## **Electronic supplementary materials**

# Spectroelectrochemical study of the reduction of 2-methyl-9H-thioxanthene-9one and its S,S-dioxide and electronic absorption spectra of their molecular ions

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**Figure S1**. Optically transparent spectroelectrochemical cell with an ITO working electrode and a Pt dick testing electrode.

### 1. Cyclic voltammetry data and determination of diffusion coefficients of 1 and 2.



Figure S2. CVs of 1 (*a*) and 2 (*b*, first CV-wave) in CH<sub>3</sub>CN at various potential sweep rates (indicated by color) and the corresponding Randles-Sevcik calculations (*c*, *d*) (Blue rectangles – experiment, red curves – calculations). Calibrated area of the Pt dick working electrode is A= 0.0143 cm<sup>2</sup>. Initial bulk concentrations of 1 and 2 were 9.94·10<sup>-4</sup> and 6.54·10<sup>-4</sup> mol/dm<sup>3</sup>, respectively.

Figure S2 demonstrates the determination of the diffusion coefficients of compounds 1 and 2 in MeCN using Randles-Sevcik equation [1]:

$$I_{\rm p} = 0.4463 \ nFAC_0 (\frac{nFv \ D}{RT})^{1/2} \tag{1}$$

where  $I_p$  is current maximum, *n* is number of electrons transferred in the redox event, A - electrode area in cm<sup>2</sup>, *F* –Faraday constant in C·mol<sup>-1</sup>, *D* is diffusion coefficient in cm<sup>2</sup>/s,  $C_0 -$  concentration in mol/cm<sup>3</sup>, *v* – potential scan rate in V/s, *R* – gas constant in J·K<sup>-1</sup>·mol<sup>-1</sup>, *T* – temperature in K. The corresponding diffusion coefficients were found to be  $(1.75 \pm 0.05) \times 10^{-5}$  and  $(2.37 \pm 0.04) \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>, respectively (see also Table 1, main text).



2. Illustrations of the results of time-dependent DFT calculations with B2PLYP and B3LYP functionals.

**Figure S3.** The electronic absorption spectrum of **1** (red spectrum) registered at E = -1.0 V in CH<sub>3</sub>CN and its change upon reduction registered at E = -1.78 V (blue spectrum). In both figures the vertical bars indicate the positions and oscillator strengths (right axis) of the electronic transitions calculated at the TD-B2PLYP/def2-TZVP level of theory (a) and TD-B3LYP/def2-TZVP level of theory (b) for **1** (red bars), **1**<sup>-•</sup> (blue bars) and **1**<sup>2–</sup> (green bars).



**Figure S4**. The electronic absorption spectrum of **2** (red spectrum) registered at E = -1.0 V in CH<sub>3</sub>CN and its changes upon reduction registered at E = -1.35 V (blue spectrum) and at E = -1.61 V (green spectrum). In both figures the vertical bars indicate the positions and oscillator strengths (right axis) of the electronic transitions calculated at the TD-B2PLYP/def2-TZVP level of theory (a) and TD-B3LYP/def2-TZVP level of theory (b) for **2** (red bars), **2**<sup>-•</sup> (blue bars) and **2**<sup>2–</sup> (green bars).

**Table S1a**. Maxima of absorption bands ( $\lambda_{max}$  and  $\nu_{max}$ ) in the experimental electronic absorption spectra of neutral compound 1 and its RA 1<sup>-•</sup>, and positions ( $\lambda_{max}$  and  $\nu_{max}$ ) and oscillator strengths (f) of the electronic transitions calculated at the TPSSh/def2-TZVP level, as well as positions ( $\lambda_{max}$ ) and oscillator strengths (f) of the electronic transitions calculated at the TD-B2PLYP/def2-TZVP and TD-B3LYP/def2-TZVP levels of theory, for 1, RA 1<sup>-•</sup> and DA 1<sup>2–</sup> (only electronic transition with f > 0.005 are presented).

