Supporting Information

Chemiluminescence from the Biomimetic Reaction of 1,2,4-Trioxolanes and 1,2,4,5-Tetroxanes with Ferrous Ions

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Content: The Supporting Information (SI) material consists of the chemiluminescence procedure for the reaction of the cyclic peroxides with ferrous ions, the fluorescence and chemiluminescence spectra (taken by means of cut-off filters) recorded in the peroxide reactions (see Figures S-1, S-2, S-4, and S-5), and the kinetics of the chemiluminescence decay (see Figure S-3).

Measurement of the Chemiluminescence in the Reaction of Cyclic Peroxides **1**-**3**, OZ03 and Artemisinin with Ferrous Ion in CH_3CN/H_2O Solution.

In a typical procedure, an aliquot of the cyclic peroxide in a CH_3CN:H_2O (1:1) mixture was transferred to a cuvette, which was placed above the photocathode of the photomultiplier. Subsequently, an aliquot of $FeSO_4$/rhodamine G in CH_3CN:H_2O (1:1) mixture was rapidly (ca. 1 s) injected into the peroxide solution and immediately the CL was recorded. Similarly, in another set of experiments, a solution of $FeCl_3$/rhodamine G in aqueous (50%) acetonitrile was added rapidly to a mixture of *L*-cysteine hydrochloride and the cyclic peroxide in CH_3CN:H_2O (1:1) solution, and immediately the CL was recorded. All reactions were carried out at 70 ^oC (for peroxides **1**-**3** and OZ03) or 60 ^oC (for artemesinin) by bubbling a slow stream of oxygen gas through the CH_3CN/H_2O solution. Solutions in the cuvette and in the injector were thermostated at the required temperature for ca. 5 min prior to initiating the reaction.

The following concentrations of the reagents in the cuvette were chosen:

[peroxides **1** or **2**] = [$FeCl_3$] = [Rhodamine G] = 1.5×10^{-3} M, [*L*-cysteine]= 3×10^{-3} M;

[peroxide **3**] = 2×10^{-3} M, [$FeCl_3$]= 3×10^{-3} M, [*L*-cysteine] = 5×10^{-3} M, [rhodamine G] = 3×10^{-3} M;

[artemisinin] = 2×10^{-2} M, [$FeSO_4$]= 4×10^{-3} M, [rhodamine G] = 1×10^{-3} M or

[artemisinin] = 2×10^{-2} M, [$FeCl_3$]= 1×10^{-2} M, [*L*-cysteine] = 2×10^{-2} M, [rhodamine G] = 1×10^{-2} M;

[OZ03] = 2×10^{-3} M, [$FeSO_4$] = 1×10^{-3} M, [rhodamine G] = 5×10^{-4} M or

[OZ03] = [$FeCl_3$] = 1.5×10^{-3} M, [*L*-cysteine] = 3×10^{-3} M, [rhodamine G] = 1.5×10^{-3} M.

