

Electronic Supplementary Information

A Water-Soluble Octahedral Molybdenum Cluster Complex as a Potential Agent for X-Ray Induced Photodynamic Therapy

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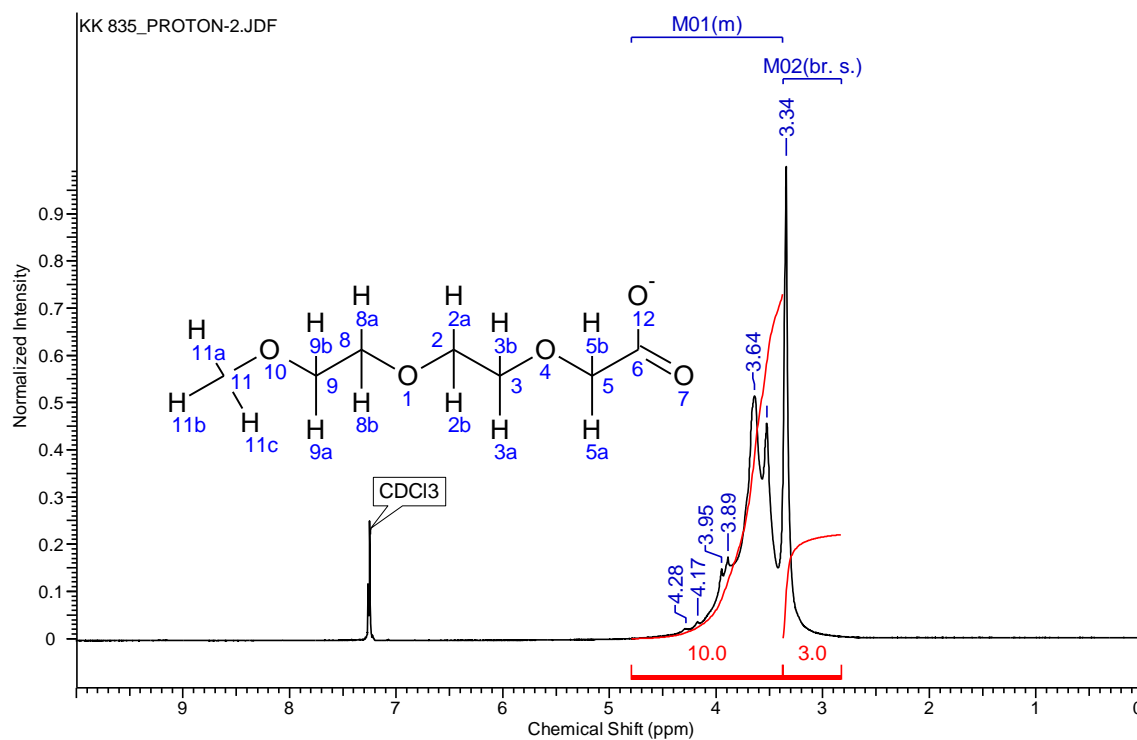
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Figure S1. ^1H NMR spectrum of **1** in CDCl_3 and the corresponding assignment.



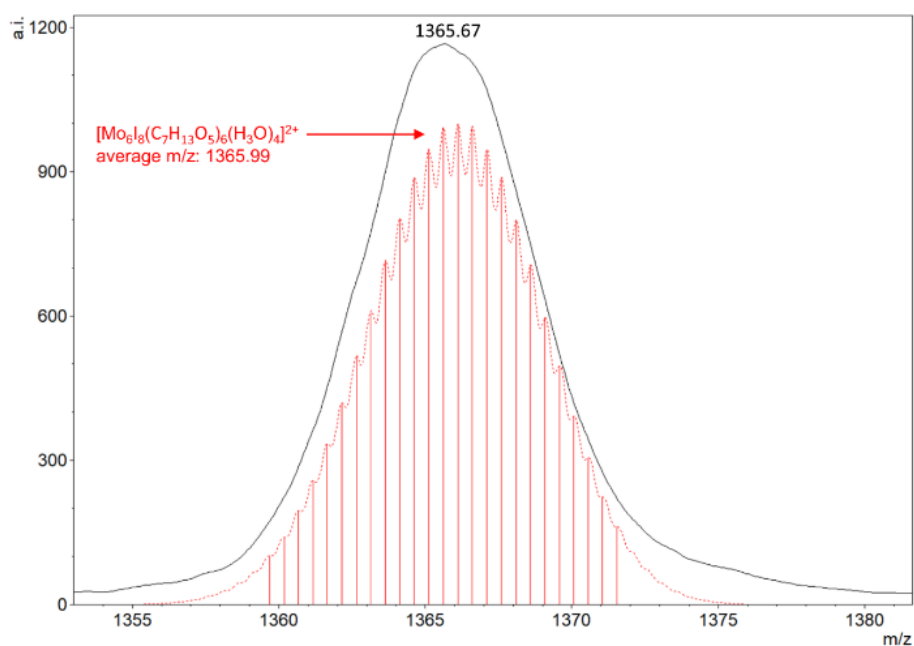
Multiplet	δ (ppm)	Proton assignment	Number of protons
M01 (m)	3.34	11a, 11b, 11c	3
M02 (br. s.)	3.38 - 4.79	2a, 2b, 3a, 3b, 5a, 5b, 8a, 8b, 9a, 9b	10
Total number of protons			13

Figure S2. Electrospray ionization-mass spectrum of **1** in the positive mode:

(A) fresh solution of **1**, revealing a peak with m/z of 1365.67 corresponding to $[\text{Mo}_6\text{I}_8(2\text{-}[2\text{-}(2\text{-methoxyethoxy})\text{ethoxy}]\text{acetate})_6(\text{H}_3\text{O})_4]^{2+}$ ($m/z = 1365.99$).

