

Supplementary information

New supramolecular hypoxia-sensitive complexes based on azo-thiacalixarene

Farida Galieva, Mohamed Khalifa, Zaliya Akhmetzyanova, Diana Mironova, Vladimir Burilov, Svetlana Solovieva and Igor Antipin

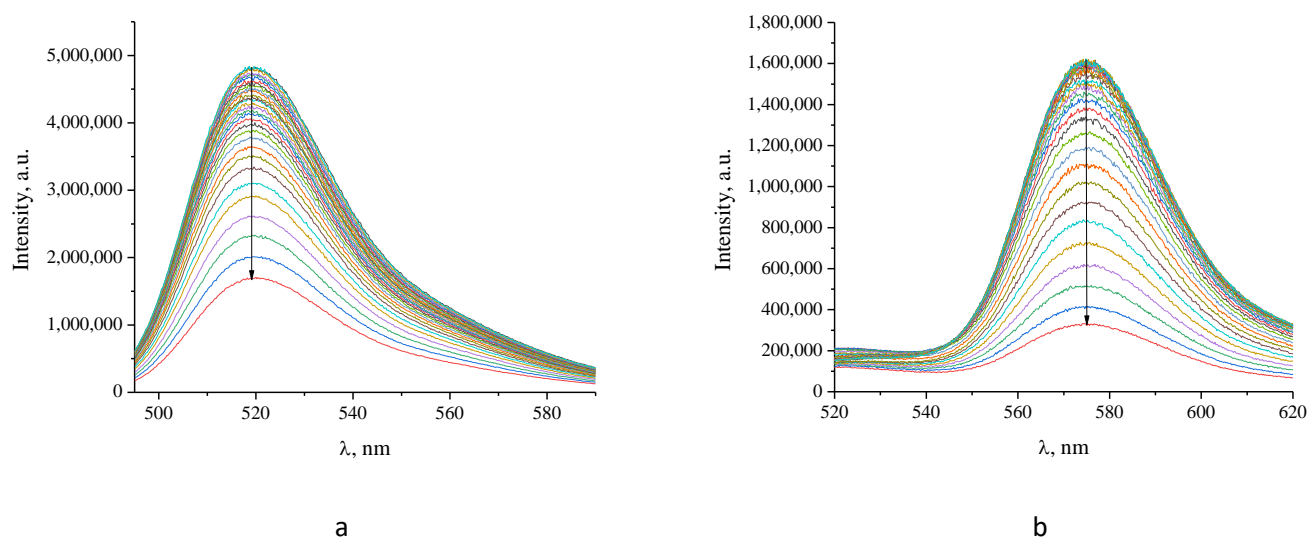


Figure S1. Direct fluorescence titration of **Rh123** (a) and **RhB** (b) with **L** (up to 10.7 μM) in PBS buffer (pH 7.4) at 37°C.

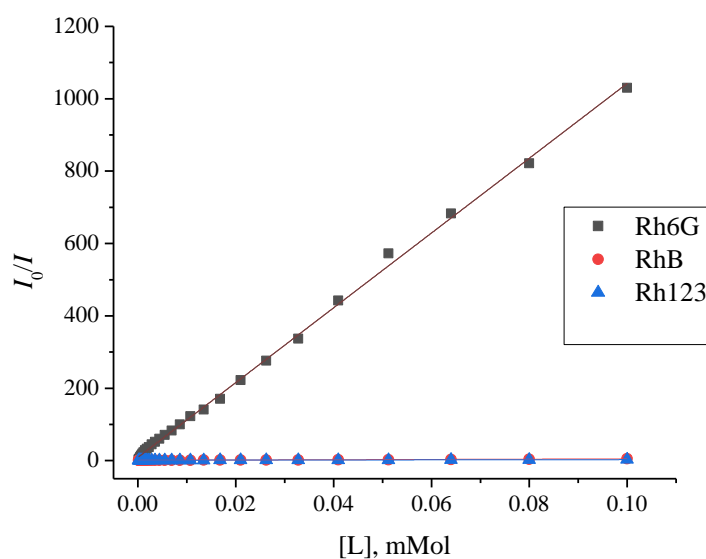


Figure S2. Volmer plots for **Rh6G**, **RhB** and **Rh123** with thiacalix[4]arene **L**. $C(\text{dye}) = 1 \mu\text{M}$, PBS buffer (pH 7.4) at 37°C.

