Supplementary Information for

Copper-Incorporated Mono- and Di-$TeRu_5$ Metal Carbonyl Complexes: Syntheses, Structures, and an Unusual Skeletal Arrangement

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Contents

Explanations for the checkCIF alerts for $[PPh_4]_2$[1]:

Alert level B

PLAT331_ALERT_2_B Small Average Phenyl C-C Dist. C71-C76 1.36 Ang.
PLAT342_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.0365 Ang.
PLAT430_ALERT_2_B Short Inter D...A Contact O3 .. O14 .. 2.83 Ang.
PLAT430_ALERT_2_B Short Inter D...A Contact O13 .. O21 .. 2.84 Ang.

Explanation: Crystals were diffracted extremely weakly because of the low quality of the crystals (R(int) = 0.1771). This lack of high resolution data therefore affected the precision on C-C bonds and O…O contacts. SIMU and DELU restraints were applied to the C atoms in the phenyls. Some atoms were still not ideally shaped, however, this does not indicate an incorrect atom-type assignment.

Explanations for the checkCIF alerts for $[PPh_4]_4$[2]·3Et_2O:

Alert level A

PLAT430_ALERT_2_A Short Inter D...A Contact O21 .. O21 .. 2.10 Ang

Alert level B

PLAT342_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.0268 Ang

Explanation: Crystals were diffracted extremely weakly because of the low quality of the crystals (R(int) = 0.1119). In addition, disorder of the solvent should weaken the reflections with low theta angle. One Et_2O molecule, chaotically disordered around the inversion centre, was approximated by arbitrary O and C positions with fractional occupancies, totalling one OC_4 for the void. This lack of high resolution data therefore affected the precision on the O…O contact and C-C bonds. The enhanced rigid-bond restraint RIGU was applied to all the atoms. Some atoms were still not ideally shaped, however, this does not indicate an incorrect atom-type assignment.

Computation details

All calculations reported in this study were performed via the density functional theory (DFT) with the modified Perdew−Wang exchange functional with Perdew−Wang's 91 gradient-correlation functional (MPW1PW91)[2] using the Gaussian 03[3] series of packages or the periodic code of Dmol[3] 6.0 package[4] with the general gradient approximation (GGA) plus the RPBE functional.[5] The geometries of $[TeRu_5(CO)_{14}]^{2-}$, **1**, **3a**, and **3b** taken from single-crystal X-ray diffraction data were fully optimized via the periodic code of Dmol[3] 6.0 package,[4] because of a better structural converge and correlation with experimental structural parameters (Table S2). Effective core potentials (ECP) and a DND basis set were used in the calculations. The lattice parameter for lengths was a = b = c = 30 Å and the lattice parameter for angles was $\alpha = \beta = \gamma = 90^o$. The self-consistent-field interaction was performed with a convergence criterion 10^{-5} a.u. on the total energy. Further, our analyses for the Cartesians coordinates of these optimized Te─Ru─Cu complexes (in gas phase) were used to perform on the newer generation functional, MPW1PW91, with the LanL2DZ/ECP[6] basis set for Te, Ru, Cu, and Cl atoms and the 6-31+G* basis set for C, O, N, and H atoms by using the Gaussian 03 series of packages, which the functional has been shown to have the better correlation for some heavy transition metal complexes.[7,8] Natural charges[9] and Wiberg bond indices[10] were evaluated with Weinhold's NBO method.[11]

The nature of all stationary points provided positive eigenvalues for reactant **3a**, product **3b**, and the intermediate **I1** and one imaginary eigenvalue for transition state **TS** and **I2** (anharmonic effect for the methyl rotation)[12] through vibration frequencies calculations which were calculated at the MPW1PW91 functional with LanL2DZ basis set for all the atoms. The potential energy surface scan calculations were done by increasing the selected Ru─Cu bond of **I1** with a 0.10 Å step size and were used to verify that the **TS** found was linked to the intermediates **I1** and **I2** or product **3b**. For the electronic absorption spectrum,

on the basis of the experimental coordinates of **1**, low-lying 150 singlet states were employed to produce the vertical excitation for all of the molecules in the CH_2Cl_2 media using the time-dependent DFT (TDDFT) method[13] at the same level associated with the conductor-like polarizable continuum model (CPCM).[14] Calculation of UV−vis spectra was accomplished using GaussSum 2.2.[15] Electronic transitions were expanded as Gaussian curves, with a full width at half maximum (fwhm) for each peak set to 3000 cm^{-1}. Graphical representations of the molecular orbitals were obtained using GaussView 5.0. For orbital contributions, the molecular orbital compositions were analyzed using the AOMIX program.[16]

Electrochemistry details

The cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed at room temperature under a nitrogen atmosphere and recorded using a CHI 621D electrochemical potentiostat. A glassy carbon working electrode, a platinum wire auxiliary electrode, and a non-aqueous Ag/Ag^+ electrode were used in a three-electrode configuration. For the controlled-potential coulometry (CPC) measurements, the working electrode, auxiliary electrode, and reference electrode were the same as those used for CV and DPV measurements. Tetra-*n*-butylammonium perchlorate (TBAP) was used as the supporting electrolyte, and the solute concentration was ~10^{-3}-10^{-4} M. The redox potentials were calibrated with a ferrocenium/ferrocene (Fc^+/Fc) couple in the working solution and referenced to SCE.

The electronic stoichiometry is determined by the measurement of the peak width at half-height ($W_{1/2}$) of the DPVs (Table S7) and by the CPC experiments (Fig. S6).[17] As shown in Table S7, the widths of the DPV peaks at half-height of **1**, **3a**, and **3b** are a bit greater than the value ($W_{1/2}$ = 90 mV) expected for one-electron reversible redox reactions, indicating that these DPV responses are quasi-reversible.[18] However, the CPC experiments indicated that **1**,

3a, and **3b** each possessed 0.2, 0.2, and 0.5 electrons per molecular (Fig. S6), which was not adequate to determine the electronic stoichiometry in our experimental conditions so as in many other cases due to the difficulty in controlling the complicated experimental parameters. Therefore, the $W_{1/2}$ of DPV peaks still remained a practical approach to determine the electronic stoichiometry as mentioned in our and others' studies.

Electronic absorption and diffuse reflectance spectra.

The electronic absorption spectra of solution samples of $[TeRu_5(CO)_{14}]^{2-}$ and **1** (Fig. S7) were scanned at room temperature with a Varian Cary 5000 UV−vis−NIR spectrophotometer between 200−800 nm in CH_2Cl_2 solution (10^{-4} M) with a conventional 1.0 cm quartz cell. The diffuse reflectance spectra of solid samples of $[TeRu_5(CO)_{14}]^{2-}$ and **1—4** (Fig. S8) were measured at room temperature between 200−2500 nm with Al_2O_3 powder for the 100% reflectance reference by using a Varian Cary 5000 UV−vis−NIR spectrophotometer and the room temperature optical absorption spectra of those solid compounds were obtained from diffuse reflectance experiment. The reflectance spectrum was converted to the absorption by using the Kubelka-Munk function, $F = (1-R)^2/2R$.[19,20] The band gap was determined in the F-versus-E plot, by extrapolating the linear portion of starting rising curve to zero, which provided the onset of absorption.

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Table S1 The Ru─Cu and Cu─Cu bond lengths (Å) of di-Cu-capped isomers **3a** and **3b**·0.5CH_2Cl_2

3a	Bond lengths	**Δ**[a]	**3b**·0.5CH_2Cl_2	Bond lengths	**Δ**[a]
Ru(1)─Cu(1)	2.5953(4)	0.0630(4)	Ru(1)─Cu(1)	2.588(1)	0.067(1)
Ru(2)─Cu(1)	2.6502(4)		Ru(2)─Cu(1)	2.655(1)	
Ru(5)─Cu(1)	2.6583(4)				
Ru(2)─Cu(2)	2.6304(4)	0.0310(4)	Ru(1)─Cu(2)	2.6321(9)	0.028
Ru(3)─Cu(2)	2.6250(4)		Ru(2)─Cu(2)	2.6445(9)	
Ru(5)─Cu(2)	2.6560(4)		Ru(5)─Cu(2)	2.660(1)	
Cu(1)─Cu(2)	3.8896(6)		Cu(1)─Cu(2)	2.645(1)	

[a] Difference between the longer Ru─Cu and the shorter Ru─Cu bond

Table S2 Comparison of selected structural parameters of the optimized geometries for $[TeRu_5(CO)_{14}]^{2-}$, **1**, **3a**, and **3b** with the experimental structural parameters, calculated by using Dmol^3 package with the general gradient approximation (GGA) plus the RPBE functional

	$[TeRu_5(CO)_{14}]^{2-}$	
bond distances	X-ray	optimized geometry
Te(1)─Ru(2)	2.665	2.751
Te(1)─Ru(3)	2.723	2.773
Te(1)─Ru(4)	2.748	2.843
Te(1)─Ru(5)	2.686	2.760
Ru(2)─Ru(3)	2.877	2.966
Ru(2)─Ru(5)	2.899	3.019
Ru(4)─Ru(3)	2.815	2.897
Ru(4)─Ru(5)	2.846	2.929
Ru(6)─Ru(2)	2.843	2.939
Ru(6)─Ru(3)	2.869	3.018
Ru(6)─Ru(4)	2.882	2.967
Ru(6)─Ru(5)	2.841	2.917
	1	
bond distances	X-ray	optimized geometry
Te(1)─Ru(6)	2.674	2.762
Te(1)─Ru(7)	2.663	2.762
Te(1)─Ru(8)	2.744	2.837
Te(1)─Ru(9)	2.728	2.801
Te(2)─Ru(1)	2.731	2.812
Te(2)─Ru(2)	2.748	2.819
Te(2)─Ru(3)	2.675	2.764
Te(2)─Ru(4)	2.677	2.768
Ru(6)─Ru(7)	3.070	3.306
Ru(6)─Ru(9)	2.838	2.912
Ru(8)─Ru(7)	2.823	2.896
Ru(8)─Ru(9)	2.818	2.916
Ru(10)─Ru(6)	2.890	2.998
Ru(10)─Ru(7)	2.912	2.996
Ru(10)─Ru(8)	2.847	2.979
Ru(10)─Ru(9)	2.842	2.952
Ru(1)─Ru(2)	2.832	2.922
Ru(1)─Ru(4)	2.834	2.903
Ru(3)─Ru(2)	2.809	2.911
Ru(3)─Ru(4)	3.071	3.221
Ru(5)─Ru(1)	2.826	2.951
Ru(5)─Ru(2)	2.889	2.939
Ru(5)─Ru(3)	2.900	3.032
Ru(5)─Ru(4)	2.880	3.006
Cu(1)─Ru(3)	2.653	2.751
Cu(1)─Ru(4)	2.694	2.765
Cu(1)─Ru(5)	2.691	2.781
Cu(2)─Ru(6)	2.670	2.708
Cu(2)─Ru(7)	2.655	2.740
Cu(2)─Ru(10)	2.661	2.861
Cu(3)─Ru(4)	2.583	2.710
Cu(3)─Ru(6)	2.568	2.668
Cu(3)─Cu(1)	2.599	2.589

