Supporting Information for Fragment-based Quantum Mechanical/Molecular Mechanical Simulations of Thermodynamic and Kinetic Process of the Ru^{2+}-Ru^{3+} Self-Exchange Electron Transfer

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Supplemental Figures

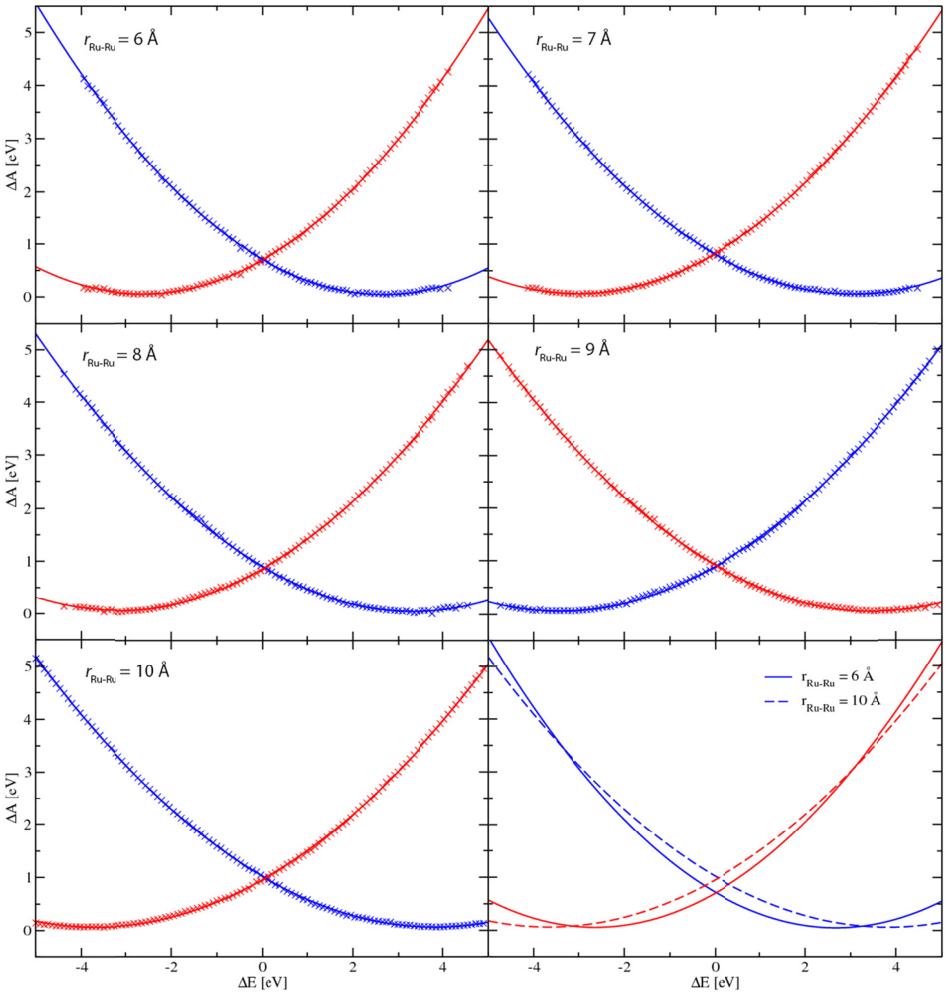

Fig. S1 Diabatic energy profiles of Ru^{2+}-Ru^{3+} self-exchange at different distances (6.0 Å, 7.0 Å, 8.0 Å, 9.0 Å, and 10.0 Å)