(B) 3-days old solution of **1**, revealing a peak with m/z of 1266.50 corresponding to partially hydrolyzed $[\text{Mo}_6\text{I}_8(2\text{-}[2\text{-}(2\text{-methoxyethoxy})\text{ethoxy}]\text{acetate})_5(\text{H}_2\text{O})(\text{H}_3\text{O})_2]^{2+}$ ($m/z = 1266.38$).

A



B

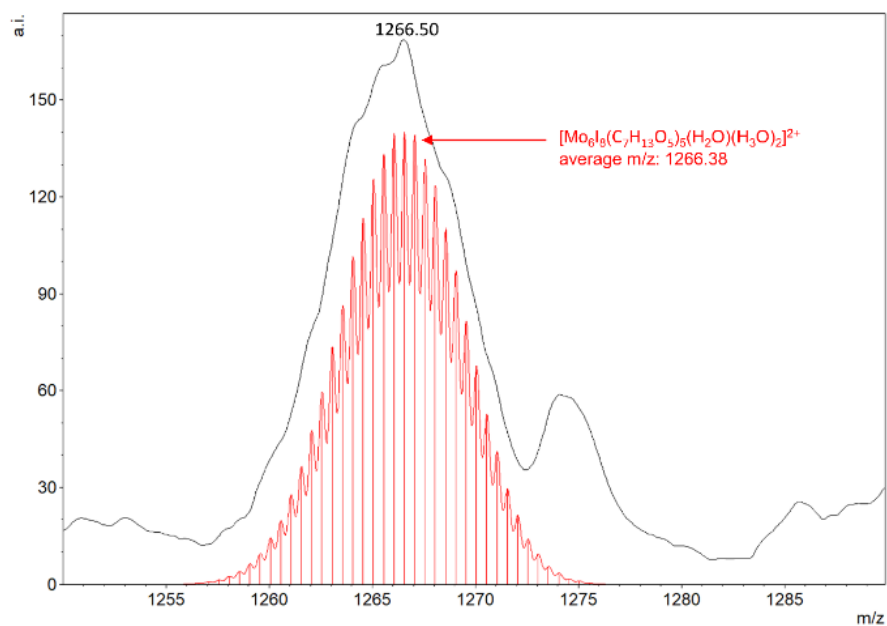


Figure S3. Absorption spectrum of **1** in DMSO.

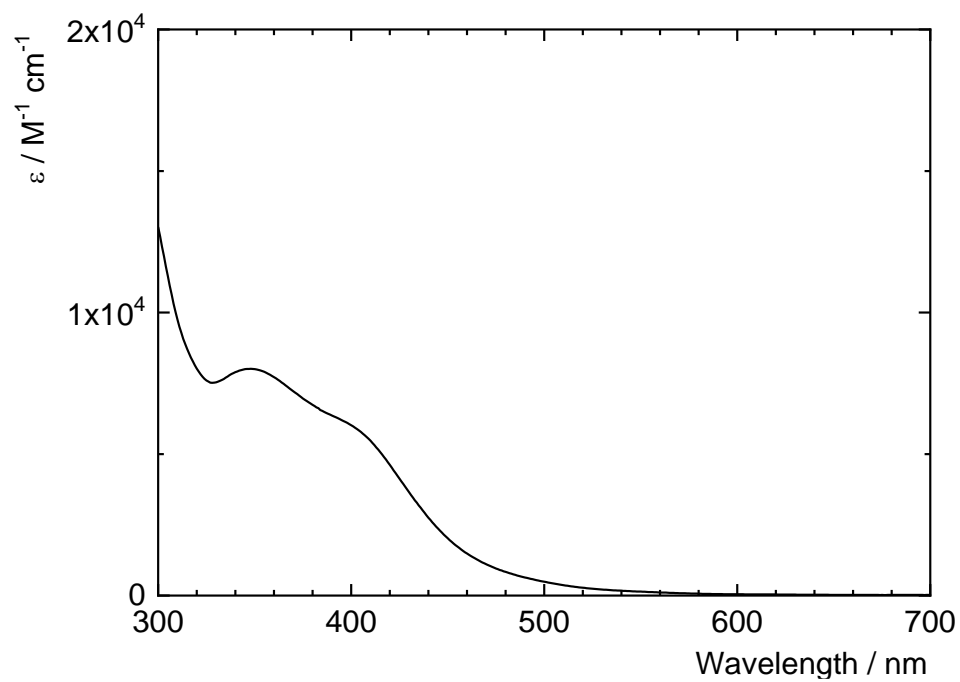


Figure S4. Luminescence emission spectrum of **1** in air-saturated (black) and Ar-saturated DMSO (red). The samples were excited at 400 nm.

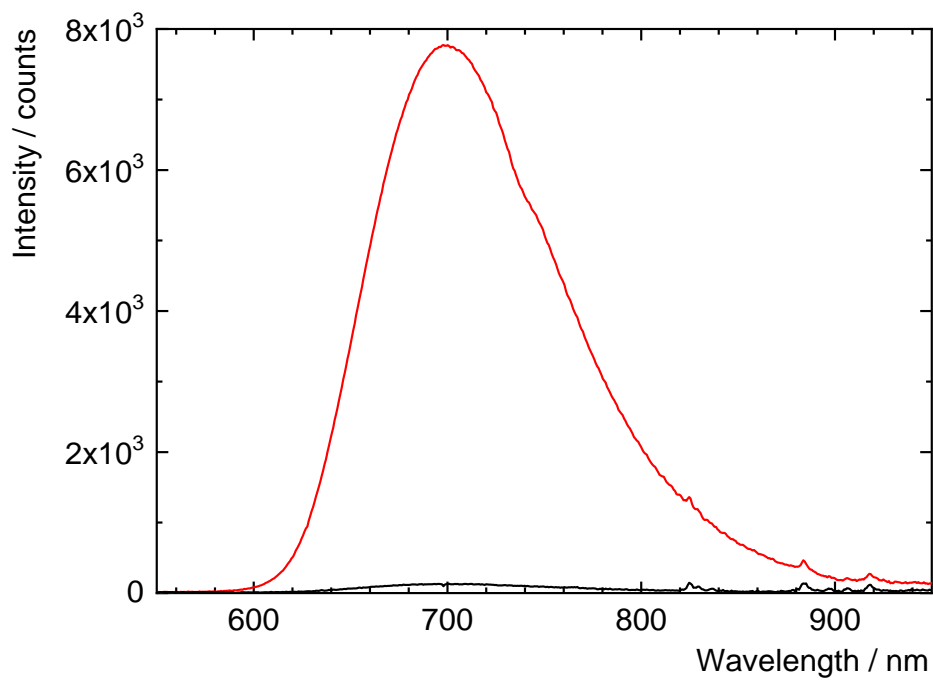


Figure S5. Absorption spectrum of **1** in PBS, fresh solution (a) and three-days old solution (b).

