

Phosphorogenic Rhenium(I) Polypyridine Dinitrophenylsulfonamide Complexes as Biothiol-selective Imaging Reagents and Photosensitizers

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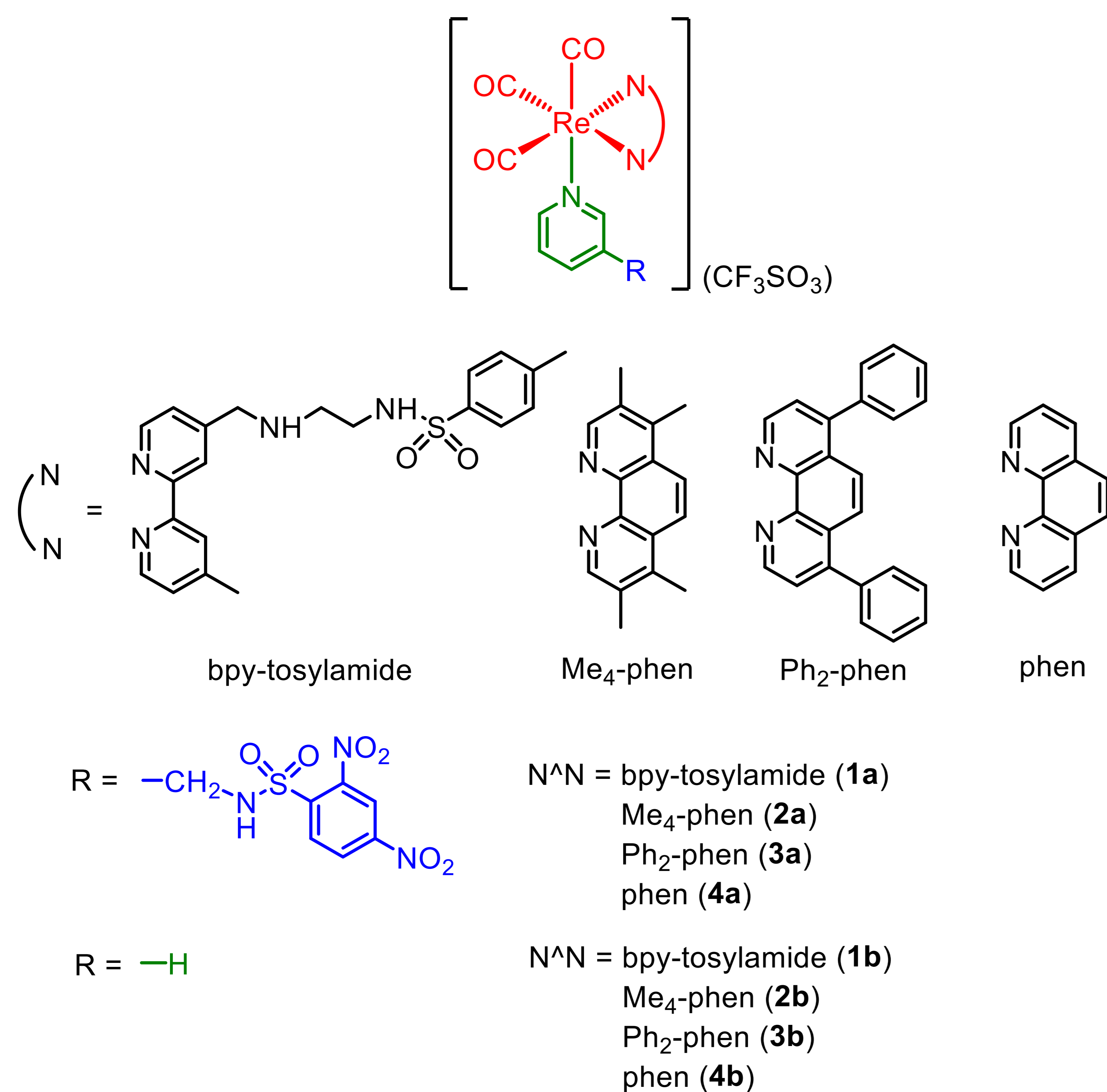
Guang-Xi Xu, Lawrence Cho-Cheung Lee, Cyrus Wing-Ching Kwok, Peter Kam-Keung Leung, Jing-Hui Zhu, Kenneth Kam-Wing Lo*

Department of Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, P. R. China (Email: bhkenlo@cityu.edu.hk)

