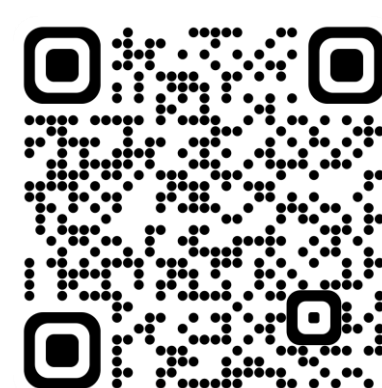
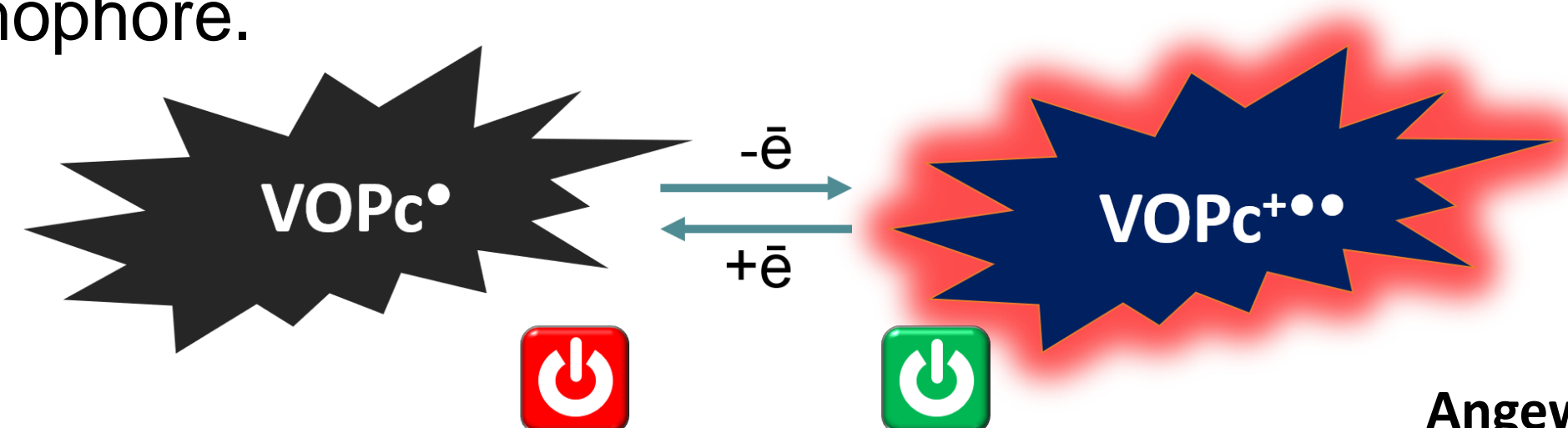


## Abstract

Elucidating electrofluorochromism phenomena at the molecular level is essential for understanding and improving the performance of optoelectronic devices. Here we report the strongly **charge-state-dependent photoluminescence (PL)** of **vanadyl phthalocyanine (VOPc)**. We describe vibrationally resolved absorption and laser-induced fluorescence (LIF) spectra of samples comprising both the neutral molecule (VOPc<sup>•</sup>, a stable radical) and its cation isolated in 5 K neon matrices. Ionization of the essentially **non-emissive VOPc<sup>•</sup> forms a high-spin diradical cation (VOPc<sup>••+</sup>) which shows profound PL** in the near-infrared (NIR) spectral range. This has implications for **future NIR-emitting electro-optical devices** based on this commonly available chromophore.