Cu(3)─Cu(2)	2.483	2.706
Cu(1)─Cl(1)	2.236	2.277
Cu(2)─Cl(1)	2.218	2.299
	3a	
bond distances	X-ray	optimized geometry
Te(1)─Ru(1)	2.672	2.769
Te(1)─Ru(2)	2.672	2.751
Te(1)─Ru(3)	2.681	2.766
Te(1)─Ru(4)	2.762	2.848
Ru(1)─Ru(2)	3.000	3.141
Ru(1)─Ru(4)	2.808	2.891
Ru(3)─Ru(2)	3.002	3.149
Ru(3)─Ru(4)	2.804	2.884
Ru(5)─Ru(1)	2.887	3.016
Ru(5)─Ru(2)	2.915	3.079
Ru(5)─Ru(3)	2.899	3.010
Ru(5)─Ru(4)	2.869	2.971
Cu(1)─Ru(1)	2.595	2.706
Cu(1)─Ru(2)	2.650	2.727
Cu(1)─Ru(5)	2.658	2.697
Cu(2)─Ru(2)	2.630	2.709
Cu(2)─Ru(3)	2.625	2.670
Cu(2)─Ru(5)	2.656	2.735
Cu(1)─N(1)	1.899	1.925
Cu(2)─N(2)	1.909	1.932
	3b	
bond distances	X-ray	optimized geometry
Te(1)─Ru(1)	2.671	2.778
Te(1)─Ru(2)	2.674	2.769
Te(1)─Ru(3)	2.708	2.808
Te(1)─Ru(4)	2.712	2.804
Ru(1)─Ru(2)	3.015	3.141
Ru(1)─Ru(4)	2.823	2.888
Ru(3)─Ru(2)	2.818	2.905
Ru(3)─Ru(4)	2.846	2.914
Ru(5)─Ru(1)	2.901	3.016
Ru(5)─Ru(2)	2.897	3.016
Ru(5)─Ru(3)	2.819	2.913
Ru(5)─Ru(4)	2.825	2.930
Cu(1)─Ru(1)	2.588	2.651
Cu(1)─Ru(2)	2.655	2.724
Cu(2)─Ru(1)	2.632	2.741
Cu(2)─Ru(2)	2.645	2.751
Cu(2)─Ru(5)	2.660	2.695
Cu(1)─Cu(2)	2.645	2.643
Cu(1)─N(1)	1.909	1.902
Cu(2)─N(2)	1.915	1.929

Table S3 Results of natural bond order and natural population analyses of $[TeRu_5(CO)_{14}]^{2-}$, **1**, **3a**, **3b**, **I1**, and **I2**

complex	Wiberg bond index					Natural charge					
	Te─Ru	Ru─Ru	Ru─Cu	Cu─Cu	Cu─Cl or Cu─N	Te	Ru	Cu	Cl or N	$TeRu_5(CO)_{14}$ (sum)	Cu_mX_n (sum)
$[TeRu_5(CO)_{14}]^{2-}$ (m = 0, n = 0)	0.323	0.131				−0.105	−0.315			−2	0
1 (X = Cl, m = 3, n = 1)	0.338	0.127	0.092	0.068	0.168	0.038	−0.392	0.560	−0.692	−2.989	0.989
3a (X = MeCN, m = 2, n = 2)	0.354	0.137	0.096		0.176	0.066	−0.421	0.574	−0.538	−1.247	1.247
3b (X = MeCN, m = 2, n = 2)	0.352	0.137	0.114	0.065	0.184	0.059	−0.433	0.540	−0.550	−1.191	1.191
I1[a] (X = MeCN, m = 2, n = 2)	0.341	0.124	0.071		0.183	0.190	−0.432	0.727	−0.534	−1.565	1.565
I2[a] (X = MeCN, m = 2, n = 2)	0.338	0.121	0.082	0.049	0.171	0.183	−0.407	0.710	−0.535	−1.534	0.534

[a] Calculated by MPW1PW91/LanL2DZ.

Table S4 Calculated results for the optimized geometries of one-electron and two-electron oxidized species of **1** (**1'**, **1''**)

	1 (S = 0)	**1'** (S = 1/2)	**1''** (S = 0)	**1''** (S = 1)
relative energy (kcal mol^{-1})			0.00	0.07
bond lengths (Å)				
Te─Ru (av.)	2.791 (2.705)[c]	2.791	2.788	2.791
Ru─Ru (av.)	2.990 (2.880)[c]	2.980	2.976	2.981
Ru─Cu (av.)	2.748 (2.647)[c]	2.739	2.717	2.734
Cu─Cl (av.)	2.288 (2.227)[c]	2.276	2.256	2.274
Cu─Cu[a] (av.)	2.648 (2.541)[c]	2.640	2.628	2.644
Cu─Cu[b]	3.245 (2.938)[c]	2.971	2.889	3.021
metal spin density				
$Ru_5/Cu_3/Ru_5$		0.63/0.08/0.06		0.77/0.04/0.95

[a] Bridged by Ru atom. [b] Bridged by Cl atom. [c] From single-crystal diffraction data.

Table S5 Selected low-lying singlet excited states (S_n) in **1**, calculated by TD-MPW1PW91/LanL2DZ/6-31+G*/CPCM (CH_2Cl_2), with the orbital involved in the dominant excitations, transition (percentage contribution), vertical excitation energies (nm), oscillator strength (*f*)

complex	S_n	major transition (percentage contribution)	vertical excitation energy (nm)		oscillator strength (*f*)
			expt	calcd	
1	5	HOMO−1→LUMO+2 (47%) HOMO−3→LUMO+2 (18%)	595	565.67	0.0103
	8	HOMO−2→LUMO+2 (26%) HOMO−3→LUMO (14%) HOMO−3→LUMO+3 (-10%)		538.43	0.0238
	27	HOMO−2→LUMO+4 (13%) HOMO−2→LUMO (-8%) HOMO−3→LUMO+3 (8%) HOMO−2→LUMO+3 (7%) HOMO−5→LUMO (-6%) HOMO−1→LUMO+3 (-4%)	426	428.21	0.0423
	40	HOMO−10→LUMO (17%) HOMO−9→LUMO (17%) HOMO−5→LUMO+4 (5%) HOMO−7→LUMO (4%) HOMO−5→LUMO+2 (3%)		393.95	0.1161

Table S6 Cartesian coordinates of all optimized geometries. The optimized geometries of $[TeRu_5(CO)_{14}]^{2-}$, **1**, **3a**, and **3b** were performed via the periodic code of DMol^3 package with the general gradient approximation (GGA) plus the RPBE functional. In addition, for the mechanism study, the optimized geometries of **3a**, **3b**, **I1**, **I2**, and **TS** were further performed via Gaussian 03 series of packages with MPW1PW91/LanL2DZ method

$[TeRu_5(CO)_{14}]^{2-}$ (DMol^3)
Total energy = −2071.3299922 a.u.

	x	y	z
Te	8.717600	13.437800	7.001800
Ru	6.031400	13.892900	6.617800
Ru	7.493400	11.760800	5.163800
Ru	9.495600	13.656700	4.276500
Ru	8.173000	15.827000	5.731700
Ru	6.643600	14.300700	3.772700
O	4.780400	16.592300	7.344100
O	5.288600	12.764500	9.371000
O	3.557600	12.656900	5.296100
O	8.077100	9.402500	7.009000
O	5.469700	9.941000	3.779300
O	9.597800	10.689600	3.257400
O	10.222300	13.777600	1.319600
O	12.422000	13.127300	5.007400
O	10.585000	16.603600	4.067700
O	6.841000	18.324100	4.582800
O	9.392100	17.530700	7.969200
O	5.813700	12.394700	1.515900
O	7.846100	16.159200	1.659300
O	3.995100	15.858000	3.650700
C	5.341700	15.612400	7.017300
C	5.613500	13.185200	8.321800
C	4.570200	13.107100	5.690600
C	7.842200	10.322500	6.312800
C	6.231000	10.691400	4.267700
C	9.050200	11.518200	3.918500
C	9.917900	13.772000	2.452300
C	11.294200	13.334900	4.751600
C	9.764300	15.873900	4.532100
C	7.313000	17.337700	5.011500
C	8.913700	16.844800	7.140200
C	6.137000	13.037800	2.444200
C	7.471200	15.439700	2.506800
C	4.993700	15.256300	3.782500

$[\{TeRu_5(CO)_{14}\}_2Cu_3Cl]^{2-}$ (**1**) (DMol^3)
Total energy = −5195.2493388 a.u.

	x	y	z
C	9.321400	4.367200	-3.241800
C	9.093100	3.665800	-5.962100
C	9.580500	6.315100	-5.331600
C	7.248400	5.638000	-6.807300
C	5.166500	7.542100	-6.293400
C	4.487500	5.050800	-7.153700
C	3.470900	5.734200	-4.666600
C	3.050400	4.135100	-2.442400
C	3.752600	6.675500	-2.005200
C	8.400200	5.478100	-0.859100
C	8.023600	2.731200	-1.492000
C	7.140200	1.607000	-4.084200
C	4.388000	2.159800	-4.263600
C	6.127800	2.772700	-6.308400
C	3.669900	5.114000	1.471100
C	5.805800	6.846700	1.284700
C	4.254000	6.740700	3.606800
C	5.724400	7.595400	5.953700
C	3.621400	5.822600	6.173500
C	6.212400	5.000700	7.047300
C	8.921100	4.189700	6.582200
C	6.987700	2.266900	6.906800
C	8.339000	2.248900	4.476500
C	7.264900	1.417500	2.074100
C	9.110300	3.355000	1.986800
C	4.205900	2.846100	6.097600
C	2.970200	3.314900	3.719800
C	4.901300	1.245700	3.977600
O	10.466100	4.108200	-3.070200
O	9.690500	2.867500	-6.565300
O	10.452200	7.055300	-5.560200
O	7.584800	5.818900	-7.930200
O	4.971900	8.629000	-6.671500
O	3.851900	4.694800	-8.063300
O	2.384900	5.939500	-5.102200
O	2.069600	3.583800	-2.136900
O	3.264400	7.573400	-1.441300
O	9.080600	6.170700	-0.199600
O	8.445600	1.731400	-1.063800
O	7.754500	0.618600	-4.002500
O	3.431800	1.487500	-4.292700
O	6.194600	2.388400	-7.410700
O	2.658300	5.069800	0.895700
O	6.059100	7.807900	0.670600
O	3.456800	7.613900	3.523700
O	5.930000	8.662600	6.378100
O	2.588600	5.883300	6.709900
O	6.131200	5.164000	8.218400
O	9.924800	4.427700	7.126500
O	6.885000	1.376100	7.650500
O	9.077100	1.364900	4.765100
O	7.315000	0.337500	1.640100
O	10.148900	3.435700	1.461500
O	3.743400	2.589900	7.139500
O	1.823800	3.341800	3.503600
O	4.870100	0.080800	3.893700
Te	7.670400	5.730500	3.797200
Te	6.740400	6.792900	-3.385900
Ru	8.204200	5.035200	-5.002700
Ru	5.468600	5.762300	-5.703200
Ru	4.471400	5.257900	-3.031600
Ru	7.568300	4.426600	-2.226600
Ru	6.027900	3.121700	-4.442500
Ru	5.274200	5.434400	2.443100
Ru	7.470000	3.122900	2.901700
Ru	7.273100	3.728800	5.742500
Ru	5.307000	5.847700	5.316300
Ru	4.782200	3.125700	4.304800
Cu	5.313800	3.031900	-1.673200