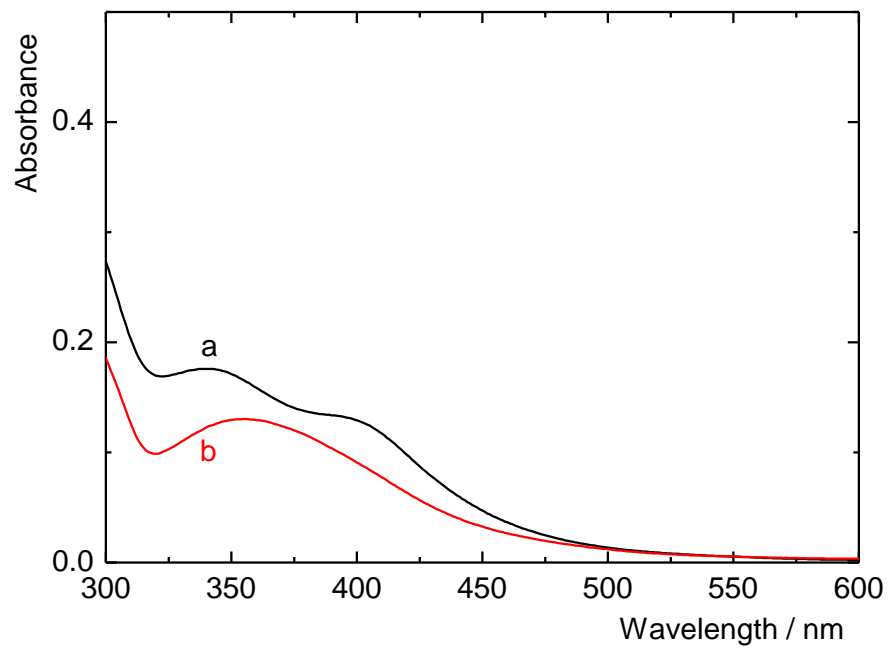
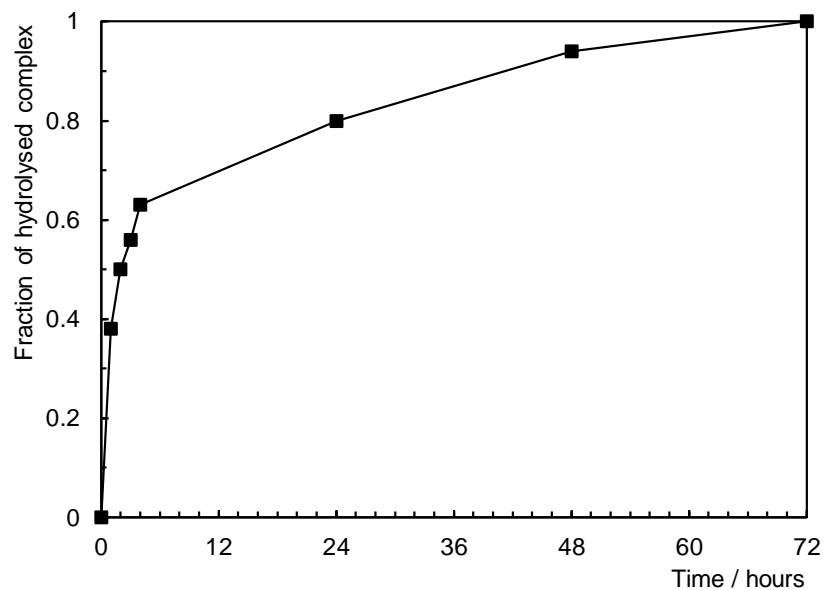


Figure S6. Hydrolysis of **1**:

(A) Kinetics of hydrolysis of micromolar concentrations of **1** in argon-saturated PBS measured by the time dependence of luminescence quantum yields (Table 1 for details).

(B) Luminescence emission band of $O_2(^1\Delta_g)$ produced by **1** in three-days old oxygen-saturated PBS (excited at 400 nm).