Redox	Experiment <sup>a</sup>		TD-TPSSh/def2-TZVP			TD-B2PLYP		TD-B3LYP	
state	$\lambda_{\max},$ nm	$v_{max}$ , cm <sup>-1</sup>	$\lambda_{max},$ nm	$v_{max}$ , cm <sup>-1</sup>	f	$\lambda_{max},$ nm	f	$\lambda_{\max},$ nm	f
	385	25970	379	26400	0.172	365	0.102	368	0.078
	302	33120	297	33680	0.061	281	0.028	292	0.028
Neutral	290	34490	280	35760	0.008	257	0.022	270	0.001
1	263	38020	272	36740	1.229	248	1.231	262	0.488
-	205	50020	270	37110	0.055	244	0.080	261	0.043
	258	38760	266	37590	0.349	242	0.035	254	0.232
		38700	258	38820	0.511	240	0.065	251	0.258
	_	_	841	11900	0.020	753	0.070	813	0.028
	_	_	658	15190	0.008	616	0.023	641	0.014
	675	14800	602	16620	0.162	592	0.077	598	0.154
	_	_	483	20710	0.005	398	0.005	472	0.005
	417	23980	407	24590	0.011	360	0.009	399	0.012
	339		339	29520	0.020	314	0.013	333	0.023
RA 1-•		29500	316	31620	0.017	300	0.049	311	0.024
			314	31810	0.005	291	0.010	294	0.012
			298	33530	0.007	281	0.064	291	0.013
	289	289 34600	295	33870	0.015	280	0.005	286	0.021
			276	36200	0.070	278	0.030	271	0.285
	268	37300	276	36270	0.356	264	0.159	271	0.042
	200	57500	270	37110	0.062	262	0.133	267	0.149
	259	38600	266	37630	0.017	258	0.075	264	0.043

		262	38120	0.042	254	0.158	260	0.043
		256	39130	0.042	246	0.016	256	0.005
		820	12200	0.018	770	0.077	646	0.009
		669	14950	0.007	647	0.017	499	0.341
		435	22990	0.005	526	0.414	432	0.021
		419	23860	0.281	415	0.142	418	0.254
		340	29450	0.014	374	0.005	369	0.006
		308	32520	0.037	338	0.010	321	0.008
DA 1 <sup>2-</sup>	- Not detected	298	33530	0.009	327	0.006	320	0.015
		298	33570	0.116	306	0.021	301	0.005
		283	35330	0.011	305	0.008	293	0.060
		276	36300	0.0232	293	0.042	290	0.040
		265	37730	0.021	291	0.066	289	0.101
		264	37820	0.008	283	0.159	266	0.035
		259	38550	0.009	281	0.010	265	0.009
		251	39920	0.076	259	0.082	256	0.024
		259 251	38550 39920	0.009	281 259	0.010	265 256	0.009

<sup>a</sup>Assignment of the experimental band maxima were performed based on the results of the TD-TPSSh/def2-TZVP calculations.

**Table S1b**. Maxima of absorption bands ( $\lambda_{max}$  and  $\nu_{max}$ ) in the experimental electronic absorption spectra of neutral compound **2**, its RA **2**<sup>-•</sup> and DA **2**<sup>2–</sup>, and positions ( $\lambda_{max}$  and  $\nu_{max}$ ) and oscillator strengths (f) of the electronic transitions calculated at the TPSSh/def2-TZVP level, as well as positions ( $\lambda_{max}$ ) and oscillator strengths (f) of the electronic transitions calculated at the TD-B2PLYP/def2-TZVP and TD-B3LYP/def2-TZVP levels of theory for 2, its RA 2<sup>-•</sup> and DA 2<sup>2–</sup> (only electronic transition with f > 0.005 are presented).

Paday	Experimen	nt <sup>a</sup>	TD-TPS	Sh/def2-TZ	ZVP	TD-B2P	LYP	TD-B3LYP		
state	$\lambda_{max}$ , nm	v <sub>max</sub> , cm <sup>-1</sup>	λ <sub>max</sub> , nm	v <sub>max</sub> , cm <sup>-1</sup>	f	$\lambda_{max},$ nm	f	$\lambda_{max},$ nm	f	
	375 <sup>b</sup>	26640	382	26210	0.003	360	0.004	368	0.003	
	359	27870	358	27960	0.006	306	0.006	339	0.006	
Neutral		_	321	31110	0.016	279	0.210	302	0.020	
2	284	35211	303	33040	0.194	283	0.018	294	0.209	
-			269	37160	0.073	247	0.132	260	0.091	
	260	38390	261	38260	0.142	228	0.448	246	0.013	
			255	39170	0.005	244	0.042	241	0.194	
			754	13260	0.007	659	0.019	716	0.008	
	631	15850	571	17530	0.123	550	0.200	556	0.159	
	0.51	15650	516	19370	0.105	469	0.015	504	0.079	
	378	26450	357	28030	0.012	328	0.019	349	0.010	
	570	20100	352	28450	0.013	317	0.040	344	0.019	
			321	31190	0.056	283	0.032	312	0.066	
RA <b>2</b> -•	321	31153	314	31860	0.047	282	0.068	304	0.047	
			302	33150	0.013	273	0.027	292	0.009	
			297	33650	0.007	-	_	_	_	
	285	35060	291	34320	0.007	269	0.061	277	0.036	
	205	55000	286	34990	0.028	262	0.006	275	0.010	
			274	36520	0.006	262	0.005	272	0.015	
			271	36880	0.016	262	0.008	271	0.016	

