ELECTROCHEMICAL, SPECTROSCOPIC, AND DFT INVESTIGATION OF A PYRIDINE-MODIFIED PHENOTHIAZINIUM PHOTOSENSITIZER

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Phenothiazinium dyes are widely used as photosensitizers in photodynamic antimicrobial chemotherapy, electrochemical sensing, and textile applications. Methylene blue (**MB**$^+$) is one of the most extensively studied representatives due to its strong absorption in the therapeutic window (600–800 nm) and efficient generation of reactive oxygen species (ROS). However, limitations in photostability and lipophilicity motivate the development of new derivatives. In this work [1], we investigate a newly synthesized pyridine-modified phenothiazinium derivative, **QMB**$^+$ (Fig. 1), and compare its electrochemical, spectroscopic, and electronic properties with those of **MB**$^+$.

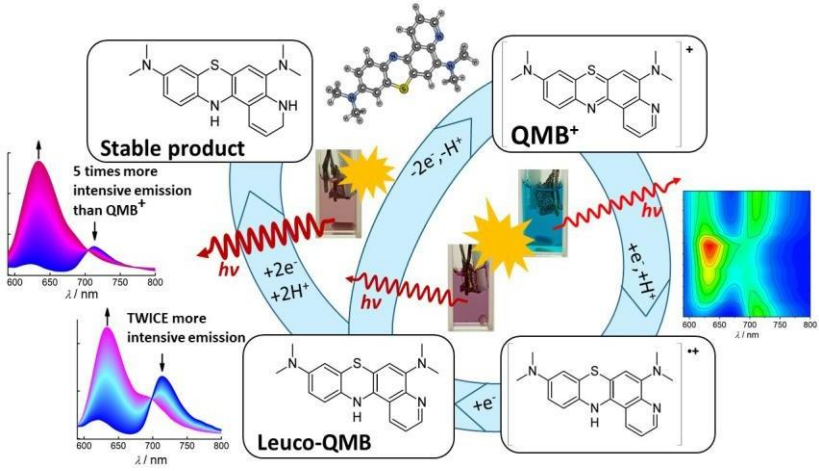

*Fig. 1. Proposed photoredoxcycle and redox-induced fluorescence switching of **QMB**$^+$ revealed by spectroelectrochemistry and density functional theory (DFT) calculations*

Electrochemical studies demonstrated that **QMB**$^+$ undergoes a reversible electron-proton coupled reduction process [1]. The first reduction leads to the formation of a violet radical intermediate (**QMB**$^{\bullet}$**)**, while the second reduction yields leuco-QMB. In contrast to leuco-MB, the leuco-QMB remains colored because of the additional pyridine chromophore. The reduction process is facilitated by proton donors, which shift the reduction potential toward more positive values.

In situ fluorescence spectroelectrochemical measurements revealed unique emission behavior during reduction. The original fluorescence band of **QMB**$^+$ at 713 nm gradually decreased, while a new emission band appeared at 633 nm. The reduced species retained strong red emission and exhibited an approximately five-fold increase in fluorescence intensity compared to the parent cation (Fig. 1). These observations indicate that **QMB**$^+$ preserves emissive properties throughout its catalytic redox cycle.

The molecular orbital distributions showed that the HOMO is mainly localized on the phenothiazine core in both dyes, while the LUMO of **QMB**$^+$ extends toward the fused pyridine ring [1]. This additional delocalization stabilizes the electronic structure and contributes to the observed bathochromic shift of the absorption spectrum. The calculated HOMO-LUMO energy gap of **QMB**$^+$ (2.39 eV) is slightly smaller than that of **MB**$^+$ (2.40 eV), which supports the experimentally observed red-shifted absorption and emission characteristics.

The natural charge distribution for **MB**$^+$ and **QMB**$^+$ in Figure 2 demonstrated a more delocalized charge distribution in **QMB**$^+$. The strongly electron-rich pyridine nitrogen atom plays a role in charge stabilization and provides additional sites for protonation and intermolecular interactions. This enhanced delocalization explains the increased stability of **QMB**$^+$ and its distinct redox behavior. Upon one-electron reduction, the radical intermediate **QMB**$^{\bullet}$ exhibits significant spin and charge delocalization over the phenothiazine and pyridine fragments. Further reduction leads to the formation of leuco-QMB and stable product (P1), accompanied by disruption of the aromatic π-conjugated system and increased molecular distortion. The calculated electronic structure of P1 indicates a larger HOMO-LUMO energy gap and pronounced intramolecular charge-transfer character, which reduces non-radiative relaxation pathways and promotes fluorescence emission.