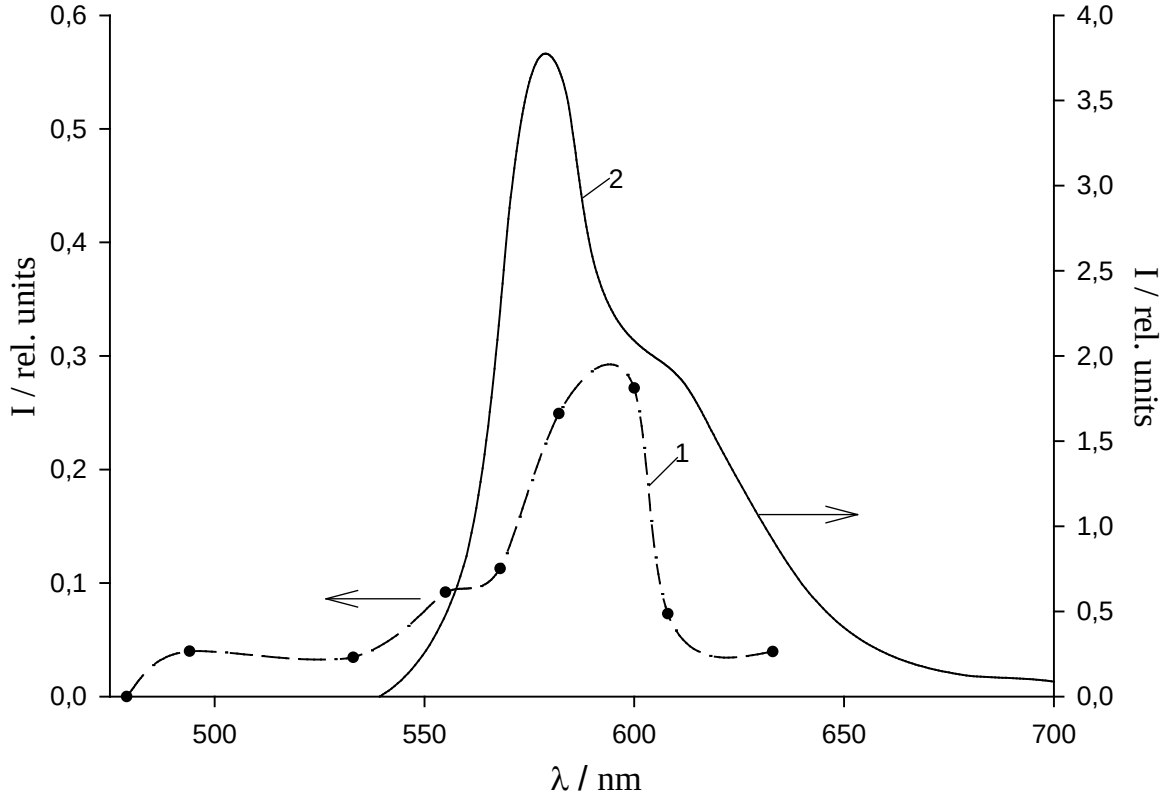

Figure S-1. Curve 1 (dashed line) represents the CL spectrum for the reaction of peroxide **1** with $FeCl_3$ in the prescence of L-cysteine and rhodamine G ([peroxide **1**] = [$FeCl_3$] = [Rhodamine G] = 1.5×10^{-3} M, [*L*-cysteine]= 3×10^{-3} M, CH_3CN/H_2O (1:1), 70 °C, O_2 atmosphere). Curve 2 (solid line) represents the fluorescence spectrum of rhodamine G ([Rhodamine G] = 1×10^{-5} M, CH_3CN/H_2O (1:1), λ_{ex}= 488 nm.)

