Redox State Sensitive Spectroscopy of the Model Compound $[(H\text{-}dcbpy)_2Ru^{II}(NCS)_2]^{2-}$ (dcbpy = 2,2´-bipyridine-4,4´-dicarboxylato)

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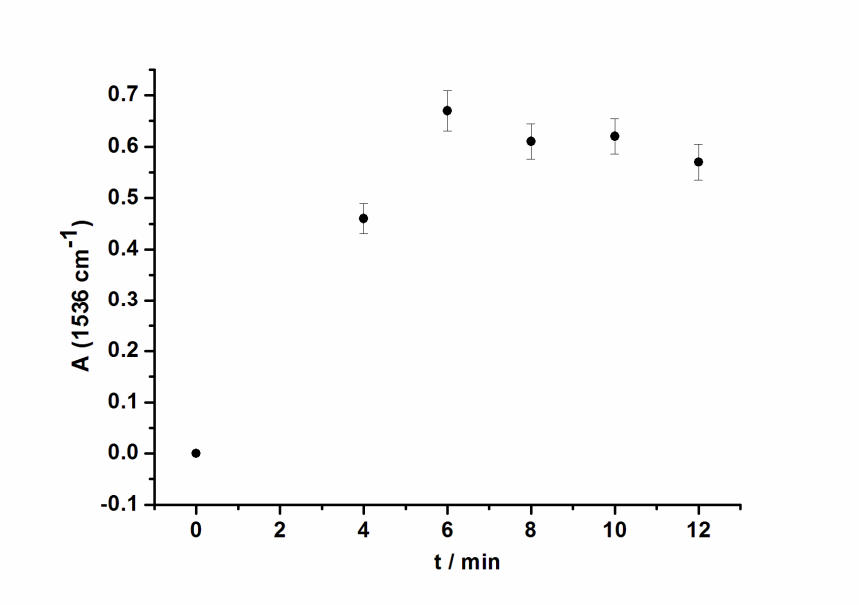
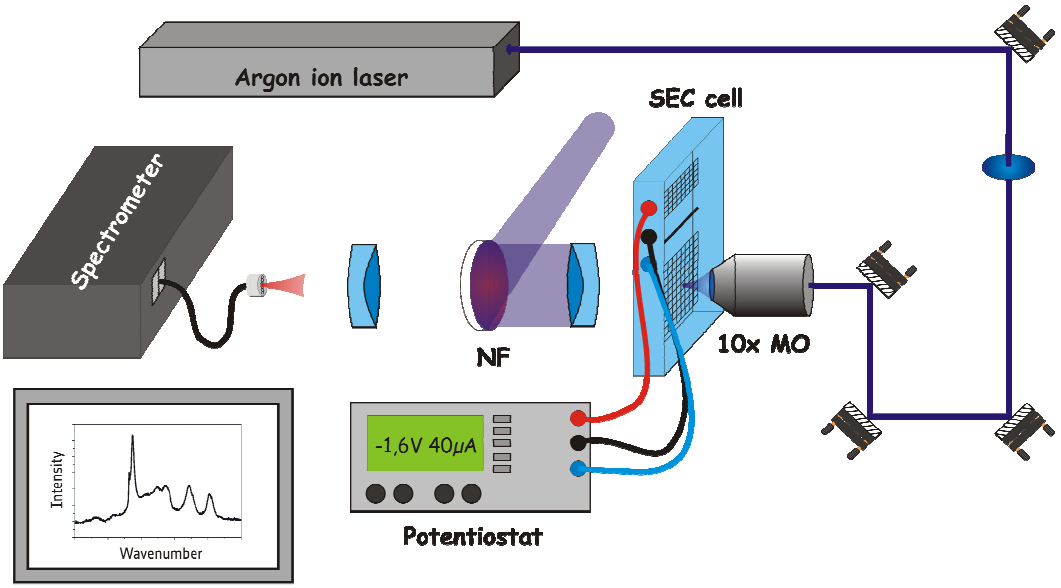
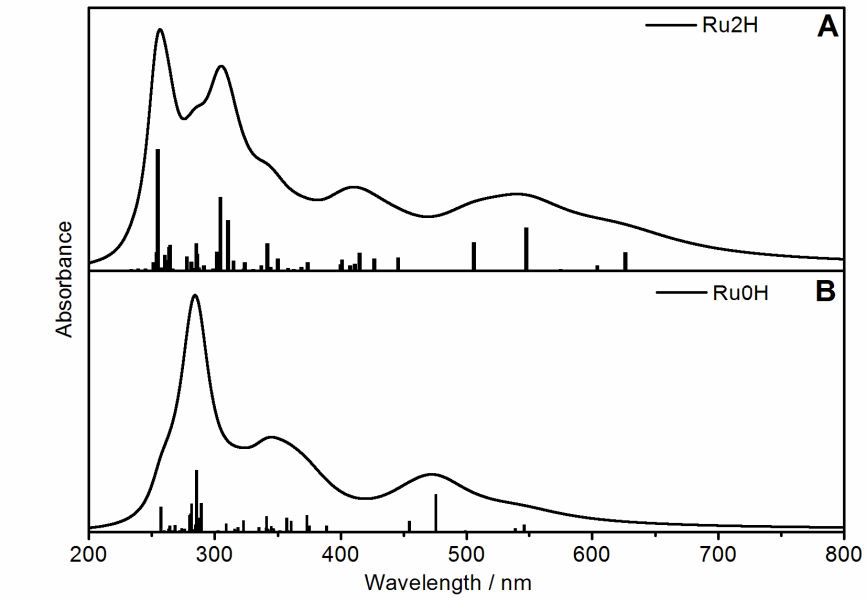
Supplementary material section