Introduction

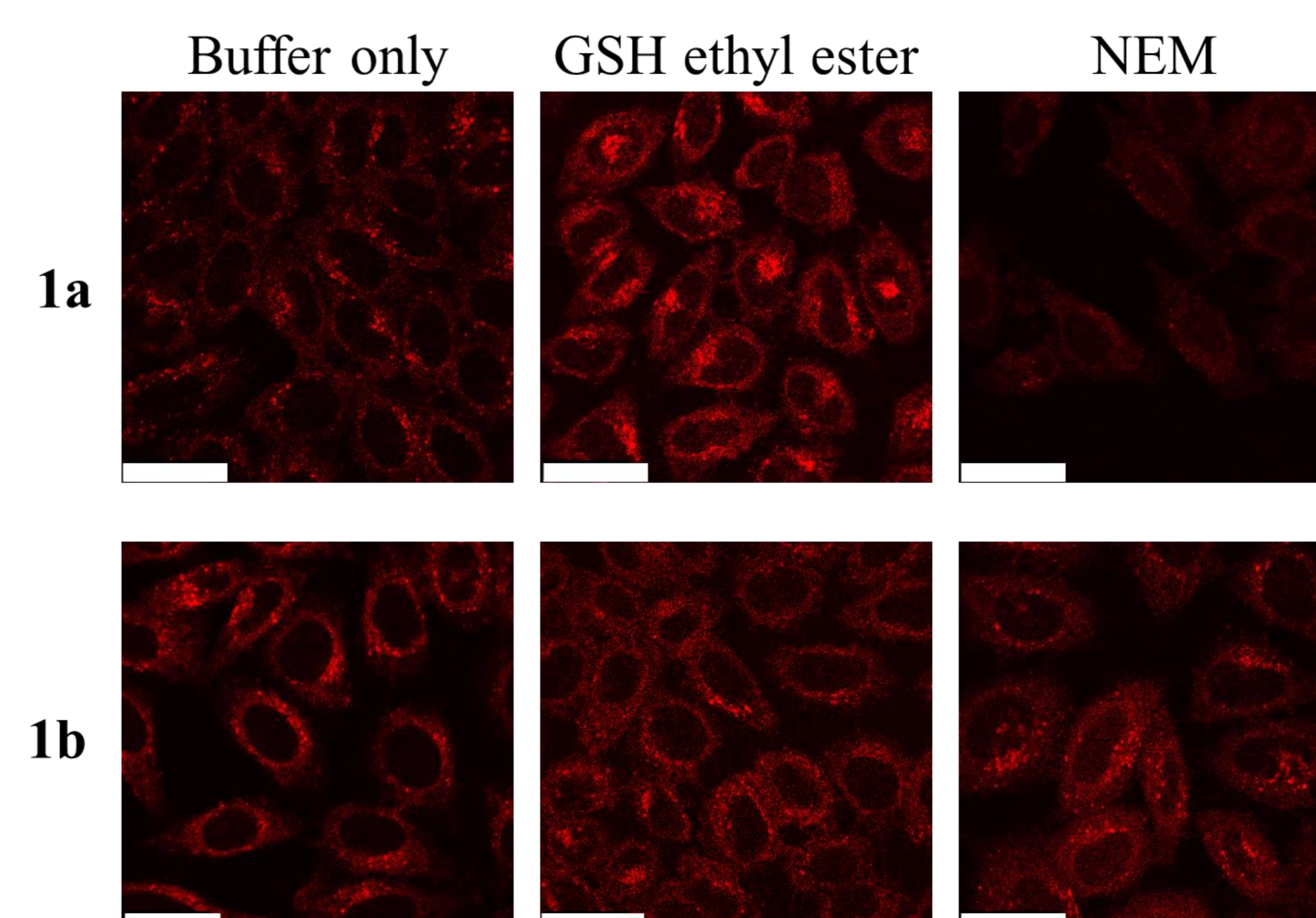
Glutathione (GSH) plays a crucial role in biological processes. Due to the high reactivity of the sulfhydryl group of GSH, significant effort has been devoted to the design of GSH-responsive bioimaging probes. Additionally, the introduction of a GSH-responsive unit to the photosensitizers is expected to modulate their singlet-oxygen (¹O₂) generation efficiency and allow them to selectively produce cytotoxic ¹O₂ in cancer cells, which are known to display elevated GSH level compared to normal cells. In this work, we describe new rhenium(I) polypyridine complexes containing a dinitrophenylsulfonamide (DNPS) moiety as GSH-sensitive phosphorogenic sensors, imaging reagents, and ¹O₂ photosensitizers.

