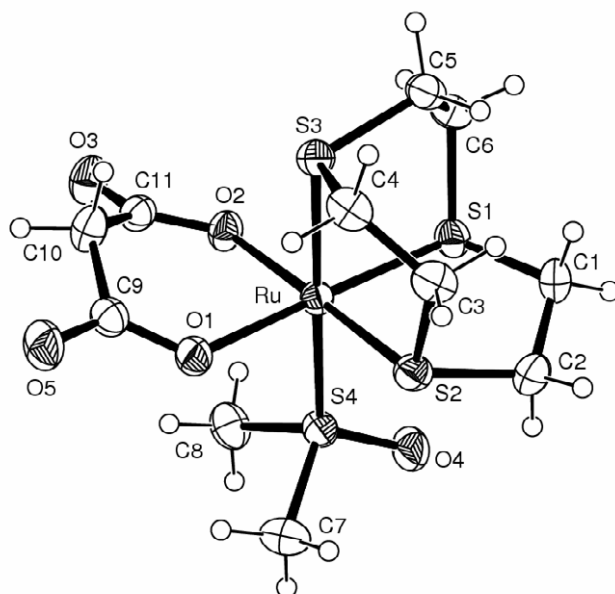


# Half-sandwich Ru<sup>II</sup>-[9]aneS<sub>3</sub> complexes with dicarboxylate ligands: synthesis, characterization and chemical behavior.

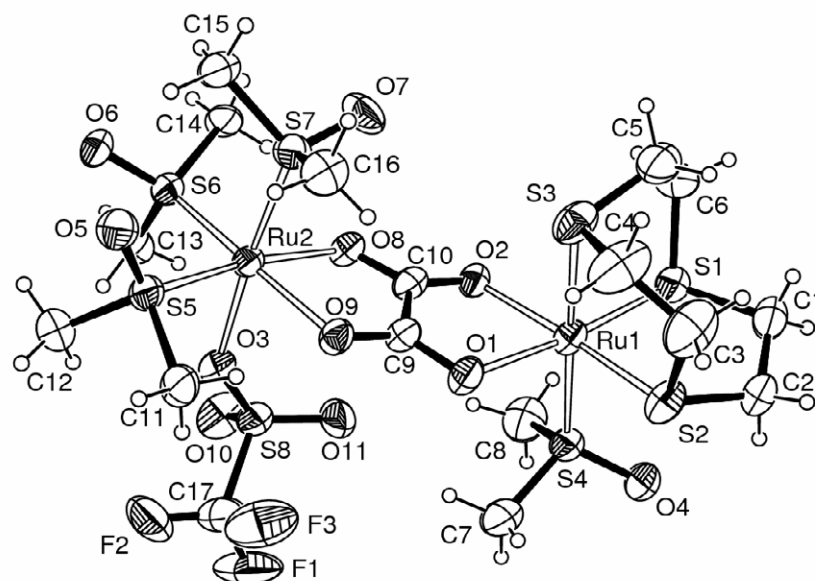
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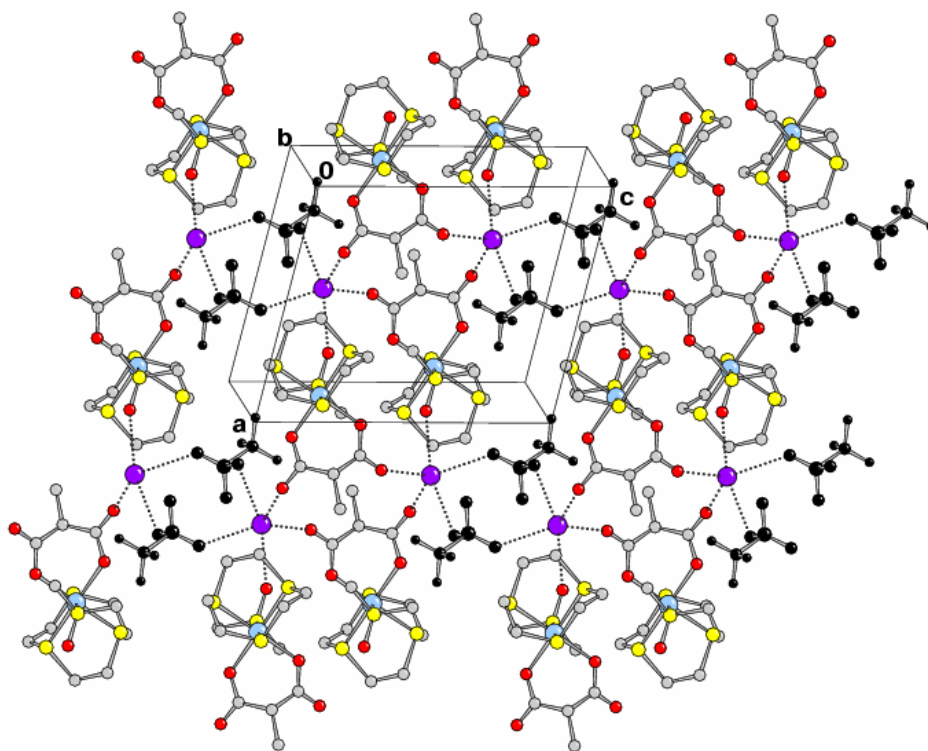
SUPPORTING INFORMATION