A



B

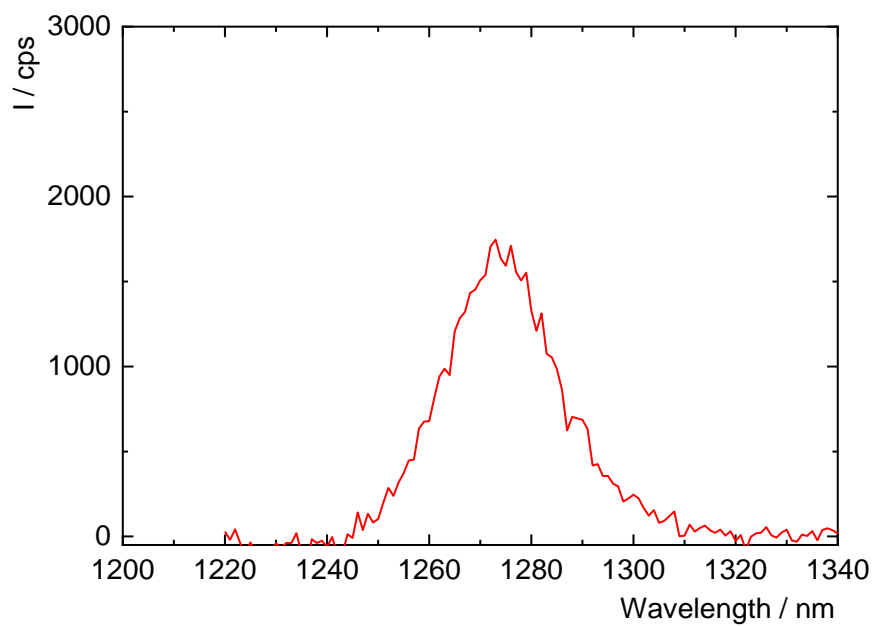
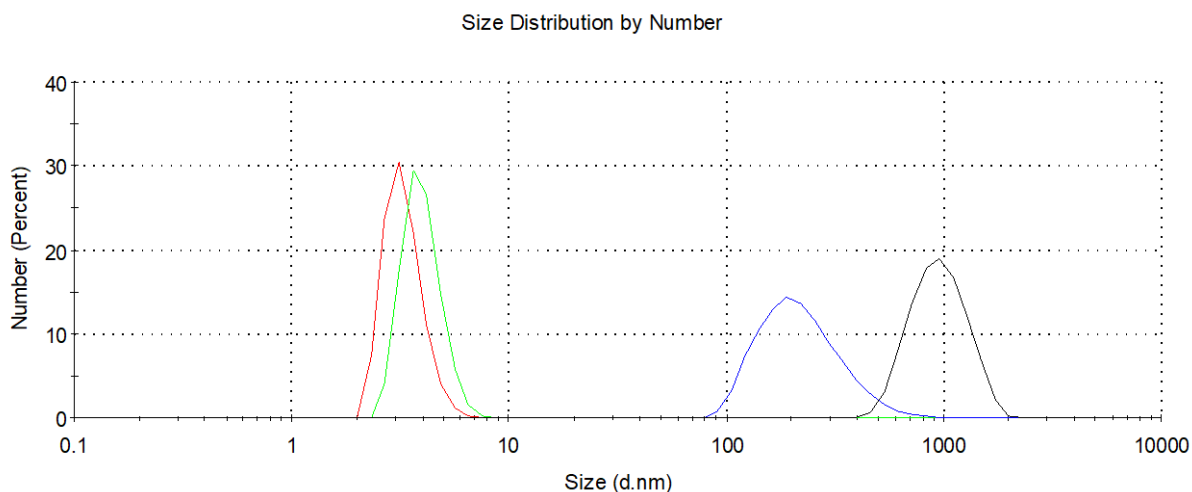


Figure S7. Nanoparticle size distribution by number (A) and by intensity (B) of PBS solutions of approximately 10 μM **1** obtained by dynamic light scattering at different aging times (red: fresh solution, green: after 4 h, blue: after 2 days, black: after 3 days). The results are summarized in Table S1 at the bottom.

A



B

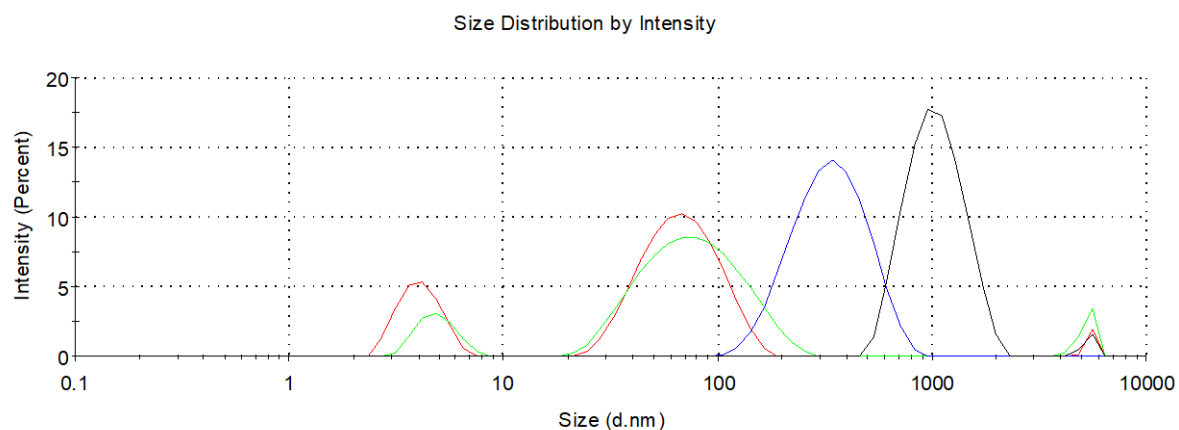


Table S1. Size distributions and zeta potentials of **1** in PBS obtained by dynamic light scattering at different aging times. PdI is the polydispersity index.

Time	Diameter / nm	Z-average / nm	PdI	Zeta potential / mV
Fresh	3.3 ± 0.7	117	0.15	-3.8 ± 1.2
4 h	4.0 ± 0.8	105	0.18	-5.8 ± 0.8
1 day	232 ± 104	313	0.29	-7.8 ± 0.5
3 days	976 ± 278	1064	0.26	-12.3 ± 1.1

Figure S8. Phototoxicity of 0.08 mM **1** towards Hep-2 (A) and MRC-5 (B) cells with indicated incubation time. Phototoxicity of **1** (red) after irradiation with a 500 W halogen lamp ($\lambda \geq 400$ nm, light dose of approximately 20 J cm^{-2}) was compared with corresponding experiments in dark (black) The bars labeled “control” represent negative control experiments in the absence of **1**. Data are presented with the corresponding standard error of the mean.