Cu	5.088400	2.821700	1.557400
Cu	6.540900	4.508200	0.234000
Cl	4.351800	1.561500	-0.190100

$[\{TeRu_5(CO)_{14}\}_2Cu_3Cl]^-$ (**1'**, S = 1/2) ($DMol^3$)
Total energy = −5195.1043569 a.u.

	x	y	z
C	9.406100	4.338400	-3.226100
C	9.083400	3.501700	-5.853400
C	9.653300	6.186800	-5.427800
C	7.281200	5.509500	-6.792200
C	5.429400	7.593800	-6.331500
C	4.487600	5.082600	-7.017300
C	3.594200	6.086600	-4.576200
C	3.047300	4.420000	-2.429600
C	3.974800	6.846600	-1.868400
C	8.474500	5.468700	-0.811800
C	8.107000	2.732500	-1.500300
C	6.784200	1.505400	-3.843800
C	4.166500	2.458200	-4.362800
C	6.162600	2.752200	-6.160500
C	3.695300	5.265400	1.457100
C	5.925300	6.900700	1.338200
C	4.315000	6.784000	3.645100
C	5.752100	7.441000	6.050300
C	3.576400	5.753200	6.138700
C	6.131500	4.817500	7.025200
C	8.820200	3.990400	6.564300
C	6.851100	2.095700	6.820100
C	8.229000	2.109500	4.401400
C	7.211400	1.414400	1.950700
C	9.107300	3.320600	1.988900
C	4.101400	2.771500	5.907400
C	2.902300	3.294000	3.535800
C	4.817700	1.197600	3.792400
O	10.544100	4.072100	-3.048900
O	9.624100	2.635400	-6.408900
O	10.525300	6.898400	-5.715300
O	7.609400	5.575400	-7.926300
O	5.337000	8.673100	-6.753400
O	3.797300	4.650800	-7.845100
O	2.556900	6.477500	-4.987800
O	2.036300	3.933400	-2.126800
O	3.556600	7.739500	-1.251700
O	9.186400	6.163900	-0.189900
O	8.527100	1.723900	-1.099000
O	7.230000	0.442700	-3.685500
O	3.131300	1.943700	-4.499700
O	6.253400	2.351500	-7.251000
O	2.681500	5.280300	0.887100
O	6.249800	7.861000	0.760700
O	3.571400	7.701000	3.592000
O	6.004200	8.476800	6.512900
O	2.546600	5.827100	6.672400
O	6.037900	4.945900	8.197000
O	9.818200	4.217100	7.115300
O	6.717300	1.202300	7.549500
O	8.930800	1.194900	4.667100
O	7.226300	0.351600	1.480200
O	10.178700	3.431400	1.545500
O	3.622400	2.494700	6.933000
O	1.763300	3.346600	3.301400
O	4.780800	0.040400	3.668600
Te	7.685300	5.652600	3.848500
Te	6.911100	6.840500	-3.370000
Ru	8.264400	4.964700	-4.960100
Ru	5.569600	5.820800	-5.643000
Ru	4.568700	5.427700	-2.984400
Ru	7.640500	4.437000	-2.212300
Ru	5.941700	3.168500	-4.315400
Ru	5.309700	5.474500	2.444500
Ru	7.424400	3.089500	2.839900
Ru	7.178100	3.576300	5.678900
Ru	5.281100	5.743500	5.306200
Ru	4.715000	3.083000	4.128300
Cu	5.365100	3.211400	-1.547700
Cu	5.078200	2.953200	1.398300
Cu	6.754400	4.586100	0.321300
Cl	4.227500	1.689500	-0.284600

$[\{TeRu_5(CO)_{14}\}_2Cu_3Cl]$ (**1''**, S = 0) ($DMol^3$)
Total energy = −5194.9146189 a.u.

	x	y	z
C	9.375400	4.361800	-3.411600
C	9.047600	3.658700	-6.071500
C	9.405300	6.335400	-5.562300
C	7.036800	5.508900	-6.856700
C	5.073400	7.458000	-6.370700
C	4.289900	4.887800	-6.957500
C	3.402100	5.881700	-4.481900
C	3.099000	4.205200	-2.335500
C	3.919200	6.718600	-1.819100
C	8.527700	5.587900	-0.967400
C	8.195700	2.849100	-1.521400
C	6.855200	1.448400	-3.796900
C	4.185500	2.286200	-4.320800
C	6.167000	2.666600	-6.100100
C	3.775000	5.195000	1.485700
C	5.993600	6.869100	1.288200
C	4.334800	6.796300	3.597800
C	5.634300	7.440300	6.136800
C	3.482900	5.707600	5.995600
C	5.986000	4.812200	7.039800
C	8.733600	4.281900	6.774700
C	6.969500	2.177900	6.872700
C	8.480800	2.313200	4.542800
C	7.506300	1.472900	2.125000
C	9.222300	3.517900	2.041100
C	4.198400	2.695600	5.844400
C	3.002400	3.166500	3.490000
C	5.016300	1.150700	3.780900
O	10.511500	4.080500	-3.277900
O	9.636000	2.880300	-6.694000
O	10.180300	7.143400	-5.858200
O	7.327400	5.596300	-7.996100
O	4.872500	8.510800	-6.811800
O	3.610000	4.429200	-7.775200
O	2.336500	6.194200	-4.870100
O	2.138100	3.652300	-1.992400

O	3.506700	7.605500	-1.195200
O	9.249900	6.285300	-0.366600
O	8.662100	1.894000	-1.054500
O	7.356000	0.417000	-3.620200
O	3.174600	1.729100	-4.433900
O	6.257600	2.276100	-7.191200
O	2.762000	5.171400	0.918000
O	6.246200	7.862800	0.730100
O	3.573800	7.687500	3.479500
O	5.841600	8.449300	6.666700
O	2.414100	5.710700	6.441100
O	5.759800	4.891000	8.194000
O	9.653800	4.612100	7.399000
O	6.878200	1.265500	7.580100
O	9.270400	1.503600	4.876500
O	7.599700	0.410400	1.665100
O	10.240600	3.660200	1.501000
O	3.707000	2.411000	6.857600
O	1.871100	3.154300	3.232300
O	5.027000	-0.002800	3.656700
Te	7.711700	5.780000	3.930700
Te	6.767300	6.853200	-3.460500
Ru	8.144800	4.996600	-5.052400
Ru	5.383500	5.721000	-5.638000
Ru	4.527000	5.314100	-2.961500
Ru	7.645200	4.504900	-2.296600
Ru	5.932500	3.081800	-4.253900
Ru	5.398500	5.458200	2.449800
Ru	7.594800	3.179000	2.976400
Ru	7.217900	3.705600	5.761400
Ru	5.244500	5.778700	5.268400
Ru	4.834500	3.040300	4.077200
Cu	5.474200	3.187600	-1.504400
Cu	5.358500	3.002300	1.376200
Cu	6.675100	4.878400	0.170700
Cl	4.556600	1.595300	-0.190700

[{$TeRu_5(CO)_{14}$}$_2Cu_3Cl$] (**1''**, S = 1) ($DMol^3$)
Total energy = −5194.9145050 a.u.

	x	y	z
C	9.398500	4.384000	-3.323500
C	9.119000	3.683100	-5.993000
C	9.524500	6.347200	-5.462500
C	7.172600	5.565300	-6.814800
C	5.238200	7.556800	-6.349400
C	4.410800	4.994200	-6.999900
C	3.500400	5.973200	-4.558100
C	3.071400	4.267000	-2.441800
C	3.937500	6.728900	-1.838600
C	8.490100	5.563500	-0.886000
C	8.167600	2.817000	-1.513200
C	6.882200	1.482100	-3.855300
C	4.232500	2.343600	-4.372200
C	6.216300	2.726200	-6.150000
C	3.723800	5.068700	1.422200
C	5.662700	7.044900	1.515200
C	4.039400	6.468400	3.726600
C	5.469700	7.510300	5.949200
C	3.584100	5.549300	6.295200
C	6.239900	4.955600	7.056400
C	8.968400	4.155500	6.455800
C	7.044200	2.271300	6.874300
C	8.229600	2.292400	4.381600
C	7.335400	1.639100	1.891100
C	9.239100	3.560700	2.126200
C	4.170400	2.627600	5.987300
C	3.007200	2.959600	3.492800
C	4.976000	1.114900	3.824100
O	0.531400	4.100600	-3.156400
O	9.709400	2.896700	-6.604400
O	0.336700	7.121200	-5.750800
O	7.491900	5.655000	-7.946400
O	5.075100	8.623900	-6.770700
O	3.737000	4.554000	-7.832500
O	2.439000	6.310900	-4.942900
O	2.085700	3.732200	-2.144200
O	3.518900	7.603900	-1.200400
O	9.174300	6.264900	-0.244400
O	8.627400	1.847200	-1.067300
O	7.345000	0.431000	-3.687500
O	3.220400	1.787300	-4.483400
O	6.316100	2.345700	-7.243700
O	2.713100	5.001600	0.852600
O	5.885500	8.050000	0.977000
O	3.099200	7.177100	3.663700
O	5.587400	8.601100	6.317600
O	2.580900	5.528800	6.872800
O	6.232700	5.130300	8.220500
O	9.980500	4.399400	6.962400
O	6.963100	1.399700	7.631800
O	8.901600	1.340700	4.571200
O	7.419200	0.563700	1.461700
O	0.330500	3.654800	1.744100
O	3.728000	2.320400	7.015200
O	1.895600	2.902100	3.163600
O	5.034100	-0.035400	3.684200
Te	7.627700	5.870600	3.865900
Te	6.817900	6.870500	-3.402200
Ru	8.218500	5.035000	-4.992100
Ru	5.476800	5.795000	-5.637900
Ru	4.551700	5.345700	-2.993800
Ru	7.648300	4.498100	-2.248600
Ru	5.982000	3.129000	-4.301700
Ru	5.291900	5.430800	2.448500
Ru	7.466200	3.335200	2.768900
Ru	7.276200	3.727800	5.664600
Ru	5.234500	5.701800	5.351000
Ru	4.783000	2.981200	4.202400
Cu	5.405300	3.223900	-1.535700
Cu	5.138200	2.869600	1.452300
Cu	6.721200	4.625500	0.298300
Cl	4.396400	1.611100	-0.287500

[$TeRu_5(\mu$-$CO)_2(CO)_{12}(CuMeCN)_2$] (**3a**) ($DMol^3$)
Total energy = −2731.7844680 a.u.

	x	y	z
C	4.276700	0.487000	5.245700
C	6.821900	1.522300	6.176100
C	4.617200	2.661400	7.067300