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Angew. Chem.Int. Ed.2022,61, e2022015

## Method

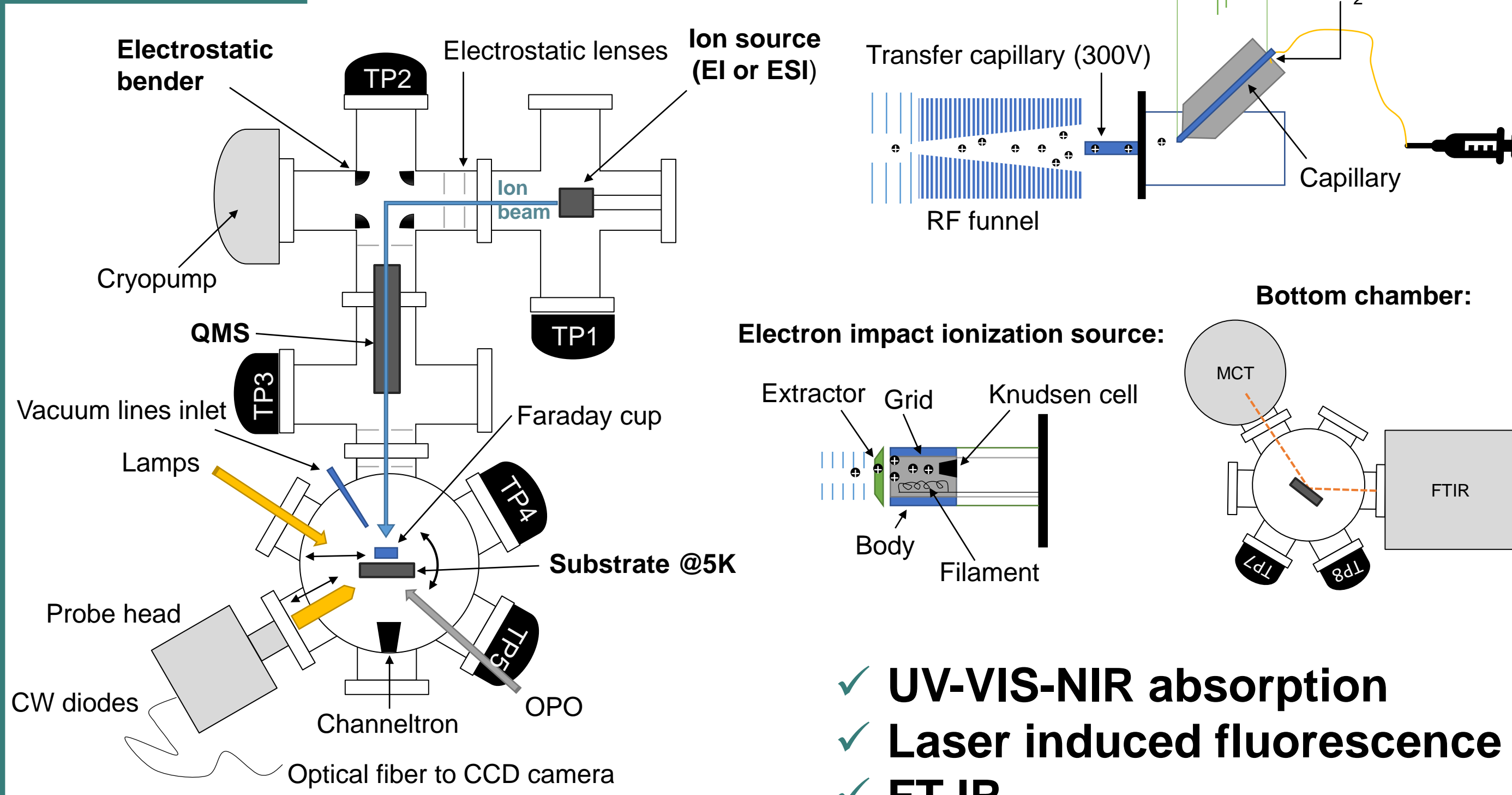


Fig 1. Schematic of Depo-II-lite instrument

- ✓ UV-VIS-NIR absorption
