



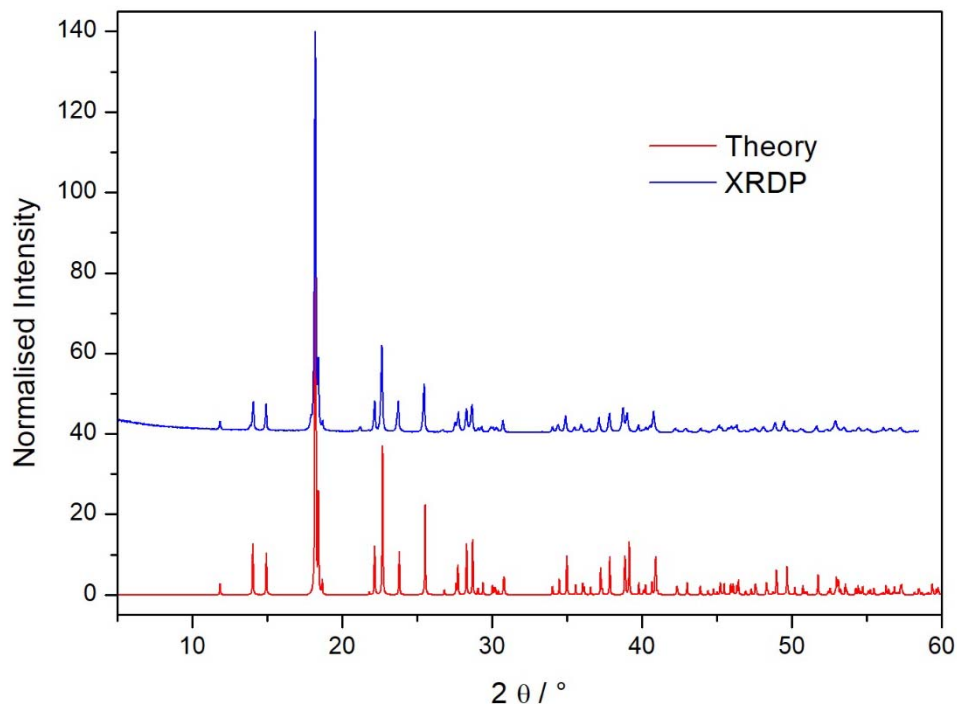
STRUCTURAL SCIENCE  
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MATERIALS

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**Supporting information for article:**

**Combining photoinduced linkage isomerism and nonlinear optical properties in ruthenium nitrosyl complexes**

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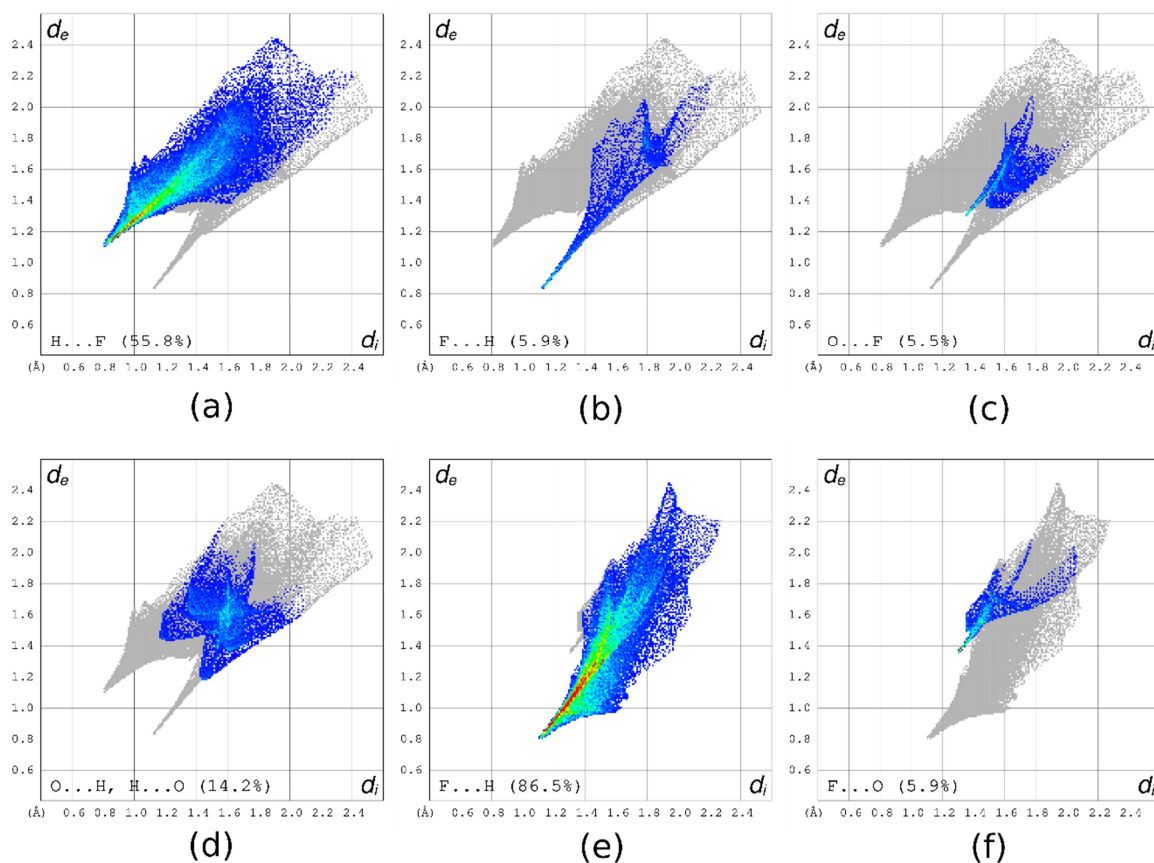