C	7.484600	4.686100	4.802800
C	5.503400	6.445700	3.815300
C	7.254400	5.144900	2.042700
C	2.192900	2.928700	5.205100
C	2.531600	5.495800	4.151100
C	1.775700	3.339400	2.529600
C	3.472000	3.917100	0.042600
C	5.826100	2.757300	-0.208200
C	3.614000	1.257800	0.996700
C	2.185200	0.308500	3.295800
C	4.603700	-0.818300	2.709300
C	4.296400	6.910700	8.026400
C	2.943300	8.115200	0.656800
C	2.340700	9.309800	0.093500
H	2.047800	9.124800	-0.947100
H	3.057500	10.139100	0.117500
H	1.453600	9.587500	0.674600
Cu	4.613900	4.829100	5.764700
Cu	4.069900	5.519800	1.916500
N	4.424700	6.097500	7.200200
N	3.413300	7.148200	1.110100
O	3.950200	-0.411700	5.943300
O	7.749700	1.068600	6.714600
O	4.247200	2.764800	8.171600
O	8.370500	4.792400	5.547600
O	5.342200	7.585200	4.030700
O	8.002100	5.467300	1.215800
O	1.475600	2.537900	6.035200
O	1.954600	6.486300	4.397400
O	0.816000	3.160000	1.894600
O	2.763900	4.350300	-0.781000
O	6.551100	2.606400	-1.107300
O	3.048500	0.643400	0.158500
O	1.104100	-0.109100	3.382900
O	4.981000	-1.886800	2.454000
Ru	5.286400	2.243200	5.339100
Ru	6.098400	4.644500	3.484600
Ru	3.963900	0.927600	3.130400
Ru	4.629800	2.998800	1.236600
Ru	3.175200	3.719800	3.771300
Te	6.592800	1.999800	2.909400
C	4.126000	7.924800	9.053400
H	4.116900	7.453000	10.042900
H	4.951200	8.645400	9.008500
H	3.178700	8.455100	8.899600

[$TeRu_5(\mu\text{-}CO)_3(CO)_{11}Cu_2(MeCN)_2$] (**3b**) ($DMol^3$)
Total energy = −2731.7827685 a.u.

	x	y	z
C	1.042000	8.384500	4.368200
C	0.117900	8.322500	1.820600
C	2.910700	8.602500	2.324900
C	4.359200	7.669200	-0.001800
C	5.503700	7.618400	2.504000
C	5.202700	5.162200	1.114400
C	3.676600	2.950000	0.133900
C	4.843000	2.772900	2.631800
C	2.080500	2.556300	2.565700
C	0.228200	3.425200	4.492100
C	-0.525500	3.539500	1.938100
C	3.470000	6.942300	5.483600
C	5.238600	5.227900	4.256400
C	3.056800	4.096300	5.481900
C	-4.030100	6.099200	3.220700
C	-5.479300	6.020200	3.288100
H	-5.783800	4.978600	3.448500
H	-5.921900	6.382000	2.352800
H	-5.847700	6.632800	4.119800
C	-0.357500	6.155000	7.938500
C	-0.811300	6.281200	9.312000
H	-1.388100	7.205800	9.434000
H	0.054600	6.312400	9.984400
H	-1.438300	5.423500	9.583300
N	-2.863400	6.144300	3.176200
N	0.016800	6.069800	6.836100
O	0.830700	9.156100	5.219100
O	-0.605100	9.002000	1.205400
O	3.159400	9.757100	2.331400
O	4.618800	8.206000	-0.998000
O	6.433000	8.141200	2.962500
O	6.276300	5.008200	0.648500
O	3.719000	2.335100	-0.851000
O	5.569000	2.006400	3.115900
O	2.038600	1.381000	2.677600
O	-0.283500	2.829300	5.357900
O	-1.410700	3.060100	1.347400
O	3.654500	7.763800	6.292200
O	6.379000	5.059900	4.421400
O	2.985100	3.235900	6.266400
Cu	-0.961000	6.137700	3.166200
Cu	0.828500	5.890800	5.095500
Ru	1.384800	7.324000	2.826000
Ru	3.987800	6.823000	1.679800
Ru	3.608600	3.935100	1.778000
Ru	0.951600	4.214300	2.917900
Ru	3.347600	5.506100	4.217700
Te	1.672700	5.625300	0.646700

[$TeRu_5(\mu\text{-}CO)_2(CO)_{12}(CuMeCN)_2$] (**3a**)
(MPW1PW91/LanL2DZ, Gaussian 03)
G = −2721.798938 a.u.

	x	y	z
C	2.312396	-2.234983	-0.894914
C	1.327832	-3.293723	1.610624
C	-0.193079	-3.551219	-0.504542
C	-1.222481	-1.365723	2.812704
C	-2.889667	0.114076	1.110902
C	-1.107666	1.465348	2.804777
C	-0.056348	-1.364695	-2.549035
C	-2.320464	0.094258	-1.823541
C	0.043840	1.394226	-2.534990
C	0.096067	3.564335	-0.465939
C	1.599501	3.162435	1.636743
C	2.485821	2.046209	-0.878392
C	2.755885	-0.100139	-2.696287
C	4.202522	-0.168979	-0.389492
C	-4.304091	-3.776601	-0.732585
C	-4.005934	4.080933	-0.766292

C	-4.974825	5.089143	-1.166486
H	-4.461998	6.023632	-1.407480
H	-5.685413	5.274172	-0.357290
H	-5.524616	4.751391	-2.048436
Cu	-1.914815	-1.843932	-0.103529
Cu	-1.760042	1.997071	-0.096595
N	-3.467262	-3.018028	-0.439563
N	-3.223889	3.273080	-0.454279
O	2.983594	-3.075013	-1.419483
O	1.715569	-4.051620	2.420547
O	-0.621682	-4.543020	-0.981967
O	-1.392508	-2.187961	3.631728
O	-4.070568	0.161915	1.043078
O	-1.214613	2.299322	3.622864
O	0.121120	-2.151319	-3.405958
O	-3.394617	0.137045	-2.321938
O	0.278492	2.175132	-3.383385
O	-0.251365	4.593773	-0.929484
O	2.052372	3.878692	2.450648
O	3.221954	2.833594	-1.397634
O	3.031408	-0.105796	-3.834080
O	5.337327	-0.216114	-0.104675
Ru	0.701347	-2.095345	0.299692
Ru	-1.033174	0.040816	1.548882
Ru	2.361575	-0.092150	-0.855075
Ru	0.869972	2.031073	0.319744
Ru	-0.472104	0.025434	-1.333080
Te	1.658750	-0.075787	1.854258
C	-5.339794	-4.727434	-1.105073
H	-4.890798	-5.699039	-1.325888
H	-6.055451	-4.846846	-0.288058
H	-5.871895	-4.375019	-1.992068

$[TeRu_5(\mu\text{-}CO)_3(CO)_{11}Cu_2(MeCN)_2]$ (**3b**)
(MPW1PW91/LanL2DZ, Gaussian 03)
G = − 2721.800041 a.u.

	x	y	z
C	-2.040478	0.461136	-2.409331
C	-1.600539	-2.150931	-2.097017
C	0.561993	-0.479088	-2.946482
C	2.882489	-2.047174	-2.185386
C	2.988869	0.683898	-2.541062
C	3.607999	-0.345615	-0.007354
C	2.949478	-1.420211	2.562074
C	3.077981	1.303324	2.195982
C	0.656894	0.324875	2.957376
C	-1.970662	1.077063	2.280665
C	-1.509869	-1.526331	2.657039
C	0.006450	2.544771	-1.766445
C	2.366202	2.455614	-0.348144
C	0.033934	2.926257	1.038586
C	-5.408461	-2.712395	0.272118
C	-6.591380	-3.559541	0.279934
H	-6.917765	-3.742149	1.306701
H	-6.366432	-4.518642	-0.193347
H	-7.404601	-3.079207	-0.269627
C	-4.154963	3.697241	-0.392598
C	-5.050787	4.836959	-0.510784
H	-5.527799	4.840533	-1.493902
H	-4.489173	5.766644	-0.389537
H	-5.824081	4.791765	0.259888
N	-4.454039	-2.038258	0.263934
N	-3.427851	2.789960	-0.299024
O	-2.823149	0.987037	-3.119824
O	-2.089612	-3.126295	-2.543419
O	0.591894	-0.439609	-4.140283
O	3.385177	-2.980439	-2.683652
O	3.573220	1.378128	-3.279534
O	4.800995	-0.354337	-0.025124
O	3.464109	-2.198476	3.270254
O	3.689937	2.155220	2.713889
O	0.725641	0.689858	4.092936
O	-2.737342	1.769683	2.851770
O	-1.967501	-2.351528	3.363175
O	-0.307266	3.177654	-2.709178
O	3.365933	3.067450	-0.439090
O	-0.264480	3.789215	1.783116
Cu	-2.751056	-1.098466	0.207573
Cu	-1.974735	1.444981	-0.154631
Ru	-0.786492	-0.577651	-1.443772
Ru	2.059629	-0.508778	-1.407013
Ru	2.105925	-0.128876	1.436066
Ru	-0.736981	-0.178467	1.582918
Ru	0.653466	1.646403	-0.222501
Te	0.608763	-2.142561	0.280079

Intermediate **I1** (MPW1PW91/LanL2DZ, Gaussian 03)
G = − 2721.796720 a.u.

	x	y	z
C	-2.669176	1.936656	-0.748552
C	-1.703747	3.083257	1.726364
C	-0.337501	3.561584	-0.484073
C	1.213649	0.682337	3.217691
C	2.897591	0.329821	1.185510
C	1.203184	-1.914954	1.858224
C	-0.274479	1.485521	-2.566794
C	2.213197	0.470747	-1.840626
C	0.119697	-1.251114	-2.657618
C	0.384466	-3.518768	-0.535175
C	-1.278770	-3.376384	1.559341
C	-2.133151	-2.294280	-0.925953
C	-2.823368	-0.186702	-2.595662
C	-4.186560	-0.456613	-0.230280
C	3.797555	4.365894	-0.455352
C	4.599486	-3.368415	-0.786041
C	5.766875	-4.227265	-0.905207
H	5.477910	-5.194754	-1.323161
H	6.215448	-4.388112	0.078165
H	6.509090	-3.766223	-1.561316
Cu	1.595492	2.149844	-0.032673
Cu	2.040723	-1.604650	-0.495388
N	3.023841	3.514565	-0.259450
N	3.660505	-2.684068	-0.686222
O	-3.513690	2.625750	-1.237432
O	-2.113126	3.772973	2.585487
O	-0.055041	4.604996	-0.961353
O	1.335704	1.103808	4.307094

O	4.070484	0.486512	1.153029
O	1.769883	-2.749103	2.506321
O	-0.591501	2.260806	-3.391917
O	3.273517	0.690550	-2.327466
O	0.001238	-2.048269	-3.514417
O	0.820270	-4.471919	-1.070140
O	-1.749680	-4.165591	2.284598
O	-2.660765	-3.214092	-1.473877
O	-3.139257	-0.157557	-3.722102
O	-5.306246	-0.586780	0.085986
Ru	-1.015314	2.003114	0.342337
Ru	1.052758	0.018585	1.459592
Ru	-2.368835	-0.251851	-0.765975
Ru	-0.486851	-2.114399	0.390069
Ru	0.379109	0.143675	-1.394273
Te	-1.626275	-0.120184	1.908524
C	4.759318	5.427303	-0.709540
H	4.243898	6.318046	-1.077183
H	5.292878	5.682182	0.209315
H	5.484332	5.104387	-1.460619

Intermediate **I2** (MPW1PW91/LanL2DZ, Gaussian 03)
G = − 2721.774846 a.u.