- ✓ Laser induced fluorescence
- ✓ FT-IR
- ✓ Raman

## Results and discussion

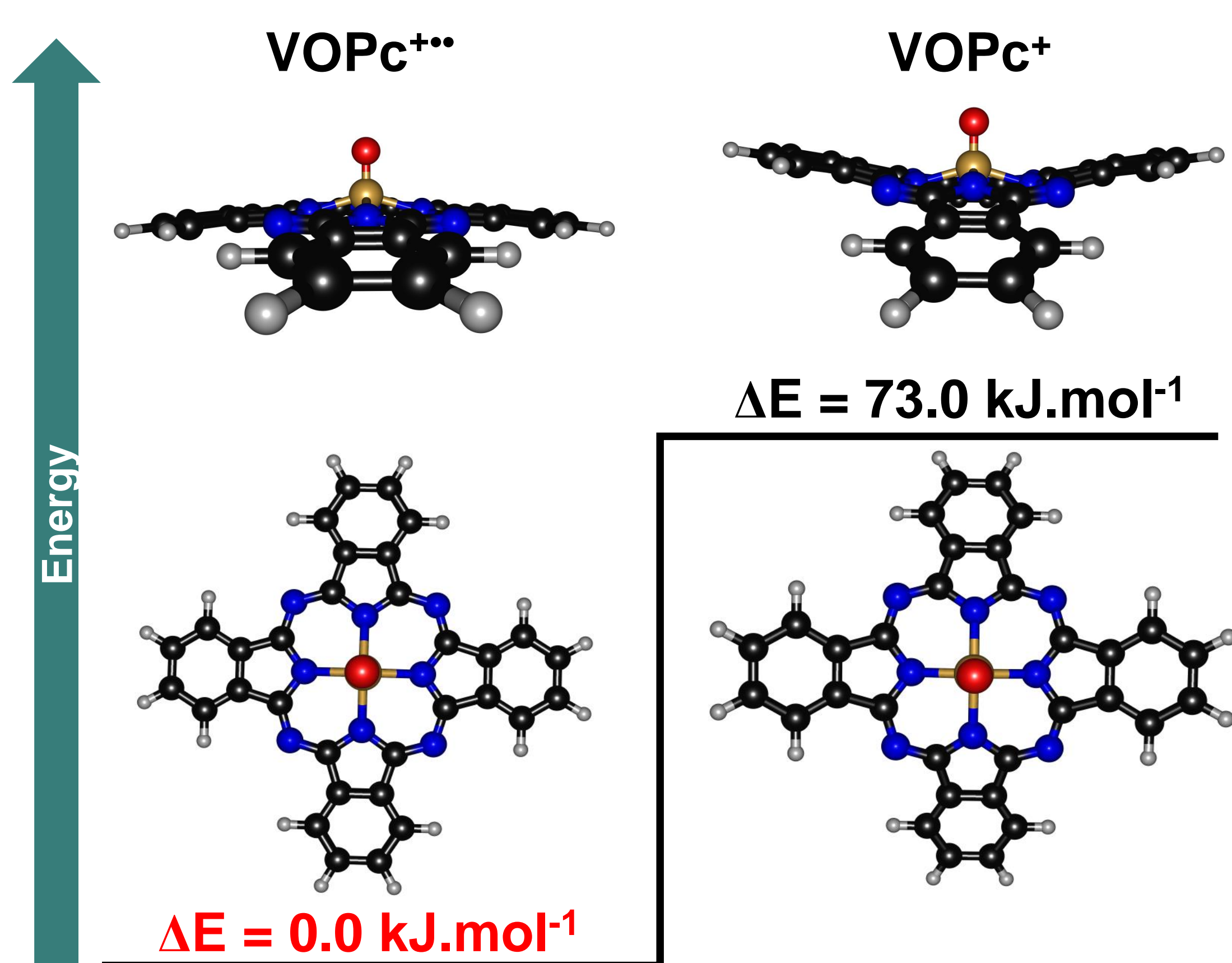


Fig 2. Structure and relative energy of triplet and singlet VOPc cation.