**Figure S1** Experimental (XRPD) and theoretical (SCXRD) diffraction patterns.

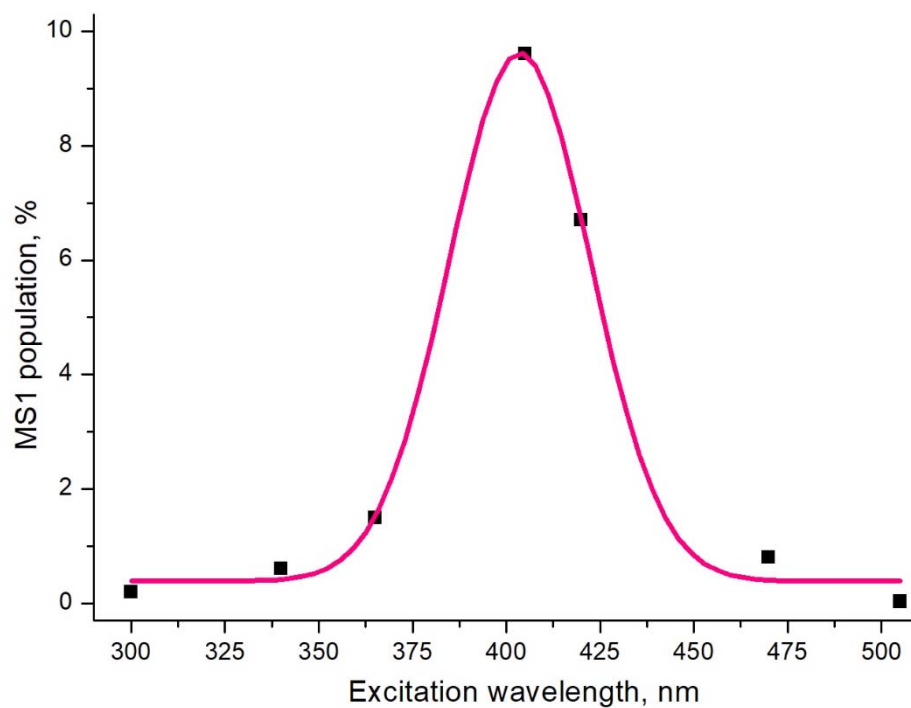
**Table S1** Experimental and refinement details.

	GS		GS+MS1		
			GS	MS1	GS/MS1
Formula			N <sub>5</sub> H <sub>12</sub> OF <sub>7</sub> Si <sub>1</sub> Ru <sub>1</sub>		
Formula weight			360.27		
Temperature/K			100		
Crystal system			Monoclinic		
Space group			<i>Pn</i>		
<i>a</i> /Å	6.7036(4)			6.7242(4)	
<i>b</i> /Å	7.4260(4)			7.4249(4)	
<i>c</i> /Å	10.1296(7)			10.1347(7)	
$\alpha$ /°	90			90	
$\beta$ /°	107.469(6)			107.135(7)	
$\gamma$ /°	90			90	
Volume/Å <sup>3</sup>	481.01(5)			483.53(6)	
Z			2		
$\rho_{\text{calc}}/\text{g}\cdot\text{cm}^{-3}$	2.4873			2.4743	

