Chemistry–A European Journal

Supporting Information

Proton Conduction at High Temperature in High-Symmetry Hydrogen-Bonded Molecular Crystals of Ru^{III} Complexes with Six Imidazole-Imidazolate Ligands

Makoto Tadokoro,* Masaki Itoh, Ryota Nishimura, Kensuke Sekiguchi, Norihisa Hoshino, Hajime Kamebuchi, Jun Miyazaki, Fumiya Kobayashi, Motohiro Mizuno, and Tomoyuki Akutagawa

Supporting Information

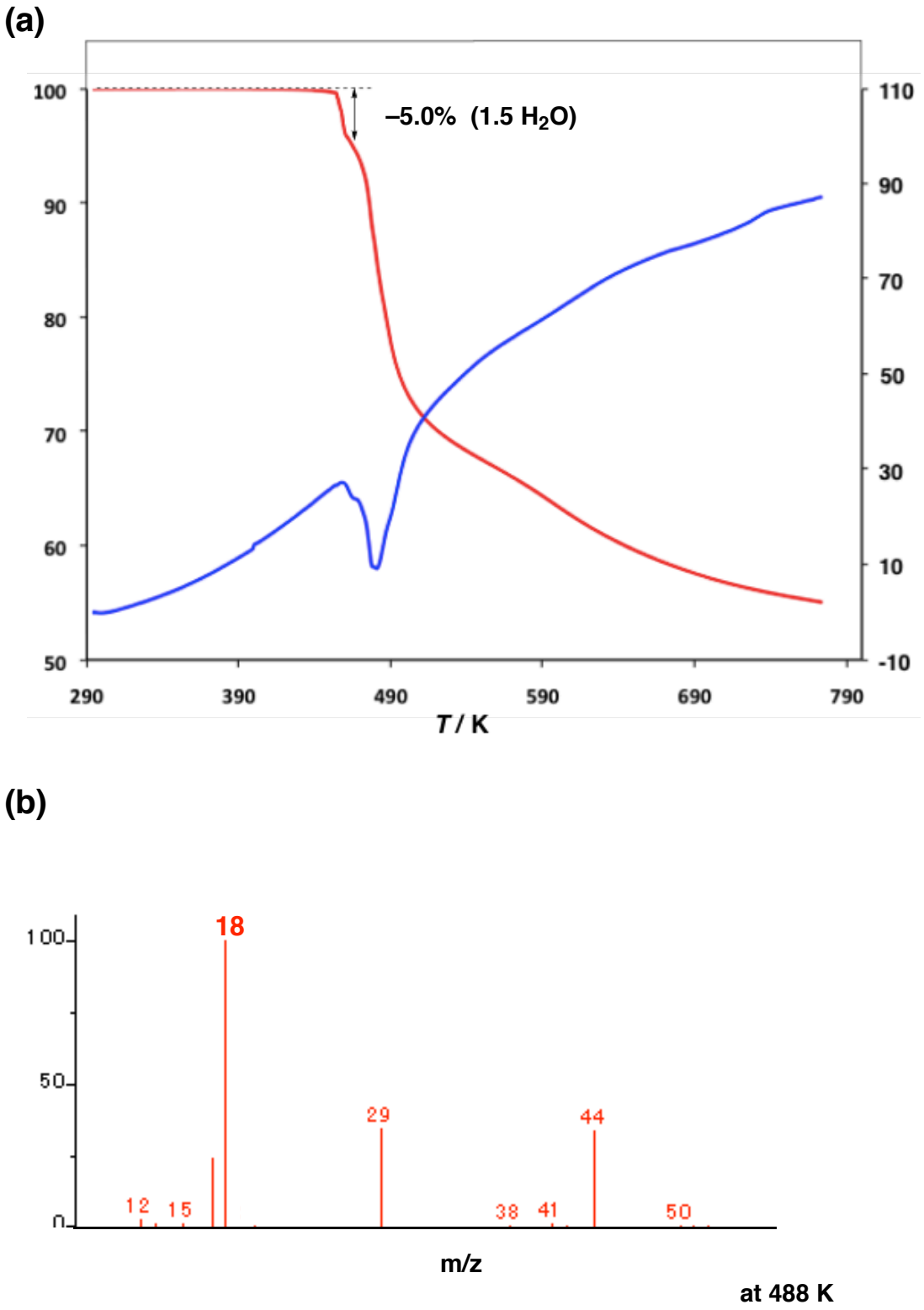


Figure 1S

(a) TG image of 1: at 453 K H_2O molecules evaporate from the crystal of 1.
(b) TG-EI-mass image at 488 K: The molecular weight 18 of H_2O are observed.