	-								
	268	37310	252	39660	0.152	249	0.056	244	0.015
	260	38500	232	57000	0.152	240	0.058	242	0.086
	242	41350	243	41190	0.023	237	0.120	242	0.093
	_	-	788	12690	0.014	923	0.013	742	0.016
	_	-	552	18130	0.014	620	0.057	529	0.020
	525	19050	455	21990	0.512	603	0.185	448	0.549
			334	29970	0.006	551	0.368	_	-
DA <b>2</b> <sup>2–</sup>	313	313 32000	296	33780	0.010	331	0.018	328	0.007
	515		291	34330	0.016	551	0.010	520	0.007
		36900	268	37330	0.031	-	_	-	-
	271		264	37950	0.022	271	0.095	276	0.030
			260	38506	0.092	270	0.040	254	0.187
			240	41670	0.415	250	0.218		
	1		1			1		1	

<sup>a</sup> Assignment of the experimental band maxima were performed based on the results of the TD-TPSSh/def2-TZVP calculations.

<sup>b</sup> These band and electronic transition are of  $n\pi^*$  type (more precisely  $(n+\sigma)\pi^*$  type, see for details natural transition orbitals in Figure 5 of main text).



Figure S5. Atomic spin population for radical anions  $1^{-\bullet}$  and  $2^{-\bullet}$  calculated at the UB3LYP/def2-TZVP level of theory.



# 4. Illustrations of 3D UV-VIS-NIR measurements in "normal mode" and the measurements using optically transparent electrode (OTE) method.

Figure S6. Spectroelectrochemical surfaces in the reduction area of potentials for compounds 1 (*a*) and 2 (*c*); electronic absorption spectra registered at various potentials for 1 (*b*) and 2 (*d*) when  $CH_3CN$  was taken as blank.



**Figure S7.** The images of an ITO working electrode under OTE measurements of compound **2**: (*a*) E=-1.2 V, one-electron process: t=10 s (potential ON), 30 sec (potential OFF), 40 sec (end of observation); (*b*) E=-2.0 V, two electron process: t=10 s (potential ON), 30 sec (potential OFF), 40 sec (end of observation)

Figure S7 demonstrates the images of an ITO working electrode at different periods of time under OTE measurements (see also Fig. 4*b*, *c*, main text). Images at 40 s (end of observation) show a violation of chronoamperometric conditions and, as a consequence, the appearance of vortex flows. The image (*b*) at 40 s shows a color change due to oxidation of DA  $2^{2-}$  to form RA  $2^{-\bullet}$  (compare images (*a*) and (*b*); see also Fig.4*c*, main text).

5. Experimental time dependences of the currents used in empirical charge transfer kinetic models.



Figure S8. Current *versus* time observed in the 3D UV-VIS-NIR spectroelectrochemical reduction of 1 in CH<sub>3</sub>CN. Initial bulk concentration of 1 was  $7.0 \cdot 10^{-4}$  M.



**Figure S9.** Current versus time dependence, I(t), registered in the 3D UV-VIS-NIR spectroelectrochemical reduction of **2** in MeCN. Initial bulk concentration of **2** was  $7.2 \cdot 10^{-4}$  M. The optimized time domains of **h**, **g** functions are indicated by color.

Figure S9 illustrates the dependence of current on time observed in the 3D UV-VIS-NIR spectroelectrochemical experiment of **2**. The time domains (in seconds) for determining the functions **h** and **g** (see main text) were found to be as follows:  $210 < [t_1, t_2] \le 389$ ;  $389 < [t_2, t_3] \le 432$ ;  $432 < [t_3, t_4] \le 602$ ;  $602 < [t_4, t_5] \le 692$ ;  $692 < [t_5, t_6] \le 1020$ .



Figure S10. Spectroelectrochemical reduction kinetics at the selected wavelengths for compound
2 together with the corresponding modeling in the approximation of the EE-process for ECR of
2. (solid curves – experiment, curves with circles - modeling).

Figure S10 shows the time dependences of optical densities, obtained in 3D reductive spectroelectrochemical experiment of compound **2**, together with the corresponding modeling of these time dependences using approximation of the EE-process for ECR of **2** (the rate constant  $k_1$  was taken equal to 0, Scheme 1, main text). In this approximation, an adequate description of the increase in the optical density at 288 nm is impossible. This fact clearly indicates that negative optical absorption at 288 nm (time period 400<t<750 s) is associated not only with the neutral form of compound **2**, but also with the product formed at the stage of **2**<sup>2-</sup> formation (ThSO<sub>2</sub>H<sup>-</sup>, Scheme 1, main text).

#### References

[1] A. J. Bard, L. R. Faulkner, Electrochemical Methods: Fundamentals and Applications (2nd ed.), John Wiley & Sons, 2001