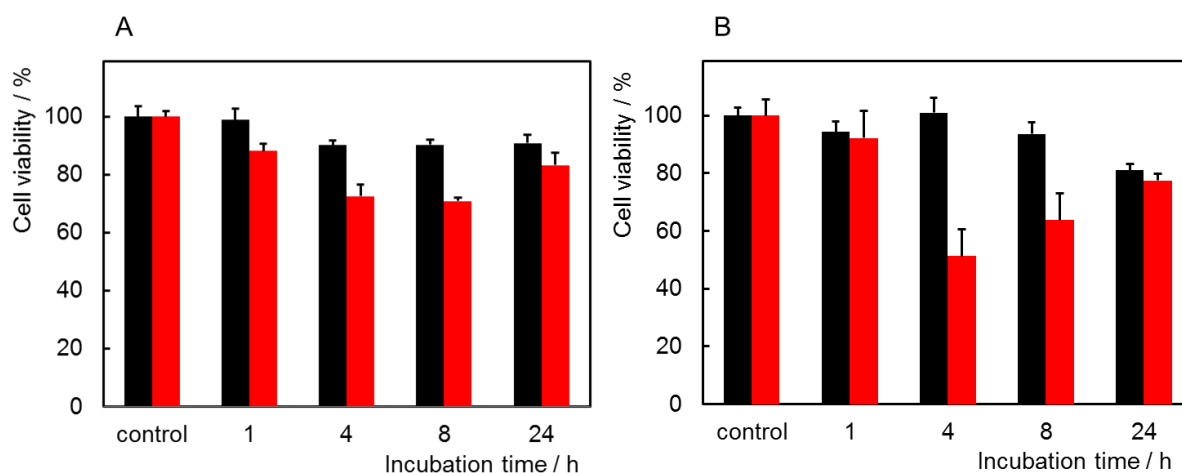


Figure S9. Survival rate of BALB/C mice injected intravenously with 200 μL of **1** dissolved in water in concentrations 24, 47, 95, 189, and 284 mg mL^{-1} , i.e. 158, 315, 630, 1260, and 1890 mg of **1** *per* kg of the mouse model (5 mice in a group). The animals were monitored for 2 weeks. The death of animals that received doses of 315 and 630 mg/kg occurred within 3 days, and doses of 1260 and 1890 mg/kg led to the death within a day after administration.

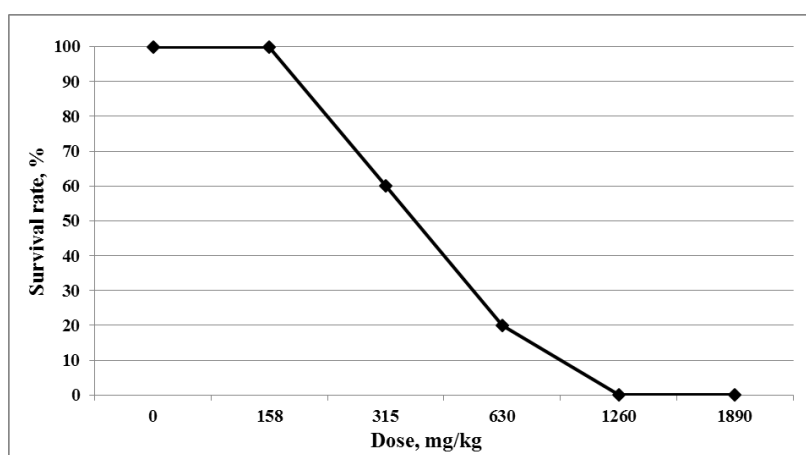


Figure S10. Histological analysis of the kidney, magnification $\times 20$.

A – control (physiological saline);

B – dose 158 mg/kg;

C – dose 315 mg/kg;

D – dose 630 mg/kg.

After administration of the maximal dose, a large hemorrhage into the internal tissues of the kidney (blue arrow) and the site of renal glomerular necrosis are noticeable (green arrow).