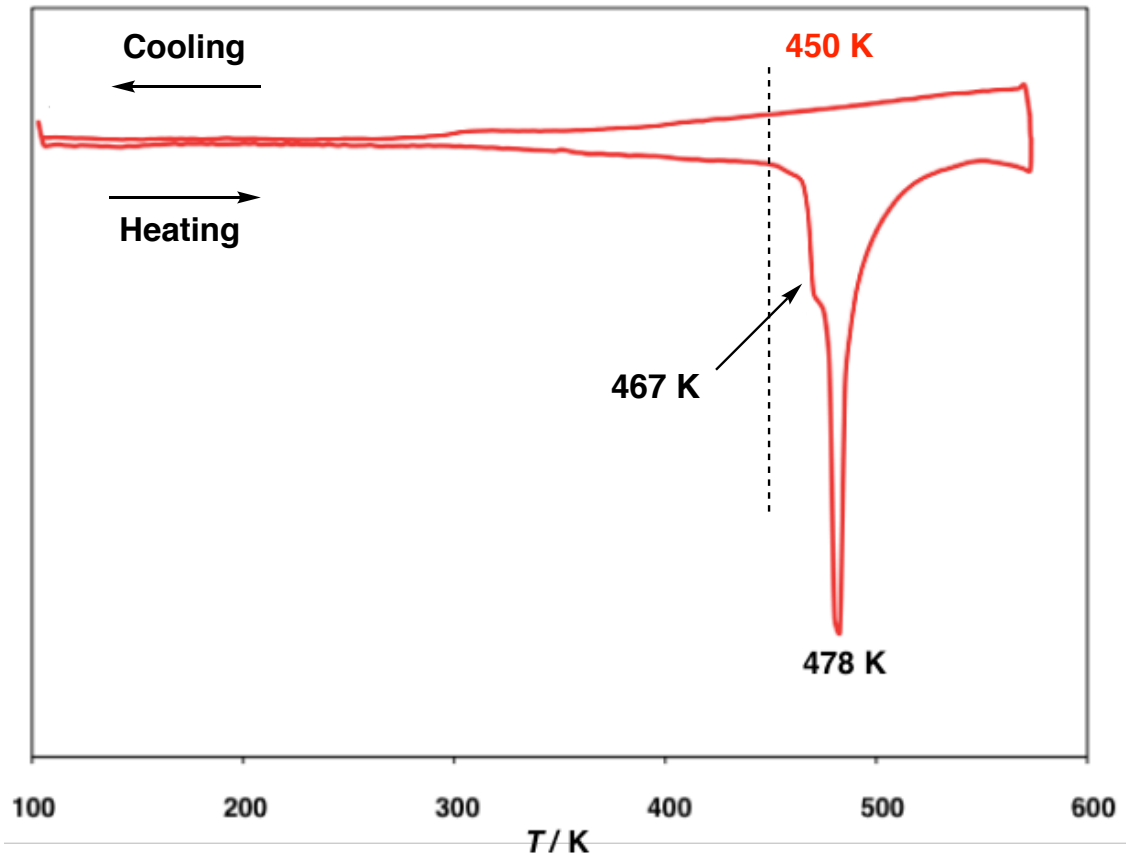


Figure 2S

The DSC image of the crystal of **1**: two endothermic peaks were observed at 467 K and 478 K to occure two kinds of H_2O by decomposition.