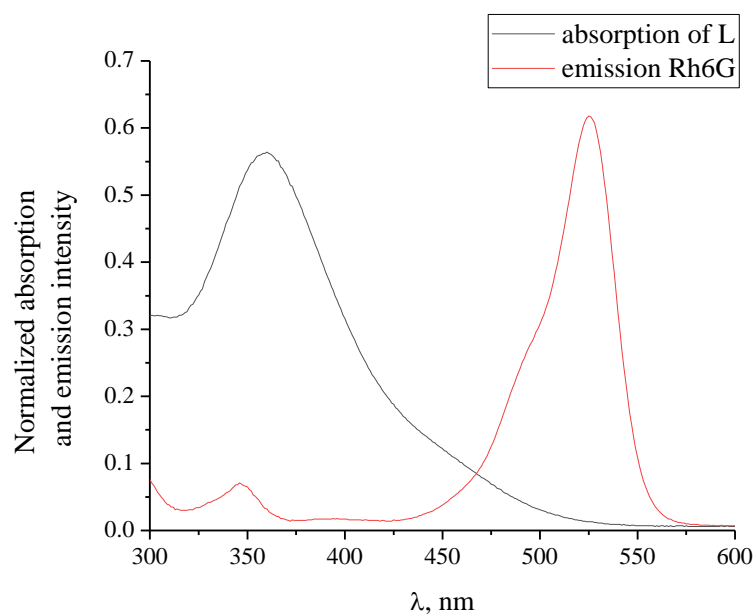


Figure S3. Normalized emission spectrum of **Rh6G** and absorption spectrum of thiacalix[4]arene **L** in PBS buffer (pH 7.4) at 37 °C.

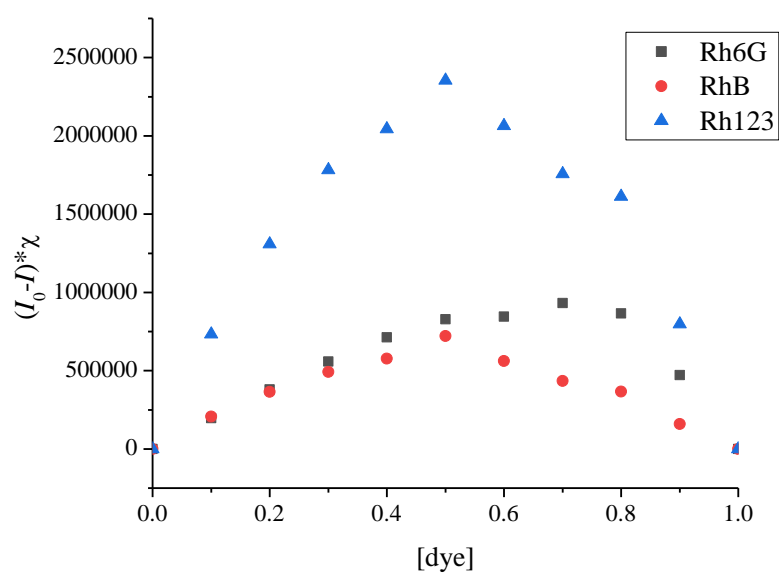


Figure S4. Job's plot for solutions rhodamine dyes and thiacalix[4]arene **L**. C [total] = 2 μ M, PBS buffer (pH 7.4) at 37 °C.