	x	y	z
C	-2.178222	2.509643	-0.573459
C	-0.801115	3.131085	1.944869
C	0.432800	3.450664	-0.338239
C	0.971684	-0.830369	3.362976
C	2.798057	-0.141602	1.681025
C	0.863618	-2.402016	0.965385
C	0.936162	1.416575	-2.356800
C	1.545153	-1.298344	-2.298522
C	-0.912036	-0.657687	-2.737879
C	-0.650415	-3.317817	-1.127319
C	-1.923582	-3.250380	1.341288
C	-2.901796	-1.715453	-0.865150
C	-3.259124	0.731288	-2.396932
C	-4.243248	0.608523	0.071768
C	4.337349	3.559146	-0.415748
C	5.217664	-2.687313	-0.714805
C	6.334855	-3.615793	-0.784654
H	7.102336	-3.237086	-1.463857
H	5.988432	-4.585528	-1.150653
H	6.773060	-3.750319	0.207224
Cu	2.004289	1.503073	0.052937
Cu	2.602682	-0.986261	-0.480329
N	3.587553	2.683595	-0.232368
N	4.313897	-1.952481	-0.650828
O	-2.790365	3.450925	-0.985885
O	-0.949861	3.816993	2.887552
O	0.928382	4.433521	-0.764155
O	1.036176	-1.058250	4.513362
O	3.909399	0.047974	2.066851
O	1.522833	-3.405836	1.053270
O	1.296439	2.259743	-3.099817
O	2.024483	-1.963042	-3.156215
O	-1.434644	-1.085234	-3.706158
O	-0.374392	-4.163250	-1.889104
O	-2.405093	-4.038941	2.061431
O	-3.769106	-2.377577	-1.345316
O	-3.778487	0.999639	-3.408040
O	-5.301650	0.771481	0.544200
Ru	-0.542767	2.033296	0.440085
Ru	0.937685	-0.483528	1.502806
Ru	-2.529635	0.360008	-0.683784
Ru	-1.107404	-2.005129	0.147259
Ru	0.307426	-0.101565	-1.403198
Te	-1.660369	0.054644	1.926490
C	5.252164	4.664727	-0.652174
H	4.696411	5.527459	-1.028354
H	5.754208	4.945737	0.276795
H	6.006279	4.382855	-1.390886

TS (MPW1PW91/LanL2DZ, Gaussian 03)
G = − 2721.770974 a.u.

	x	y	z
C	-1.542814	2.676430	-1.156970
C	-0.035880	3.458968	1.236929
C	1.206740	2.952681	-1.041854
C	0.814629	-0.569877	3.413280
C	2.709728	-0.823000	1.705057
C	0.272201	-2.467252	1.296642
C	1.173963	0.510737	-2.583068
C	0.957731	-2.210630	-1.762420
C	-1.185285	-0.967986	-2.635551
C	-1.639030	-3.320173	-0.517562
C	-2.610703	-2.486131	1.921372
C	-3.342728	-1.163236	-0.520919
C	-3.189452	0.914951	-2.507495
C	-3.989394	1.576086	-0.059113
C	5.103163	2.729716	0.148955
C	5.032807	-2.757369	-1.371982
C	6.104865	-3.647631	-1.788586
H	6.750597	-3.883690	-0.939353
H	6.705095	-3.178751	-2.572051
H	5.682705	-4.577234	-2.178777
Cu	2.345039	1.245812	0.367436
Cu	2.472118	-1.180400	-0.506700
N	4.144859	2.069043	0.240500
N	4.163043	-2.055041	-1.037345
O	-1.891788	3.618365	-1.805518
O	-0.005709	4.354122	1.998955
O	1.914333	3.655225	-1.673567
O	0.845620	-0.593296	4.587161
O	3.808247	-1.003086	2.133548
O	0.688091	-3.573801	1.493614
O	1.779078	1.037810	-3.446321
O	1.262046	-3.263898	-2.209668
O	-1.813711	-1.415058	-3.529343
O	-1.689068	-4.329861	-1.106718
O	-3.210951	-2.980135	2.797702
O	-4.379746	-1.660131	-0.839741
O	-3.703137	1.090188	-3.541651
O	-4.932231	2.110130	0.384321
Ru	-0.069083	2.031882	0.010305
Ru	0.830770	-0.565181	1.518835
Ru	-2.452574	0.732117	-0.767317
Ru	-1.611226	-1.720936	0.485979
Ru	0.135738	-0.518703	-1.365895

Te	-1.530699	0.690377	1.841074
C	6.288758	3.564170	0.028639
H	6.279707	4.087998	-0.930467
H	6.309103	4.304635	0.832145
H	7.192464	2.953240	0.090982

Table S7 Cyclic voltammetry and differential pulse voltammetry of **1**, **3a**, and **3b**

Cyclic Voltammetry	oxidation process		reduction process	
complex	Ep^{ox}/V^{a}	Ep^{red}/V^{b}	Ep^{ox}/V^{a}	Ep^{red}/V^{b}
1	0.225	- [d]	−0.048	
	~ 0.363[e]	- [d]	−0.199	
				−0.894
				−1.144
				−1.329
				~ −1.817
3a	0.117	- [d]	−0.010	
	0.411[e]		- [d]	
				−0.767
				−1.100
			- [d]	−1.810
3b	0.129	- [d]	−0.030	
			−0.120	
				−0.799
				−1.090
			−1.720	−1.830

Differential Pulse Voltammetry	oxidation process		reduction process	
complex	Ep^{ox}/V^{a} ($W_{1/2}$/mV[c])	Ep^{red}/V^{b} ($W_{1/2}$/mV[c])	Ep^{ox}/V^{a} ($W_{1/2}$/mV[c])	Ep^{red}/V^{b} ($W_{1/2}$/mV[c])
1	~ 0.133, 0.197 (184)	0.124, 0.184 (217)	−0.339[f] (163)	
	~ 0.377[e] (br)	0.366[e] (96)	−1.047 (183)	−0.674 (82)
				−1.112 (174)
			−1.275 (116)	−1.294 (97)
			−1.375 (102)	−1.396 (108)
			−1.743 (123)	−1.760 (122)
			−1.905[g] (116)	−1.916[g] (91)
3a	0.088 (78)	0.134 (119)	−0.376[f] (291)	
	0.388[e] (120)	0.446[e] (120)		−0.528 (102)
				−0.680 (60)
				−1.148 (141)
			−1.376 (135)	−1.376 (108)
			−1.770 (100)	−1.776 (85)
3b	0.102 (88)	0.154 (120)	−0.376[f] (333)	
	0.414[e] (128)	- [d,e] (br)		−0.636 (51)
				−1.116 (br)
			−1.354 (106)	−1.342 (111)
			−1.770 (109)	−1.800 (98)

[a] Ep^{ox} = oxidative peak potential. [b] Ep^{red} = reductive peak potential. [c] $W_{1/2}$ = width at half-height. [d] Difficult to determine. [e] A metal-centered Cu(I) → Cu(II) oxidation. [f] The irreversible desorption of Cu. [g] The interference of $[PPh_4]^+$.

Table S8 Selected bond distances (Å) and bond angles (deg) for $[PPh_4]_2$[**1**], $[PPh_4]_4$[**2**]·$3Et_2O$, **3a**, and **3b**·$0.5CH_2Cl_2$

$[PPh_4]_2$[**1**]			
Te(1)─Ru(6)	2.674(2)	Te(1)─Ru(7)	2.663(2)
Te(1)─Ru(8)	2.744(2)	Te(1)─Ru(9)	2.728(2)
Te(2)─Ru(1)	2.731(2)	Te(2)─Ru(2)	2.748(2)
Te(2)─Ru(3)	2.675(2)	Te(2)─Ru(4)	2.677(2)
Ru(1)─Ru(2)	2.832(2)	Ru(1)─Ru(4)	2.834(2)
Ru(2)─Ru(3)	2.809(2)	Ru(3)─Ru(4)	3.071(2)
Ru(6)─Ru(7)	3.070(2)	Ru(6)─Ru(9)	2.839(2)
Ru(7)─Ru(8)	2.823(2)	Ru(8)─Ru(9)	2.819(2)
Ru(5)─Ru(1)	2.826(2)	Ru(5)─Ru(2)	2.889(2)
Ru(5)─Ru(3)	2.900(2)	Ru(5)─Ru(4)	2.880(2)
Ru(10)─Ru(6)	2.890(2)	Ru(10)─Ru(7)	2.912(2)
Ru(10)─Ru(8)	2.847(2)	Ru(10)─Ru(9)	2.842(2)
Cu(1)─Ru(3)	2.653(3)	Cu(1)─Ru(4)	2.693(3)
Cu(1)─Ru(5)	2.691(3)	Cu(3)─Ru(4)	2.583(7)
Cu(3)─Ru(6)	2.568(7)	Cu(2)─Ru(6)	2.670(3)
Cu(2)─Ru(7)	2.655(3)	Cu(2)─Ru(10)	2.661(3)
Cu(1)─Cu(3)	2.600(7)	Cu(1)─Cu(2)	2.938(4)
Cu(2)─Cu(3)	2.484(8)	Cu(1)─Cl(1)	2.235(6)
Cu(2)─Cl(1)	2.218(6)	Te(1)─Ru(7)	2.663(2)
Cu(2)─Ru(7)─Ru(10)	56.89(7)	Cu(1)─Ru(4)─Ru(1)	116.46(9)
Cu(2)─Ru(7)─Cu(3)	52.4(2)	Cu(3)─Ru(4)─Ru(5)	115.8(2)
Te(1)─Ru(7)─Cu(3)	83.9(2)	Cu(1)─Ru(4)─Ru(5)	57.63(7)
Ru(8)─Ru(7)─Cu(3)	136.9(2)	Cu(3)─Ru(4)─Ru(3)	78.0(2)
Ru(10)─Ru(7)─Cu(3)	97.9(2)	Cu(1)─Ru(4)─Ru(3)	54.33(7)
Cu(2)─Ru(7)─Ru(6)	55.03(7)	Cu(1)─Ru(5)─Ru(1)	116.81(9)
Cu(3)─Ru(7)─Ru(6)	50.5(1)	Cu(1)─Ru(5)─Ru(4)	57.71(7)
Cu(1)─Ru(3)─Te(2)	110.58(8)	Cu(1)─Ru(5)─Ru(2)	114.42(9)
Cu(1)─Ru(3)─Ru(2)	118.40(9)	Cu(1)─Ru(5)─Ru(3)	56.50(7)
Cu(1)─Ru(3)─Ru(5)	57.77(7)	Cu(3)─Ru(6)─Cu(2)	56.6(2)
Cu(1)─Ru(3)─Ru(4)	55.57(7)	Cu(3)─Ru(6)─Te(1)	91.3(2)
Cu(3)─Ru(4)─Cu(1)	59.0(2)	Cu(2)─Ru(6)─Te(1)	109.26(8)
Te(2)─Ru(4)─Cu(1)	109.28(8)	Cu(3)─Ru(6)─Ru(9)	147.0(2)
Cu(3)─Ru(4)─Ru(1)	163.4(2)	Cu(2)─Ru(6)─Ru(9)	116.16(9)
Cu(3)─Ru(6)─Ru(10)	107.7(2)	Cl(1)─Cu(2)─Ru(7)	132.9(2)

