4-(2-carboxylethyl)-4'-methyl-2,2'-bipyridyl)$(PF_6)_2$ (Ru-COOH).** $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (268 mg, 0.515 mmol), 4-(2-carboxylethyl)-4'-methyl-2,2'-bipyridine (150 mg, 0.615 mmol) were suspended in anhydrous ethanol (55 ml) and the mixture was refluxed for 8 h under Ar atmosphere. The reaction mixture was cooled to room temperature and colorless precipitate was removed by filtration. To the filtrate was added $H_2O$ (8 ml) and the ethanol was removed under reduced pressure.

The pH of the mixture was adjusted to 1 by the addition of conc. HCl. To the solution was added an aqueous solution of $NH_4PF_6$ (6.6 M, 0.5 ml) until no further precipitation was formed. The product was obtained by red precipitate and was collected by filtration and washed with $H_2O$ and diethyl ether. Yield: 396 mg (82 %). $^1$H NMR (400 MHz ,DMSO-$d_6$): δ = 12.3 (1H, s), 8.83 (4H, d, *J* = 8.3 Hz), 8.76 (2H, s), 8.16 (4H, t, *J* = 7.8 Hz), 7.72 (4H, m), 7.60–7.47 (6H, m), 7.42(1H, d, *J* = 5.5 Hz), 7.38(1H, d, *J* = 5.5 Hz), 3.02 (2H, t, *J* = 7.8 Hz), 2.73 (2H, t, *J* = 7.4 Hz), 2.52 (3H, s). ESI TOF-MS ($CH_3CN$): calcd. for $[M–PF_6]^+$ *m/z* 801.11; found 801.08.

**Ru(bpy)$_2$(3-(4'-methyl-2,2'-bipyridyl-4-yl)propionc acid *N*-succinimidyl ester) (PF$_6$)$_2$. (Ru-OSu)** To a distilled $CH_3CN$ solution (0.67 ml) of Ru(bpy)$_2$(4-(2-carboxylethyl)-4'-methyl-2,2'-bipyridyl)(PF$_6$)$_2$ (300 mg, 0.317 mmol) and *N*-hydroxysuccinimide (43.5 mg, 0378 mmol) was added 1,3-Dicyclohexylcarbodiimide (96.5 mg, 0.468 mmol) with stirring at room temperature under Ar atmosphere. To the solution was added distilled $CH_3CN$ (6 ml) and the mixture was stirred for 20 h. Colorless precipitate was removed by filtration and the filtrate was concentrated under reduced pressure. The mixture was filtrated again and the solution was concentrated to 5 ml. To the mixture was added 2-propanol (55 ml) and the mixture was stored at –20ºC for 5 h. The product was obtained as red solid and washed with diethyl ether. Yield: 148 mg (45 %). $^1$H NMR (400 MHz, $CD_3CN$): δ = 8.49 (4H, d, *J* = 7.9 Hz), 8.40 (2H, s), 8.01 (4H, t, *J* = 7.6 Hz), 7.72 (4H, t, *J* = 5.0 Hz), 7.60 (1H, d, *J* = 5.5 Hz), 7.54 (1H, d, *J* = 5.8 Hz), 7.40 (4H, m), 7.30 (1H, d, *J* = 5.5 Hz), 7.24 (1H, d, *J* = 5.8 Hz), 3.21 (2H, t, *J* = 6.6 Hz), 3.12 (2H, t, *J* = 6.8 Hz), 2.75 (4H, s), 2.54 (3H, s). ESI TOF-MS ($CH_3CN$): calcd. for $[M–P_2F_{12}]^{2+}$ *m/z* 376.58; found 376.56.

**Re(4-(2-carboxylethyl)-4'-methyl-2,2'-bipyridyl)(CO)$_3$Cl.** A distilled toluene (40 ml) solution of 4-(2-carboxylethyl)-4'-methyl-2,2'-bipyridine (500 mg, 2.06 mmol) and $Re(CO)_5Cl$ (746 mg, 2.06 mmol) was refluxed for 2 h under Ar atmosphere. The product was obtained as yellow solid and washed twice with diethyl ether. Yield: 1.09 mg (96%). $^1$H NMR (270MHz, DMSO-$d_6$) : δ = 12.3 (1H, s), 8.86 (1H, d, *J* = 5.4 Hz), 8.83 (1H, d, *J* = 5.9 Hz), 8.67 (2H, s), 7.63 (1H, d, *J* = 5.2 Hz), 7.58 (1H, d, *J* = 5.7 Hz), 3.06 (2H, t, *J* = 7.3 Hz), 2.79 (2H, t, *J* = 7.5 Hz), 2.56 (3H, s). ESI-TOF MS ($CH_3CN$): calcd. for $[M–Cl]^+$ *m/z* 513.05; found 513.05.