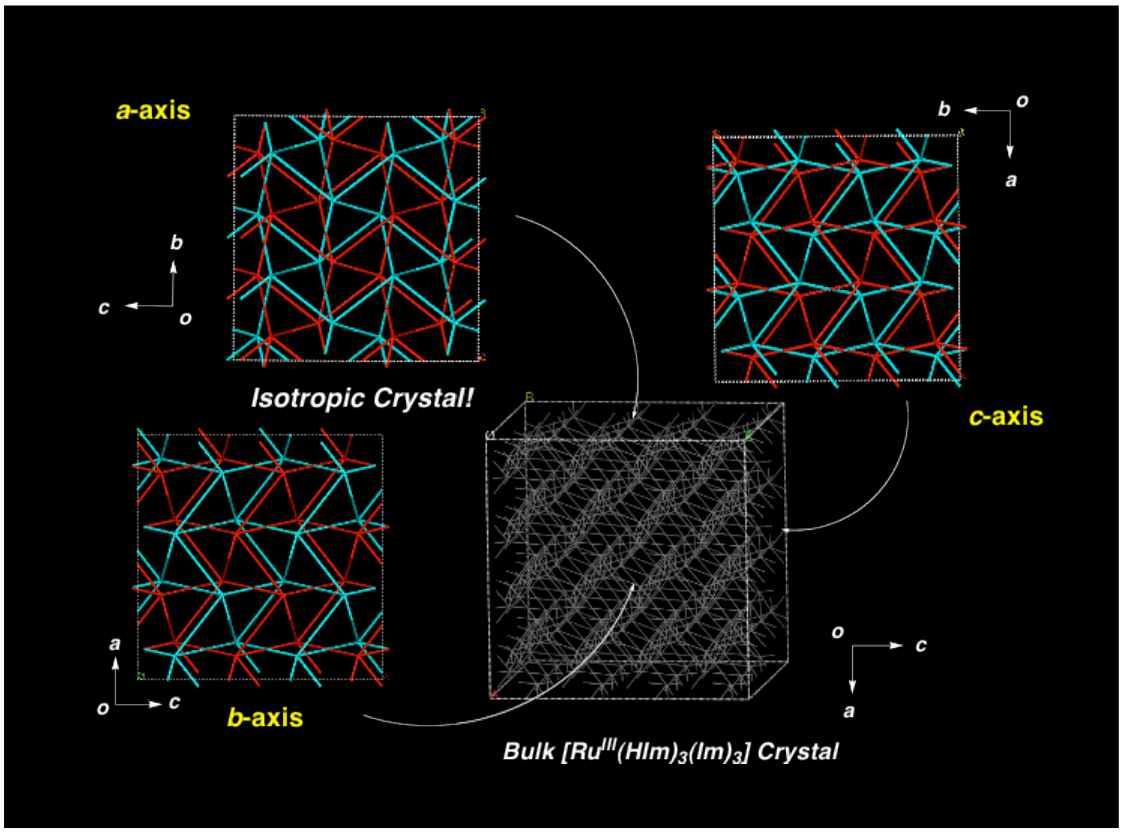


Figure 3S

The apperarences of H-bonding networks show three 2-D down veiews along each axis networks

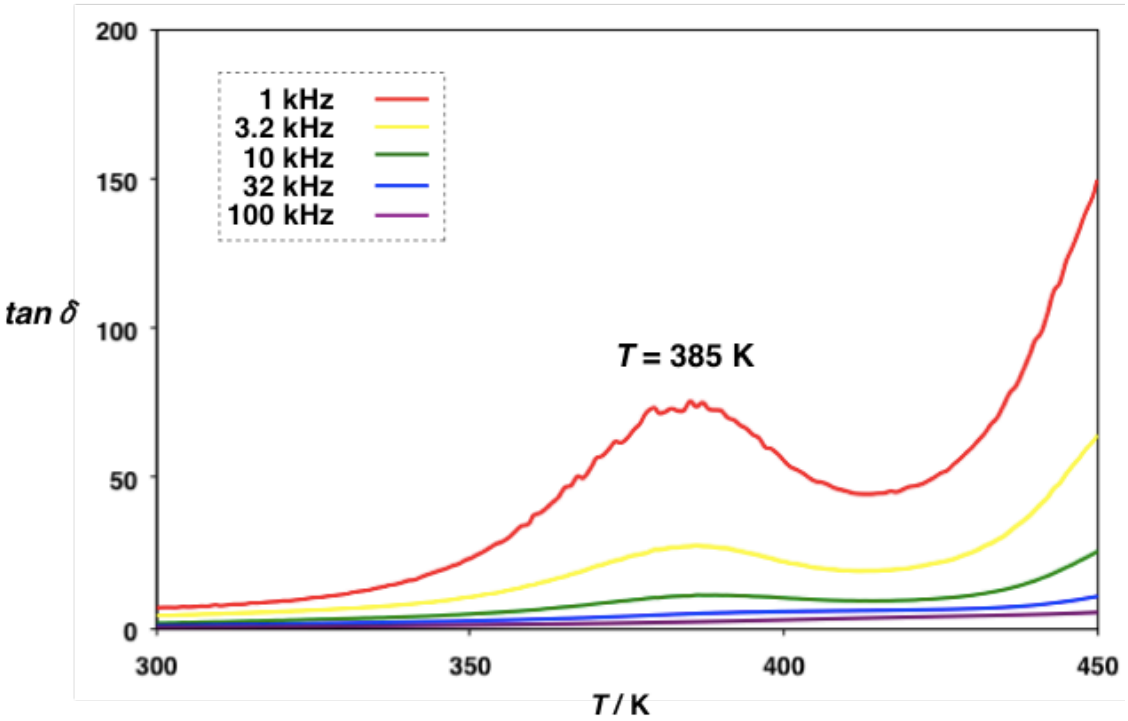


Figure 4S

tanδ (ε'/ε") image of dielectric constant on frequency moodulation depending upon temperatures

