Supporting Information

Side-effect of ancillary ligand on electron transfer and photodynamics of dinuclear valence tautomeric complex

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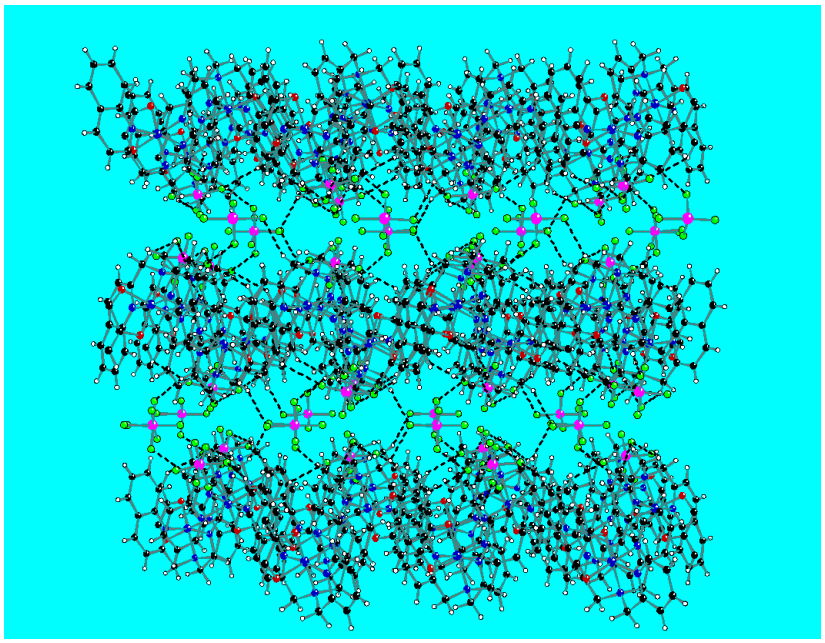

Fig. S1 Three-dimensional structure of $\mathbf{1}\cdot(PF_6)_3$ featuring alternating layers of $\mathbf{1}^{3+}$ and counterions.

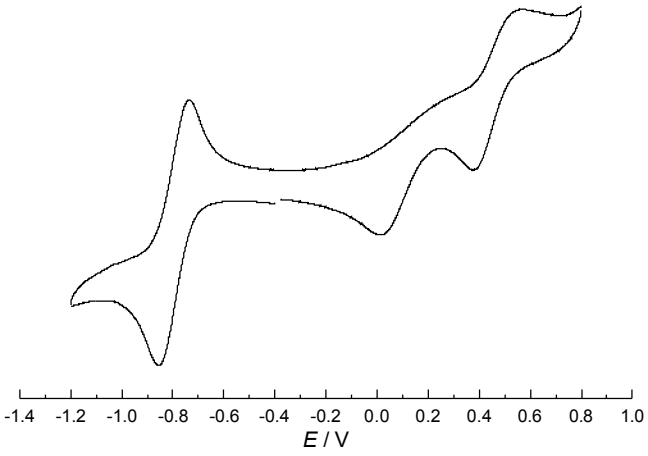

Fig. S2 CV of $\mathbf{1}\cdot(PF_6)_3$.

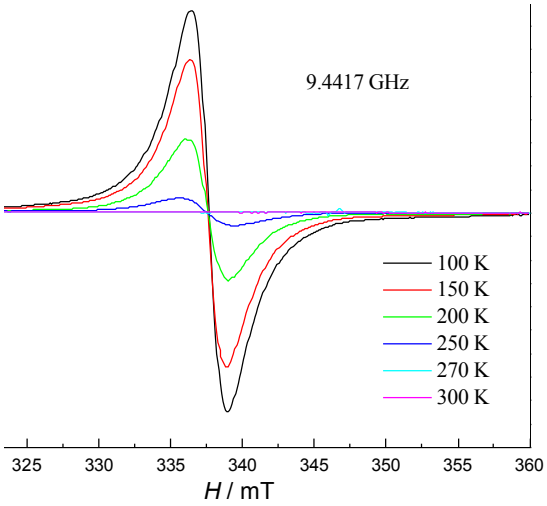

Fig. S3 ESR spectra of **1**·$(PF_6)_3$ measured from 100 to 300 K.