Structure of the complexes

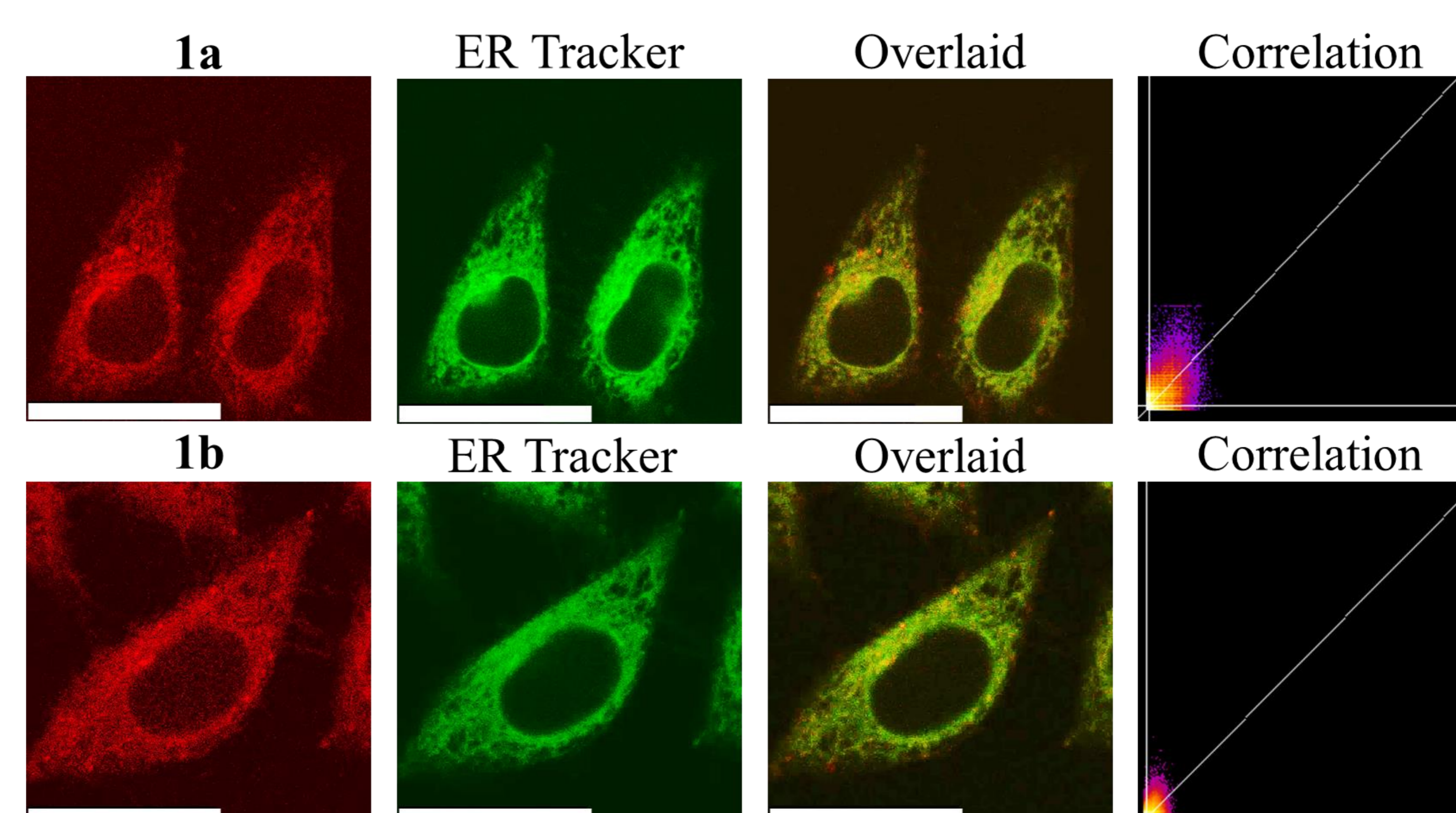


Intracellular imaging

Intracellular GSH sensing (scale bar = 25 μm)