**Re(3-(4'-methyl-2,2'-bipyridyl-4-yl)propionc acid *N*-succinimidyl ester)(CO)$_3$Cl. (Re-OSu)** To an anhydrous DMF (12.5 ml) solution of Re(4-(2-carboxylethyl)-4'-methyl-2,2'-bipyridy)(CO)$_3$Cl (949 mg, 1.73 mmol) and *N*-hydroxysuccinimide (202 mg, 1.76 mmol) was added 1,3-dicyclohexylcarbodimide (428 mg, 2.08 mmol) and the mixture was stirred at room temperature for 9 h. Colorless precipitate was removed by filtration and to the filtrate was added 2-propanol (300 ml) with stirring and stored at –20ºC for 1.5 h. The product was obtained as yellow solid and washed twice with diethyl ether. Yield: 839mg (75%). Anal. Calcd for $C_{21}H_{17}ClN_3O_7Re$: C, 39.10; H, 2.66, N; 6.51. Found: C, 39.10; H, 2.81; N, 6.43. $^1$H NMR (270 MHz, $CD_3CN$): δ = 8.89 (1H, d, *J* = 5.2 Hz), 8.83 (1H, d, *J* = 5.5 Hz), 8.33 (2H, s), 7.53 (1H, d, *J* = 4.9 Hz), 7.46 (1H, d, *J* = 5.0 Hz), 3.24 (2H, d, *J* = 6.1 Hz), 3.17 (2H, d, *J* = 6.1 Hz), 2.77 (4H, s), 2.57 (3H, s). ESI-TOF MS (MeCN): calcd. For $[M-Cl]^+$ m/z 610.06; found 610.08.

**Modification of cysteines with Re-MI. K41C_Re$_{Cys}$**: To an aqueous solution of $[(gp5\beta f\_K41C)_3]_2$ (5.0 μM, 38 ml in 20 mM MES buffer pH 6.5) was added slowly a

DMSO solution of Re-MI (1.8 mM, 1.9 ml) and the mixture was stirred gently for 15 h at room temperature. After the dialysis against 20 mM MES buffer pH 6.5, **K41C_Re$_{Cys}$** was passed through a Sephadex G25 equilibrated with a 100 mM $NaHCO_3$ aqueous solution to remove an excess amount of Re-MI. The protein concentration was determined by a BCA protein assay and the concentration of rhenium was determined by ICP measurements. The protein recovery after the modification was 70 %. UV/Vis: $\lambda_{max}$ 360 nm ($\tilde{\varepsilon}M^{-1}cm^{-1}$ 23200), 286 nm (205000). MS (MALDI-TOF): calcd for $[gp5\beta f\_K41C + Re\text{-}MI - Cl^-]^+$, 15327; found, 15340. (Fig. S2) **N57C_Re$_{Cys}$:** The protein recovery after the modification was 76 %. UV/Vis: $\lambda_{max}$ 363 nm ($\tilde{\varepsilon}M^{-1}cm^{-1}$ 24100), 286 nm (219000). MS (MALDI-TOF): calcd for $[gp5\beta f\_N57C + Re\text{-}MI - Cl^-]^+$, 15341; found, 15355. **D69C_Re$_{Cys}$:** The protein recovery after the modification was 100 %. UV/Vis: $\lambda_{max}$ 363 nm ($\tilde{\varepsilon}M^{-1}cm^{-1}$ 21000), 286 nm (186000). MALDI-TOF MS: calcd. for $[gp5\beta f\_D69C + Re\text{-}MI - Cl^-]^+$ m/z 15340; found, 15349.