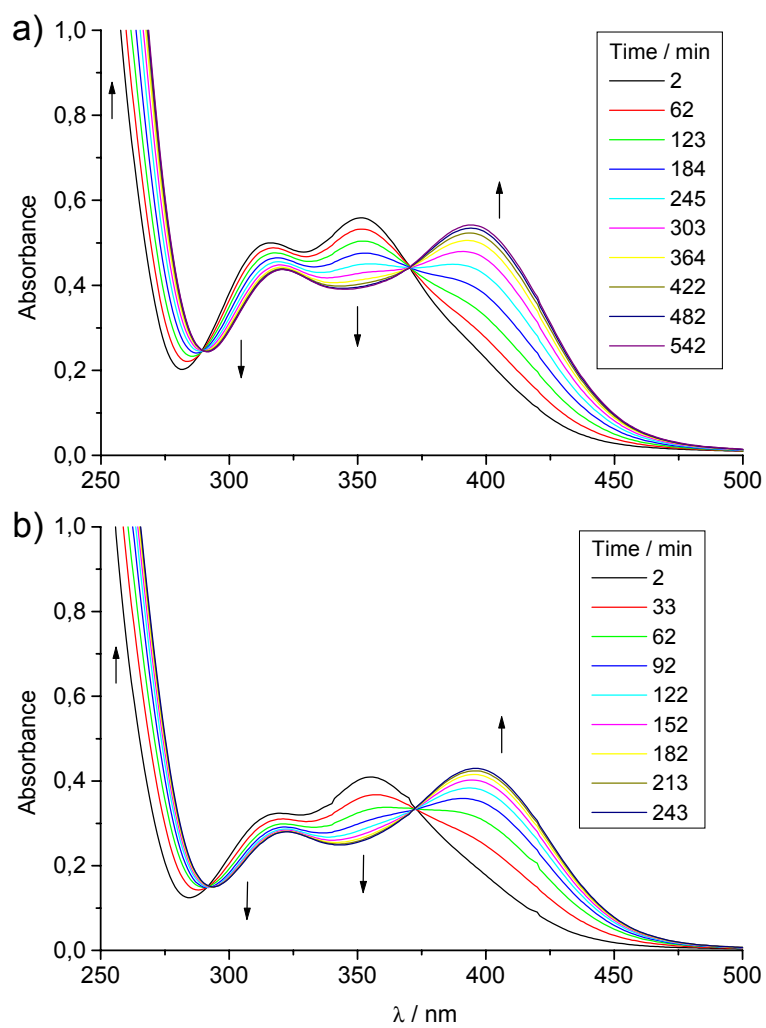
**Figure S1.** ORTEP drawing (40% probability level) of [Ru([9]aneS<sub>3</sub>)(dmsO-S)(η<sup>2</sup>-mal)]·(H<sub>2</sub>O) (**2**).