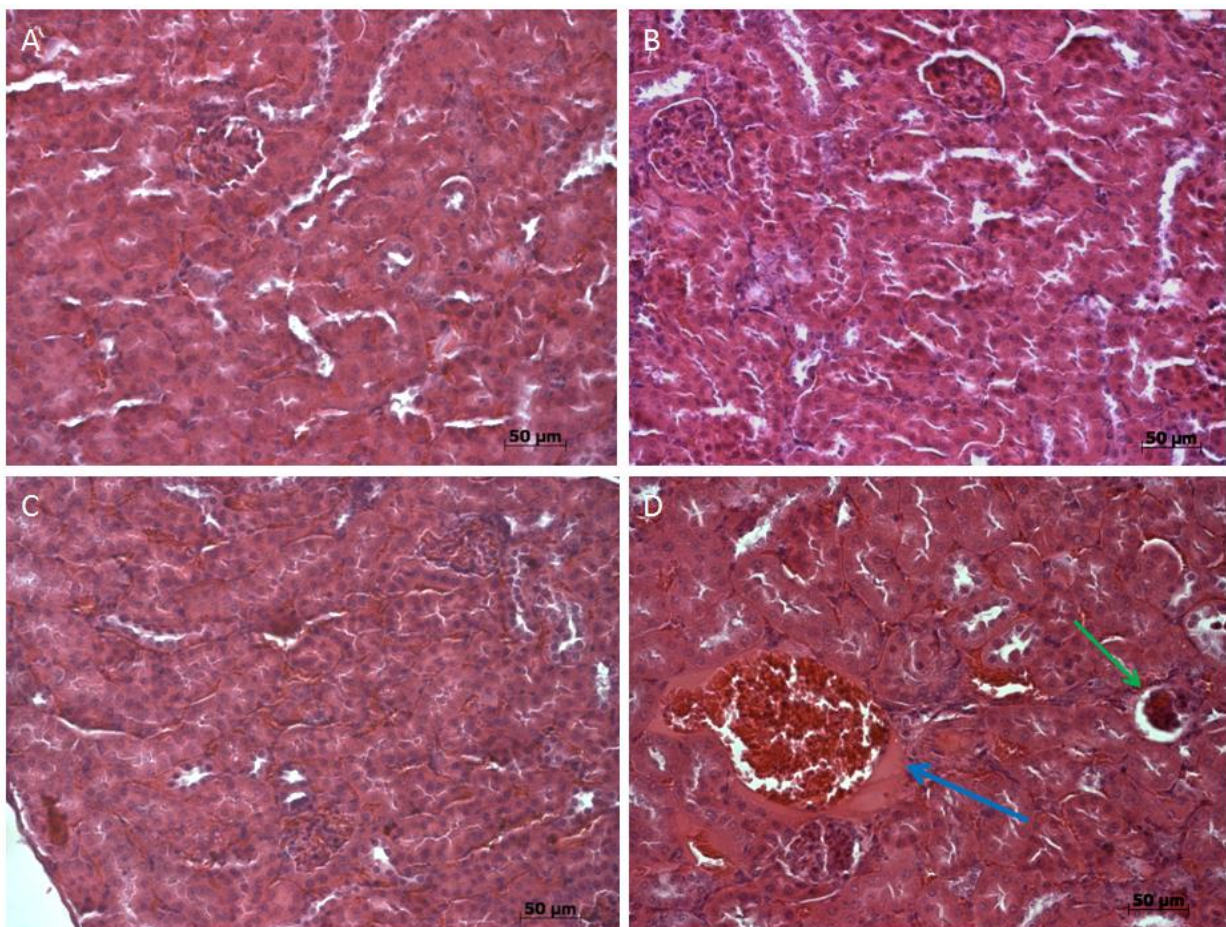


Figure S11. Histological analysis of the kidney, magnification $\times 40$.

A – control (physiological saline);

B – dose 158 mg/kg;

C – dose 315 mg/kg;

D – dose 630 mg/kg.

After administration of doses of 315 and 630 mg/kg, the areas of renal tubular cell dystrophy (red arrows) are noticeable. In addition, renal glomerular necrosis (green arrow) is often observed in the kidney after administration of a dose of 630 mg/kg.

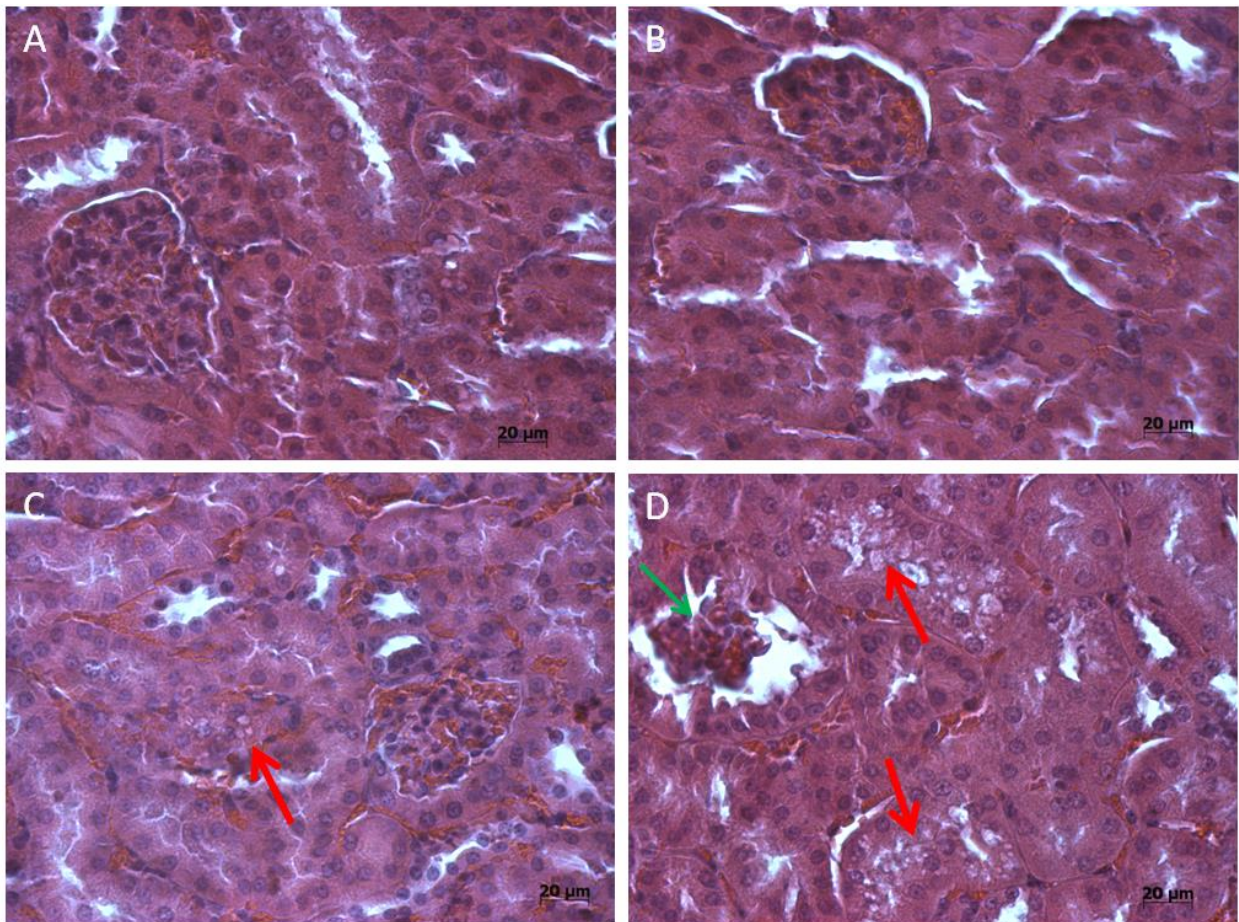


Figure S12. Histological analysis of the liver, magnification $\times 10$.

A – control (physiological saline);

B – dose 158 mg/kg;

C – dose 315 mg/kg;

D – dose 630 mg/kg.

