Ionic-Caged Heterometallic Bismuth–Platinum Complex Exhibiting Electrocatalytic CO_2 Reduction

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[#] *These authors contributed equally to this work.*

1. TDDFT calculation.

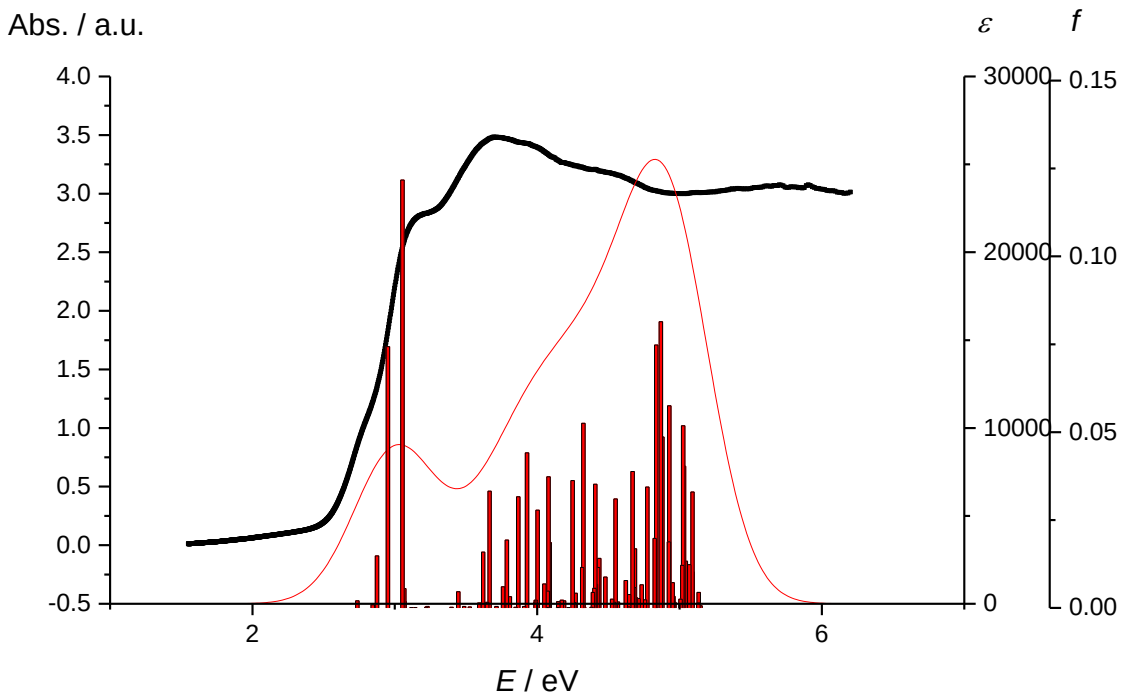

Fig. S1. The solid-state UV/vis spectra of **1** (black: experimental; red: calculation).

2. NBO analysis.

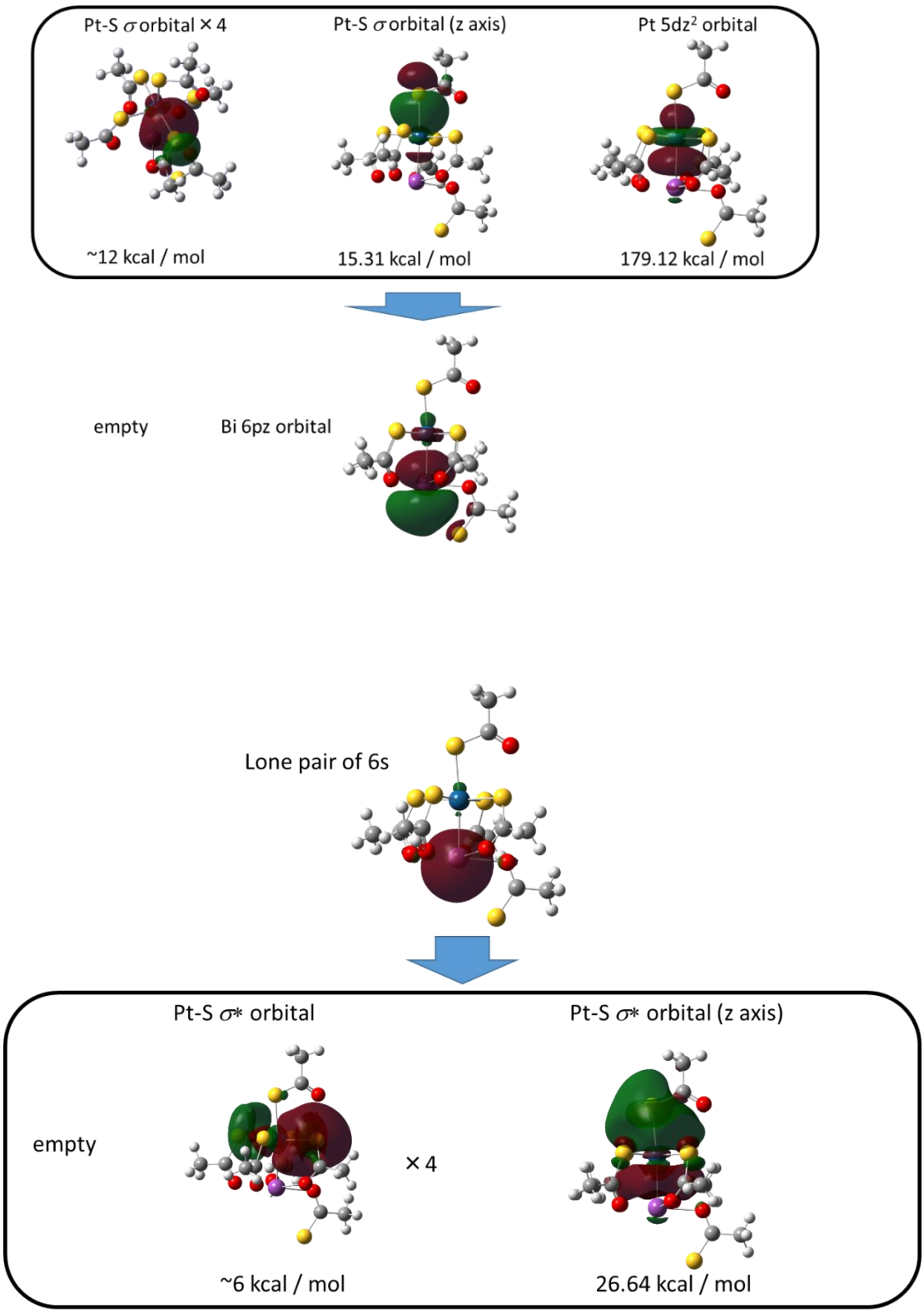

Fig. S2. NBO analysis of **1** (the orbitals and energies of donor-accepter interaction).