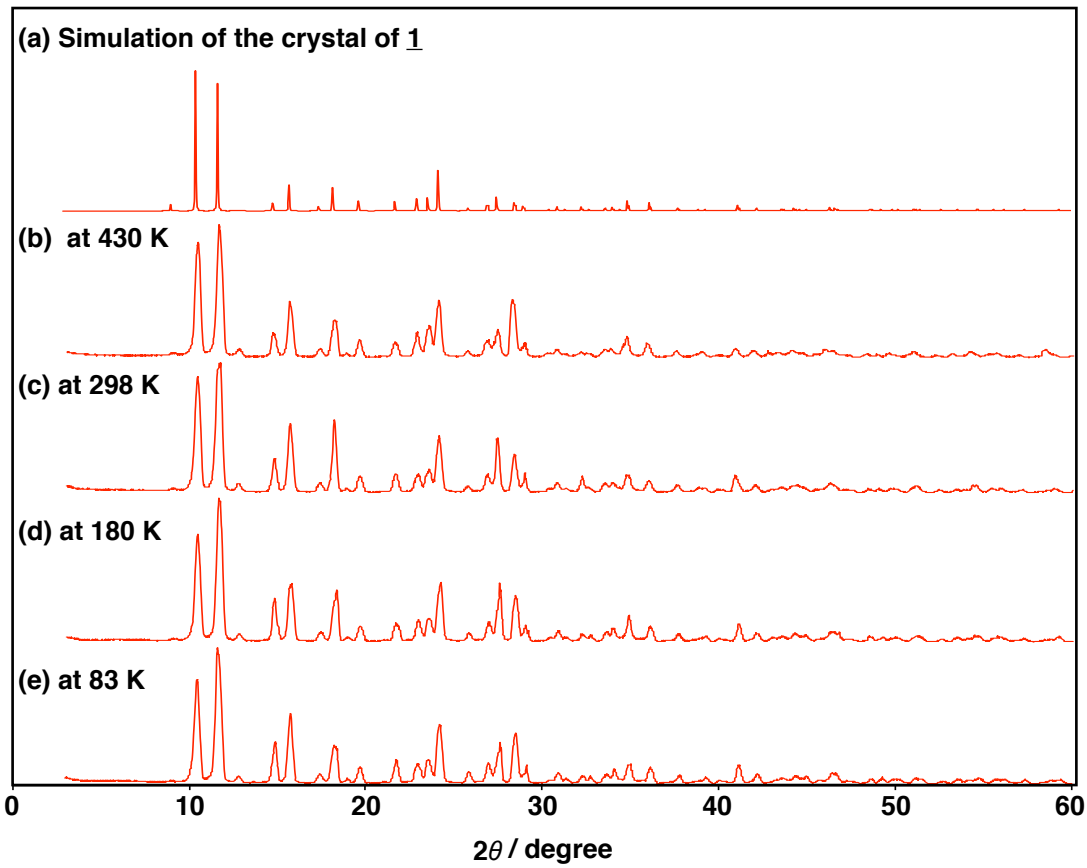
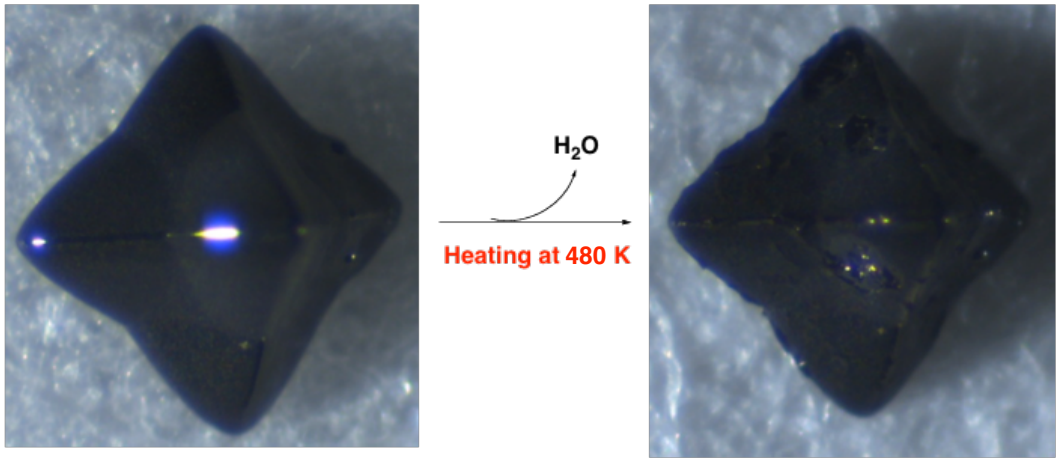


Figure 5S

(a) PXRD patterns of simulation from X-ray crystal structure analysis of 1, (b)-(e) PXRD ptterns at the temperature range of 83, 180, 298, 430 K, respectively.

(a)



(b)

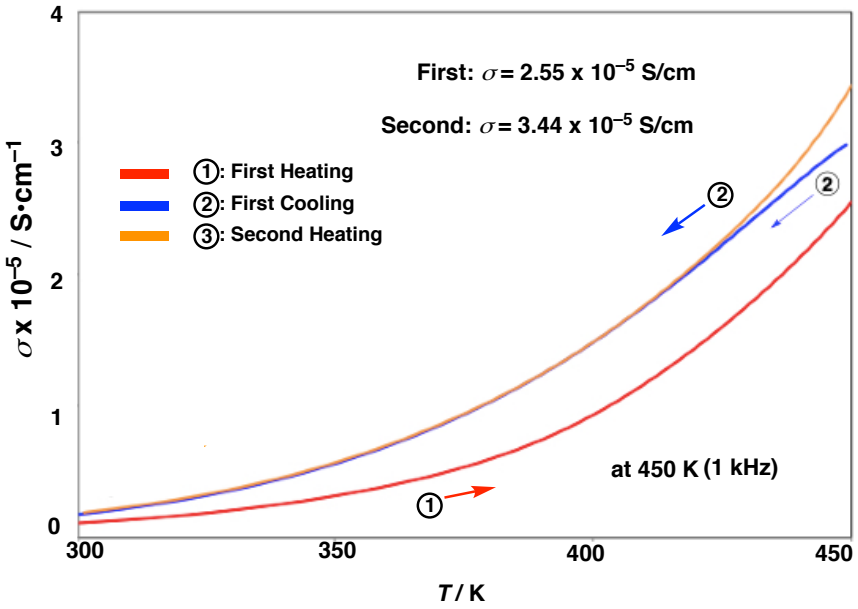


Figure 6S

(a) The appearance of crystal surface changed by heating until 480 K (b) The measurement of proton conductivity until 450 K: by a cycle measurement the proton conductivity increases from 2.55 $\times 10^{-5}$ S/cm at a first run to 3.44×10^{-5} S/cm at a second run.

