Supporting Information

Understanding the Intramolecular Vibrational Energy Transfer and Structural Dynamics of Anionic Ligands in Photo-Catalytic CO_2 Reduction Catalyst

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1. Synthesis of Re-NCS

The mixture of toluene (50 mL) and methanol (20 mL) was heated to reflux, then $Re(CO)_5Cl$ (0.200 g, 0.55 mmol) and equal molar weight of 4,4'-dicarboxy-2,2'-bipyridine were added to the solution under reflux and stirring for 4 hours at least. The mixture was transferred to the freezer for 2 hours in order to precipitate the unreacted substance. The resulting organic supernatant was got by filtering and then evaporating to give $Re(dcbpy)(CO)_3Cl$ [dcbpy=2,2'-bipyridine-4,4'-$(COOH)_2$] (Re-Cl) as bright orange solids. NMR (D_2O with Na_2CO_3, ppm): 7.78(doublet, 2H), 8.68(doublet, 2H), 9.08(doublet, 2H).

Re-Cl and NaSCN was refluxed in ethanol/water(1:1 v/v) under N_2 atmosphere

for 12 hours. The complex Re(dcbpy)$(CO)_3$NCS Re-NCS was obtained by extraction using CH_2Cl_2 as the organic solvent for three times. After washing the organic layer for three times, the Re-NCS solid was obtained by rotary evaporation. Recrystallization procedure was performed in order to remove the impurities in Re-NCS, where the solid was washed with acetone-water solution for twice and then with acetone-Et_2O solution. 1H NMR (Methyl sulfoxide-d_6): δ9.39 (d, 2H), δ9.29 (s, 2H), δ8.34 (d, 2H).

2. Characterizations of Re-NCS

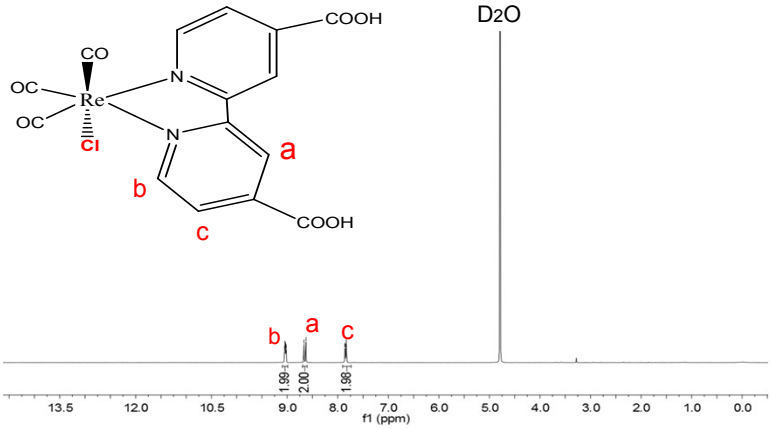

Figure S1. NMR characterization of Re-Cl complex.

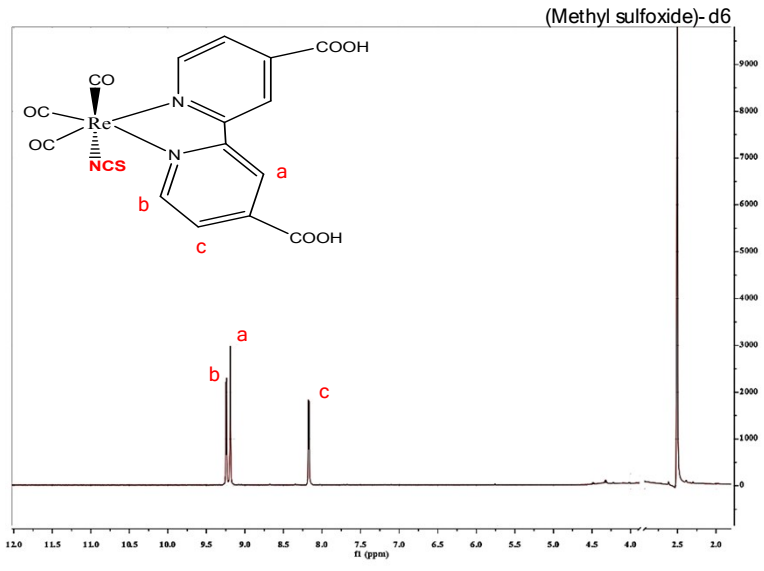

Figure S2. NMR characterization of Re-NCS complex.