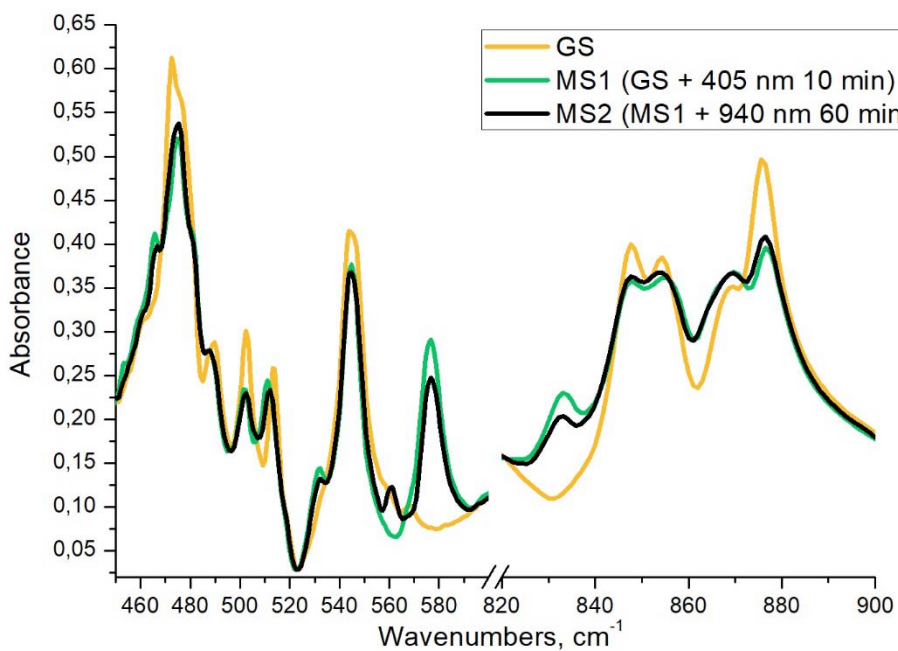
$\mu/\text{mm}^{-1}$	1.850		1.840	
F(000)			349.9	
Crystal size/ $\text{mm}^3$			$0.157 \times 0.104 \times 0.085$	
Radiation			Mo K $\alpha$ ( $\lambda = 0.71073 \text{ \AA}$ )	
2 $\theta$ range for data collection/ $^\circ$	5.48 to 65.84		5.48 to 66	
Index ranges	$-10 \leq h \leq 10,$ $-11 \leq k \leq 11,$ $-13 \leq l \leq 14$		$-10 \leq h \leq 10,$ $-11 \leq k \leq 11,$ $-13 \leq l \leq 14$	
Reflections collected	8064		8063	
Independent reflections	3165 [ $R_{\text{int}} = 0.0326,$ $R_{\text{sigma}} = 0.0390$ ]		3186 [ $R_{\text{int}} = 0.0388,$ $R_{\text{sigma}} = 0.0461$ ]	
Data/restraints/parameters	3165/2/141	3186/2/141	3186/2/141	3186/6/139
Goodness-of-fit on $F^2$	1.023	1.028	1.046	1.026
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0220,$ $wR_2 = 0.0472$	$R_1 = 0.0273,$ $wR_2 = 0.0614$	$R_1 = 0.0282,$ $wR_2 = 0.0647$	$R_1 = 0.0273,$ $wR_2 = 0.0608$
Final R indexes [all data]	$R_1 = 0.0237,$ $wR_2 = 0.0488$	$R_1 = 0.0293,$ $wR_2 = 0.0631$	$R_1 = 0.0301,$ $wR_2 = 0.0665$	$R_1 = 0.0292,$ $wR_2 = 0.0625$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.64/-0.64	0.58/-0.82	0.63/-0.83	0.47/-0.85



