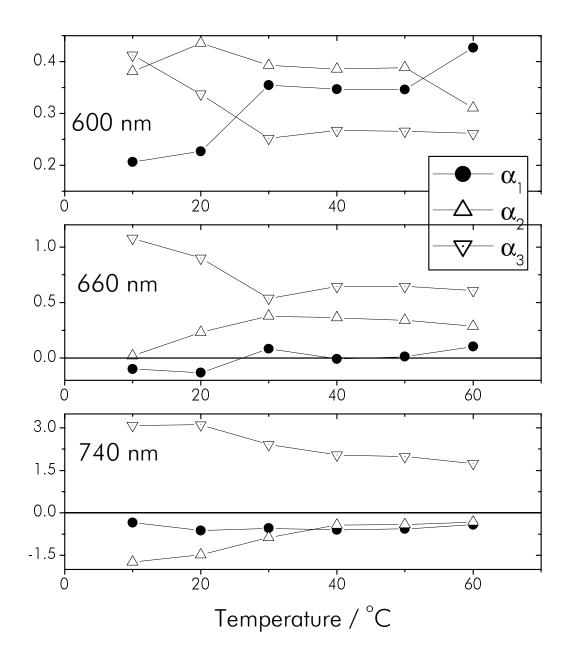
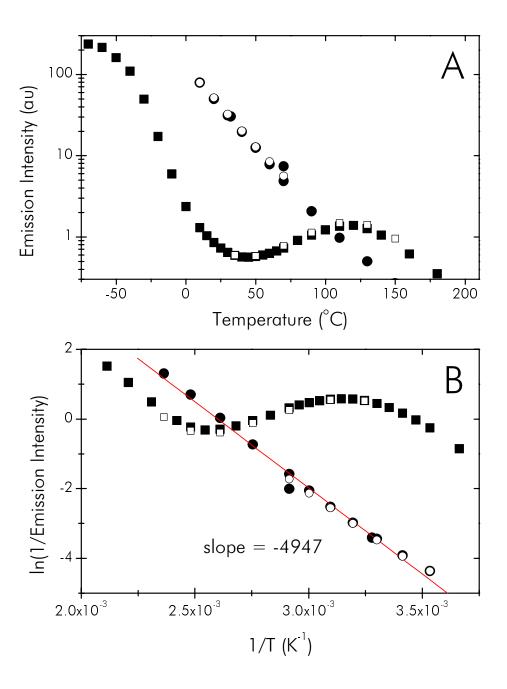


## **Supporting Information**

**Figure S1.** Arrhenius plot of macroscopic rate constants for relaxation of  $[Ru(phen)_2dppz]^{2+}$  in glycerol. Lifetimes were obtained by global fitting of the TCSPC traces at three wavelengths (600, 660 and 740 nm).



**Figure S2.** Preexponential factors corresponding to rate constants in Figure S1 ( $\alpha_1 + \alpha_2 + \alpha_3 = 1$  at all temperatures).



**Figure S3.** Panel A Plot of integrated emission intensity (500 - 850 nm) against temperature for  $[\operatorname{Ru}(\operatorname{phen})_3]^{2+}$  ( $\bullet$  = under air,  $\bigcirc$  = under argon) and  $[\operatorname{Ru}(\operatorname{phen})_2 \operatorname{dppz}]^{2+}$  ( $\bullet$  = under air,  $\square$  = under argon) in glycerol. Panel B. Same data as in panel A as an Arrhenius plot. Assuming that the integrated emission is proportional to the lifetime, the slope in the graph represent -  $\operatorname{E}_a$  / R for the ground state decay of  $[\operatorname{Ru}(\operatorname{phen})_3]^{2+}$ , corresponding to an activation energy of  $41\pm 3$  kJ/mol.