SI 1: Time course of the band area at 1536 cm^{-1} of reduced **Ru2H**. The band area and thus the concentration of reduced **Ru2H** increases for app. 4 minutes until a stationary condition is reached, i.e. the electrode surfaces are completely coated and/or an equilibrium for the reduction of **Ru2H** is established.



SI 2: General rR-SEC setup: rR-SEC measurements were performed in transmission. The laser is focussed onto the grid of the working electrode by a microscope objective (MO). Notchfilter (NF) is used to block the laser line.



SI 3: Calculated ground state absorption spectra of **Ru2H** (A) and **Ru0H** (B) with oscillator strength as histogram.

ESI Data:

Table S1: Molecular orbitals involved in the main configurations of the excited states of **Ru2H**.

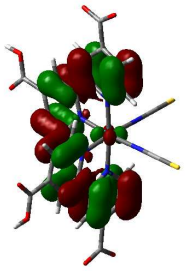
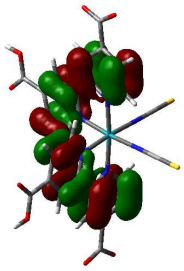
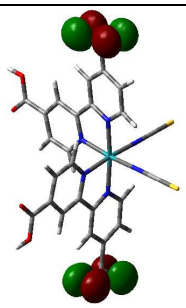
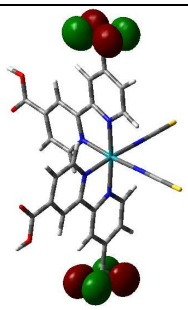
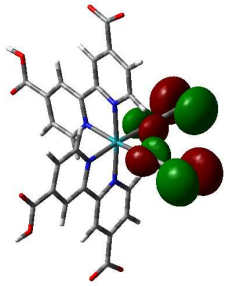
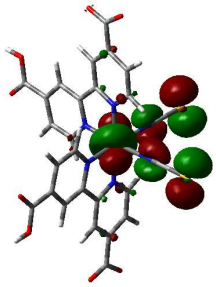
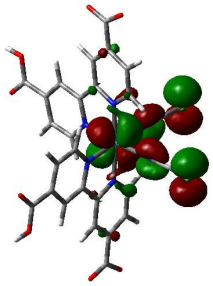
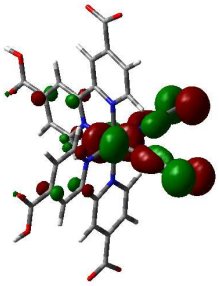
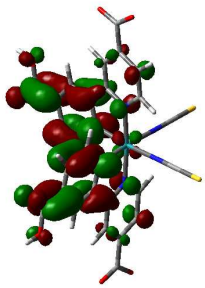
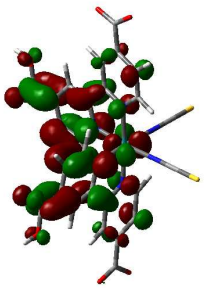
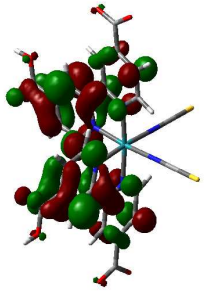
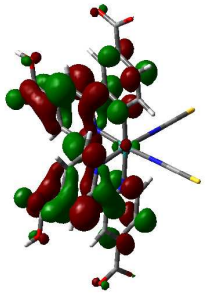
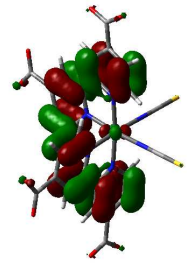
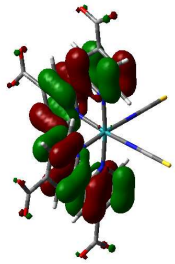
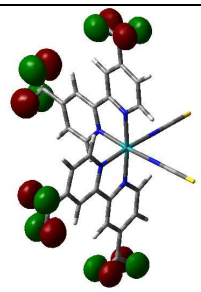
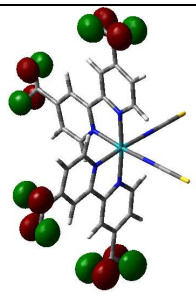
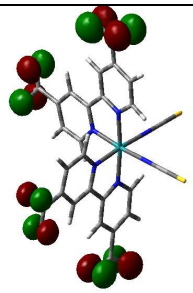
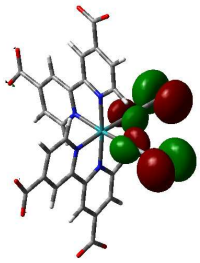
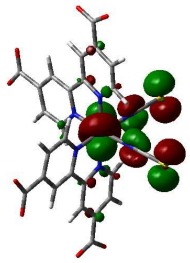
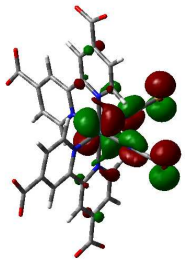
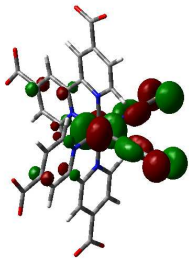
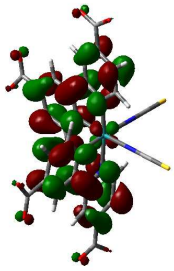