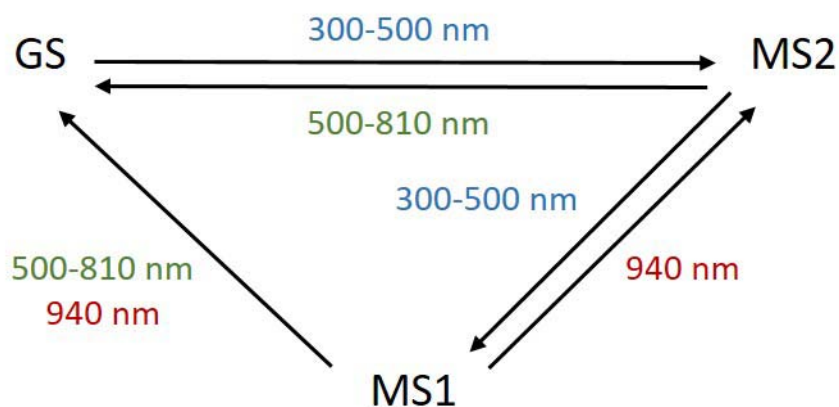
**Figure S2** Selected two-dimensional fingerprint plots for different intermolecular interactions. Plots are based on Hirshfeld surfaces of (a-d)  $[\text{Ru}(\text{NO})(\text{NH}_3)_4\text{F}]^{2+}$ , (e-f)  $\text{SiF}_6^{2-}$ .



**Figure S3** The graph represents Gaussian fit of MS1 population vs. excitation wavelength.



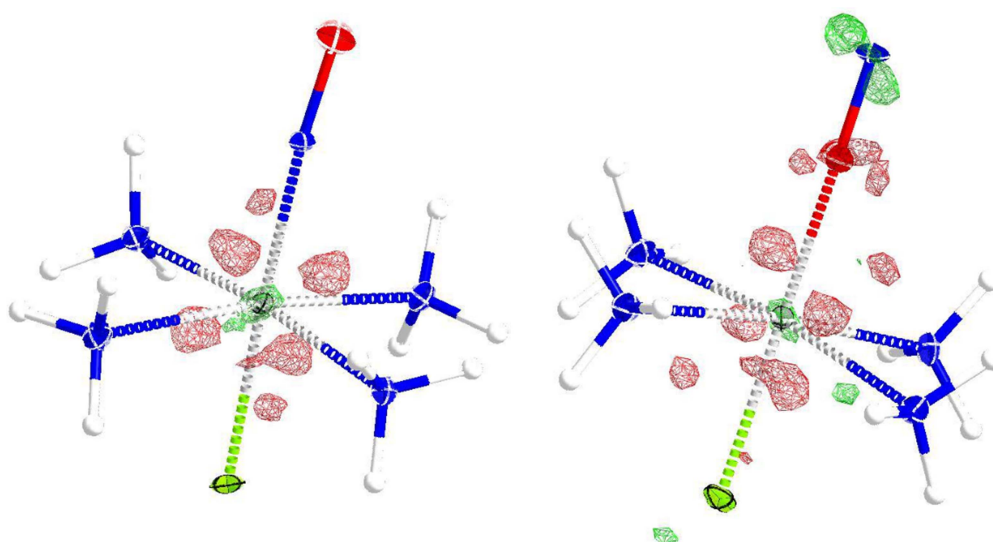
**Figure S4** IR spectra at 10 K of the GS (orange line), GS+MS1 (green line) and GS+MS1+MS2 (black line) in the range 450 - 900 cm<sup>-1</sup>.



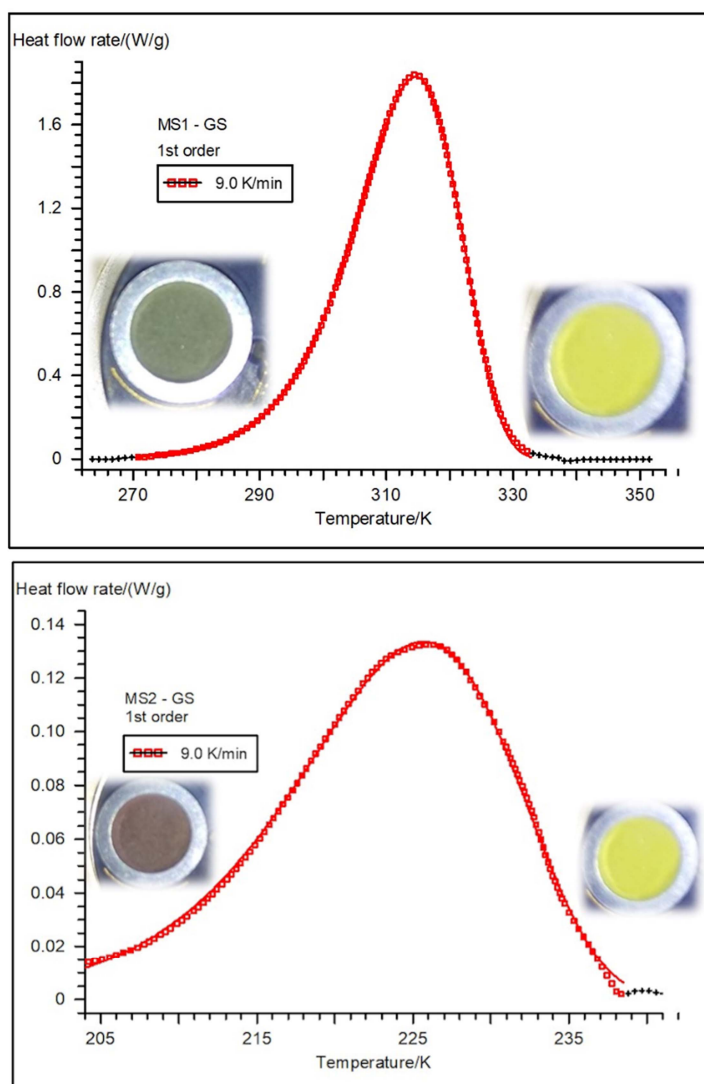
**Figure S5** Scheme of linkage isomerisation in *trans*-[RuNO(NH<sub>3</sub>)<sub>4</sub>F]SiF<sub>6</sub> indicating relevant spectral ranges for population and depopulation with light.