Cu(2)─Ru(6)─Ru(10)	57.03(7)	Cu(3)─Cu(2)─Ru(7)	69.7(2)
Cu(3)─Ru(6)─Ru(7)	62.1(2)	Cl(1)─Cu(2)─Ru(10)	136.7(2)
Cu(2)─Ru(6)─Ru(7)	54.55(7)	Cu(3)─Cu(2)─Ru(10)	118.0(2)
Cu(2)─Ru(7)─Te(1)	110.07(8)	Ru(7)─Cu(2)─Ru(10)	66.43(8)
Cu(2)─Ru(7)─Ru(8)	116.23(8)	Cl(1)─Cu(2)─Ru(6)	149.2(2)
Cu(2)─Ru(10)─Ru(9)	116.32(9)	Cu(3)─Cu(2)─Ru(6)	59.6(2)
Cu(2)─Ru(10)─Ru(8)	115.20(8)	Ru(7)─Cu(2)─Ru(6)	70.42(8)
Cu(2)─Ru(10)─Ru(6)	57.32(7)	Ru(10)─Cu(2)─Ru(6)	65.64(8)
Cu(2)─Ru(10)─Ru(7)	56.67(7)	Cl(1)─Cu(2)─Cu(1)	49.0(2)
Cl(1)─Cu(1)─Cu(3)	101.1(2)	Cu(3)─Cu(2)─Cu(1)	56.6(2)
Cl(1)─Cu(1)─Ru(3)	130.7(2)	Ru(7)─Cu(2)─Cu(1)	111.6(1)
Cu(3)─Cu(1)─Ru(3)	85.9(2)	Ru(10)─Cu(2)─Cu(1)	174.0(1)
Cl(1)─Cu(1)─Ru(5)	136.0(2)	Ru(6)─Cu(2)─Cu(1)	108.4(1)
Cu(3)─Cu(1)─Ru(5)	122.2(2)	Cu(2)─Cu(3)─Ru(6)	63.8(2)
Ru(3)─Cu(1)─Ru(5)	65.72(8)	Cu(2)─Cu(3)─Ru(4)	131.0(3)
Cl(1)─Cu(1)─Ru(4)	152.5(2)	Ru(6)─Cu(3)─Ru(4)	159.8(3)
Cu(3)─Cu(1)─Ru(4)	58.4(2)	Cu(2)─Cu(3)─Cu(1)	70.6(2)
Ru(3)─Cu(1)─Ru(4)	70.10(8)	Ru(6)─Cu(3)─Cu(1)	123.5(3)
Ru(5)─Cu(1)─Ru(4)	64.67(8)	Ru(4)─Cu(3)─Cu(1)	62.6(2)
Cl(1)─Cu(1)─Cu(2)	48.5(2)	Cu(2)─Cu(3)─Ru(7)	57.9(2)
Cu(3)─Cu(1)─Cu(2)	52.9(2)	Ru(6)─Cu(3)─Ru(7)	67.4(2)
Ru(3)─Cu(1)─Cu(2)	114.9(1)	Ru(4)─Cu(3)─Ru(7)	130.5(3)
Ru(5)─Cu(1)─Cu(2)	174.2(1)	Cu(1)─Cu(3)─Ru(7)	113.3(3)
Ru(4)─Cu(1)─Cu(2)	109.8(1)	Cu(2)─Cl(1)─Cu(1)	82.6(2)
Cl(1)─Cu(2)─Cu(3)	105.3(2)		

$[PPh_4]_4$[**2**]·3Et_2O

Te(1)─Ru(1)	2.722(2)	Te(1)─Ru(2)	2.727(2)
Te(1)─Ru(3)	2.677(2)	Te(1)─Ru(4)	2.678(2)
Te(2)─Ru(6)	2.736(2)	Te(2)─Ru(7)	2.744(2)
Ru(1)─Ru(2)	2.804(2)	Ru(1)─Ru(4)	2.862(2)
Ru(3)─Ru(2)	2.844(2)	Ru(3)─Ru(4)	2.869(2)
Ru(5)─Ru(1)	2.878(2)	Ru(5)─Ru(2)	2.888(2)
Ru(5)─Ru(3)	2.864(2)	Ru(5)─Ru(4)	2.817(2)
Ru(6)─Ru(7)	2.969(2)	Ru(6)─Ru(7a)	2.808(2)
Cu(1)─Ru(4)	2.608(2)	Cu(1)─Ru(6)	2.694(2)
Cu(1)─Ru(7)	2.675(2)	Te(1)─Cu(1)	2.912(2)
Ru(4)─Cu(1)─Ru(7)	133.04(9)	Cu(1)─Ru(7)─Te(2)	97.29(6)

Ru(4)─Cu(1)─Ru(6)	147.40(9)	Cu(1)─Ru(7)─Te(2a)	97.61(7)
Ru(7)─Cu(1)─Ru(6)	67.13(6)	Cu(1)─Ru(7)─Ru(6a)	146.44(7)
Ru(4)─Cu(1)─Te(1)	57.72(5)	Cu(1)─Ru(7)─Ru(6)	56.74(5)
Ru(7)─Cu(1)─Te(1)	168.66(8)	Cu(1)─Ru(4)─Ru(1)	123.16(6)
Ru(6)─Cu(1)─Te(1)	101.73(7)	Cu(1)─Ru(4)─Ru(3)	74.14(7)
Cu(1)─Ru(4)─Te(1)	66.85(6)	Ru(3)─Te(1)─Cu(1)	72.44(6)
Cu(1)─Ru(4)─Ru(5)	134.60(8)	Ru(4)─Te(1)─Cu(1)	55.43(5)
Cu(1)─Ru(6)─Te(2)	97.03(6)	Ru(1)─Te(1)─Cu(1)	117.30(6)
Cu(1)─Ru(6)─Te(2a)	97.34(6)	Ru(2)─Te(1)─Cu(1)	135.00(6)
Cu(1)─Ru(6)─Ru(7a)	146.42(7)		
Cu(1)─Ru(6)─Ru(7)	56.13(5)		

3a

Te(1)─Ru(1)	2.6721(3)	Te(1)─Ru(2)	2.6723(3)
Te(1)─Ru(3)	2.6814(3)	Te(1)─Ru(4)	2.7616(3)
Ru(1)─Ru(2)	2.9995(3)	Ru(1)─Ru(4)	2.8079(3)
Ru(3)─Ru(2)	3.0022(3)	Ru(3)─Ru(4)	2.8044(3)
Ru(5)─Ru(1)	2.8869(3)	Ru(5)─Ru(2)	2.9147(3)
Ru(5)─Ru(3)	2.8986(3)	Ru(5)─Ru(4)	2.8689(3)
Cu(1)─Ru(1)	2.5953(4)	Cu(1)─Ru(2)	2.6502(4)
Cu(1)─Ru(5)	2.6583(4)	Cu(2)─Ru(2)	2.6304(4)
Cu(2)─Ru(3)	2.6250(4)	Cu(2)─Ru(5)	2.6560(4)

Cu(1)─Ru(1)─Ru(2)	55.99(1)	Cu(1)─Ru(1)─Ru(5)	57.72(1)
Cu(1)─Ru(2)─Ru(1)	54.27(1)	Cu(1)─Ru(2)─Ru(5)	56.83(1)
Cu(2)─Ru(2)─Ru(5)	56.96(1)	Cu(2)─Ru(2)─Ru(3)	55.08(1)
Cu(2)─Ru(3)─Ru(2)	55.25(1)	Cu(2)─Ru(3)─Ru(5)	57.23(1)
Ru(1)─Cu(1)─N(1)	143.89(9)	Ru(2)─Cu(1)─N(1)	131.20(8)
Ru(5)─Cu(1)─N(1)	143.87(9)	Ru(2)─Cu(2)─N(2)	136.89(8)
Ru(5)─Cu(2)─N(2)	146.85(9)	Ru(3)─Cu(2)─N(2)	135.87(9)
Ru(1)─Cu(1)─Ru(2)	69.75(1)	Cu(2)─Ru(3)─Te(1)	110.900(1)
Ru(1)─Cu(1)─Ru(5)	66.65(1)	Cu(2)─Ru(3)─Ru(4)	117.54(1)
Ru(2)─Cu(1)─Ru(5)	66.61(1)	Cu(2)─Ru(5)─Cu(1)	94.09(1)
Ru(5)─Cu(2)─Ru(3)	66.58(1)	Cu(2)─Ru(5)─Ru(4)	114.33(1)
Ru(5)─Cu(2)─Ru(2)	66.92(1)	Cu(1)─Ru(5)─Ru(4)	113.99(1)
Ru(3)─Cu(2)─Ru(2)	69.68(1)	Cu(2)─Ru(5)─Ru(1)	117.86(1)
Cu(1)─Ru(1)─Te(1)	111.78(1)	Cu(1)─Ru(5)─Ru(1)	55.63(1)
Cu(1)─Ru(1)─Ru(4)	118.15(1)	Cu(2)─Ru(5)─Ru(3)	56.20(1)
Cu(1)─Ru(2)─Cu(2)	94.88(1)	Cu(1)─Ru(5)─Ru(3)	118.11(1)

Cu(1)─Ru(2)─Te(1)	110.06(1)	Cu(2)─Ru(5)─Ru(2)	56.12(1)
Cu(2)─Ru(2)─Te(1)	111.02(1)	Cu(1)─Ru(5)─Ru(2)	56.56(1)
Cu(1)─Ru(2)─Ru(3)	114.87(1)	Cu(1)─N(1)─C(15)	177.3(3)
Cu(2)─Ru(2)─Ru(1)	114.88(1)	Cu(2)─N(2)─C(17)	168.6(3)

3b·0.5CH_2Cl_2

Te(1)─Ru(1)	2.6714(6)	Te(1)─Ru(2)	2.6742(6)
Te(1)─Ru(3)	2.7080(7)	Te(1)─Ru(4)	2.7123(7)
Ru(1)─Ru(2)	3.0150(8)	Ru(1)─Ru(4)	2.8235(7)
Ru(3)─Ru(2)	2.8177(7)	Ru(3)─Ru(4)	2.8465(8)
Ru(5)─Ru(1)	2.9009(7)	Ru(5)─Ru(2)	2.8970(7)
Ru(5)─Ru(3)	2.8192(7)	Ru(5)─Ru(4)	2.8247(7)
Cu(1)─Ru(1)	2.588(1)	Cu(1)─Ru(2)	2.655(1)
Cu(2)─Ru(1)	2.6321(9)	Cu(2)─Ru(2)	2.6445(9)
Cu(2)─Ru(5)	2.660(1)	Cu(1)─Cu(2)	2.645(1)

Cu(1)─Ru(1)─Ru(2)	55.95(2)	Cu(1)─Ru(1)─Ru(5)	106.83(3)
Cu(1)─Ru(2)─Ru(1)	53.86(2)	Cu(1)─Ru(2)─Ru(5)	105.15(3)
Cu(2)─Ru(1)─Ru(2)	55.35(2)	Cu(2)─Ru(1)─Ru(5)	57.23(2)
Cu(2)─Ru(2)─Ru(1)	54.96(2)	Cu(2)─Ru(2)─Ru(5)	57.16(2)
Cu(1)─Ru(1)─Cu(2)	60.87(3)	Cu(1)─Ru(2)─Cu(2)	59.87(3)
Ru(1)─Cu(1)─Cu(2)	60.38(3)	Cu(2)─Ru(2)─Te(1)	110.52(3)
Ru(1)─Cu(1)─Ru(2)	70.19(3)	Cu(1)─Ru(2)─Te(1)	82.36(3)
Cu(2)─Cu(1)─Ru(2)	59.86(3)	Cu(2)─Ru(2)─Ru(3)	116.07(3)
Cu(2)─Ru(1)─Cu(1)	60.87(3)	Cu(1)─Ru(2)─Ru(3)	137.93(3)
Ru(2)─Ru(1)─Cu(1)	55.95(2)	Cu(2)─Ru(5)─Ru(3)	115.50(3)
Cu(1)─Ru(1)─Ru(5)	106.83(3)	Cu(2)─Ru(5)─Ru(4)	115.23(3)
Cu(1)─Ru(1)─Te(1)	83.68(3)	Cu(2)─Ru(5)─Ru(2)	56.64(2)
Cu(2)─Ru(1)─Te(1)	110.99(3)	Cu(2)─Ru(5)─Ru(1)	56.30(2)
Cu(1)─Ru(1)─Ru(4)	139.81(3)		
Cu(2)─Ru(1)─Ru(4)	116.20(3)		

Fig. S1 Variable temperature ^{1}H NMR spectra for **3a** from −40 to 50 ^{o}C in $CDCl_3$.