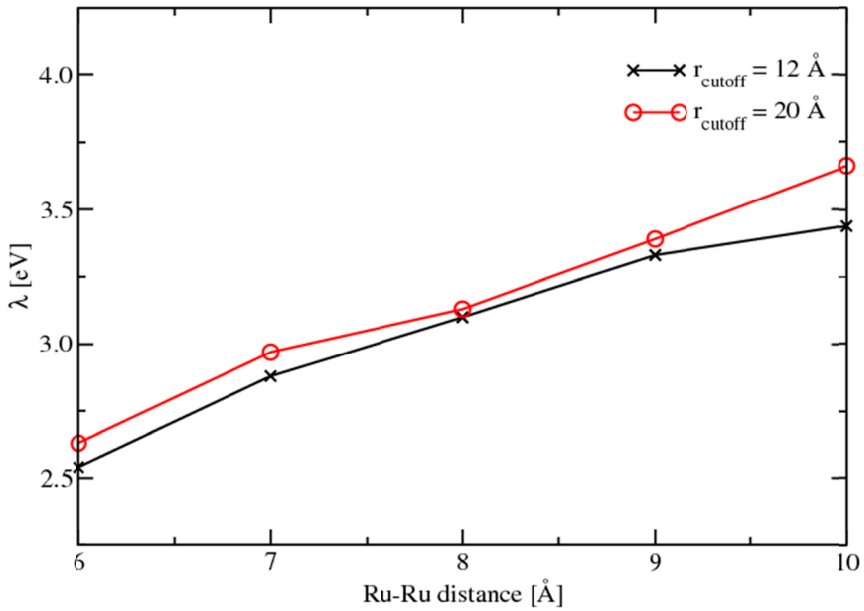

Fig. S2 Convergence of the reorganization energies with different QM/MM cutoff (12 Å and 20 Å)

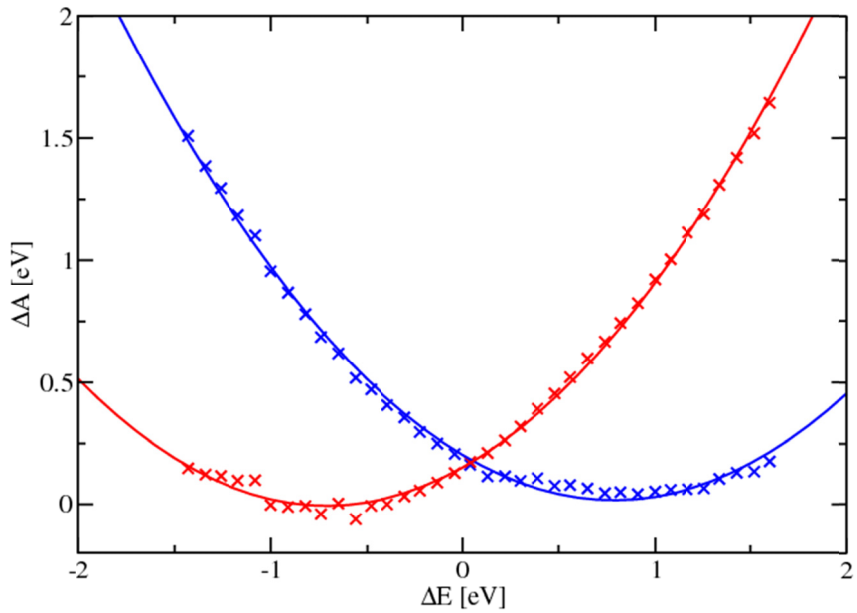

Fig. S3 Inner reorganization energy of Ru-Ru at distance of 8 Å

Supplementary Tables

Table S1. ECP parameters in Gaussian 94 ECP format for H, O, and Ru atoms using BLYP/LanL2DZ with grid=80×194 for frozen fragment pseudopotential of DFI

H	0		O	0		Ru	0	
s	potential		s	potential		s	potential	
	3			3			3	
2	52.70108	15.13984	2	0.41467	0.33298	2	0.28137	1.58928
2	10.69874	13.88517	2	39.56192	139.36823	2	25.41282	132.94691
2	62.52761	13.39176	2	4.25966	20.21308	2	17.88425	33.10262

Table S2. Dependence of the reorganization energies on the QM/MM cutoff r_{cutoff} (8 Å, 12 Å, and 20 Å)

r /Å	$\lambda(r_{cutoff}$ =8 Å)/eV	$\lambda(r_{cutoff}$ =12 Å)/eV	$\lambda(r_{cutoff}$ =20 Å)/eV
6.0	2.50	2.54	2.63
7.0	-	2.88	2.97
8.0	-	3.10	3.13
9.0	-	3.33	3.39
10.0	2.60	3.44	3.66

Table S3. Components to compute the final ET rate constant. The computed rate constant using Eq. 1 is 0.11 $M^{-1}s^{-1}$ without other corrections.

r/Å	$<H^2_{AD}>^{1/2}$/eV	$\lambda(r_{cutoff}$ =20 Å)/eV	λ_{scale}/eV	k_{ET}/s^{-1}	ΔG/eV
6.0	2.03E-03	2.63	1.66	5.88E+03	2.50E-01
7.0	3.33E-04	2.97	1.87	1.87E+01	1.70E-01
8.0	1.07E-04	3.23	2.03	3.80E-01	1.18E-01
9.0	3.75E-05	3.40	2.14	1.62E-02	8.31E-02
10.0	1.66E-05	3.66	2.31	6.28E-04	5.93E-02