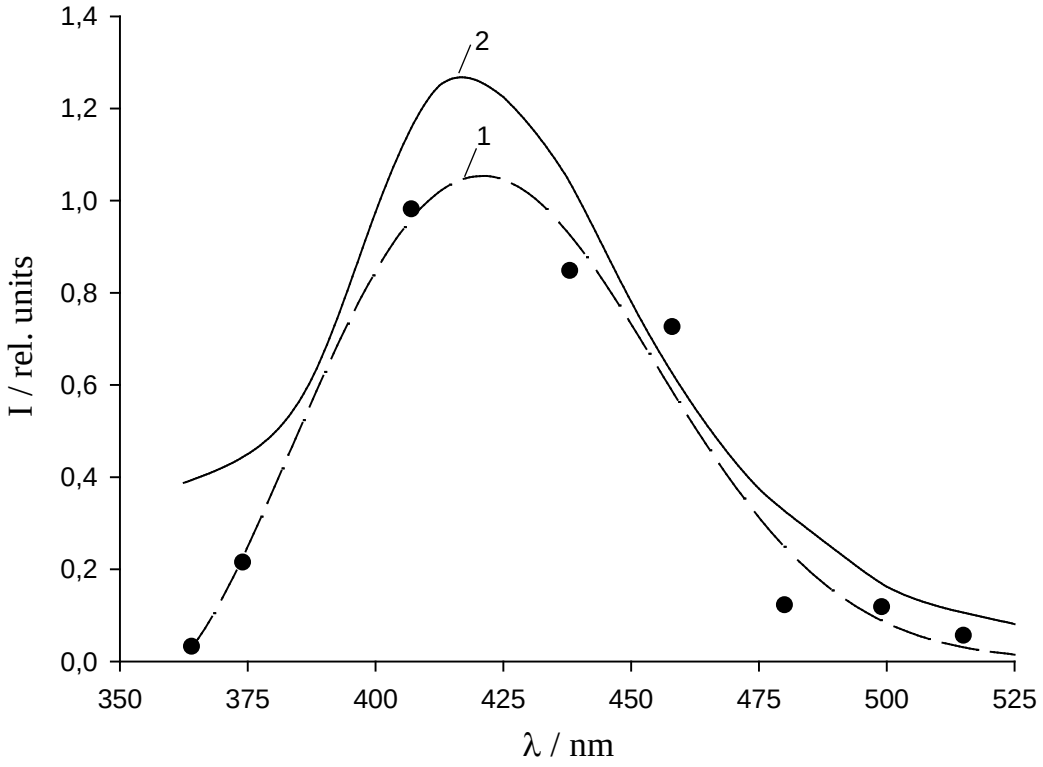

Figure S-2. Curve 1 (dashed line) represents the CL spectrum for the reaction of the trifluoroacetone tetroxane **4** with $FeSO_4$ ([peroxide **4**] = [$FeSO_4$] = 2×10^{-3} M, CH_3CN:H_2O (1:1), 30 °C). Curve 2 (solid line) represents the fluorescence spectrum of 1,1,1-trifluoroacetone in aqueous (50%) acetonitrile (1.5×10^{-2} M, 5 °C)