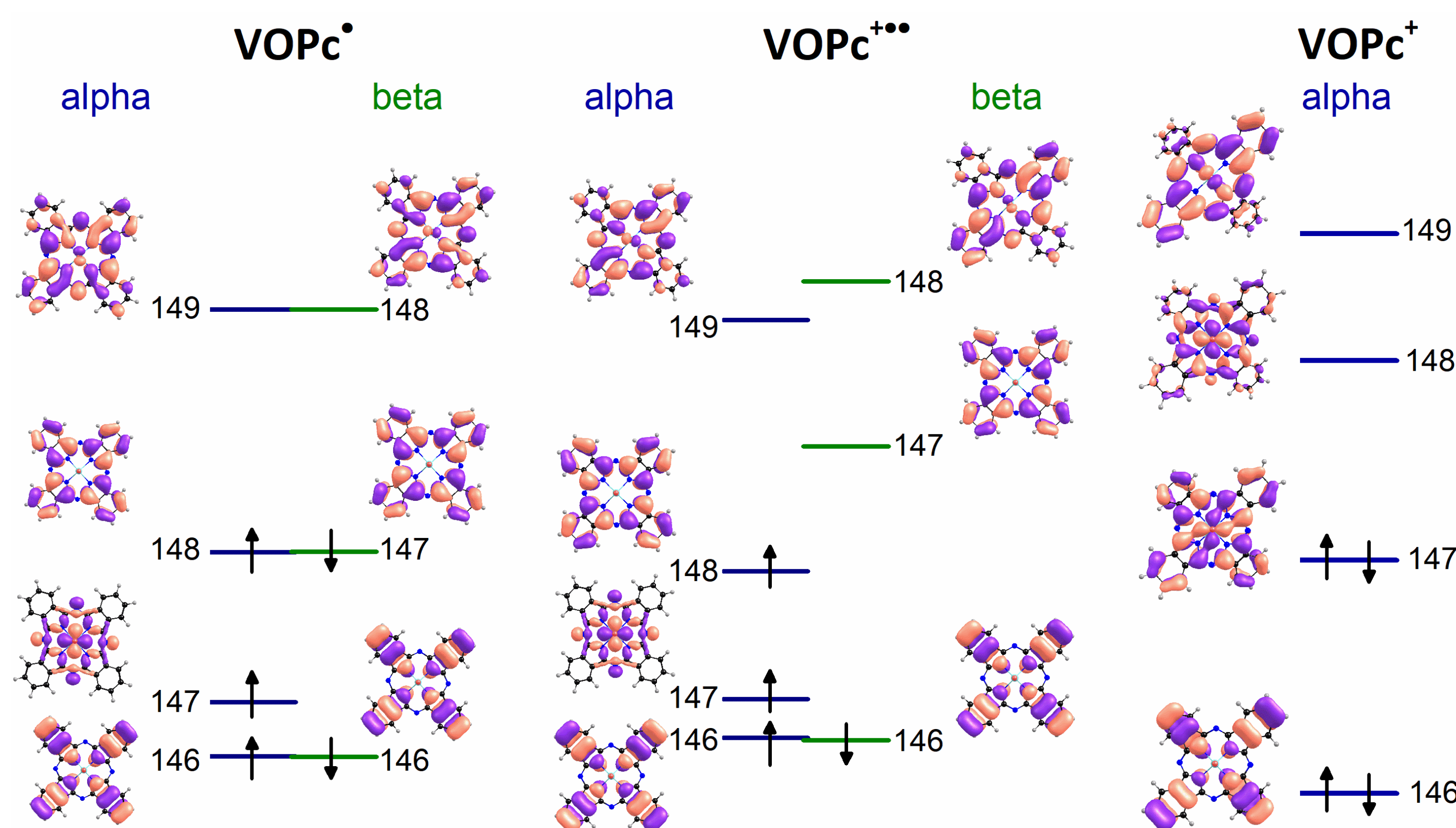


Fig 3. Frontier molecular orbitals (isosurface 0.03) and their relative energies of VOPc<sup>•</sup>/ VOPc<sup>••+</sup>/ VOPc<sup>•+</sup> together with electron occupancies calculated with TD-B3LYP/cc-pVDZ method. 'MO xxx' indicates the number of the molecular orbital;  $\alpha$  and  $\beta$  represent orbitals with occupancy of  $m_s = +1/2$  and  $m_s = -1/2$  electrons, respectively.