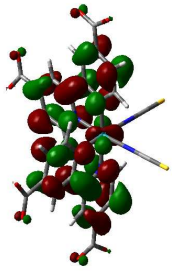
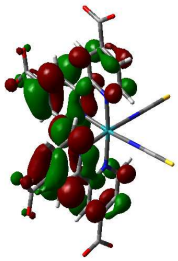
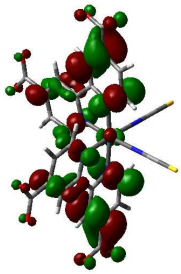
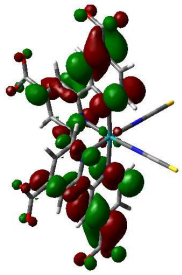
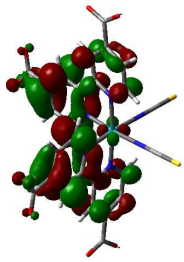
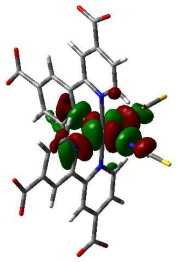
 $\pi_{dcbpy}(149)$	 $\pi_{dcbpy}(150)$	 $\pi_{COO}(154)$	 $\pi_{COO}(155)$
 $\pi_{NCS}(156)$	 $d_{Ru},\pi_{NCS}(161)$	 $d_{Ru},\pi_{NCS}(162)$	 $d_{Ru},\pi_{NCS}(163)$
 $\pi^*_{dcbpy}(164)$	 $\pi^*_{dcbpy}(165)$	 $\pi^*_{dcbpy}(166)$	 $\pi^*_{dcbpy}(167)$

Table S2: Calculated vertical excitation energies (E^e), oscillator strengths (f), and excited configurations with weights larger than 10% of the main excited states of **Ru0H**.

state	transition	weight (%)	E^e (eV)	λ (nm)	f
S_1	$d_{Ru},\pi_{NCS}(163) \rightarrow \pi^*_{dcbpy}(164)$	95	2.27	546	0.0279
S_2	$d_{Ru},\pi_{NCS}(163) \rightarrow \pi^*_{dcbpy}(165)$	88	2.30	539	0.0124
S_5	$d_{Ru},\pi_{NCS}(161) \rightarrow \pi^*_{dcbpy}(164)$ $d_{Ru},\pi_{NCS}(162) \rightarrow \pi^*_{dcbpy}(165)$	72 23	2.61	476	0.1433
S_6	$d_{Ru},\pi_{NCS}(161) \rightarrow \pi^*_{dcbpy}(165)$ $d_{Ru},\pi_{NCS}(162) \rightarrow \pi^*_{dcbpy}(164)$	64 20	2.73	455	0.0409
S_{11}	$d_{Ru},\pi_{NCS}(163) \rightarrow \pi^*_{dcbpy}(166)$	95	3.19	389	0.0225
S_{12}	$d_{Ru},\pi_{NCS}(163) \rightarrow \pi^*_{dcbpy}(167)$	83	3.31	375	0.0240
S_{15}	$d_{Ru},\pi_{NCS}(163) \rightarrow \pi^*_{dcbpy}(168)$	92	3.32	373	0.0628
S_{21}	$d_{Ru},\pi_{NCS}(163) \rightarrow \pi^*_{dcbpy}(169)$ $d_{Ru},\pi_{NCS}(162) \rightarrow \pi^*_{dcbpy}(166)$ $d_{Ru},\pi_{NCS}(162) \rightarrow \pi^*_{dcbpy}(168)$	57 17 10	3.44	361	0.0419
S_{25}	$d_{Ru},\pi_{NCS}(162) \rightarrow \pi^*_{dcbpy}(167)$	65	3.47	357	0.0531