**Modification of primary amines with Ru-OSu. K41C_Re$_{Cys}$Ru$_{NH}$**: To an aqueous solution of **K41C_Re$_{Cys}$** (4.0 μM, 21 ml in a 100 mM $NaHCO_3$ aqueous solution) was added slowly a DMSO solution of Ru-OSu (120 μM, 42 ml) and the mixture was stirred gently for 2 h at 50°C. The solution was dialyzed against the mixture of an equal amount of DMSO and 100 mM $NaHCO_3$ aqueous solution for 14 h and then dialyzed against the 1:4 mixture of DMSO and 10 mM MOPS pH 7.5 for 6 h. After the dialysis against the 1:9 mixture of DMSO and 10 mM MOPS pH 7.5, **K41C_Re$_{Cys}$Ru$_{NH}$** was passed through a G25 column equilibrated with a 1:9 mixture of DMF and 10 mM MOPS pH 7.5. The concentration of ruthenium and rhenium was determined by ICP

measurements. Protein concentration was calculated from the concentration of rhenium and the ratio of Re against **K41C_Re$_{Cys}$**. The protein recovery after the modification was 43 %. UV/Vis: $\lambda_{max}$ 454 nm ($\tilde{\varepsilon}$M$^{-1}$cm$^{-1}$ 339000), 360 nm (175000), 286 nm (2120000). **N57C_Re$_{Cys}$Ru$_{NH}$:** The protein recovery after the modification was 31 %. UV/Vis: $\lambda_{max}$ 459 nm ($\tilde{\varepsilon}$M$^{-1}$cm$^{-1}$ 364000, 361 nm (172000), 286 nm (2220000). **D69C_Re$_{Cys}$Ru$_{NH}$**: The protein recovery after the modification was 32 %. UV/Vis: $\lambda_{max}$ 454 nm ($\tilde{\varepsilon}$M$^{-1}$cm$^{-1}$ 386000), 360 nm (213000), 286 nm (2280000).

**Modification of cysteines with Ru-MI. K41C-Ru$_{Cys}$**: To an aqueous solution of [(gp5βf_K41C)$_3$]$_2$ (5.0 μM, 13.7 ml in 20 mM potassium phosphate buffer pH 7.0) was added slowly a methanol solution of Ru-MI (10 mM, 616 μl) and the mixture was stirred gently for 15 h at room temperature. After the dialysis against 20 mM potassium phosphate buffer pH 7.0, **K41C_Ru$_{Cys}$** was passed through a G25 column equilibrated with a 100 mM $NaHCO_3$ aqueous solution to remove an excess amount of Ru-MI. The protein concentration was determined by a BCA protein assay and the concentration of ruthenium was determined by ICP measurements. The protein recovery was 87 %. UV/Vis: $\lambda_{max}$ 457 nm ($\tilde{\varepsilon}$M$^{-1}$cm$^{-1}$ 81000), 286 nm (589000). MALDI-TOF MS: calcd. for [gp5βf_K41C + Ru-MI – 2$(ClO_4)^-$]$^+$, m/z 15470; found, 15397. The difference between the calcd. and the found molecular weight is in experimental error range.

**Modification of primary amines with Re-OSu. K41C_Ru$_{Cys}$Re$_{NH}$**: To an aqueous solution of **K41C_Ru$_{Cys}$** (4.0 μM, 12.5 ml in a 100 mM $NaHCO_3$ aqueous solution) was added slowly a DMSO solution of Re-OSu (144 μM, 12.5 ml) and stirred gently for 2 h

at 50°C. The solution was dialyzed against the mixture of an equal amount of DMSO and a 100 mM $NaHCO_3$ aqueous solution for 4 h and then dialyzed against the 1:4 mixture of DMSO and 20 mM MOPS pH 7.5 for 6 h. After the dialysis against 20 mM MOPS buffer pH 7.5, **K41C_$Ru_{Cys}Re_{NH}$** was passed through G25 and G200 columns equilibrated with 20 mM MOPS buffer pH 7.5. The concentration of ruthenium and rhenium was determined by ICP measurements. The protein recovery was 43 %. UV/Vis: $\lambda_{max}$ 454 nm ($\tilde{\varepsilon}M^{-1}cm^{-1}$ 93420), 360 nm (110000), 286 nm (929000).

**MALDI-TOF mass measurements.** MALDI-MS spectra were recorded on an UltraflexIII (Bruker Daltonics). For the measurements, protein samples were dialyzed against a 10 mM ammonium acetate aqueous solution and the samples were mixed with an equal volume of 70 % v/v acetonitile/water solution containing 0.03 % w/v sinapinic acid and 0.1 % v/v trifluoroacetic acid.