3. Raman spectra.

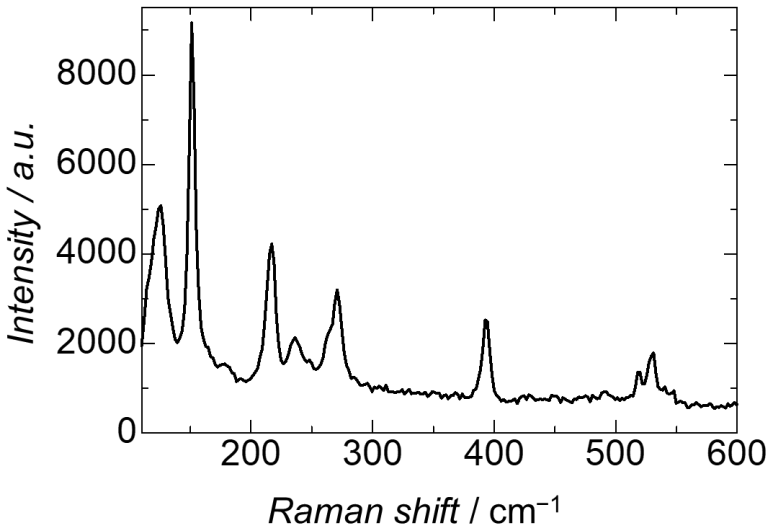

Fig. S3. Raman spectrum of **1** at room temperature (optical window of set up > 110 cm^{-1}).

4. XAFS spectra of 1.

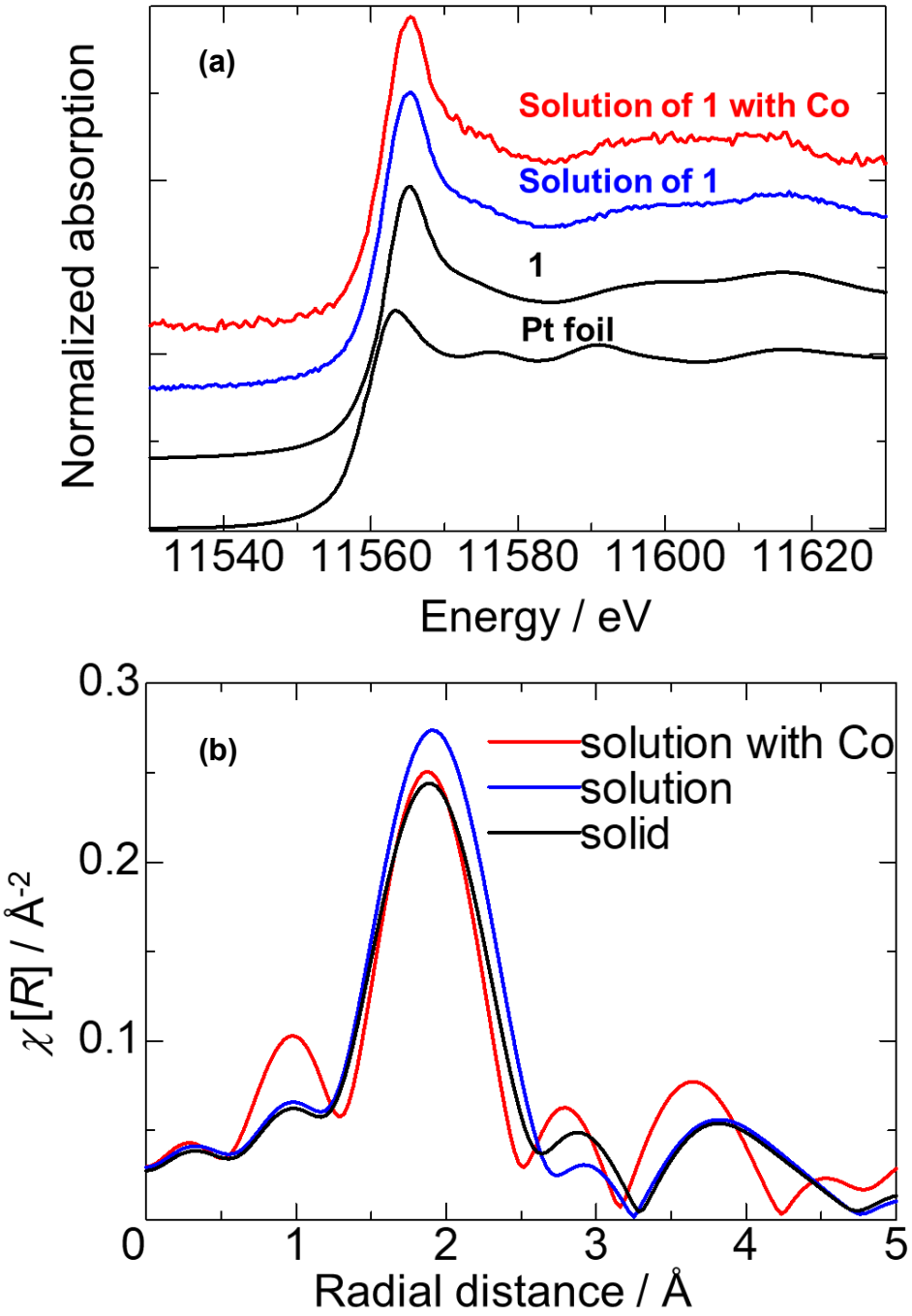

Fig. S4. (a) XANES of **1** and Pt foil. (b) Fourier transformed EXAFS spectra of **1.**