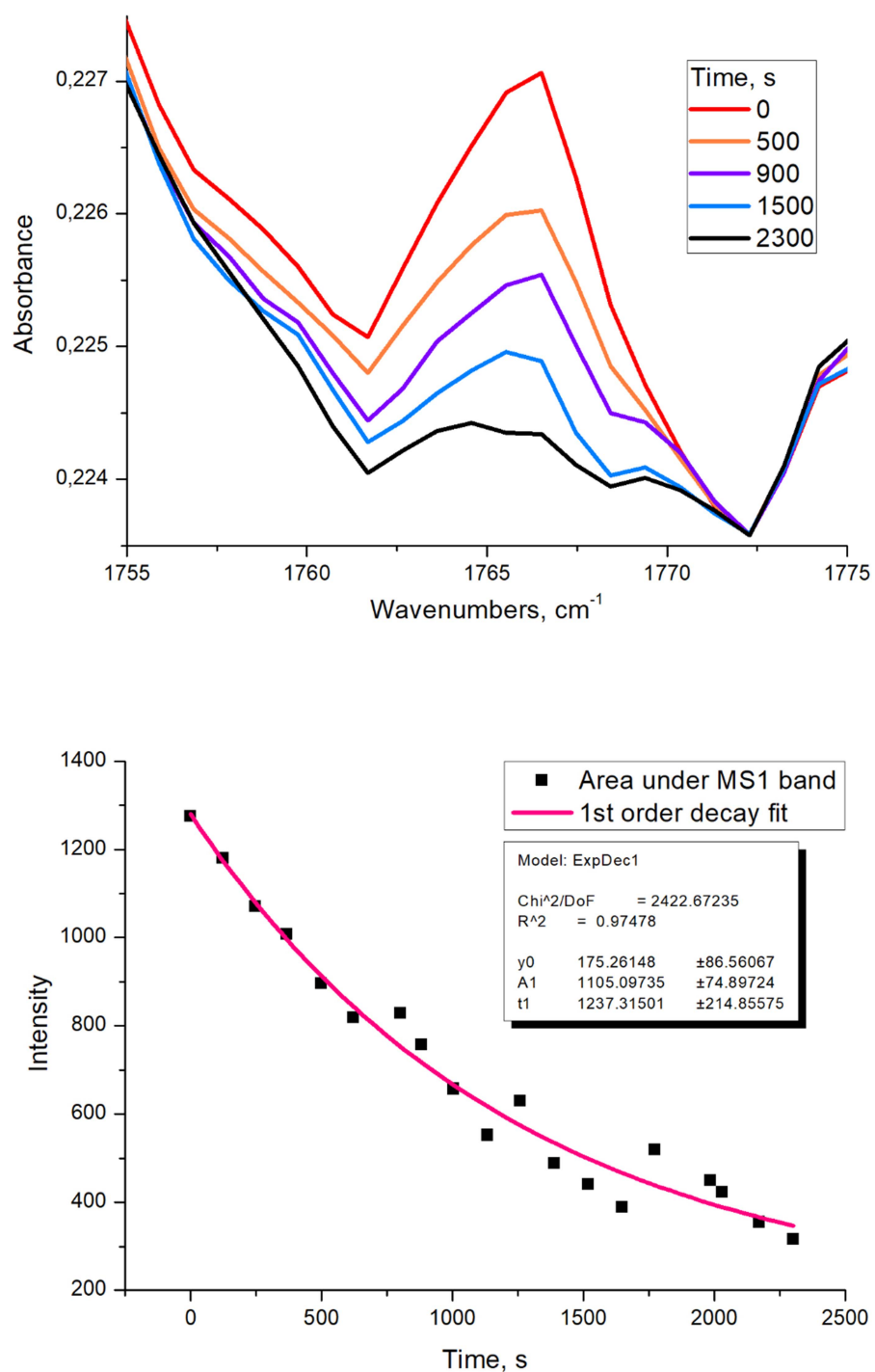
**Figure S6** The colour change of *trans*-[RuNO(NH<sub>3</sub>)<sub>4</sub>F]SiF<sub>6</sub> single crystal from bright yellow (GS, on the left) to pale yellow (GS+MS1, on the right) after 405 nm irradiation at 100 K.