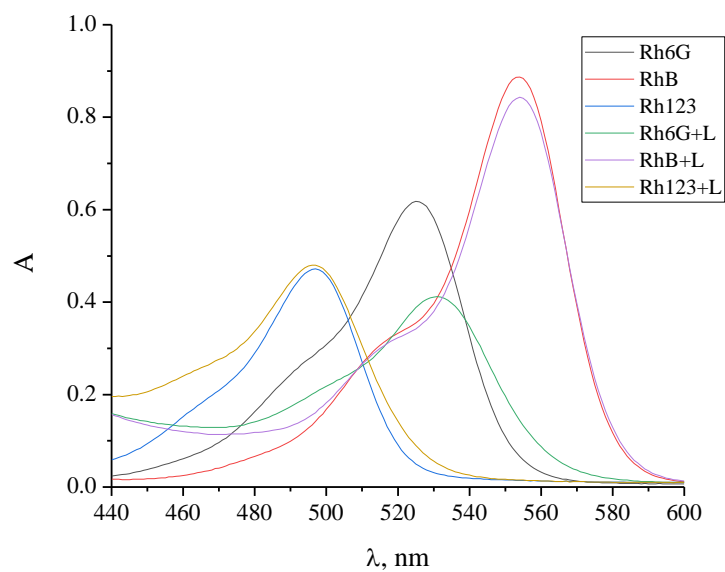
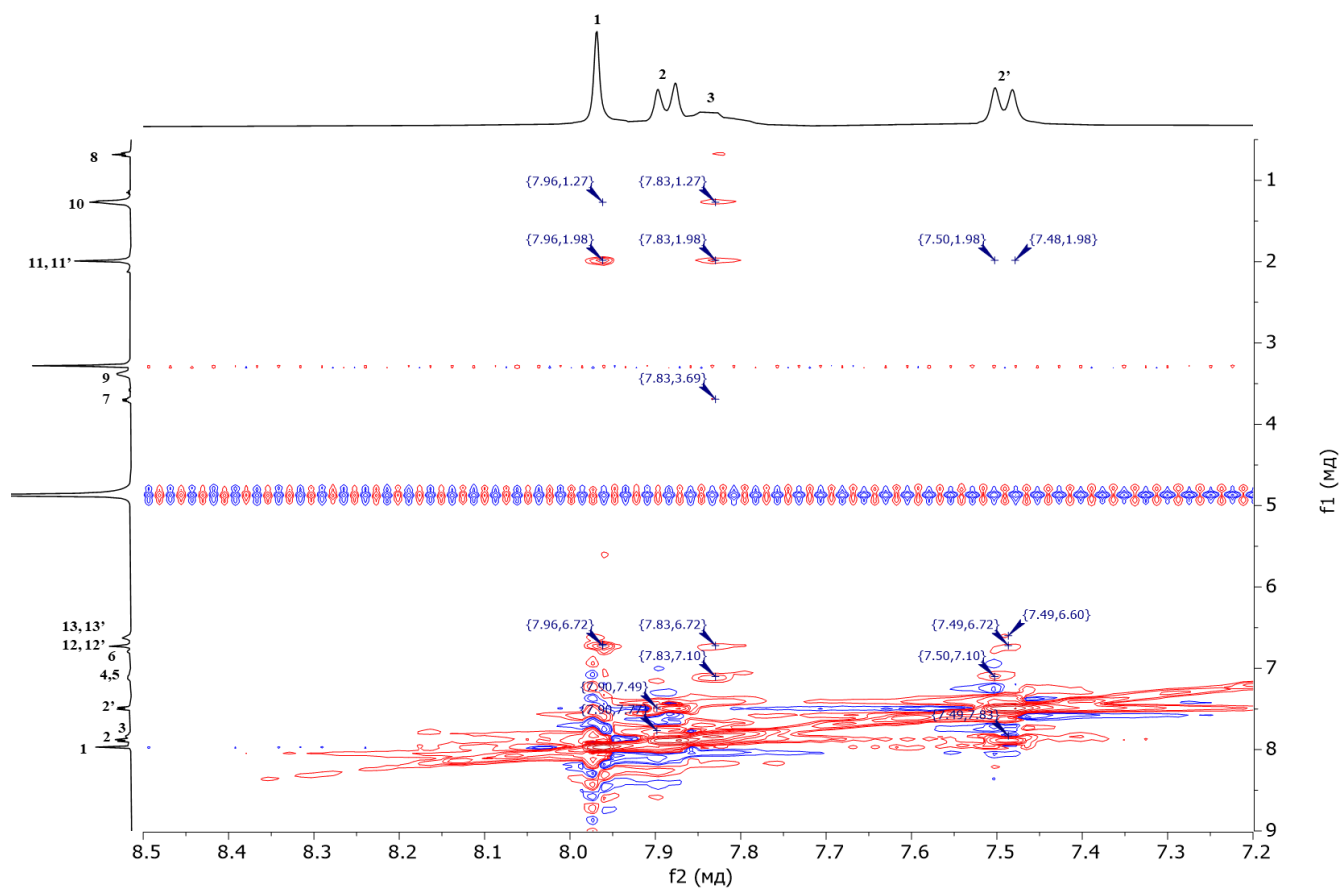


Figure S5. Absorbance spectra of dyes and binary thiacalix[4]arene L – dye systems. C [dye] = [calixarene] = 10 μ M, PBS buffer (pH 7.4) at 37 $^{\circ}$ C.