5. The results for $[BiPt(SAc)_4]^+$ paddle-wheel structure.

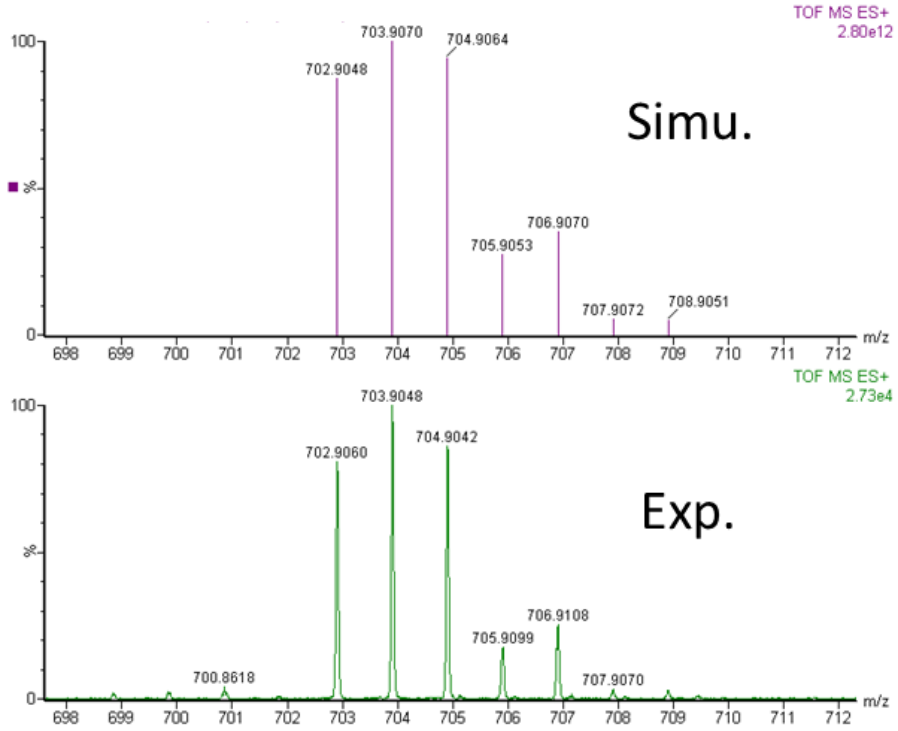

Fig. S5. Mass spectrum of **1** in the solution.

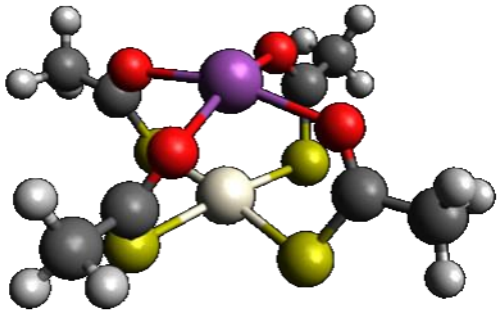

Fig. S6. Optimized structure of **1** in the solution.

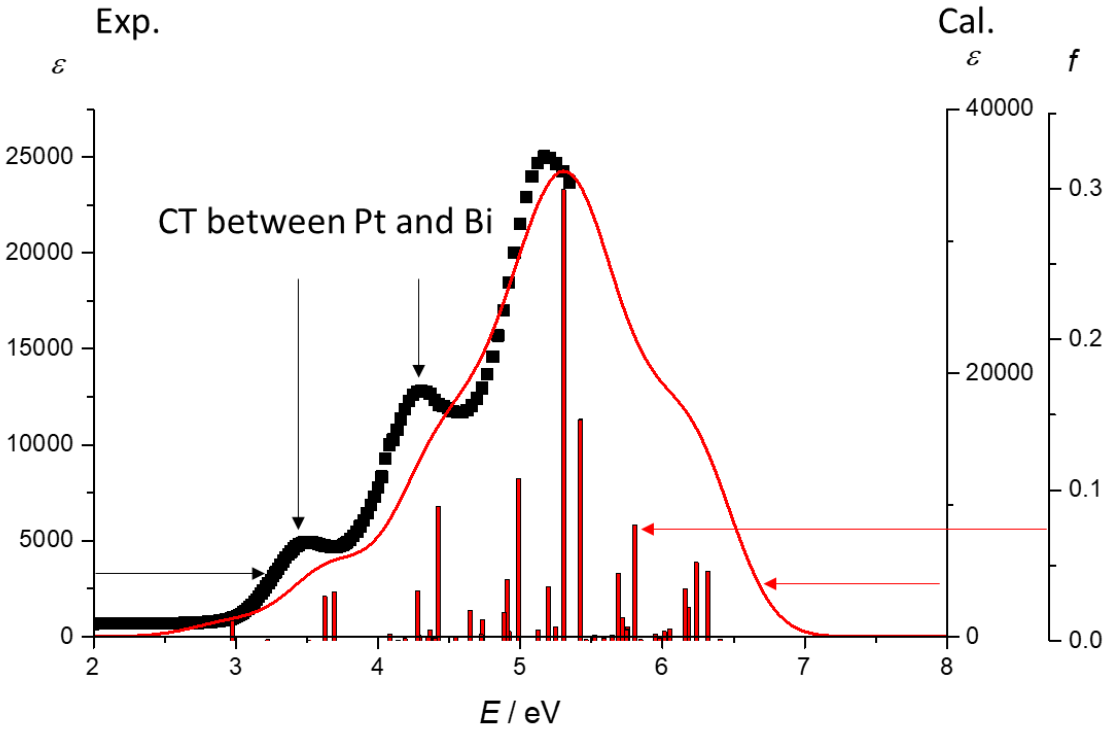

Figure S7. The UV/vis spectra of **1** in the solution (black: experimental; red: calculation).

Table S1. The coordinate of Bi-Pt complex model.