**Figure S7** 3D residual electron density maps of GS+MS1 with Ru-NO (left) and Ru-ON (right) model refinements; residual electron density surfaces are  $0.4 \text{ e}\text{\AA}^{-3}$ . Excess of electron density is shown by red contours, lack by green contours.

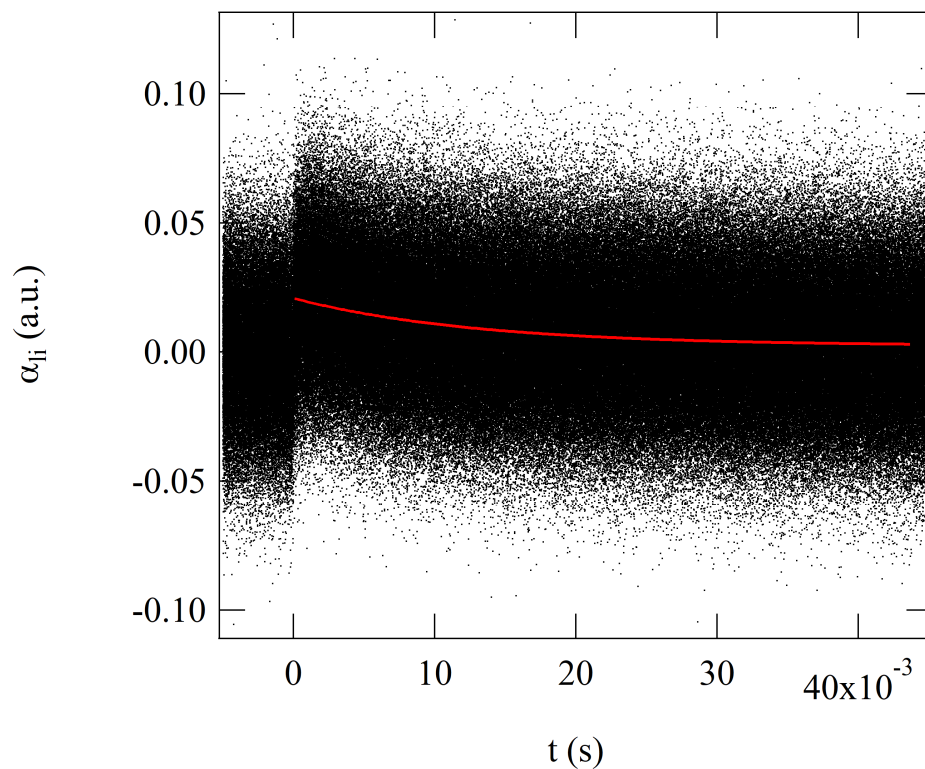


**Figure S8** Fitted DSC curves of the MS1  $\rightarrow$  GS (top) and the MS2  $\rightarrow$  GS (bottom) reactions.



**Figure S9** IR spectra of *trans*-[RuNO(NH<sub>3</sub>)<sub>4</sub>F]SiF<sub>6</sub> after 15 min of 405 nm 360 mW irradiation at 290 K as a function of time (top). Mono-exponential fit of the band area during the decay (bottom).





**Figure S10** Light-induced absorption changes in *trans*-[RuNO(NH<sub>3</sub>)<sub>4</sub>F]SiF<sub>6</sub> after pumping at 410 nm (5 ns laser pulse) and probing at 535 nm at room temperature. The experimental data are fitted by mono-exponential kinetic yielding a lifetime of 13(1) ms.