Table S1. Fitting Parameters for Rate Constants $K_{vt}(T)$ /(s^{-1}) for **1**·$(PF_6)_3$ at different temperature.

T / K	K
5	5.5E-7
10	4.9E-7
15	2.5E-7
20	6.4E-7
25	1.3E-6
30	1.1E-6
35	1.8E-6
40	2.8E-6
45	4.9E-6
50	9.1E-6
55	1.4E-5
60	1.6E-5
65	3.2E-5
70	4.3E-5

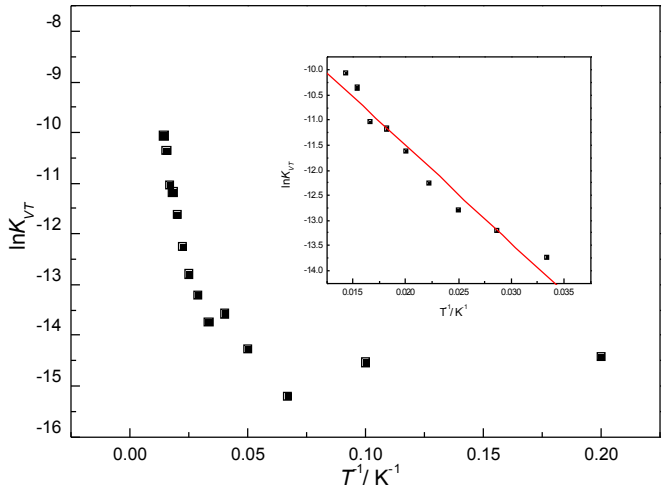

Fig. S4 Plots of $\ln K_{VT}(T)$ versus $1/T$ for **1**·$(PF_6)_3$, where the inset showing data from 30 K to 70 K with fitted line.

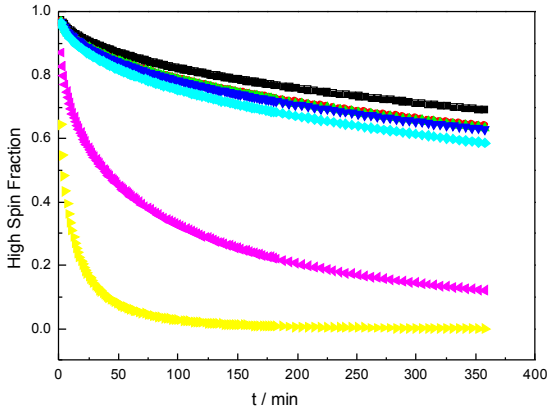

Fig. S5 Time-dependent VT relaxation of the *hs* molar fraction for $[\{Co(tpa)\}_2(dhbq)]\cdot(PF_6)_3$ at temperature:5K, 10K, 15K, 20K, 25K, 30K, 35K.

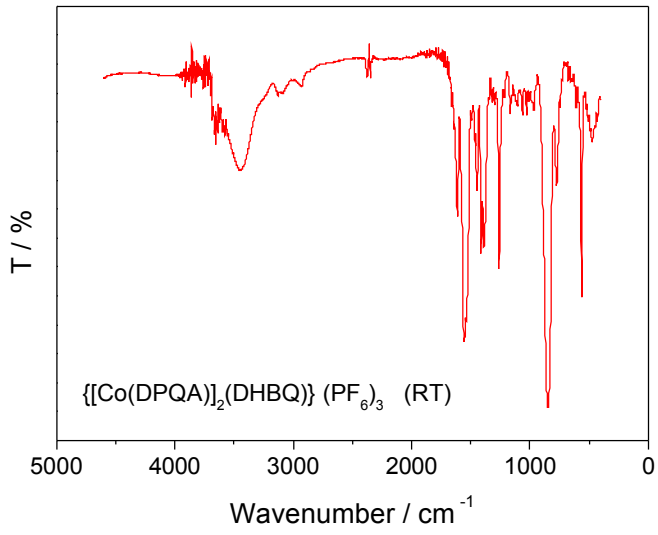

Fig. S6 IR spectra of **1**·$(PF_6)_3$ at room temperature.