Atom	X	Y	Z
Bi	-0.00002	0	1.50355
C	-3.11509	-3.24026	0.36472
H	-3.01148	-3.71744	1.34436
H	-3.09149	-3.98946	-0.4279
H	-4.09107	-2.73704	0.34303
C	-2.04115	-2.19843	0.19238
C	3.24035	-3.11501	0.36487
H	3.71745	-3.01138	1.34454
H	3.98959	-3.09137	-0.4277
H	2.73719	-4.09102	0.34314
C	2.19846	-2.04113	0.19247
C	3.11496	3.2404	0.36487
H	3.01118	3.71765	1.34446
H	3.09143	3.98952	-0.42782
H	4.09097	2.73724	0.34338
C	2.04111	2.19848	0.19247
C	-3.2404	3.11493	0.36476
H	-3.7176	3.01121	1.34438
H	-3.98956	3.09134	-0.42789
H	-2.73727	4.09096	0.34317
C	-2.19846	2.04111	0.19238
O	-1.80053	-1.38155	1.16722
O	1.3816	-1.80046	1.16731
O	1.80044	1.38163	1.16732
O	-1.38163	1.80046	1.16725
Pt	0.00003	-0.00001	-1.20958
S	-1.1557	-2.14821	-1.34709
S	2.14823	-1.15575	-1.34704
S	1.15577	2.14818	-1.34706
S	-2.14816	1.15572	-1.34712

6. LOBA calculation.

Table S2. Localized Orbital Bonding analysis for Bi-Pt showing bonding interactions involving only Bi and Pt with the corresponding number of electrons localized on each atom. (Each green shaded row represents Pt – S bonds. The purple row shows the Bi – Pt bonding interaction)

Bi-Pt asymmetric unit (Bi-Pt(C2H3OS)5)									
MO numbers	**83-Bi-alpha**	**83-Bi-Beta**	**Bi-sum**	**78-Pt-alpha**	**78-Pt-beta**	**Pt-sum**	**16-S-alpha**	**16-S-beta**	**S-sum**
26	0.986	0.986	1.972						
42				0.989	0.989	1.978			
43	0.998	0.998	1.996						
44	0.998	0.998	1.996						
45	0.992	0.992	1.984						
46				0.988	0.988	1.976			
47				0.988	0.988	1.976			
48				0.991	0.991	1.982			
49	0.998	0.998	1.996						
50	0.999	0.999	1.998						
51	0.998	0.998	1.996						
52	0.999	0.999	1.998						
53	0.999	0.999	1.998						
69	0.851	0.851	1.702						
99				0.932	0.932	1.864			
100				0.266	0.266	0.532	0.617	0.617	1.234
101				0.263	0.263	0.526	0.616	0.616	1.232
103				0.927	0.927	1.854			
104				0.927	0.927	1.854			
105	0.354	0.354	0.708	0.607	0.607	1.214			
109				0.291	0.291	0.582	0.595	0.595	1.19

112				0.291	0.291	0.582	0.597	0.597	1.194
118				0.156	0.156	0.312	0.644	0.644	1.288
			20.344			17.232			

Table S3. Localized Orbital Bonding Analysis

Alpha Spin

Occupation > 15%

Orbital 1	Orbital 2	Orbital 3	Orbital 4	Orbital 5
S3: 1.000	S2: 1.000	S4: 1.000	S1: 1.000	S5: 1.000

Orbital 6	Orbital 7	Orbital 8	Orbital 9	Orbital 10
O2: 0.997	O3: 0.998	O4: 0.998	O1: 0.998	O5: 0.998

Orbital 11	Orbital 12	Orbital 13	Orbital 14	Orbital 15
C4: 0.995	C6: 0.995	C8: 0.995	C2: 0.994	C9: 0.994

Orbital 16	Orbital 17	Orbital 18	Orbital 19	Orbital 20
C3: 0.992	C5: 0.992	C7: 0.992	C1: 0.992	C10: 0.992

Orbital 21	Orbital 22	Orbital 23	Orbital 24	Orbital 25
S3: 0.997	S2: 0.998	S4: 0.999	S1: 0.998	S5: 0.999

Orbital 26	Orbital 27	Orbital 28	Orbital 29	Orbital 30
Bi : 0.986	S3: 0.998	S2: 0.998	S3: 0.998	S4: 0.999

Orbital 31	Orbital 32	Orbital 33	Orbital 34	Orbital 35
S3: 1.000	S1: 0.999	S2: 0.998	S4: 0.995	S2: 1.000

Orbital 36	Orbital 37	Orbital 38	Orbital 39	Orbital 40
S1: 0.996	S4: 1.000	S1: 1.000	S5: 0.999	S5: 0.995

Orbital 41	Orbital 42	Orbital 43	Orbital 44	Orbital 45
S5: 1.000	Pt : 0.989	Bi : 0.998	Bi : 0.998	Bi : 0.992

Orbital 46	Orbital 47	Orbital 48	Orbital 49	Orbital 50
Pt : 0.988	Pt : 0.988	Pt : 0.991	Bi : 0.998	Bi : 0.999

Orbital 51	Orbital 52	Orbital 53	Orbital 54	Orbital 55
Bi : 0.998	Bi : 0.999	Bi : 0.999	O2: 0.792	O3: 0.800

Orbital 56	Orbital 57	Orbital 58	Orbital 59	Orbital 60
O1: 0.790	O4: 0.794	O5: 0.834	C5: 0.518 H9: 0.404	C3: 0.518 H5: 0.406

Orbital 61	Orbital 62	Orbital 63	Orbital 64	Orbital 65
C7: 0.518 H12: 0.405	C1: 0.518 H3: 0.406	C10: 0.519 H13: 0.409	S3: 0.785	S1: 0.789

Orbital 66	Orbital 67	Orbital 68	Orbital 69	Orbital 70
S4: 0.784	S2: 0.794	S5: 0.802	Bi : 0.851	C3: 0.464 C4: 0.452

Orbital 71	Orbital 72	Orbital 73	Orbital 74	Orbital 75
C6: 0.461 S3: 0.465	C7: 0.465 C8: 0.450	C1: 0.465 C2: 0.450	C9: 0.447 C10: 0.471	C6: 0.364 O3: 0.597

Orbital 76	Orbital 77	Orbital 78	Orbital 79	Orbital 80
C4: 0.365 O2: 0.597	C7: 0.516 H11: 0.407	C5: 0.518 H7: 0.402	C3: 0.519 H4: 0.402	C1: 0.517 H2: 0.407