After administration of a dose of 630 mg/kg, an increase in blood vessels filling is clearly noticeable (blue arrows). However, there are no visible areas of dystrophic changes.

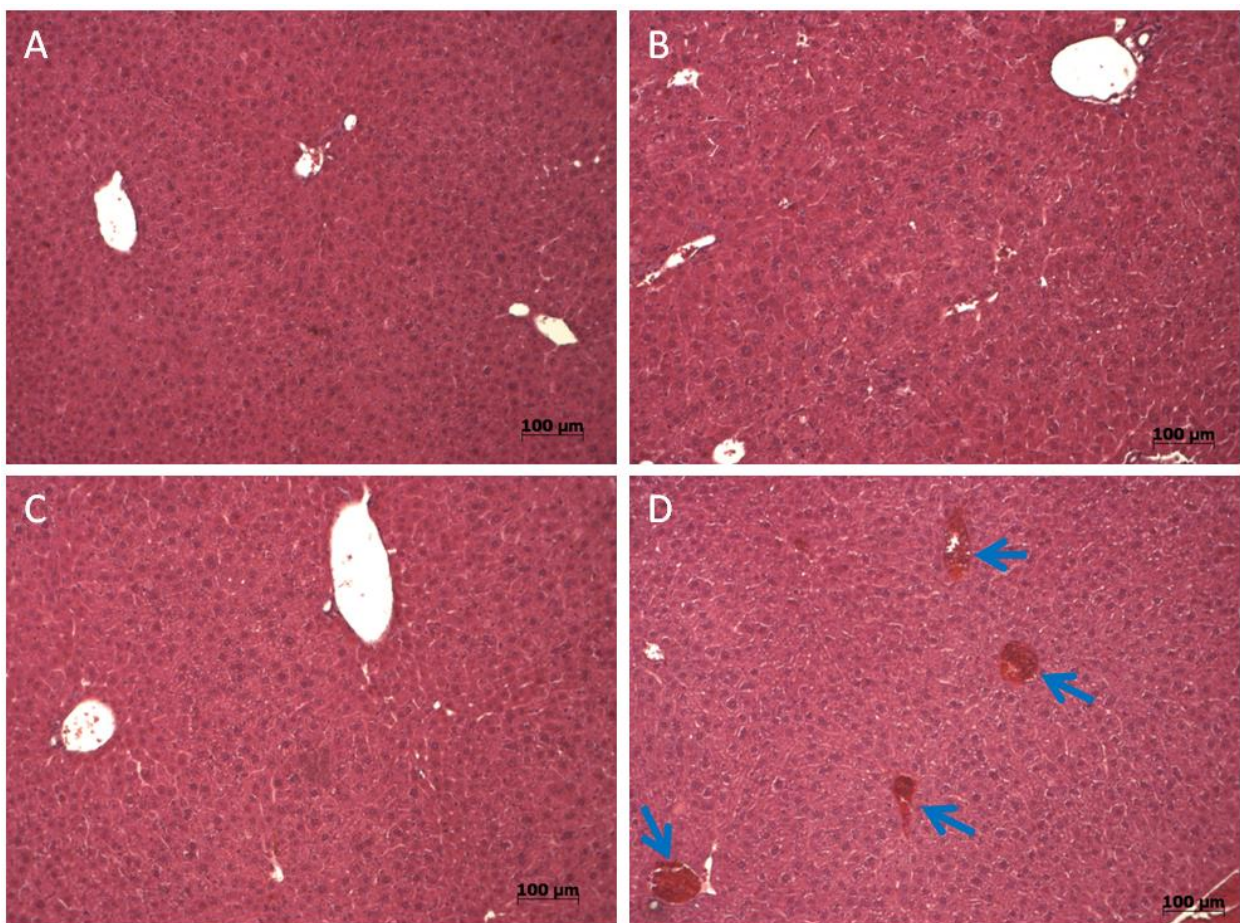


Figure S13. Histological analysis of the heart, magnification $\times 20$.

A – control (physiological saline);

B – dose 158 mg/kg;

C – dose 315 mg/kg;

D – dose 630 mg/kg.