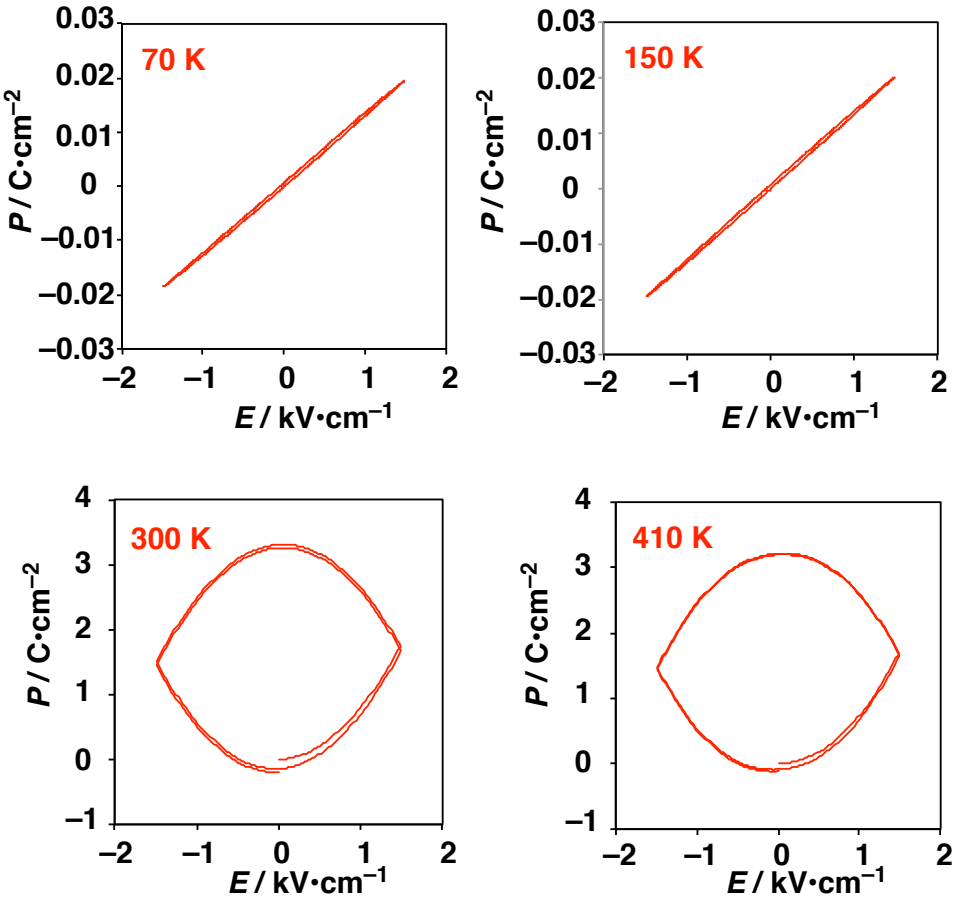


Figure 7S

P-E curve measurements of the single crystal of **1** at 70, 150, 300, 410 K: at low temperatures at 70 K and 150 K, the crystal indicates paraelectric natures. But at high temeperatures at 300 K and 400 K, the P-E curves are not hysterisis loops and open due to conductive componennts.