Orbital 81	Orbital 82	Orbital 83	Orbital 84	Orbital 85
C1: 0.520	C7: 0.519	O2: 0.770	C5: 0.464	C2: 0.366
H1: 0.404	H10: 0.404		C6: 0.451	O1: 0.598

Orbital 86	Orbital 87	Orbital 88	Orbital 89	Orbital 90
C8: 0.365	C10: 0.519	C10: 0.520	C5: 0.515	C3: 0.518
O4: 0.599	H14: 0.408	H15: 0.406	H8: 0.406	H6: 0.406

Orbital 91	Orbital 92	Orbital 93	Orbital 94	Orbital 95
C2: 0.461	C8: 0.462	C9: 0.372	C4: 0.260	C8: 0.255
S1: 0.467	S4: 0.465	O5: 0.599	O2: 0.696	O4: 0.695

Orbital 96	Orbital 97	Orbital 98	Orbital 99	Orbital 100
C2: 0.261	C6: 0.251	C9: 0.450	Pt : 0.932	Pt : 0.266
O1: 0.685	O3: 0.705	S5: 0.477		S2: 0.617

Orbital 101	Orbital 102	Orbital 103	Orbital 104	Orbital 105
Pt : 0.263	C9: 0.320	Pt : 0.927	Pt : 0.927	Bi : 0.354
S3: 0.616	O5: 0.645			Pt : 0.607

Orbital 106	Orbital 107	Orbital 108	Orbital 109	Orbital 110
O3: 0.764	C4: 0.462 S2: 0.464	C4: 0.185 S2: 0.748	Pt : 0.291 S4: 0.595	O4: 0.791

Orbital 111	Orbital 112	Orbital 113	Orbital 114	Orbital 115
O1: 0.796	Pt : 0.291 S1: 0.597	C6: 0.201 S3: 0.731	C2: 0.195 S1: 0.736	C8: 0.201 S4: 0.730

Orbital 116	Orbital 117	Orbital 118
C9: 0.153	S5: 0.790	Pt : 0.156

Beta Spin
Occupation > 15%

Orbital 1	Orbital 2	Orbital 3	Orbital 4	Orbital 5
S3: 1.000	S2: 1.000	S4: 1.000	S1: 1.000	S5: 1.000

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Orbital 26	Orbital 27	Orbital 28	Orbital 29	Orbital 30
Bi : 0.986	S3: 0.998	S2: 0.998	S3: 0.998	S4: 0.999

Orbital 31	Orbital 32	Orbital 33	Orbital 34	Orbital 35
S3: 1.000	S1: 0.999	S2: 0.998	S4: 0.995	S2: 1.000

Orbital 36	Orbital 37	Orbital 38	Orbital 39	Orbital 40
S1: 0.996	S4: 1.000	S1: 1.000	S5: 0.999	S5: 0.995

Orbital 41	Orbital 42	Orbital 43	Orbital 44	Orbital 45
S5: 1.000	Pt : 0.989	Bi : 0.998	Bi : 0.998	Bi : 0.992

Orbital 46	Orbital 47	Orbital 48	Orbital 49	Orbital 50
Pt : 0.988	Pt : 0.988	Pt : 0.991	Bi : 0.998	Bi : 0.999

Orbital 51	Orbital 52	Orbital 53	Orbital 54	Orbital 55
Bi : 0.998	Bi : 0.999	Bi : 0.999	O2: 0.792	O3: 0.800

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Orbital 61	Orbital 62	Orbital 63	Orbital 64	Orbital 65
C7: 0.518 H12: 0.405	C1: 0.518 H3: 0.406	C10: 0.519 H13: 0.409	S3: 0.785	S1: 0.789

Orbital 66	Orbital 67	Orbital 68	Orbital 69	Orbital 70
S4: 0.784	S2: 0.794	S5: 0.802	Bi : 0.851	C3: 0.464 C4: 0.452

Orbital 71	Orbital 72	Orbital 73	Orbital 74	Orbital 75
C6: 0.461	C7: 0.465	C1: 0.465	C9: 0.447	C6: 0.364
S3: 0.465	C8: 0.450	C2: 0.450	C10: 0.471	O3: 0.597

Orbital 76	Orbital 77	Orbital 78	Orbital 79	Orbital 80
C4: 0.365	C7: 0.516	C5: 0.518	C3: 0.519	C1: 0.517
O2: 0.597	H11: 0.407	H7: 0.402	H4: 0.402	H2: 0.407

Orbital 81	Orbital 82	Orbital 83	Orbital 84	Orbital 85
C1: 0.520	C7: 0.519	O2: 0.770	C5: 0.464	C2: 0.366
H1: 0.404	H10: 0.404		C6: 0.451	O1: 0.598

Orbital 86	Orbital 87	Orbital 88	Orbital 89	Orbital 90
C8: 0.365	C10: 0.519	C10: 0.520	C5: 0.515	C3: 0.518
O4: 0.599	H14: 0.408	H15: 0.406	H8: 0.406	H6: 0.406

Orbital 91	Orbital 92	Orbital 93	Orbital 94	Orbital 95
C2: 0.461	C8: 0.462	C9: 0.372	C4: 0.260	C8: 0.255
S1: 0.467	S4: 0.465	O5: 0.599	O2: 0.696	O4: 0.695

Orbital 96	Orbital 97	Orbital 98	Orbital 99	Orbital 100
C2: 0.261	C6: 0.251	C9: 0.450	Pt : 0.932	Pt : 0.266
O1: 0.685	O3: 0.705	S5: 0.477		S2: 0.617

Orbital 101	Orbital 102	Orbital 103	Orbital 104	Orbital 105
Pt : 0.263	C9: 0.320	Pt : 0.927	Pt : 0.927	Bi : 0.354
S3: 0.616	O5: 0.645			Pt : 0.607

Orbital 106	Orbital 107	Orbital 108	Orbital 109	Orbital 110
O3: 0.764	C4: 0.462	C4: 0.185	Pt : 0.291	O4: 0.791
	S2: 0.464	S2: 0.748	S4: 0.595	

Orbital 111	Orbital 112	Orbital 113	Orbital 114	Orbital 115
O1: 0.796	Pt : 0.291	C6: 0.201	C2: 0.195	C8: 0.201
	S1: 0.597	S3: 0.731	S1: 0.736	S4: 0.730