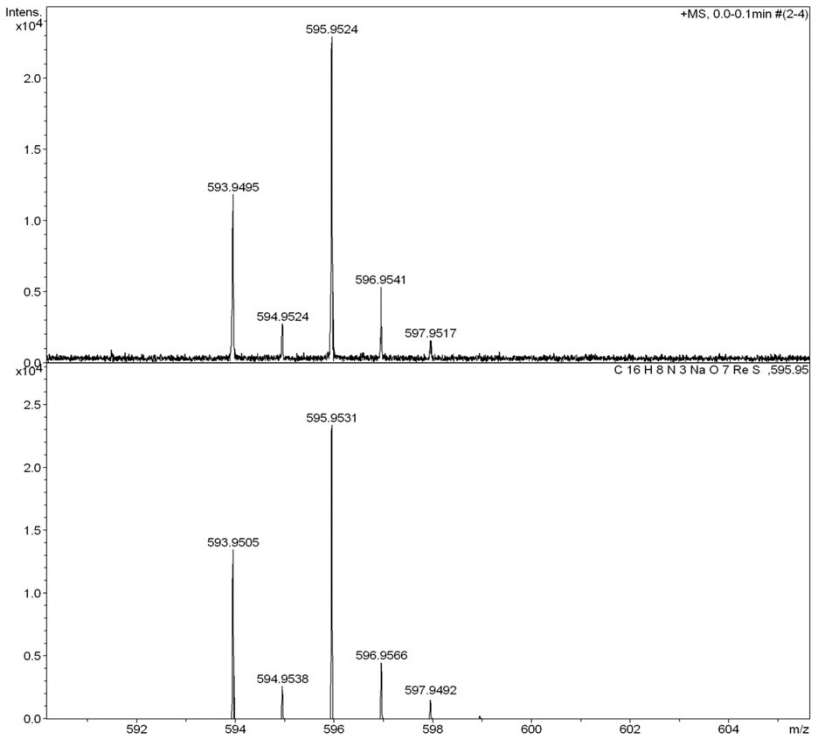

Figure S3. Mass spectrum (MS) characterization of Re-NCS complex (Top) and calculated result (Bottom).

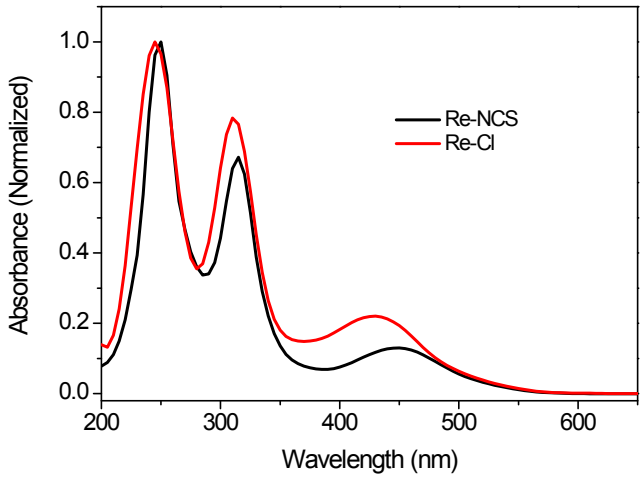

Figure S4. UV-Vis spectra of Re-NCS and Re-Cl complex.

3. Energy transfer model

To quantitatively analyze the energy transfer between CO and NCS vibrational

modes in Re-NCS, we utilized the energy transfer model which can be described in the following scheme,

$$\xleftarrow{k_a} \text{NCS} \underset{k_{ba}}{\overset{k_{ab}}{\rightleftharpoons}} \text{CO} \xrightarrow{k_b}$$

From this model, we can derive the following differential equations:

$$\frac{d[NCS]}{dt} = -(k_a + k_{ab})[NCS] + k_{ba}[CO]$$
$$\frac{d[CO]}{dt} = -(k_b + k_{ba})[CO] + k_{ab}[NCS]$$

The equations can be numerically solved. Here, it is necessary to note that the CO vibrational mode is experimentally observed to be bi-exponential. We separate the CO stretching into two subgroups following our previous reports.[1,2] The weighing factor of each subgroup is determined by the pre-factors of the bi-exponential. Each subgroup has a single-exponential-decay lifetime time and each subgroup can exchange energy. The fitted parameters are:

$$k_a = 1/40(ps^{-1});\ k_{b,fast} = 1/3.5(ps^{-1});\ k_{b,slow} = 1/45(ps^{-1});\ k_{ab} = 1/50(ps^{-1})$$

With pre-factors: $A_{CO,fast} = 0.20$ and $A_{CO,slow} = 0.80$.

4. DFT calculation of Re-NCS

Table S1. Calculated anharmonic frequencies of CN and CO vibrations in Re-NCS.

ν(CN) (cm^{-1})	Exp. (cm^{-1})	ν(CO) (cm^{-1})	Exp. (cm^{-1})
2108.4	2100	2068.1	2030 (v_3)
		2000.0	1938 (v_2)
		1977.7	1922 (v_1)

References

(1) Bian, H.; Li, J.; Wen, X.; Zheng, J. Mode-specific intermolecular vibrational energy transfer. I. Phenyl selenocyanate and deuterated chloroform mixture. *J. Chem. Phys.* **2010**, *132*, 184505.

(2) Bian, H.; Wen, X.; Li, J.; Zheng, J. Mode-specific intermolecular vibrational energy transfer. II. Deuterated water and potassium selenocyanate mixture. *J. Chem. Phys.* **2010**, *133*, 034505.