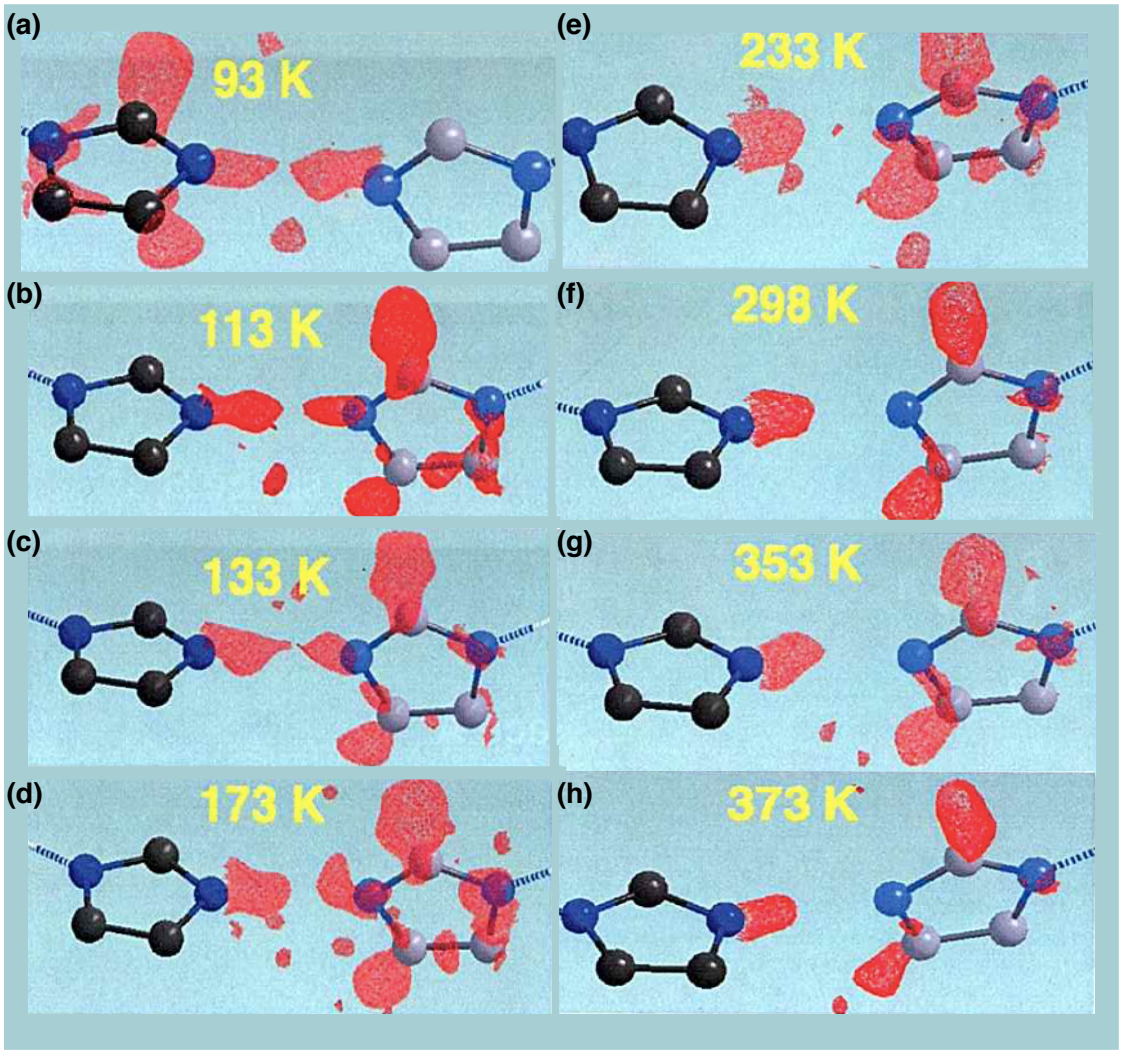


Figure 8S

The temperature-dependent X-ray crystal analyses at eight temperatures of 93, 113, 133, 173, 233, 298, 353, and 373 K: the half-tone dot meshs of a red color show electron densities of H-bonding proton on the differential Fourier map

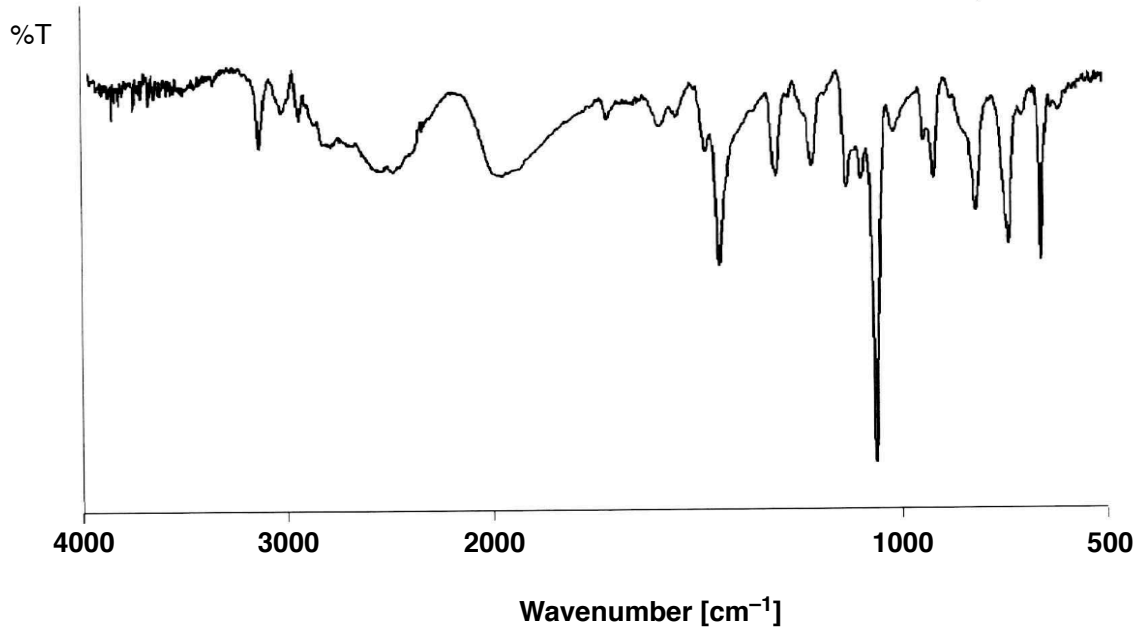


Figure 9S

IR spectrum of $[Ru^{III}(HIm)_3(Im)_3]$(**1**).