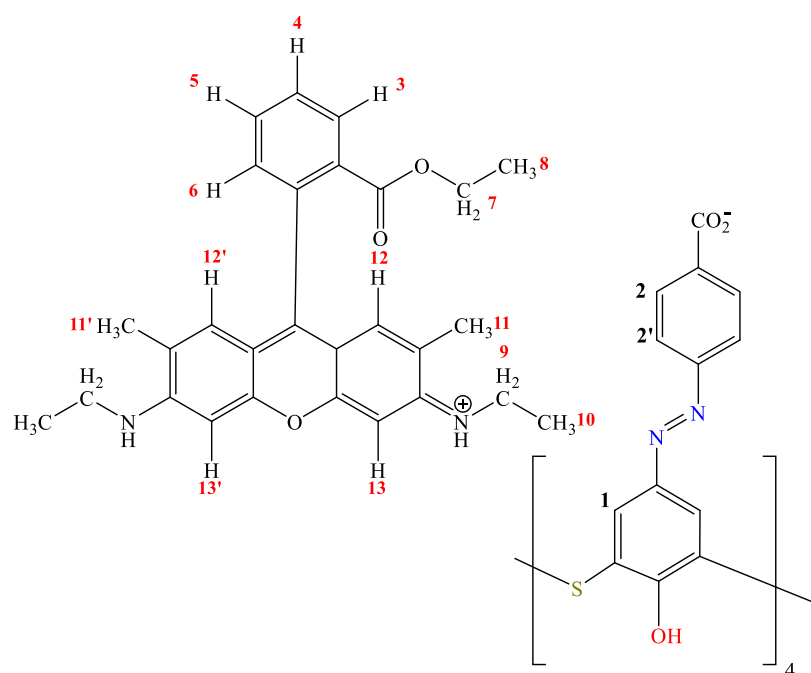


Figure S6. A fragment of 2D NOESY ^1H - ^1H spectra of thiacalix[4]arene **L** with **Rh6G**, 1.25 mM Rh6G and 2.5 mM of thiacalix[4]arene **L** in $\text{CD}_3\text{OD-d}_4$ at 25 °C.

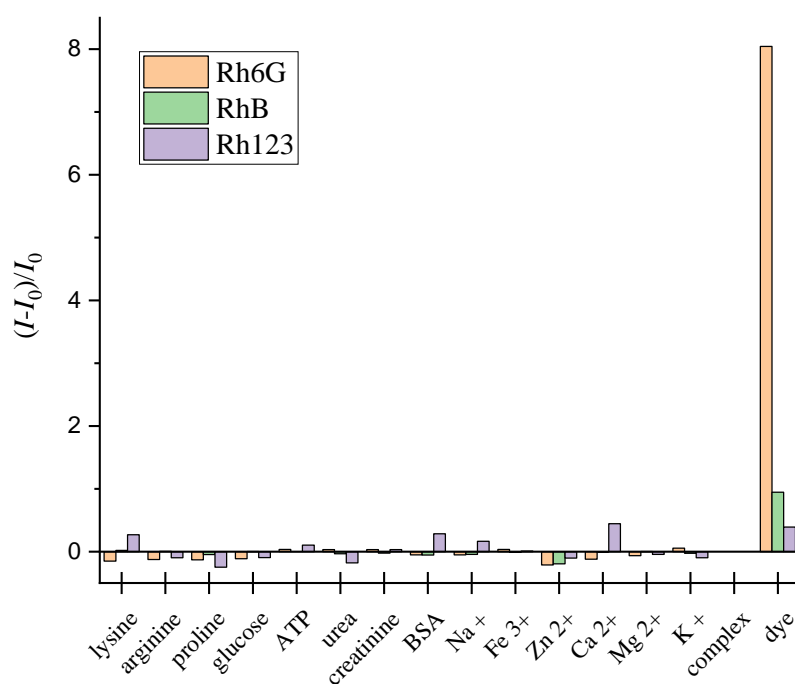


Figure S7. Fluorescent response of binary dye – thiacalix[4]arene **L** systems upon the addition of various biologically coexisting species. I_0 and I are the fluorescence intensity before and after addition of various substances present in biological media, respectively. In the last right column, I is the fluorescence intensity of free dyes. C [dye] = 1 μM , C [**L**] = 3 μM , C [substance] = 10 μM , PBS buffer (pH 7.4) at 37 °C.