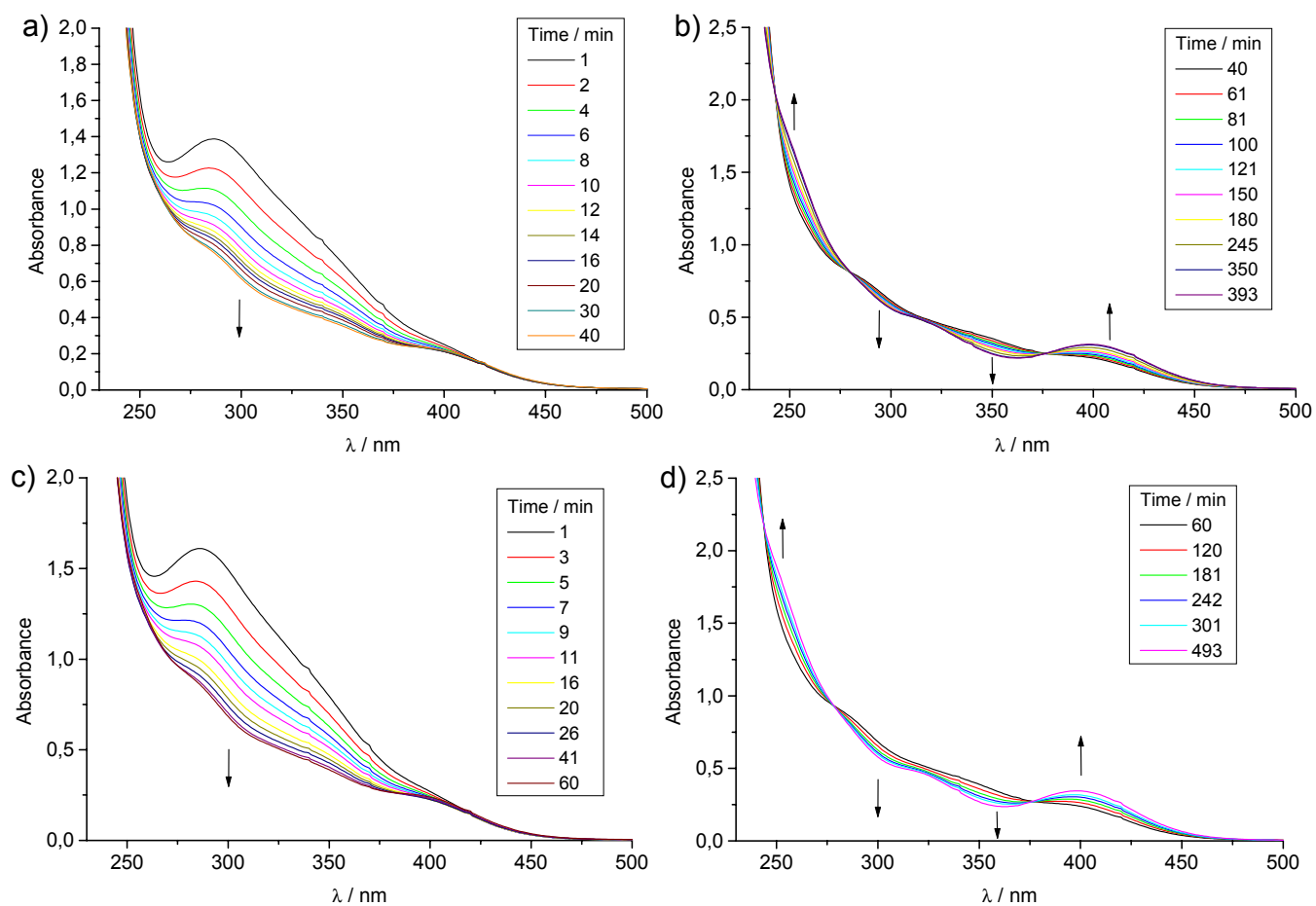
**Figure S2.** ORTEP drawing (40% probability level) of the dinuclear cation of  $[\{\text{Ru}([\text{9}]\text{aneS}_3)(\text{dms}\text{-}\text{S})\}(\eta^4, \mu\text{-ox})\{\text{Ru}(\text{dms}\text{-}\text{S})_3(\text{CF}_3\text{SO}_3)\}][\text{CF}_3\text{SO}_3] \cdot 0.5(\text{CHCl}_3)$  (**5**).