**Photo-stimulated catalytic redox reaction of $CO_2$.** A photocatalytic reaction was performed in a 6-ml test tube containing a samples solution after purging with $CO_2$ for 20 min. A sample solution was a mixture of DMF (1 ml) and 40 mM MOPS buffer pH 7.0 (1 ml) containing Ru and Re complexes and 1-benzyl-1,4-dihydronicotinamide (BNAH) (48 mg) as a sacrifice reagent. For a selective excitation of the Ru complexes, reaction solutions were irradiated at $\lambda > 500$ nm using a high pressure Hg lamp (Ushio UM452) with a $K_2CrO_4$ (30 % w/w, $d \sim 1$ cm) solution filter. The lamp was cooled in a lamp condenser (Ushio) equipped with a low temperature circulator (LAUDA RL5/RL6). During irradiations, sample solutions were tapped in an aqueous bath with

a lamp condenser and the temperatures of the aqueous bath was controlled at 30°C by a circulator. The CO production was detected by a GC-TCD (Shimadzu GC-2014).

Reference

1. S. A. Savage, A. P. Smith and C. L. Fraser, *J. Org. Chem.*, 1998, **63**, 10048-10051.
2. R. A. Krause, *Inorg. Chim. Acta*, 1978, **31**, 241-242.
3. R. H. Terbrueggen, T. W. Johann and J. K. Barton, *Inorg. Chem.*, 1998, **37**, 6874-6883.
4. J. S. Killeen, W. R. Browne, M. Skupin, J. H. Fuhrhop and J. G. Vos, *New J. Chem.*, 2003, **27**, 1078-1083.

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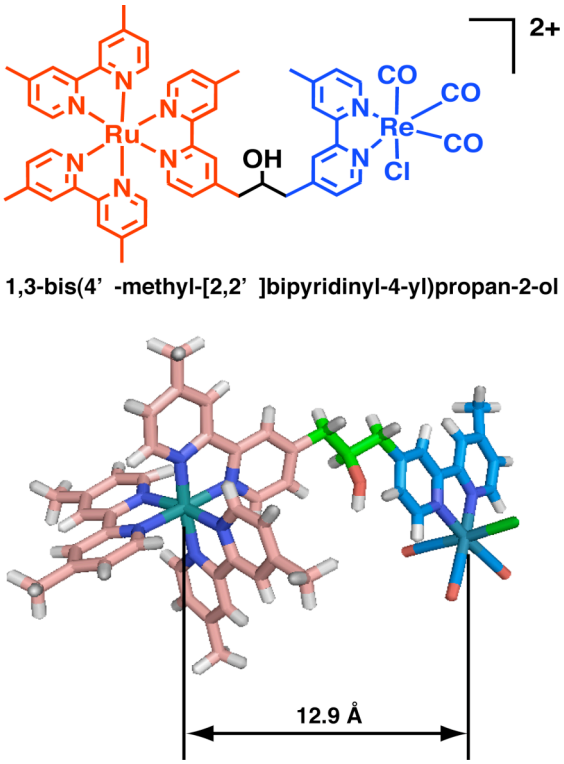


**Fig S1.** The model structure of 1,3-bis(4’-methyl-[2,2’]bipyridinyl-4-yl)propan-2-ol.

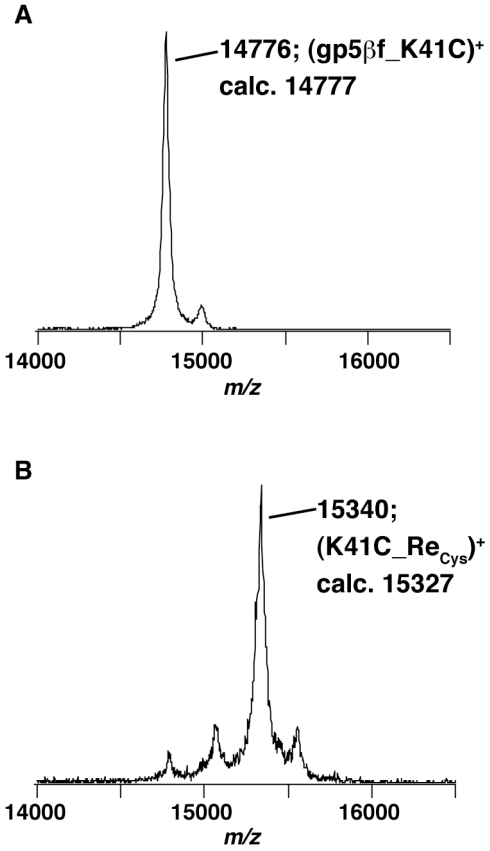


**Fig. S2.** MALDI TOF MS spectra of (A) (gp5βf_K41C)$_6$ and (B) (K41C_Re$_{Cys}$)$_6$.