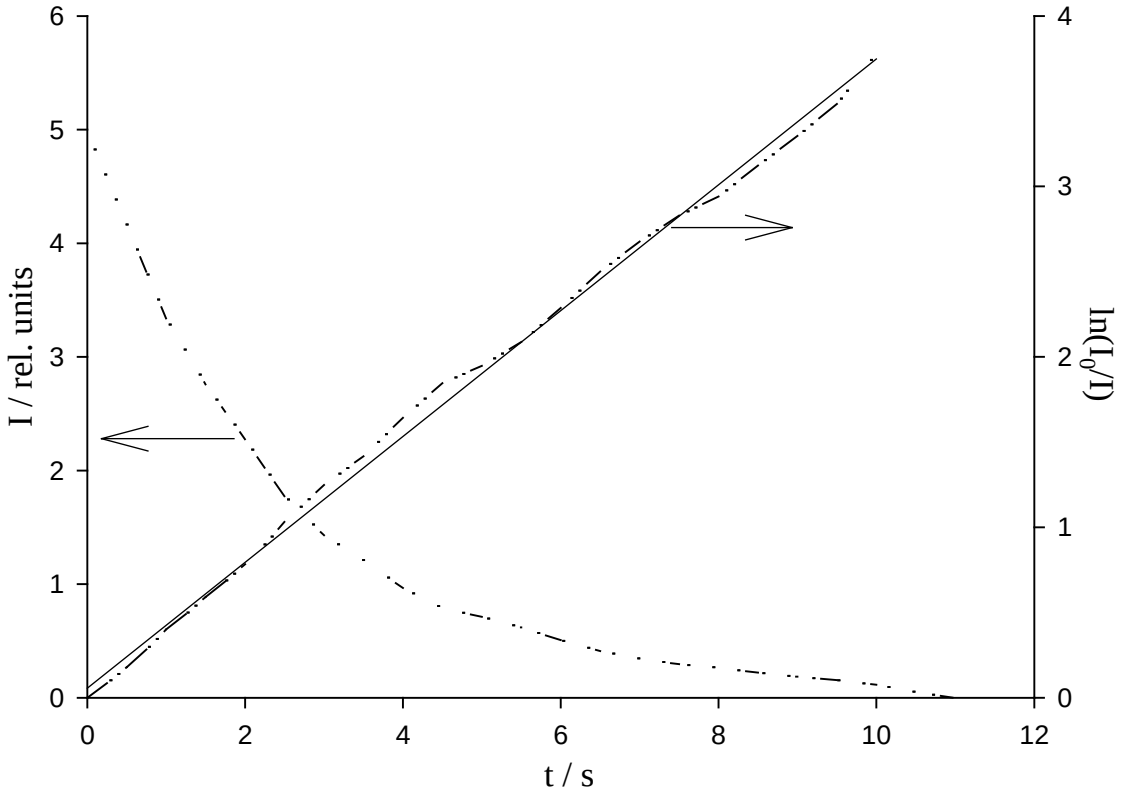

Figure S-3. Time profile of the CL decay for the reaction of the trifluoroacetone tetroxane **4** with $FeSO_4$ and its semi-logarithmic plot for the first-order kinetics ([peroxide **4**] = 2×10^{-4} M, [$FeSO_4$] = 4×10^{-3} M, CH_3CN : H_2O (1:1), 30 °C).

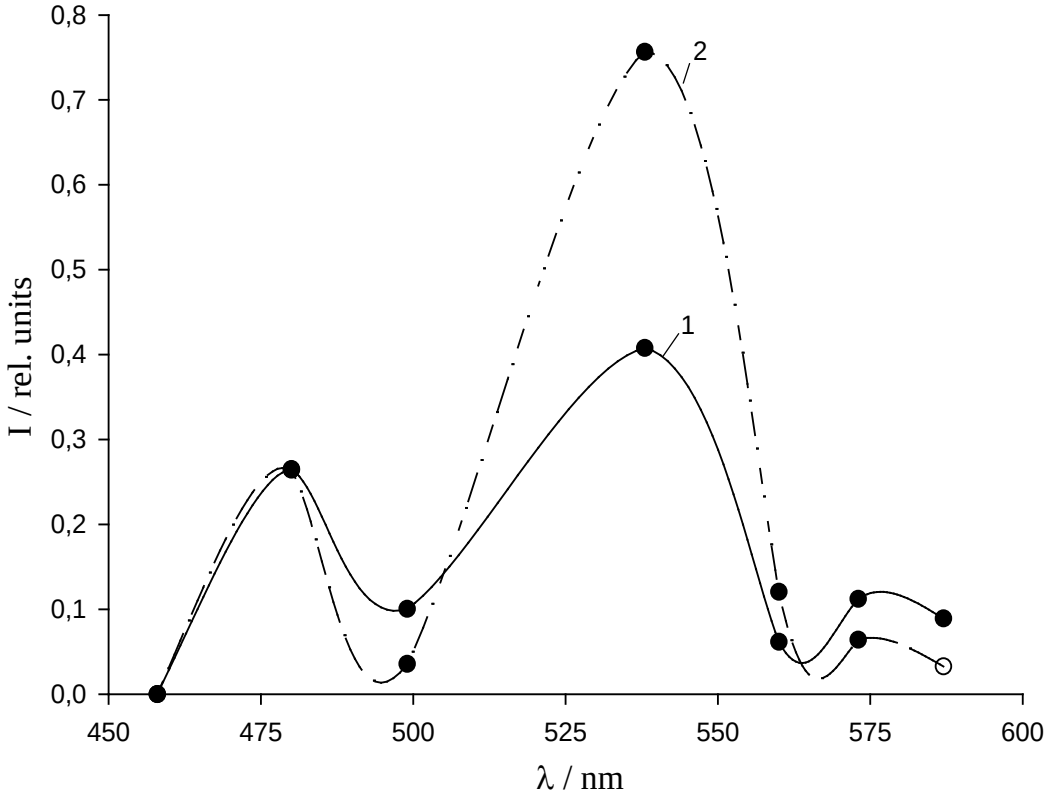

Figure S-4. CL spectrum for the reaction of the bicyclic tetroxane **5** with $FeSO_4$ ([tetroxane **5**] = [$FeSO_4$] = 2×10^{-3} M, CH_3CN : H_2O (1:1), 60 °C) taken under oxygen (curve 1, solid line) and argon (curve 2, dashed line) atmospheres.