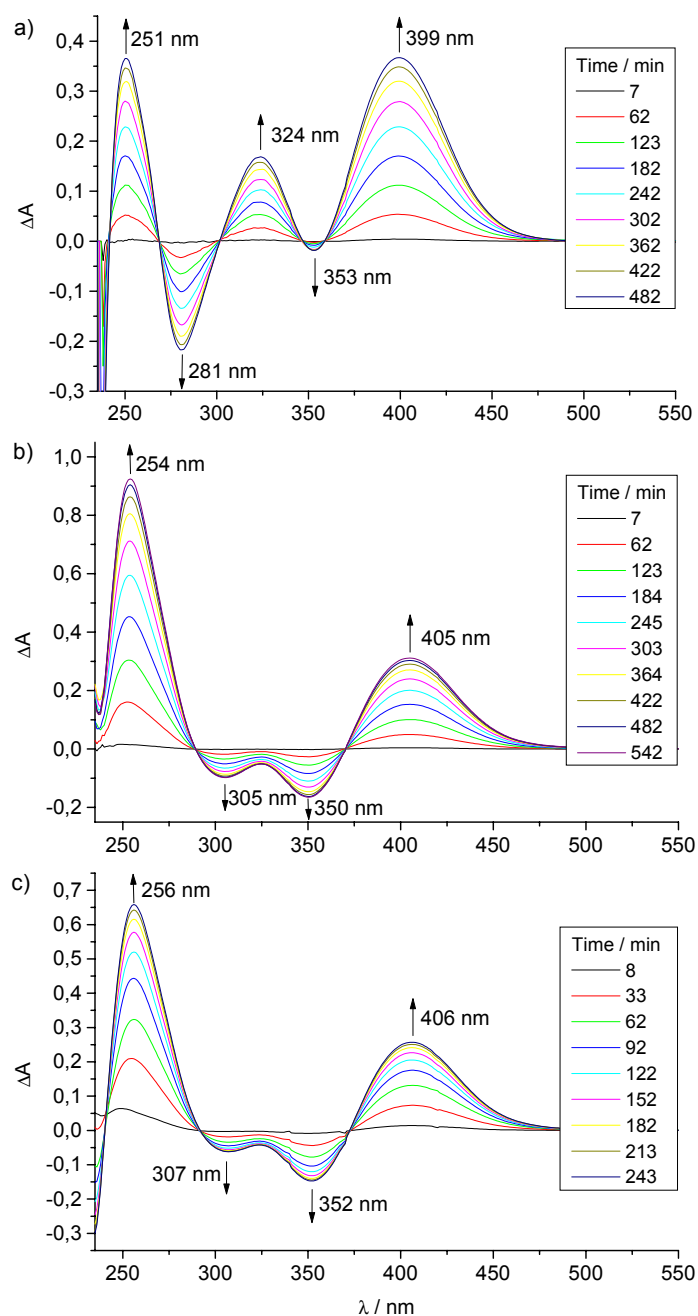
**Figure S3.** Packing arrangement of **3** in the solid state achieved through ionic  $\text{K}\cdots\text{O}$  interactions ( $\text{CF}_3\text{SO}_3$  anions colored in black). The coordination