Orbital 116	Orbital 117	Orbital 118
C9: 0.153	S5: 0.790	Pt : 0.156
O5: 0.809		S5: 0.644

7. CV with various scan rate

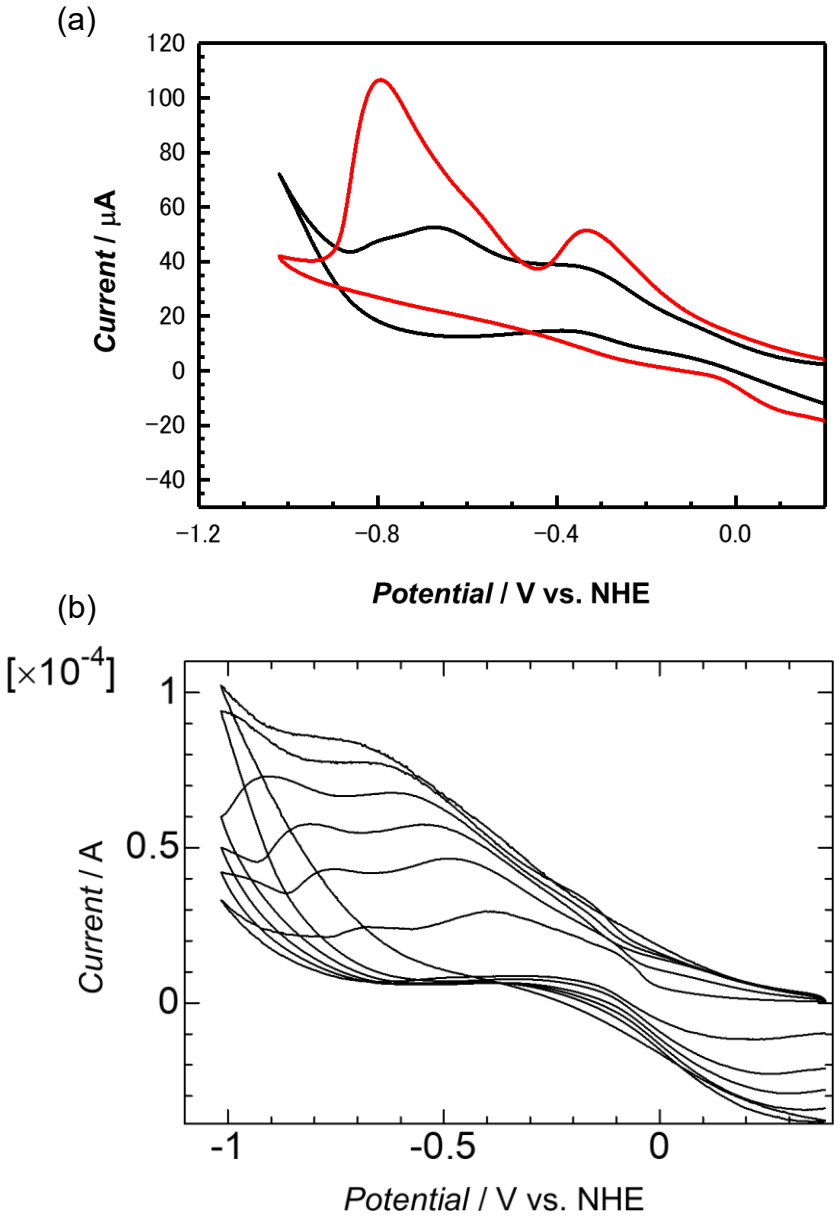

Fig. S8. CV of **1** mM **1** under N_2 in THF with 0.1 M $TBAPF_6$ supporting electrolyte (a) (b) at different rate.

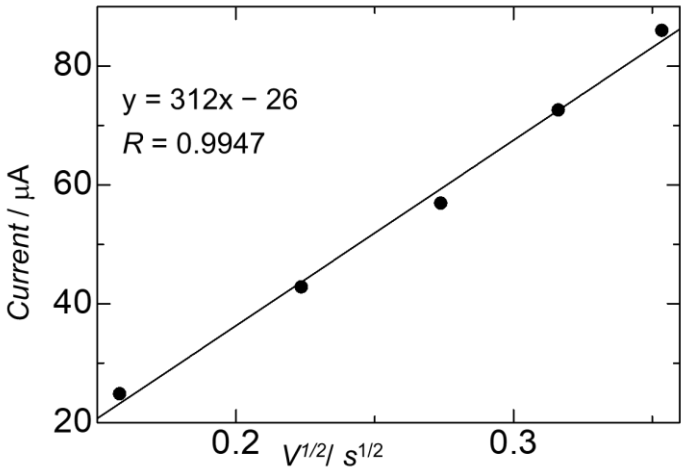

Figure. S9. i_p vs. $v^{1/2}$ plot for **1**, data collected from Figure. S7.

equation S1

$i_p = 0.4463 n_p FA[cat](n_p FvD/RT)^{1/2}$

Where, where i_p is peak current (A), n_p is the number of electron(s) involves in redox system, F is the Faraday constant (96485 $Cmol^{-1}$), A is the surface area of working electrode (0.071 cm^2), [cat] is catalysts concentration (mol/cm^3) , v is the scan rate (V/s), R is the universal gas constant (8.31 $JK^{-1}mol^{-1}$), and T is the temperature (298 K). An i_p vs $v^{1/2}$ plot (Figure S8) was made from cyclic voltammograms data at different scan rates to determine D.