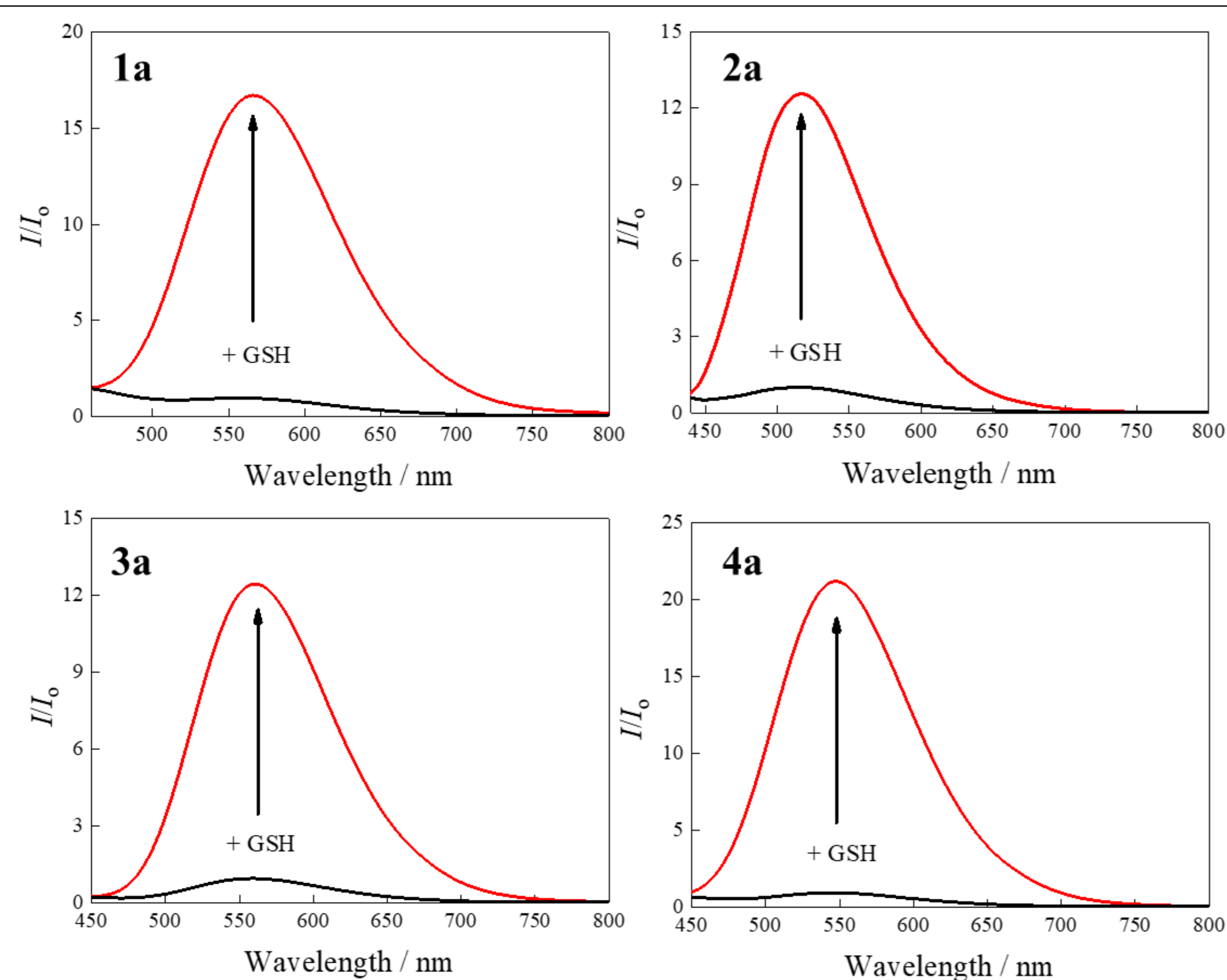
Intracellular localization (scale bar = 25 μm)



Phosphorogenic responses toward GSH

Emission enhancement factors and lifetimes of a mixture of complexes **1a** – **4a** (10 μM) and GSH (1 mM) in aerated potassium phosphate buffer (50 mM, pH 7.4)/MeOH (9:1, v/v) upon incubation at 298 K for 12 h.