sphere about K ions is a distorted trigonal bipyramid.



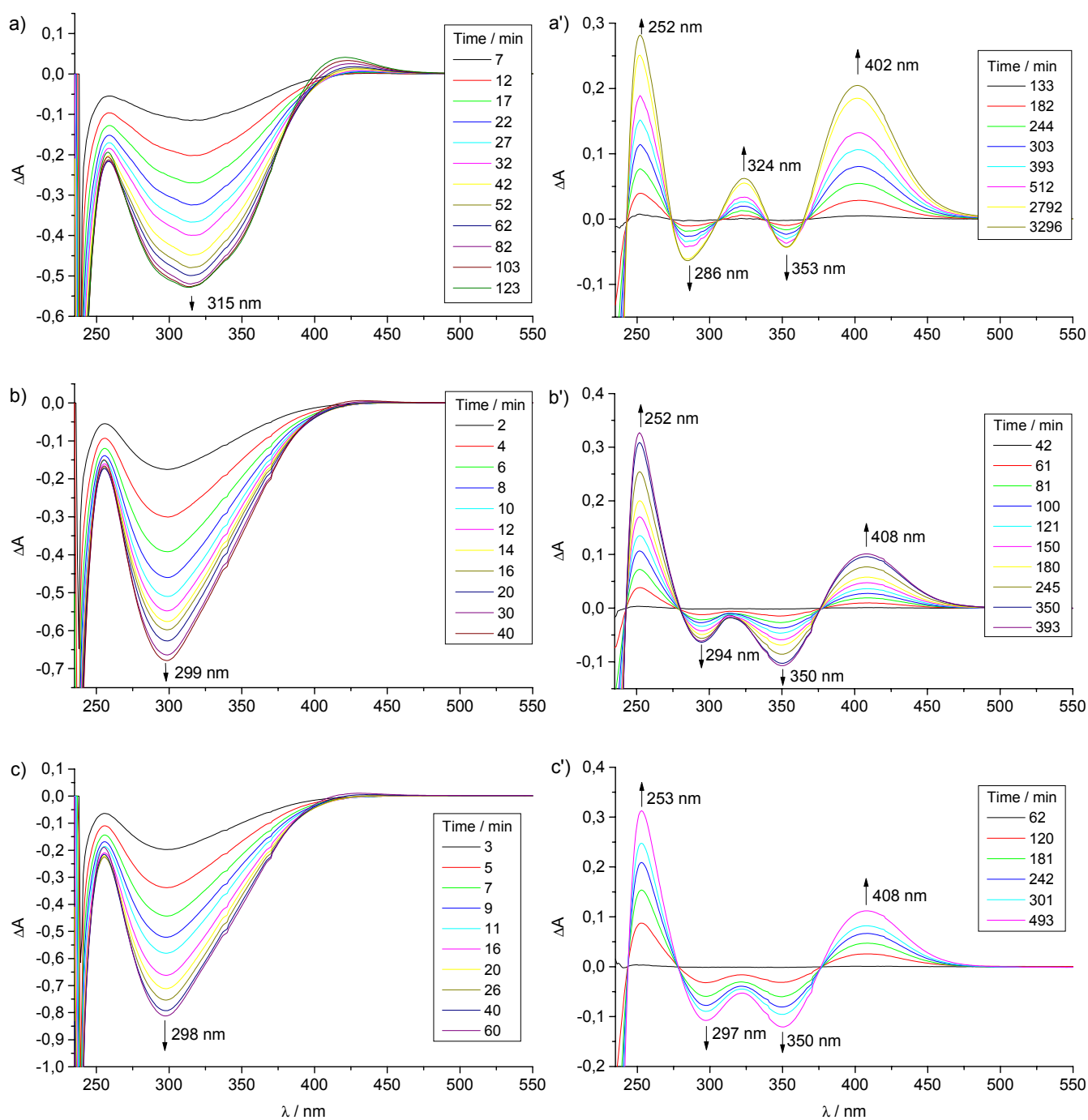
**Figure S4.** Time evolution of UV-Vis spectra of a) complex **2** (1.0 mM), and b) complex **3** (1.0 mM) in H<sub>2</sub>O at 25.0 °C.