	$d_{Ru},\pi_{NCS}(161) \rightarrow \pi^*_{dcbpy}(166)$	27			
S_{31}	$\pi_{NCS}(152) \rightarrow \pi^*_{dcbpy}(165)$ $d_{Ru},\pi_{NCS}(162) \rightarrow \pi^*_{dcbpy}(169)$ $d_{Ru},\pi_{NCS}(163) \rightarrow d_{Ru},\sigma^*(173)$	35 28 22	3.60	345	0.0222
S_{34}	$\pi_{COO}(150) \rightarrow \pi^*_{dcbpy}(164)$ $d_{Ru},\pi_{NCS}(161) \rightarrow \pi^*_{dcbpy}(168)$ $\pi_{COO}(151) \rightarrow \pi^*_{dcbpy}(165)$	35 22 20	3.64	341	0.0589
S_{67}	$\pi_{dcbpy}(144) \rightarrow \pi^*_{dcbpy}(164)$	84	4.29	289	0.1089
S_{70}	$\pi_{dcbpy}(143) \rightarrow \pi^*_{dcbpy}(164)$ $d_{Ru},\pi_{NCS}(161) \rightarrow d_{Ru},\sigma^*(173)$	41 18	4.35	285	0.2346
S_{71}	$\pi_{dcbpy}(144) \rightarrow \pi^*_{dcbpy}(165)$	75	4.35	285	0.1372
S_{81}	$\pi_{COO}(149) \rightarrow \pi^*_{dcbpy}(166)$ $\pi_{COO}(150) \rightarrow \pi^*_{dcbpy}(166)$	37 31	4.41	281	0.1069

Table S3: Molecular obitals involved in the main configurations of the excited states of **Ru0H**.

 $\pi_{dcbpy}(143)$	 $\pi_{dcbpy}(144)$	 $\pi_{COO}(149)$	 $\pi_{COO}(150)$
 $\pi_{COO}(151)$	 $\pi_{NCS}(152)$	 $d_{Ru},\pi_{NCS}(161)$	 $d_{Ru},\pi_{NCS}(162)$
 $d_{Ru},\pi_{NCS}(163)$	 $\pi^*_{dcbpy}(164)$	 $\pi^*_{dcbpy}(165)$	 $\pi^*_{dcbpy}(166)$
 $\pi^*_{dcbpy}(167)$	 $\pi^*_{dcbpy}(168)$	 $\pi^*_{dcbpy}(169)$	 $d_{Ru},\sigma^*(173)$

Complete list of co-authors for Reference 41

(41) Frisch, M. J. Trucks, G. W. Schlegel, H. B. Scuseria, G. E. Robb, M. A. Cheeseman, J. R. Scalmani, G. Barone, V. Mennucci, B. Petersson, G. A. Nakatsuji, H. Caricato, M. Li, X. Hratchian, H. P. Izmaylov, A. F. J. Bloino, G. Z. Sonnenberg, J. L. Hada, M. Ehara, M. Toyota, K. Fukuda, R. Hasegawa, J. Ishida, M. Nakajima, T. Honda, Y. Kitao, O. Nakai, H. Vreven, T. Montgomery, J. J. A. Peralta, J. E. Ogliaro, F. Bearpark, M. Heyd, J. J. Brothers, E. Kudin, K. N. Staroverov, V. N. Kobayashi, R. Normand, J. Raghavachari, K. Rendell, A. Burant, J. C. Iyengar, S. S. Tomasi, J. Cossi, M. Rega, N. Millam, J. M. Klene, M. Knox, J. E. Cross, J. B. Bakken, V. Adamo, C. Jaramillo, J. Gomperts, R. Stratmann, R. E. O. Yazyev, A. J. A. R. Cammi, C. P. Ochterski, J. W. Martin, R. L. Morokuma, K. Zakrzewski, V. G. Voth, G. A. Salvador, P. Dannenberg, J. J. Dapprich, S. Daniels, A. D. Farkas, O. Foresman, J. B. Ortiz, J. V. Cioslowski, J.; Fox, D. J. *Gaussian 09*; Gaussian, Inc., Wallingford, CT, 2009.