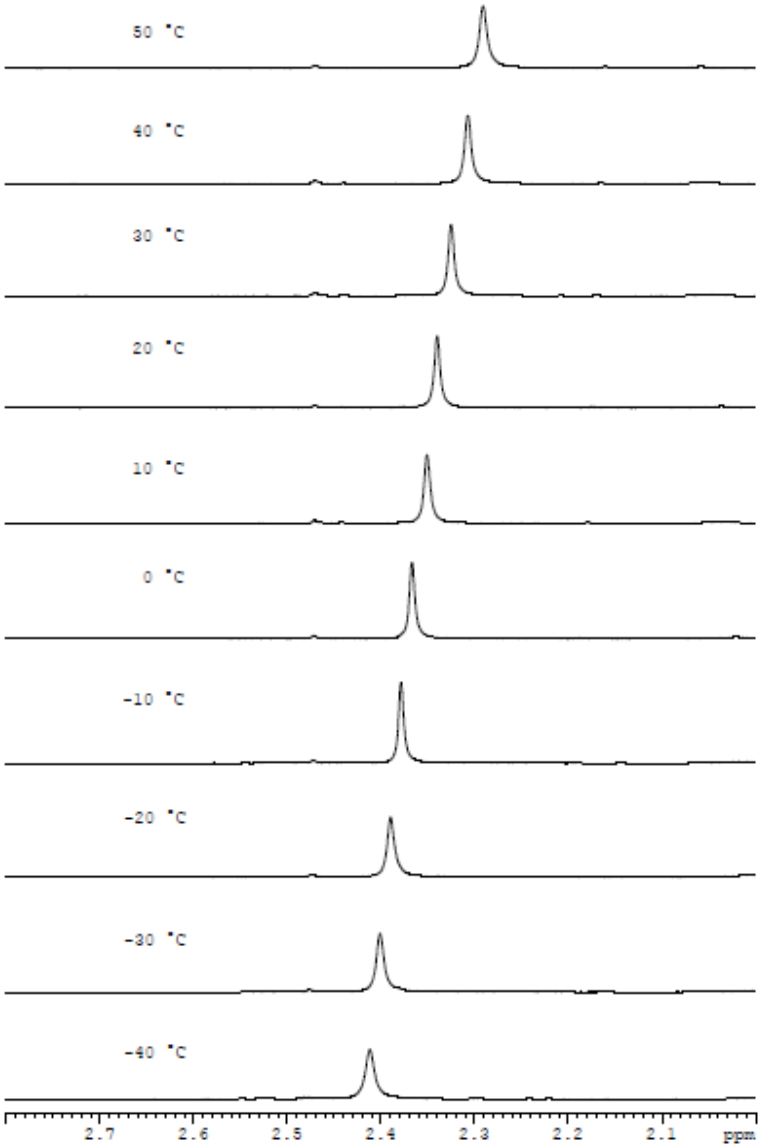


Fig. S2 Spatial graphs (isovalue = 0.02−0.03) of the frontier molecular orbitals and their associated calculated energies of $[TeRu_5(CO)_{14}]^{2-}$, **1**, **3a**, and **3b**

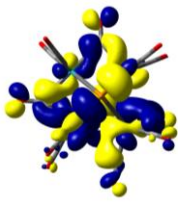
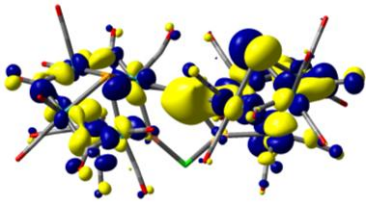
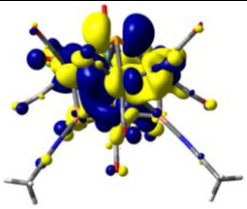
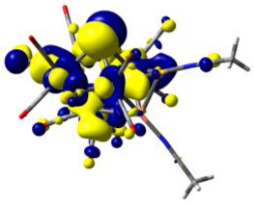
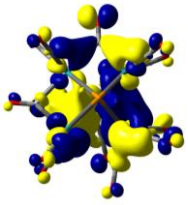
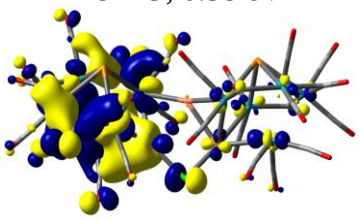
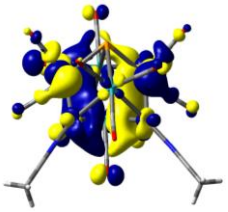
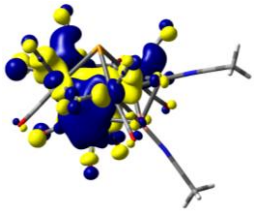
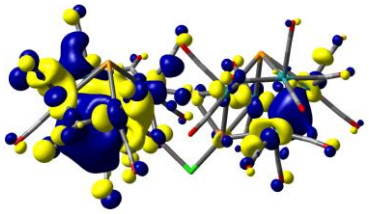
$[TeRu_5(CO)_{14}]^{2-}$	**1**	**3a**	**3b**
 LUMO, 2.68 eV	 LUMO, 0.58 eV	 LUMO, −3.06 eV	 LUMO, −2.97 eV
 HOMO, −0.32 eV	 HOMO, −2.22 eV	 HOMO, −5.93 eV	 HOMO, −5.97 eV
	 HOMO−1, −2.37 eV		

Fig. S3 Experimental (black) electronic absorption spectra of **1** in CH_2Cl_2. Vertical bars indicate the locations of calculated TD-DFT singlet-singlet excitations with oscillator strength (*f*) (blue, bar)

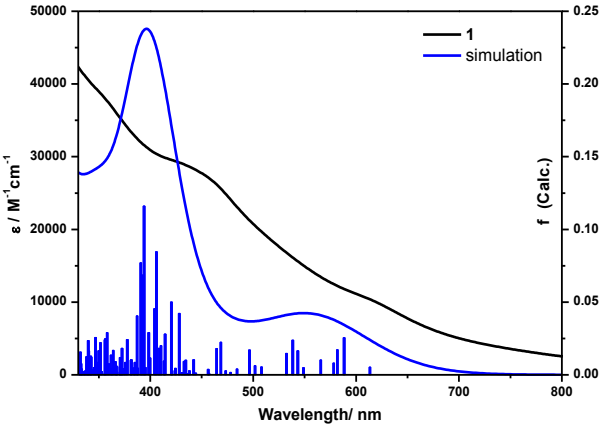


Fig. S4 Spatial plots (isovalue = 0.025) of selected frontier orbitals for **1**, with calculations in CH_2Cl_2. Calculated numerical values for the MO localization (in %) on the fragments Te/Ru/Cu/Cl/CO, respectively

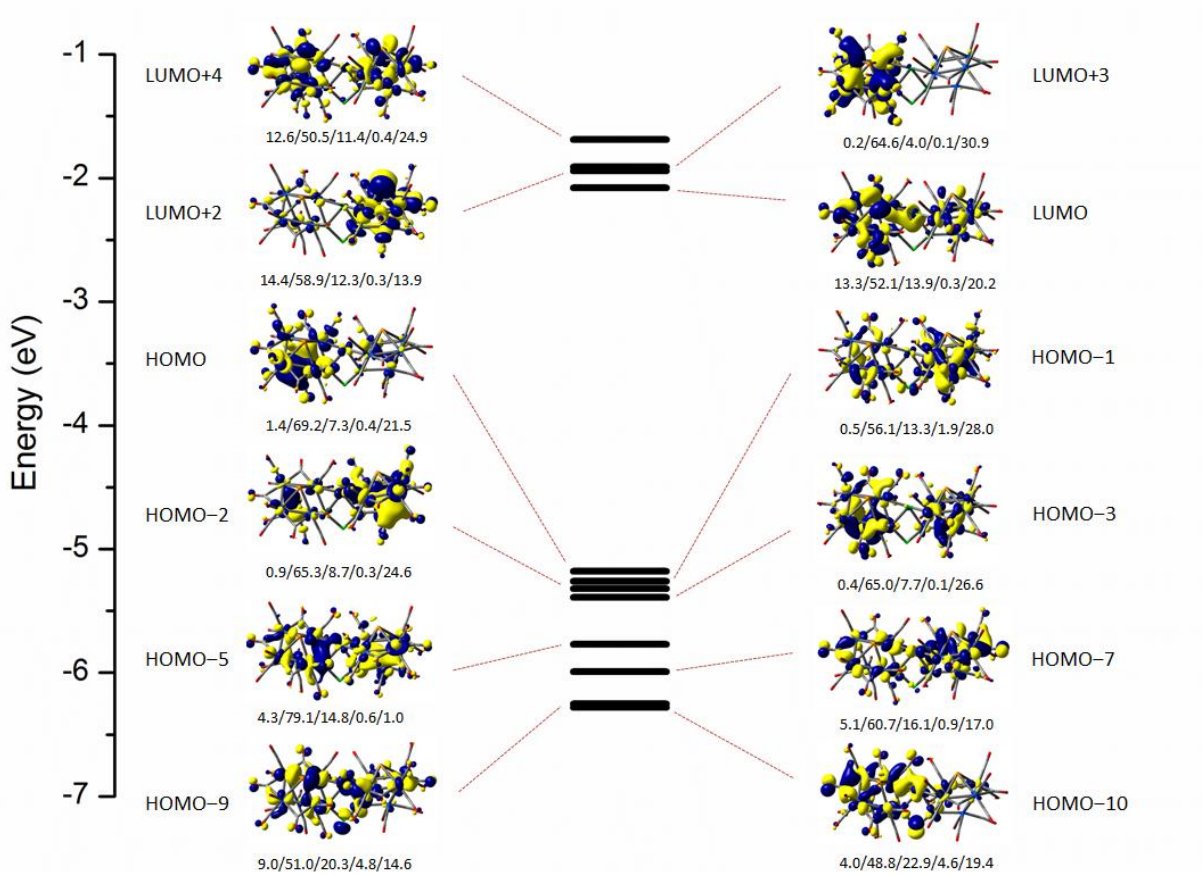


Fig. S5 CV in MeCN for **1**, **3a**, and **3b**. Conditions: electrolyte, 0.1 M Bu_4NClO_4; working electrode, glassy carbon; scan rate, 100 mV S^{-1}. Potentials are vs SCE