8. Calculation model for third redox pair

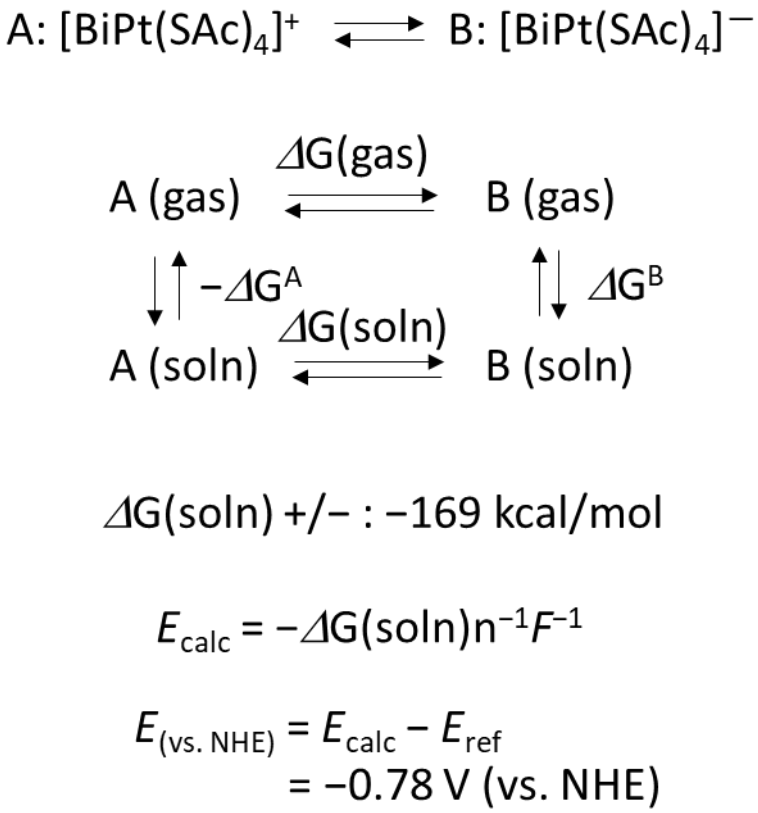

Fig. S10. Thermodynamic cycle with calculated free energy in solution ΔG(soln) and in gas ΔG(gas) from States (F: Faraday constant, n: number of moles of electrons, E_{ref}: absolute electrode potential[17b]).

9. Discussion for the Pt ion as reaction site.

A possible mechanism and the results of DFT calculations focused on axial [Bi(p_z) + Pt(d_z^2)] orbital (AO) and differences in the Gibbs free energy for the Pt ion as reaction site are shown in Figure 10. At –0.79 V, the reduced species forms ([BiPt(SAc)$_4$]$^+$ → [BiPt(SAc)$_4$]$^-$) and AO becomes occupied by electrons (a). The C atom of CO_2 molecule approaches Pt ion and stabilizes AO (b). This process has an activation barrier of –6 kcal/mol. Then, 2 H^+ approach the O atom of CO_2 stepwise, and the protonation dramatically stabilizes AO (c). The second protonation induces the H_2O and CO ligands to withdraw electrons from AO (d). These processes occur with energies of 26 kcal/mol and 58 kcal/mol, respectively. Then two additional electrons are provided to AO by the electrode. Then the Pt ion can release H_2O and CO, and the reduced species are reproduced ((d)→(a): 59 kcal/mol). Each difference in the Gibbs free energy of processes of (a) →→(d)→(a) for the Pt ion are energy disadvantage to that of (A) →→(D)→(A) for the Bi ion, because there is strong axial Pt–CO bond, whereas the Bi ion undergo the pathway via an ionic cage. Therefore, we did not conclude Pt ion as reaction site for CO_2 reduction by **1**.

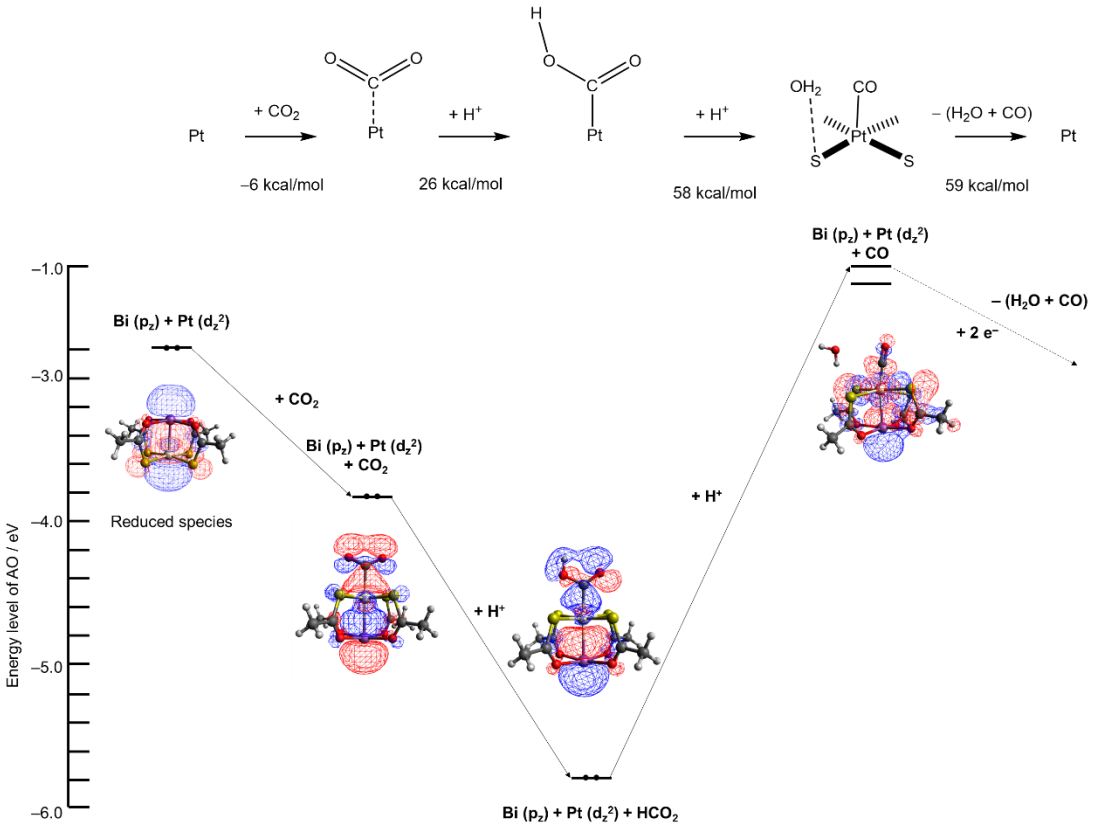

Fig. S11. A possible mechanism and results of DFT calculation (especially focus on axial [Bi(p_z) + Pt(d_z^2)] orbital (AO) and differences of Gibbs free energy).