Complex	I/I_0	τ [μs]
1a	18.2	0.13
2a	12.6	1.20
3a	12.9	1.10
4a	22.2	0.59

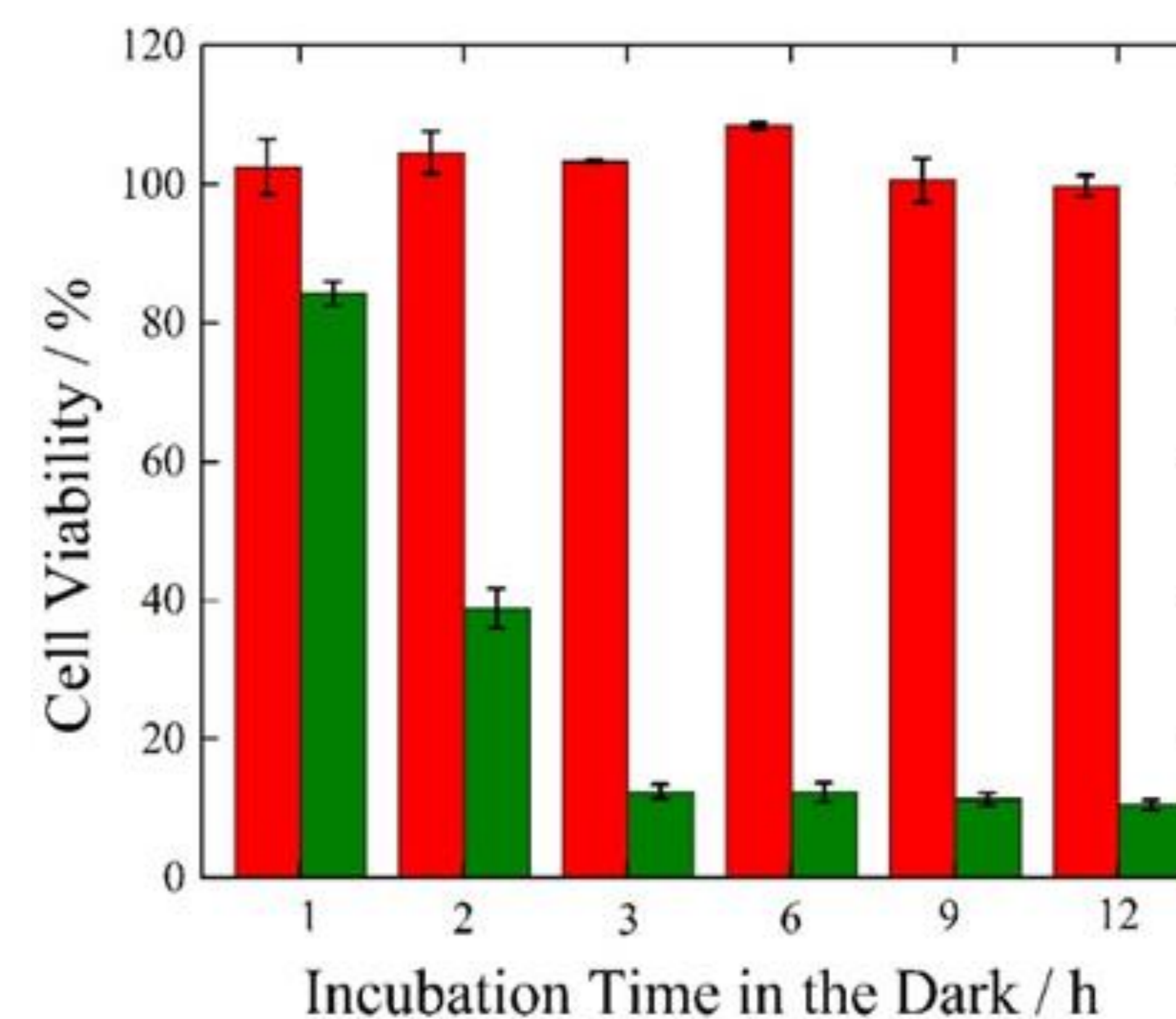


Summary

The DNPS moiety was utilized as both an emission quencher and a GSH-responsive functional group in the rhenium(I) polypyridine complexes. Due to the selective emission turn-on upon reaction with GSH, the complexes can be exploited for selective bioimaging and photocytotoxic applications.

(Photo)cytotoxicity studies

Viability of HeLa cells incubated with complex **3a** (1 μM) at 37°C for 2 h in the dark, thoroughly washed with PBS and incubated in fresh medium for different periods (1, 2, 3, 6, 9, and 12 h) in the dark, followed by further incubation in the dark (red) or under irradiation at 365 nm (green) for 5 min, and then incubated in fresh medium in the dark for 24 h.



Acknowledgement

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