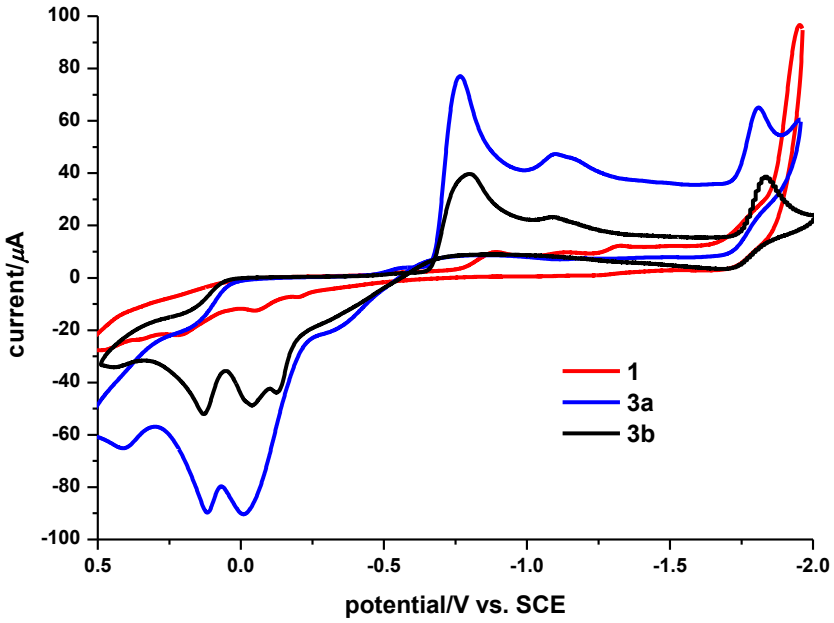


Fig. S6 Charge vs. time plots for controlled-potential coulometry (CPC) experiments of different analytes (ferrocene (Fc), tris(2,2'-bipyridine)ruthenium(II) dichloride ($Ru(bpy_3)Cl_2$), **1**, **3a**, and **3b**)

$$\frac{\Delta Q}{nF} = kC$$

$$k = m\,(2\sqrt{Dt})\,A$$

$$\frac{\Delta Q}{F} = nkC = n\,m\,(2\sqrt{Dt})\,A\,C$$

$$\frac{Q1\ (Fc \rightarrow Fc^{+})}{Q2\ (analyte\ \rightarrow\ analyte^{+})} = \frac{n1\ (n1 = 1)}{n2}$$

Q: the total charge in coulombs (C), F: Faraday's constant (C/mol),
n: the number of electrons per mole of analyte, m: proportional constant,
D: diffusion coefficient ($\approx 10^{-5}\ cm^2/sec$), t: period of time for electrolysis (sec),
A: the electrode's area, $\pi r^2 (cm^2)$, C: concentration (mol/L)

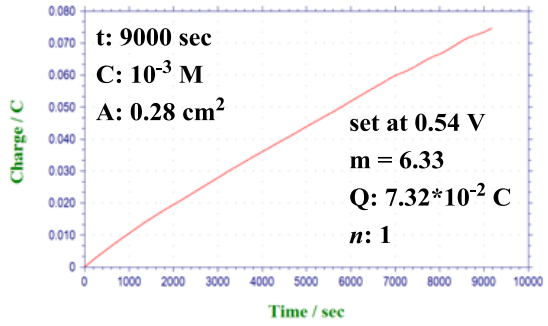
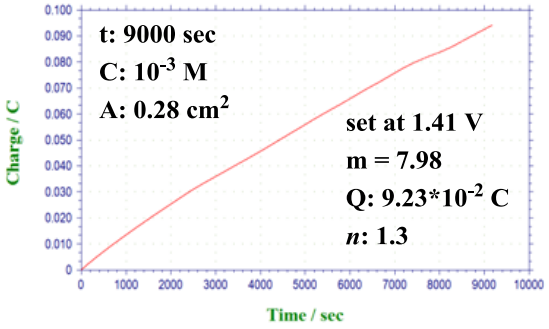
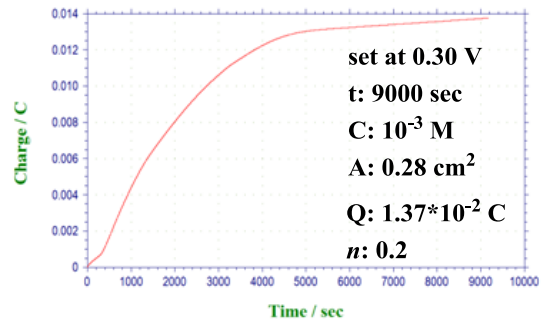
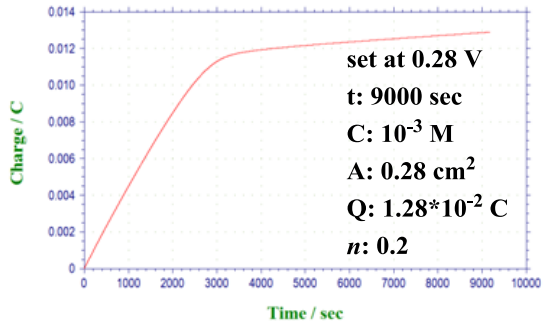
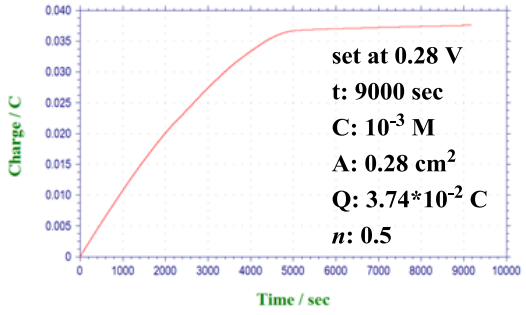
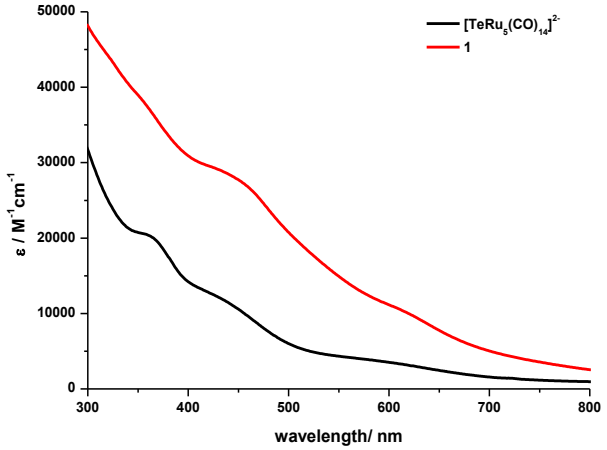
Fc	$Ru(bpy_3)Cl_2$
	
1	**3a**
	
3b	
	

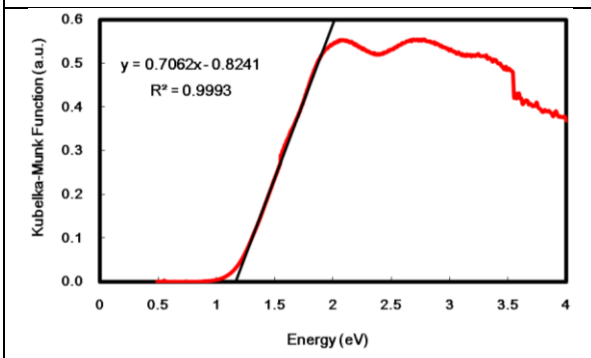
Fig. S7 UV-vis spectra of **1** (red) and the parent cluster $[TeRu_5(CO)_{14}]^{2-}$ (black) in CH_2Cl_2



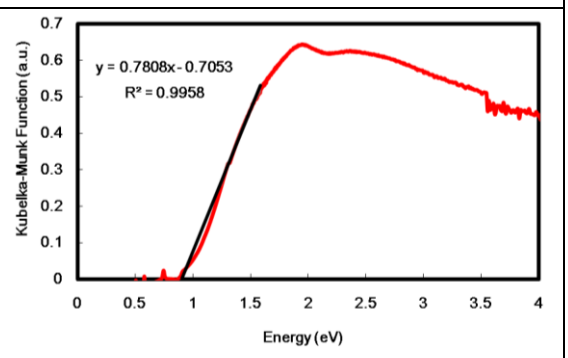
Complex	λ_{max}/nm (ε/M^{-1} cm^{-1})
$[TeRu_5(CO)_{14}]^{2-}$	353 (20662), 414 (3194), 545 (4422)
1	426 (29306), 595 (11428)

Fig. S8 The optical reflectance spectra of $[TeRu_5(CO)_{14}]^{2-}$, **1**, **2**, **3a**, **3b**, and **4**

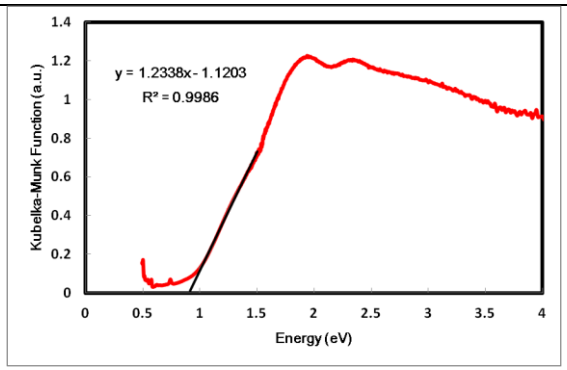
$[TeRu_5(CO)_{14}]^{2-}$



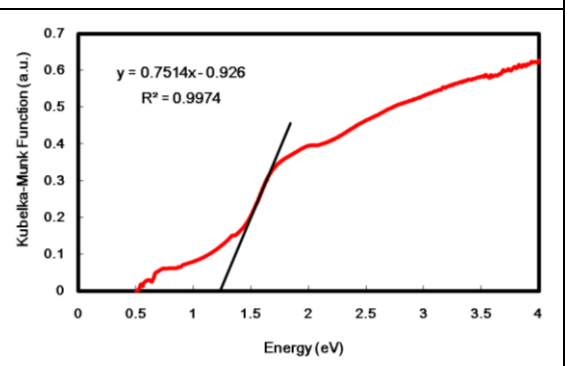
1



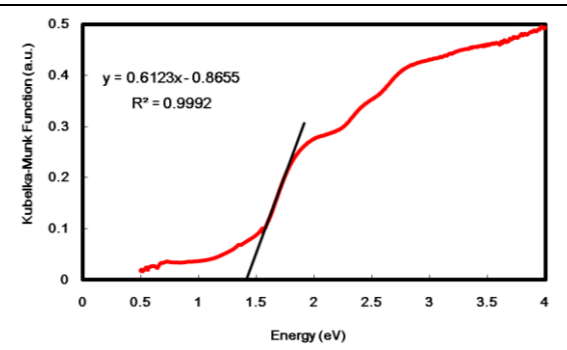
2



3a



3b



4