10. Molecular orbitals of AO at (A)-(F).

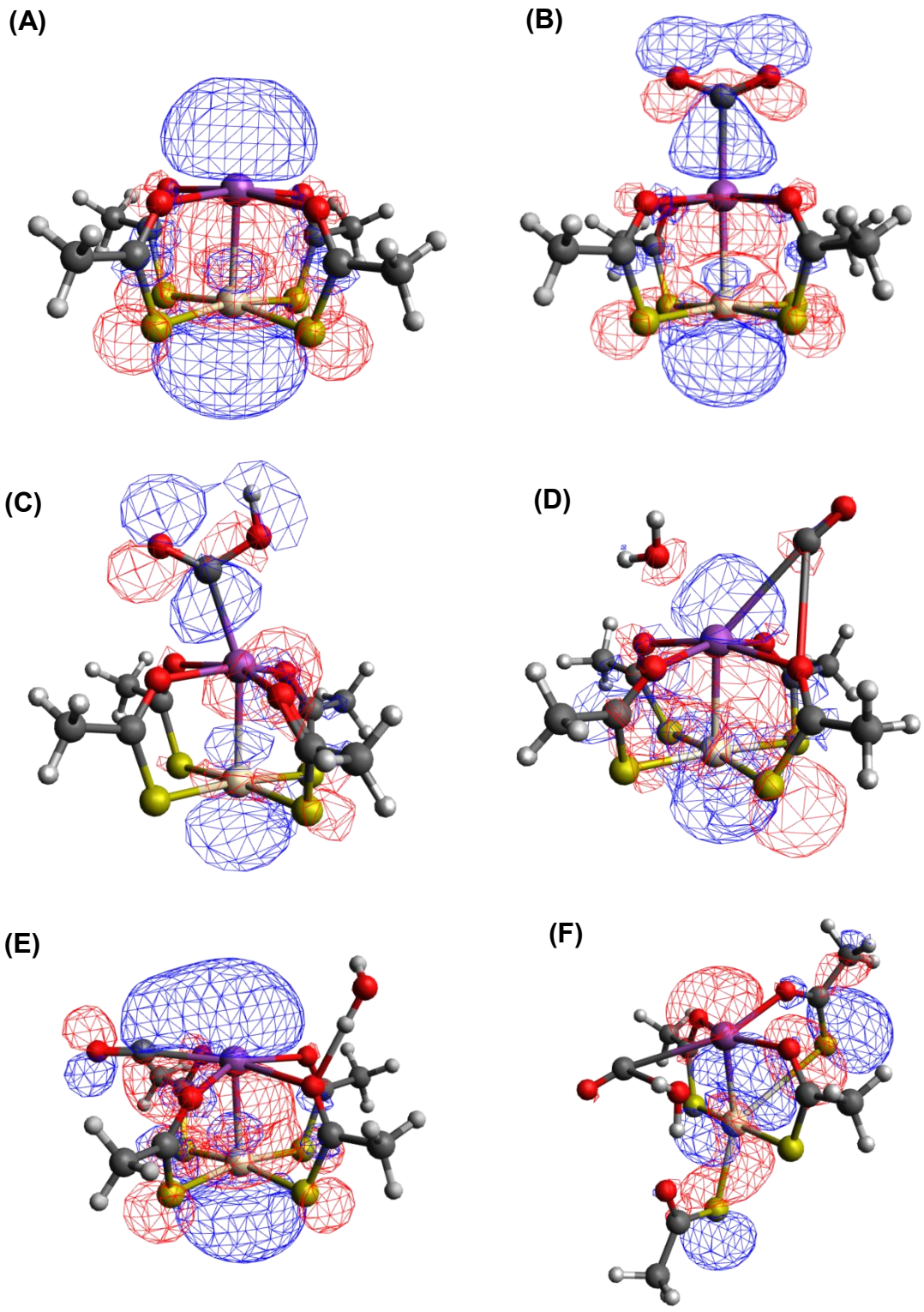

Fig. S12. Molecular orbitals of AO at (A)-(F).

11. Controlled Potential Electrolysis.

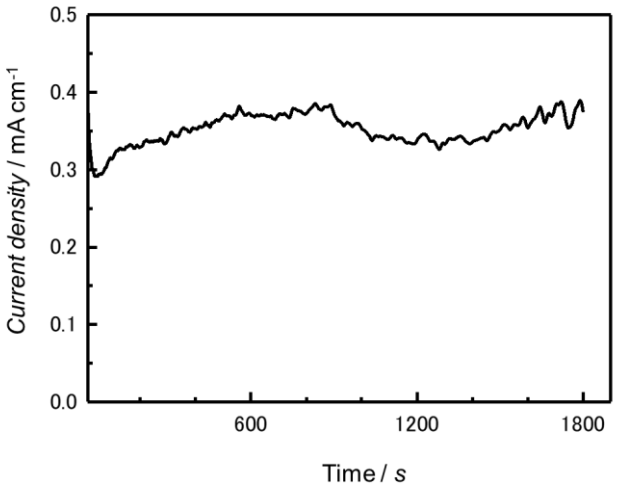

Fig. S13. CPE experiments at –0.79 V vs. NHE under CO_2 with 1 mM TFE in THF solution containing 0.1 M $TBAPF_6$ using glassy carbon working electrode (A = 0.071 cm^2).

equation S2

$$TOF = \frac{(i_{el})^2\ (1 + exp\left[\frac{F}{RT}\left(E_{app} - E_{\frac{1}{2}}\right)\right])}{F^2A^2D[cat]^2}$$

where, i_{el} is average current of CPE for CO generation (A: 6.1 × 10^{-5} A), F is faraday constant (96485 $Cmol^{-1}$), R is the universal gas constant (8.31 $JK^{-1}mol^{-1}$), T is the temperature (298 K), E_{app} is the applied potential during CPE experiments. $E_{1/2}$ (–0.80 V vs. NHE) is the standard redox potential of the catalysts, A is the surface area of working electrode (0.071 cm^2), D is the diffusion coefficient for catalyst and [cat] (8.9 × 10^{-7} mol/cm^3) is the concentration of catalyst in solution.

equation S3

energy efficiency = FE × E_n / E_{app}

where E_{app} is the applied potential during CPE experiments.