Thisexplains the spectroelectrochemical observations, where reduction of **QMB**$^+$ results in the appearance of a new emission band at 633 nm and an almost five-fold enhancement of fluorescence intensity [1]. Overall, the DFT and time-dependent (TD) DFT calculations demonstrate that incorporation of a pyridine moiety into the phenothiazinium framework significantly stabilizes the electronic structure, modifies the redox properties, and enables efficient redox-controlled fluorescence switching while preserving red-light emission.

The **QMB**$^+$ possesses significantly higher photostability than **MB**$^+$ under irradiation at 575 nm, remaining stable for at least 3000 s [1]. Although the singlet oxygen quantum yield of **QMB**$^+$ was lower than that of **MB**$^+$, its enhanced stability and expected higher lipophilicity make it a promising candidate for biological and photochemical applications.

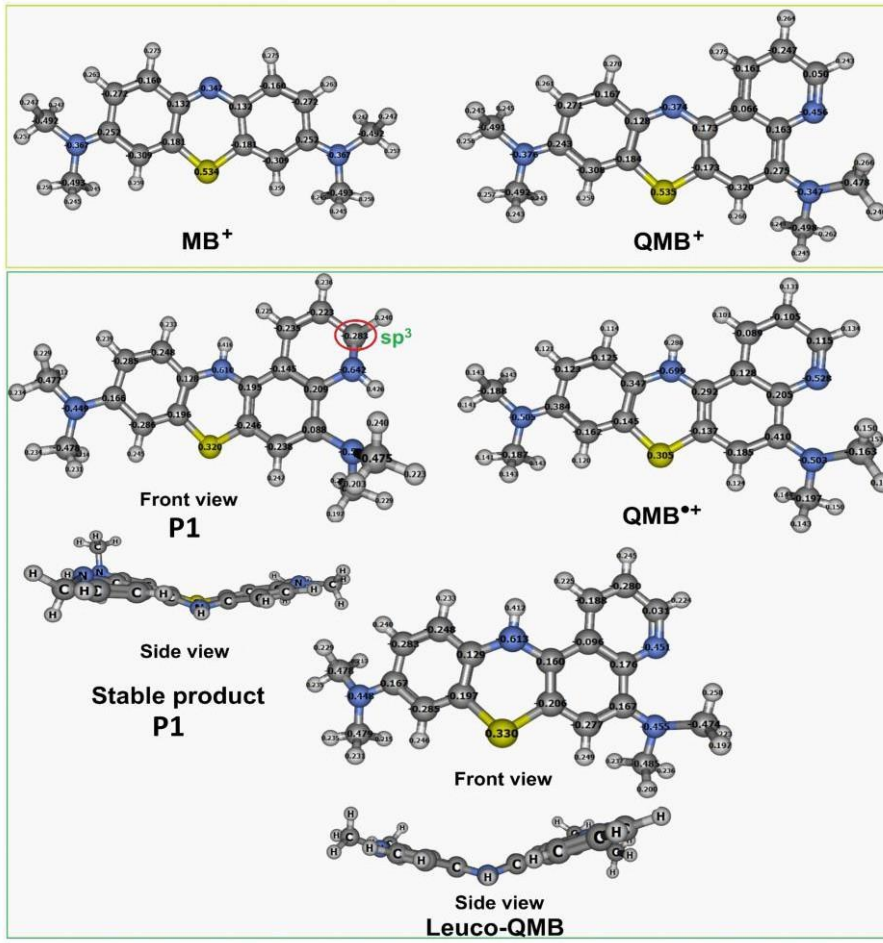

*Fig. 2. The natural charge distribution for **MB**$^+$ and **QMB**$^+$, as well as the products formed by **QMB**$^+$ during redox processes, was calculated at the B3LYP/6-31G(d,p) level of theory.*

References

1. D. Swoboda, M. Beneš, E. Jiroušková, L. Dostálková, R. Podsiadly, N. Karaush-Karmazin, R. Sokolová, J. E. Nycz, A pyridine-modified phenothiazinium photosensitizer: Electrochemical and spectroscopic behaviour upon electron transfer, Electrochim. Acta, 2026, 553, 148198.
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