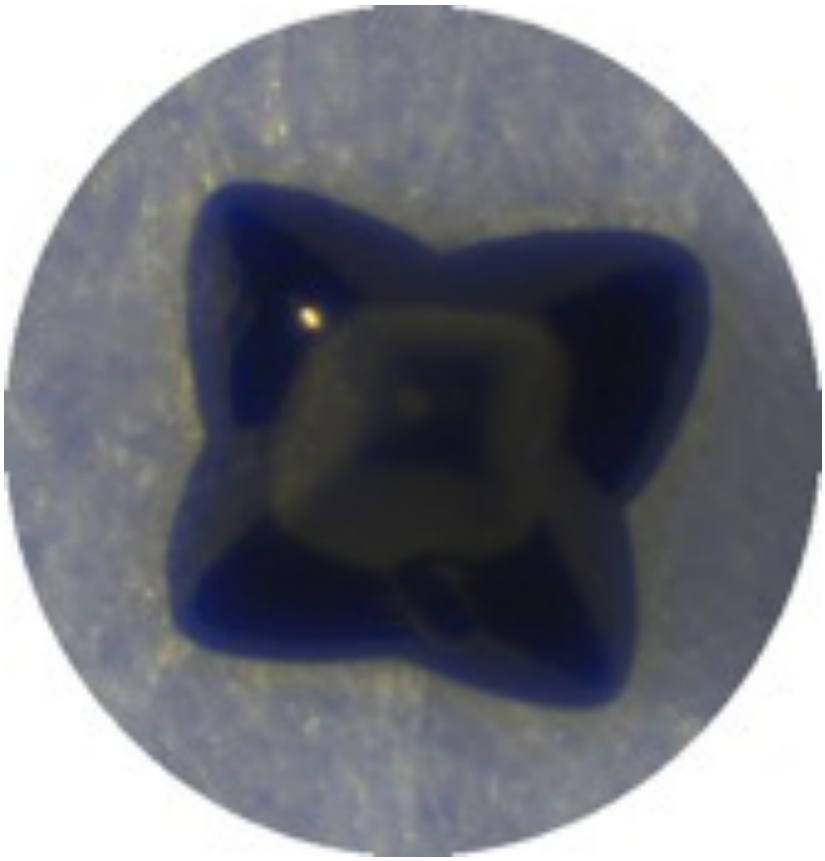


Figure 10S.

The external form of the crystal of **1** forms a five quadrangular -pyramid one.

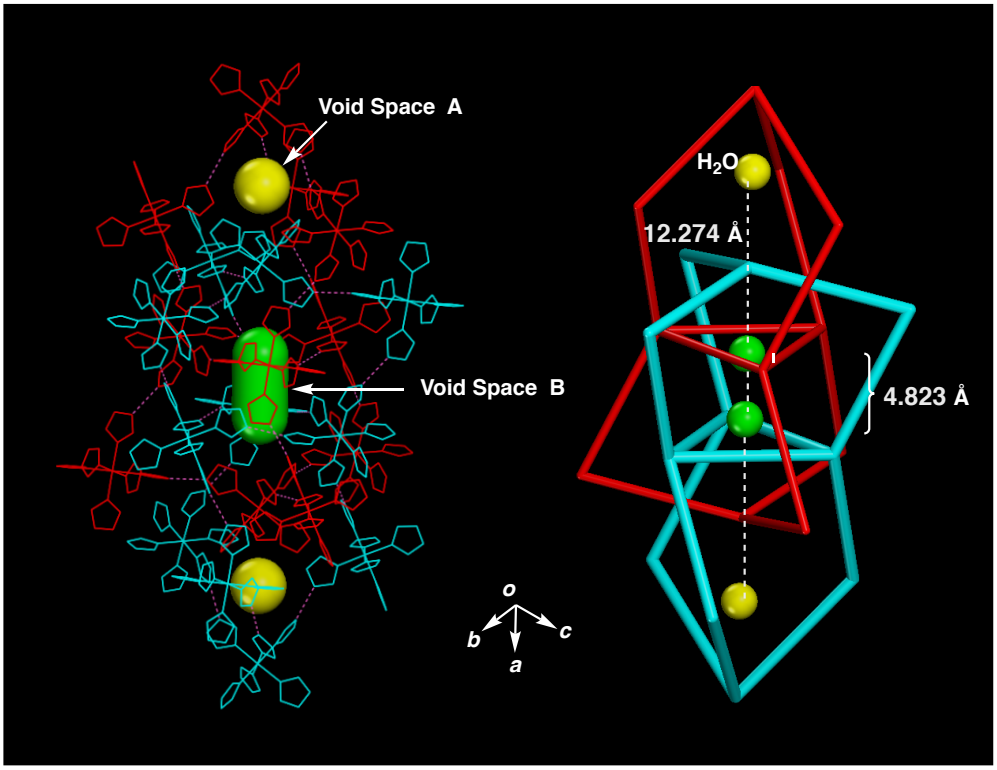
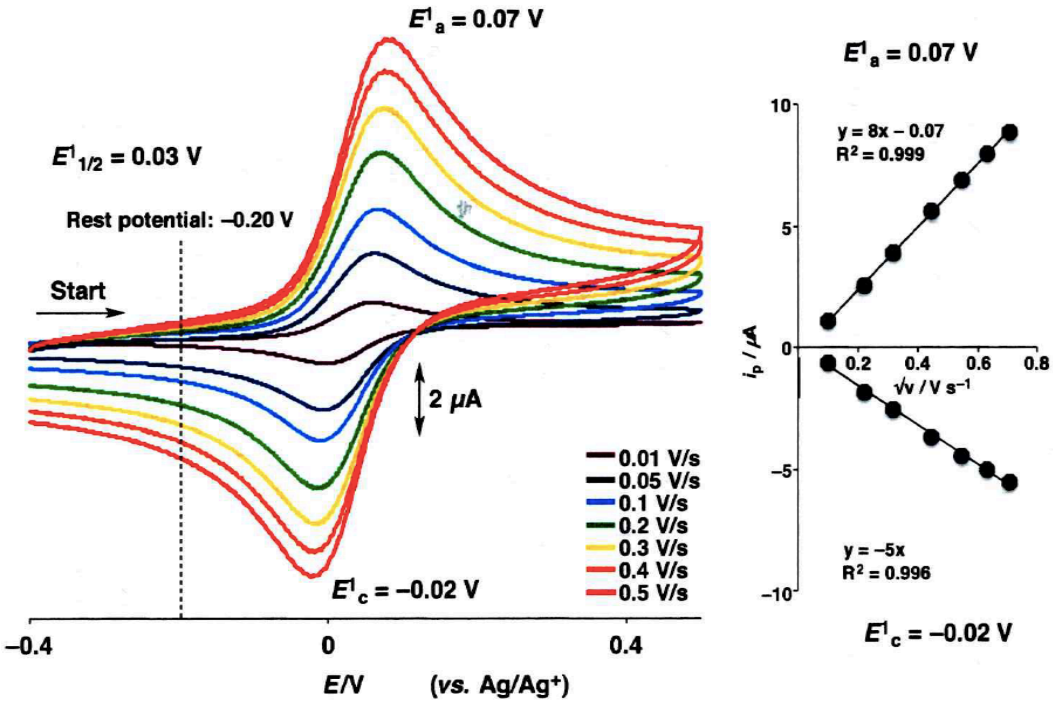