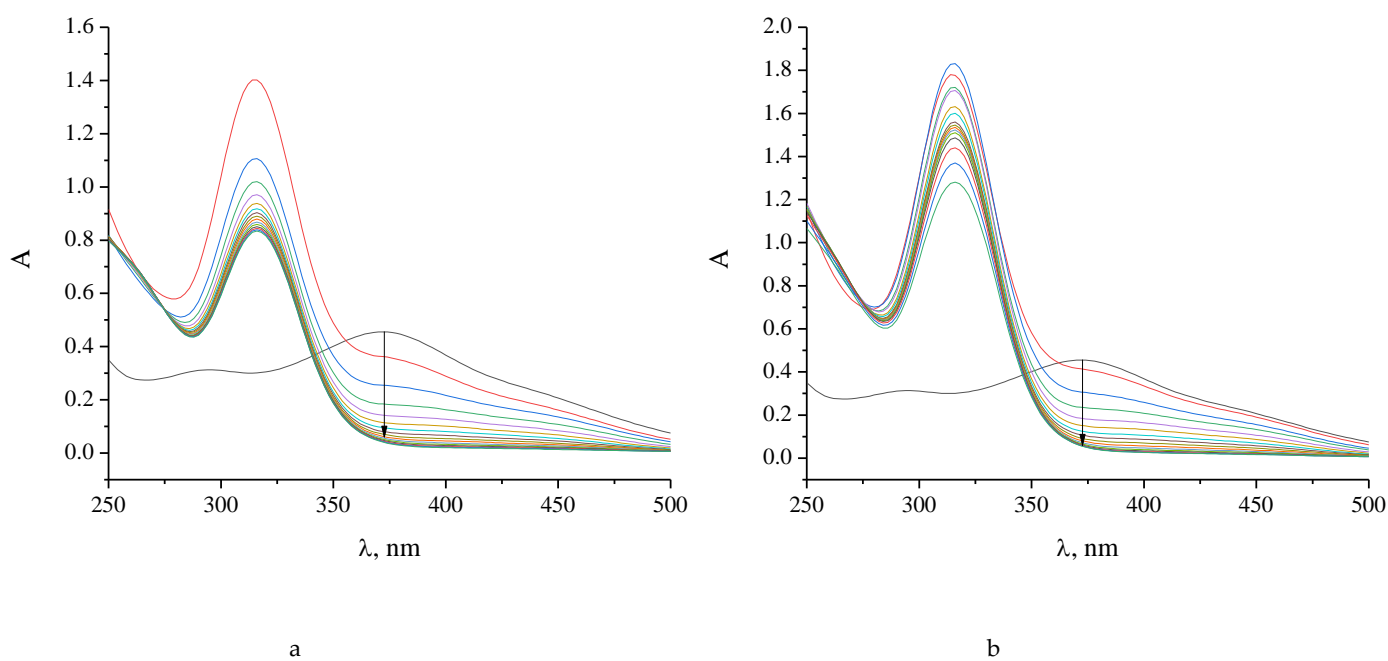
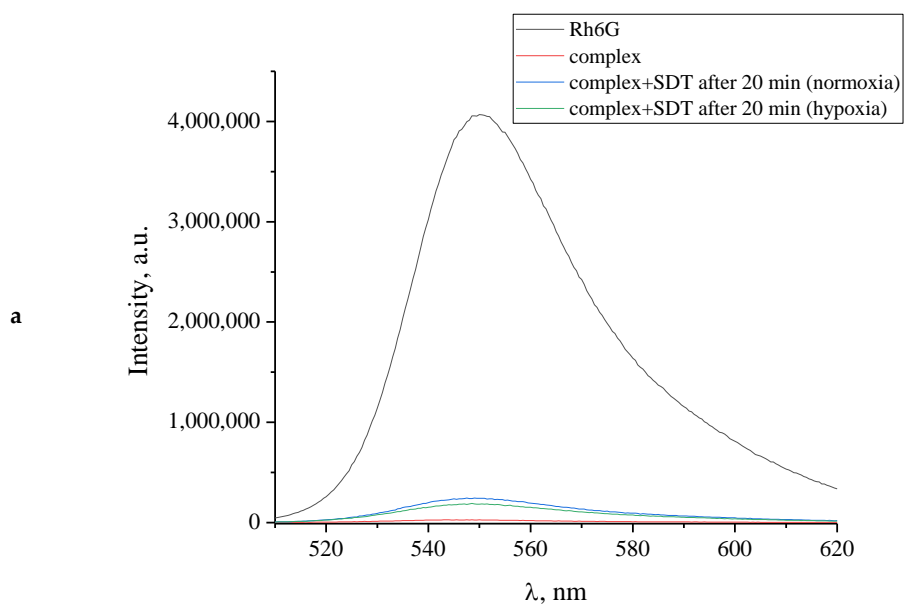


Figure S8. Absorbance spectra of L (10 μ M) before and after reduction by SDT (1.0 mM) under normoxic (20% O₂) (a) and hypoxic (less than 0.1% O₂) (b) conditions for 15 min, PBS buffer (pH 7.4) at 37 °C.



