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 CH₃CN/H₂O Solution.

In a typical procedure, an aliquot of the cyclic peroxide in a CH₃CN:H₂O (1:1) mixture was transferred to a cuvette, which was placed above the photocathode of the photomultiplier. Subsequently, an aliquot of FeSO₄/rhodamine G in CH₃CN:H₂O (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 FeCl₃/rhodamine G in aqueous (50%) acetonitrile was added rapidly to a mixture of L-cysteine hydrochloride and the cyclic peroxide in CH₃CN:H₂O (1:1) solution, and immediately the CL was recorded. All reactions were carried out at 70 °C (for peroxides 1-3 and OZ03) or 60 °C (for artemisinin) by bubbling a slow stream of oxygen gas through the CH₃CN/H₂O 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] = [FeCl₃] = [Rhodamine G] = 1.5×10⁻³ M, [L-cysteine] = 3×10⁻³ M;
- [artemisinin] = 2×10⁻² M, [FeSO₄] = 4×10⁻³ M, [rhodamine G] = 1×10⁻³ M or
- [OZ03] = 2×10⁻³ M, [FeSO₄] = 1×10⁻³ M, [rhodamine G] = 5×10⁻⁴ M or
- [OZ03] = [FeCl₃] = 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 FeCl₃ in the presence of L-cysteine and rhodamine G ([peroxide 1] = [FeCl₃] = [Rhodamine G] = 1.5×10⁻³ M, [L-cysteine] = 3×10⁻³ M, CH₃CN/H₂O (1:1), 70 °C, O₂ atmosphere). Curve 2 (solid line) represents the fluorescence spectrum of rhodamine G ([Rhodamine G] = 1×10⁻⁵ M, CH₃CN/H₂O (1:1), λₑₓ = 488 nm.)
Figure S-2. Curve 1 (dashed line) represents the CL spectrum for the reaction of the trifluoroacetone tetroxane 4 with FeSO₄ ([peroxide 4] = [FeSO₄] = 2×10⁻³ M, CH₃CN:H₂O (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 FeSO₄ and its semi-logarithmic plot for the first-order kinetics ([peroxide 4] = 2×10⁻⁴ M, [FeSO₄] = 4×10⁻³ M, CH₃CN : H₂O (1:1), 30 °C).
Figure S-4. CL spectrum for the reaction of the bicyclic tetroxane 5 with FeSO₄ ([tetroxane 5] = [FeSO₄] = 2×10⁻³ M, CH₃CN : H₂O (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 FeSO₄ in the presence of rhodamine G ([tetroxane 5] = 5×10⁻³ M, [FeSO₄] = 1×10⁻³ M, [Rd] = 2×10⁻³ M, CH₃CN/H₂O (1:1), 60 °C). Curve 2 (solid line) represents the fluorescence spectrum of rhodamine G ([Rhodamine G] = 1×10⁻⁵ M, CH₃CN/H₂O (1:1), λₑₓ = 488 nm.)