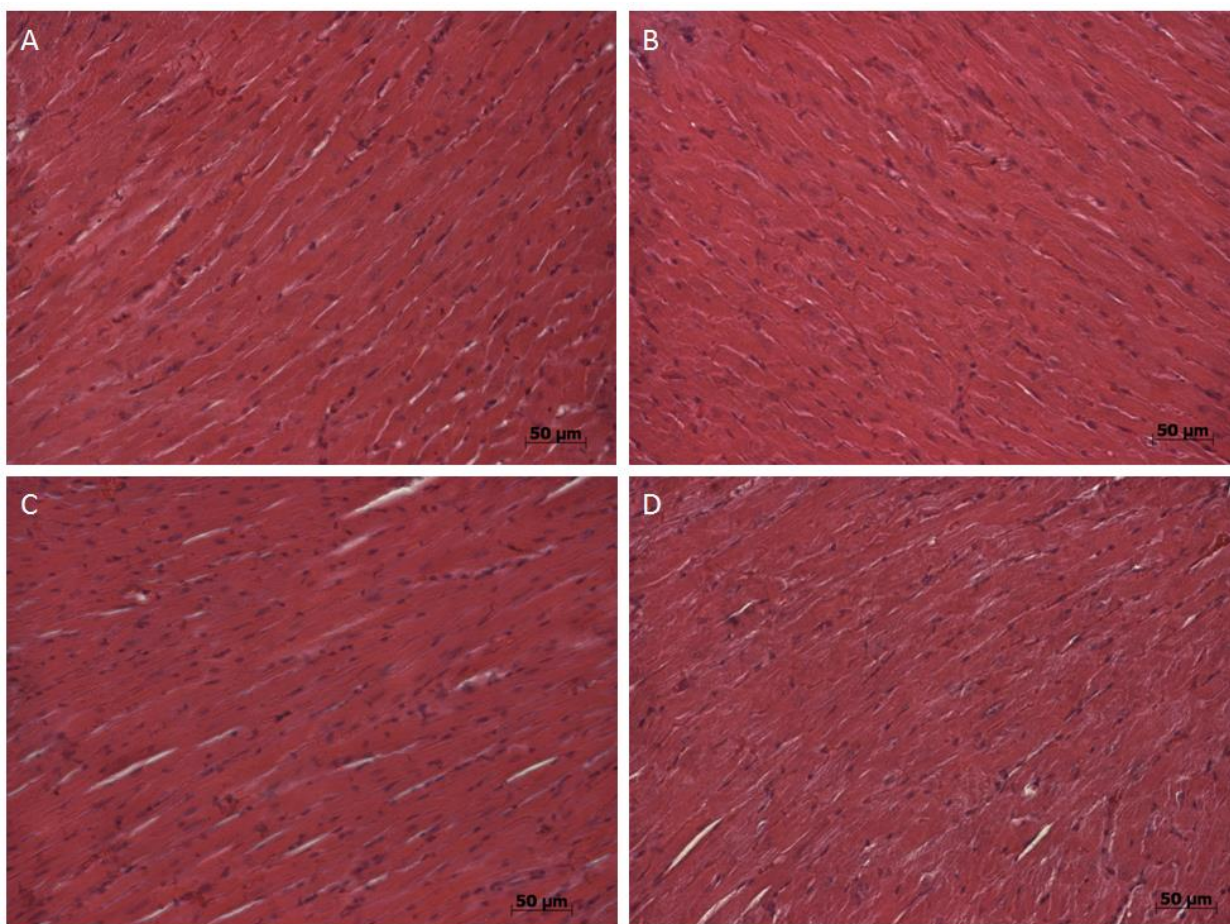


Figure S14. Histological analysis of the lung, magnification $\times 20$.

A – control (physiological saline);

B – dose 158 mg/kg;

C – dose 315 mg/kg;

D – dose 630 mg/kg.

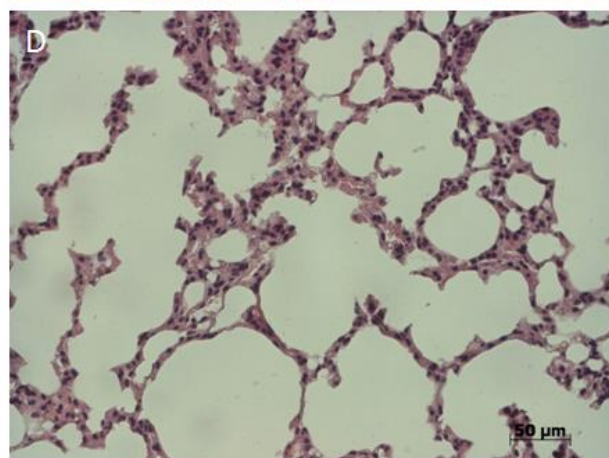
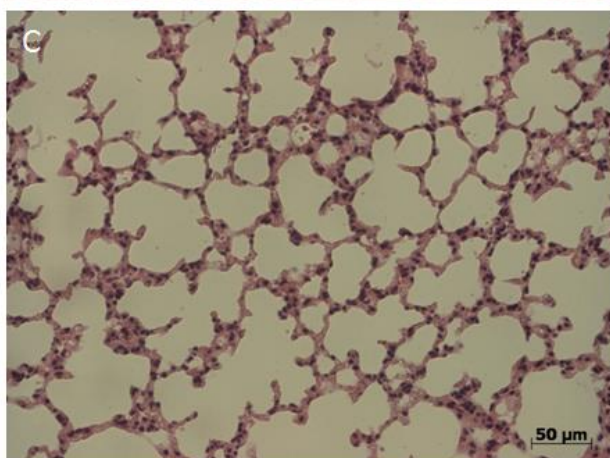
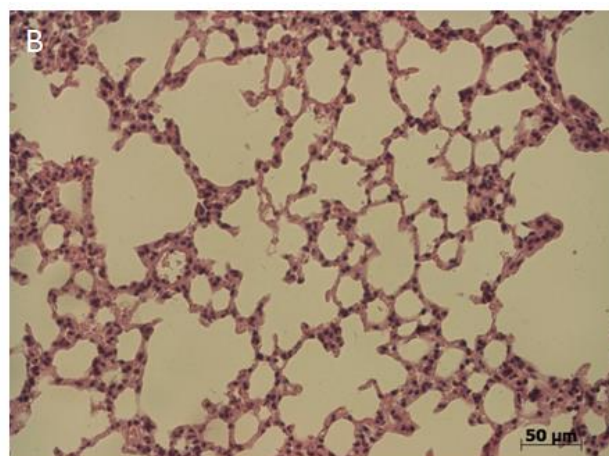
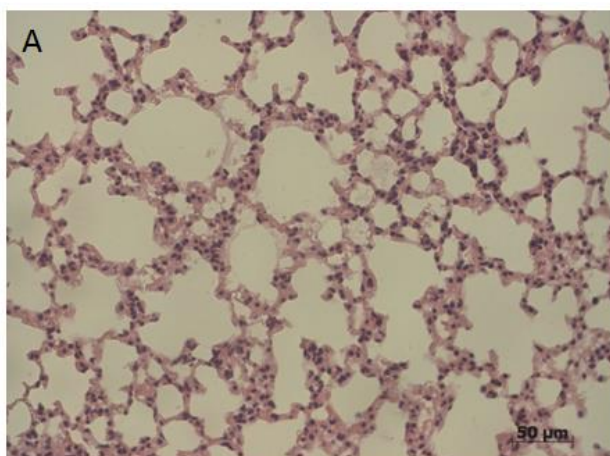


Figure S15. Histological analysis of the spleen, magnification $\times 10$.

A – control (physiological saline);

B – dose 158 mg/kg;

C – dose 315 mg/kg;

D – dose 630 mg/kg.