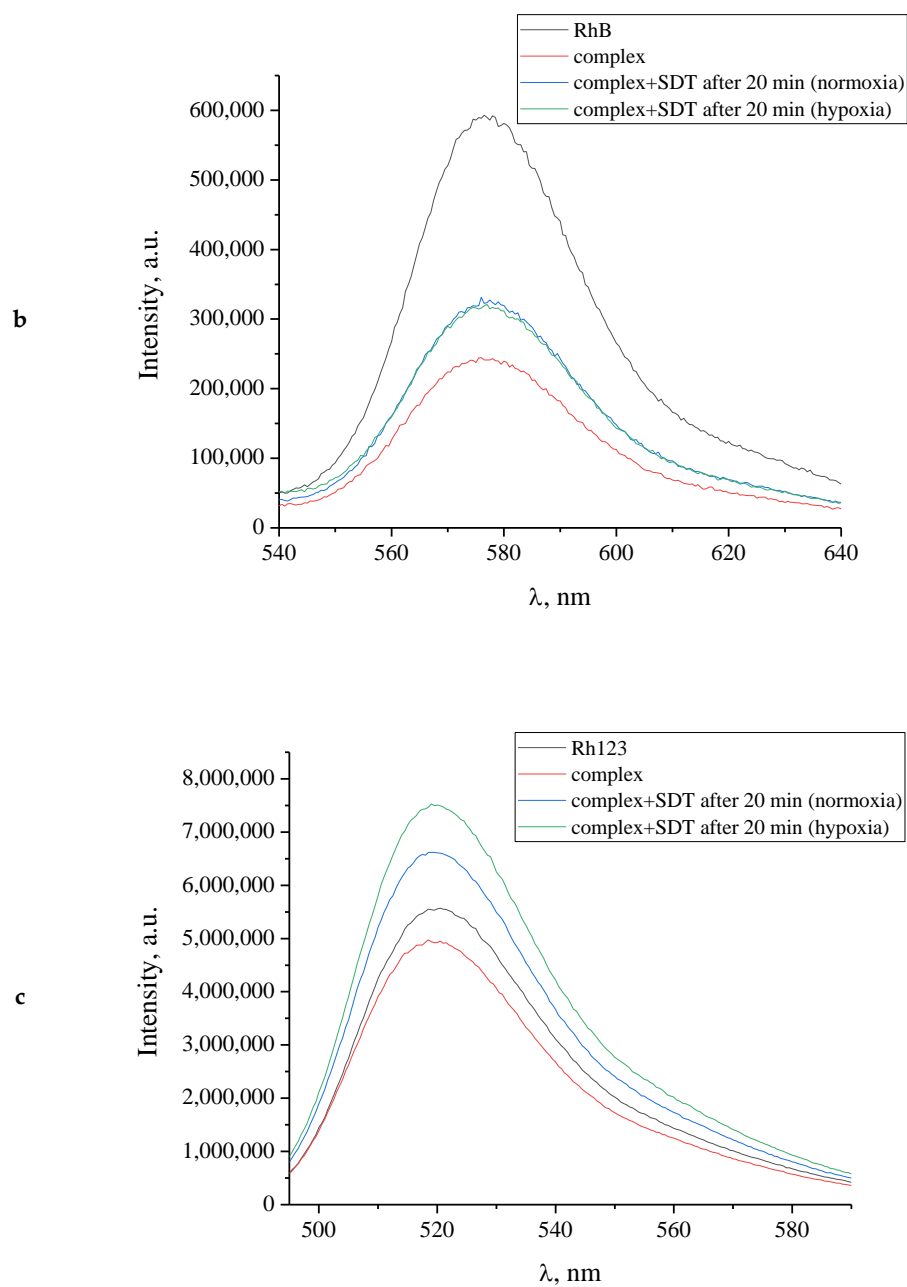


Figure S9. Fluorescent spectra of dye, the complex before the addition of SDT and after 20 minutes of exposure with the addition of SDT for systems with Rh6G (a), RhB (b) and Rh123 (c). C [dye] = 1 μ M, C [L] = 1 μ M, C [SDT] = 100 μ M, PBS buffer (pH 7.4) at 37 $^{\circ}$ C.