Figure 11S.

Water molecules are confined to two void spaces of a small A site and a wide B one. They are formed in the crossover of two different chiral hexahedrons with red and blue lines.



In MeCN Electrolyte: 0.1 M $^{n}Bu_4NPF_6$ WE: Pt (ϕ = 1.6 mm), CE: Pt, RE: Ag/Ag^+, (Fc/Fc^+ = 0.07 V)

Figure 12S.

CV image of $[Ru^{I}(HIm)_6](PF_6)_2$ in MeCN

Table 1S. Crystallographic data for **1**.

$[Ru(HIm)_3(Im)_3]\cdot 1.5H_2O$				
Formula	$C_{18}H_{24}N_{12}RuO_{1.5}$			
Crystal system	Cubic			
Space group	*P*a-3 (#205)			
Temperature/K	93	113	133	173
a, *b*, *c*/Å	16.785(17)	16.829(13)	16.830(19)	16.863(17)
V/Å^3	4729(14)	4766(11)	4767(16)	4795(15)
Z	8	8	8	8
D_{calc} /g·cm^{-3}	1.490	1.479	1.478	1.470
λ (Mo Kα)/Å	0.71073	0.71073	0.71073	0.71073
μ (Mo Kα)/mm^{-1}	0.701	0.696	0.695	0.691
F(000)	2152	2152	2152	2152
R_1, wR_2 ($I > 2\sigma(I)$)	0.0394, 0.1083	0.0366, 0.0964	0.0398, 0.1094	0.0388, 0.1016
R_1, wR_2 (for all data)	0.0438, 0.1124	0.0419, 0.1016	0.0446, 0.1152	0.0451, 0.1083
GOF	1.101	1.068	1.050	1.063
Reflections/Parameters	1815/99	1821/99	1823/99	1826/99
CCDC	2167384	2167385	2167386	2167387

Temperature / K	233	298	353	373
a, *b*, *c* / Å	16.888(19)	16.929(18)	17.000(19)	17.06(2)
V / Å^3	4817(16)	4852(15)	4913(16)	4964(17)
Z	8	8	8	8
D_{calc} / g cm^{-3}	1.463	1.453	1.435	1.420
λ (Mo Kα) / Å	0.71073	0.71073	0.71073	0.71073
μ (Mo Kα) / mm^{-1}	0.688	0.683	0.675	0.668
F(000)	2152	2152	2152	2152
R_1, wR_2 ($I > 2\sigma(I)$)	0.0376, 0.0972	0.0368, 0.0979	0.0393, 0.0971	0.0390, 0.0994
R_1, wR_2 (for all data)	0.0437, 0.1029	0.0444, 0.1058	0.0503, 0.1081	0.0506, 0.1114
GOF	1.067	1.077	1.065	1.041
Reflections/Parameters	1828/99	1846/99	1871/99	1880/99
CCDC	2167388	2167389	2167390	2167391