**Figure S5.** Time evolution of UV-Vis spectra of complex **5** (top, a: first step, b: second step, 0.5 mM), and complex **6** (bottom, c: first step, d: second step, 0.5 mM) in  $\text{H}_2\text{O}$  at  $25.0\text{ }^\circ\text{C}$ .

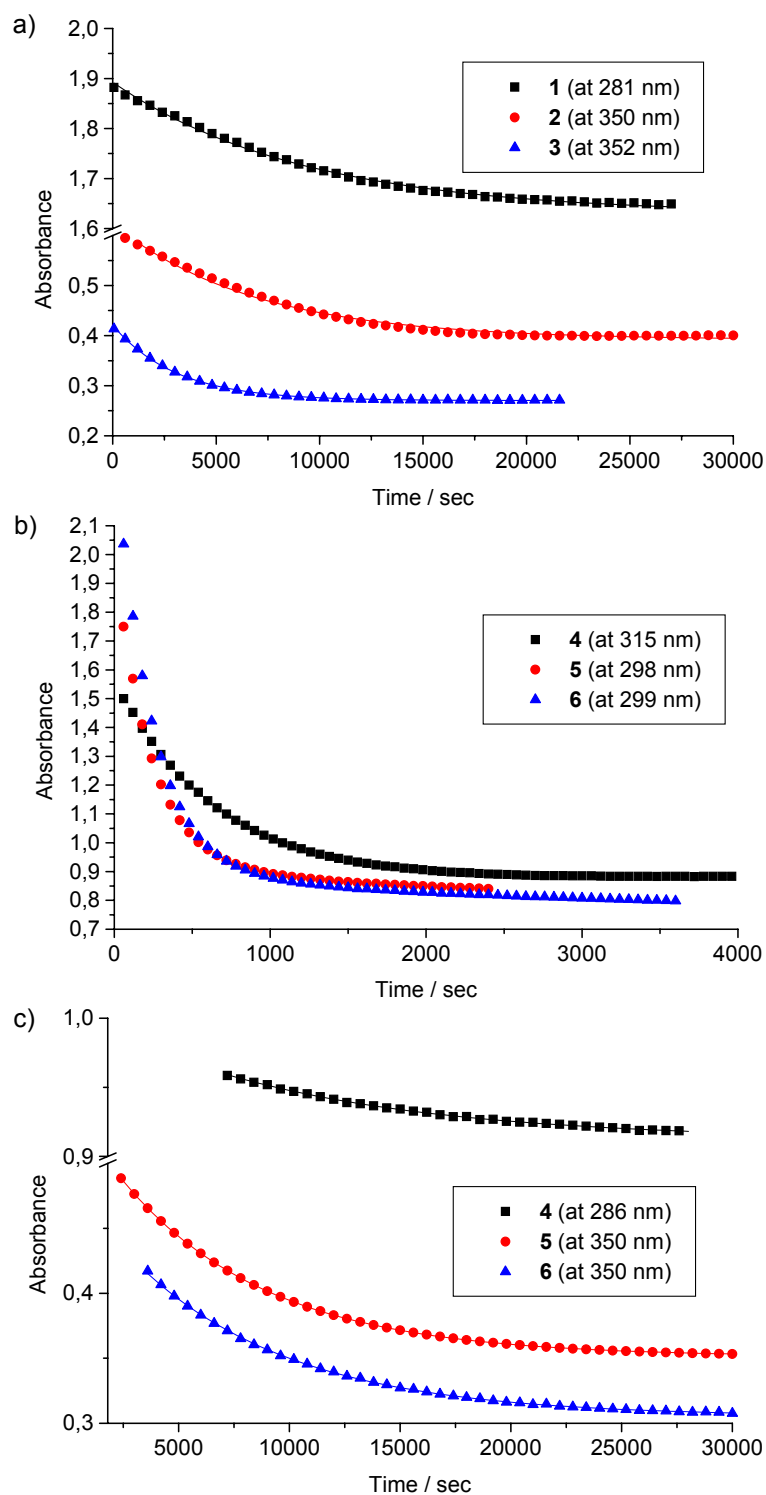


**Figure S6.** Time evolution of UV-Vis difference spectra during the hydrolysis of a) **1**, b) **2**, and c) **3** in  $H_2O$  at  $25.0\text{ }^\circ\text{C}$ .  $\Delta A = A_t - A_0$ , where  $A_t$  = absorbance at time  $t$  and  $A_0$  = absorbance at  $t = 2$  min (i.e. the time at which the first spectrum was recorded).



**Figure S7.** Time evolution of UV-Vis difference spectra during the hydrolysis of **4** (a: first step, a': second step), **5** (b: first step, b': second step), and **6** (c: first step, c': second step) in H<sub>2</sub>O at 25 °C.  $\Delta A = A_t - A_0$ , where  $A_t$  = absorbance at time  $t$  and  $A_0$  = absorbance at time obtained the first spectrum (i.e. 1 min for the first step of **4** – **6**, 123 min for second step of **4**, 40 min for second step of **5**, and 60 min for second step of **6**).





**Figure S8.** Time-dependence of the absorbance at selected wavelengths for a) the hydrolysis of complexes **1 – 3**, b) the first step of the hydrolysis of complexes **4 – 6**, and c) the second step of the hydrolysis of complexes **4 – 6** in H<sub>2</sub>O at 25.0 °C. Full lines represent computer fits giving the first-order rate constants listed in Table S1.

**Table S1.** Hydrolysis rate constants and half-lives at 25.0 °C for complexes **1 – 3** and for the second step of dimers **4 – 6**.

Compound	$\lambda_{\max}^*$ [nm]	$\lambda_{\min}^*$ [nm]	Isosbestic points [nm]	$k_{\text{H}_2\text{O}}$ [ $10^{-4} \text{ sec}^{-1}$ ]	$(t_{1/2})_{\text{H}_2\text{O}}$ [min]
<b>1</b>	251, 324, 399	<b>281</b> , 353	269, 302, 347, 359	$1.10 \pm 0.01$	$105.0 \pm 1.0$
<b>2</b>	254, 405	305, <b>350</b>	289, 370	$1.50 \pm 0.01$	$77.0 \pm 0.5$
<b>3</b>	256, 406	307, <b>352</b>	292, 372	$3.20 \pm 0.01$	$36.1 \pm 0.1$
<b>4</b>	252, 324, 402	<b>286</b> , 353	274, 306, 340, 365	$1.00 \pm 0.01$	$115.5 \pm 1.2$
<b>5</b>	252, 408	294, <b>350</b>	280, 376	$1.50 \pm 0.03$	$77.0 \pm 1.5$
<b>6</b>	253, 408	297, <b>350</b>	278, 376	$1.40 \pm 0.01$	$82.5 \pm 0.3$

\* Wavelengths obtained from the time evolution difference electronic absorption spectra.  
In bold are indicated the wavelengths selected for the kinetic studies.