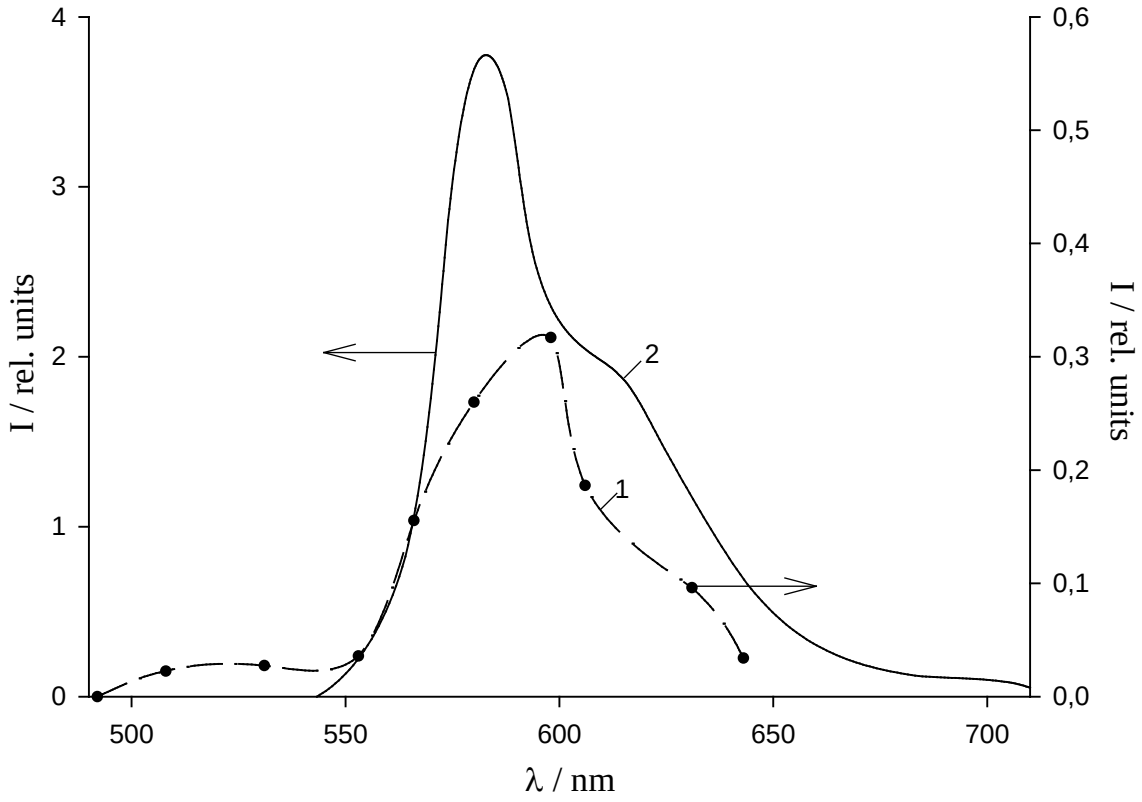

Figure S-5. Curve 1 (dashed line) represents the CL spectrum for the reaction of the bicyclic tetroxane **5** with $FeSO_4$ in the presence of rhodamine G ([tetroxane **5**] = 5×10^{-3} M, [$FeSO_4$] = 1×10^{-3} M, [Rd] = 2×10^{-3} M, CH_3CN/H_2O (1:1), 60 ºC). Curve 2 (solid line) represents the fluorescence spectrum of rhodamine G ([Rhodamine G] = 1×10^{-5} M, CH_3CN/H_2O (1:1), λ_{ex} = 488 nm.)