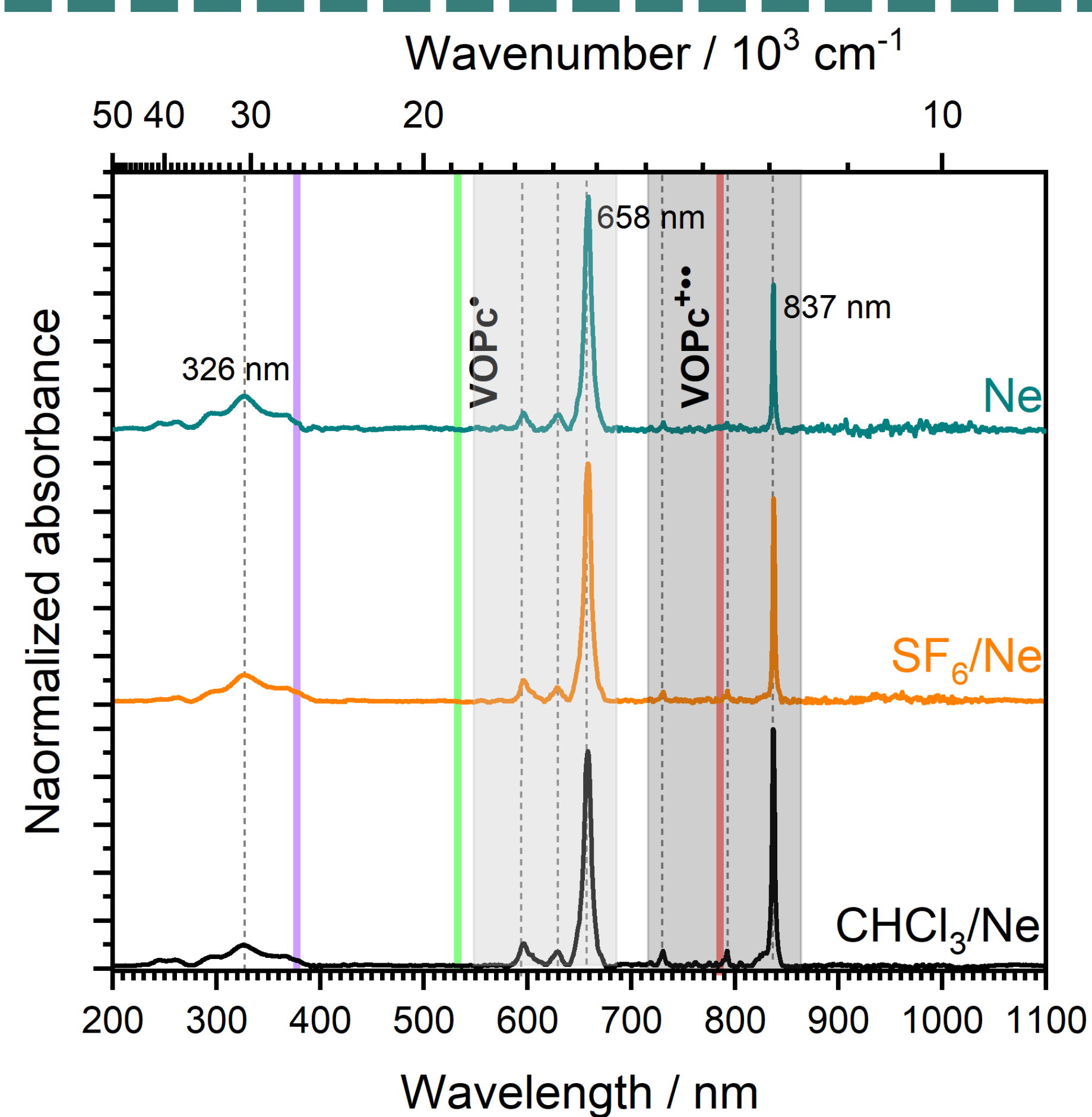


Fig 4. UV-VIS-NIR absorption spectra obtained upon depositing cationic VOPc into Ne matrix at 5K (top panel). Spectral features in the gray and deep-gray shaded regions are assigned as the signatures of VOPc<sup>•</sup> & VOPc<sup>••+</sup> respectively. Note the **presence of both neutralized and cationic VOPc in the same matrix**. Electron scavengers SF<sub>6</sub> and CHCl<sub>3</sub> were used to **enhance the concentration of the cationic species** (bottom panels). Dashed gray lines highlight the positions of absorption bands common to all three spectra. Purple, green, and red lines denote the wavelengths of laser diodes used for LIF.

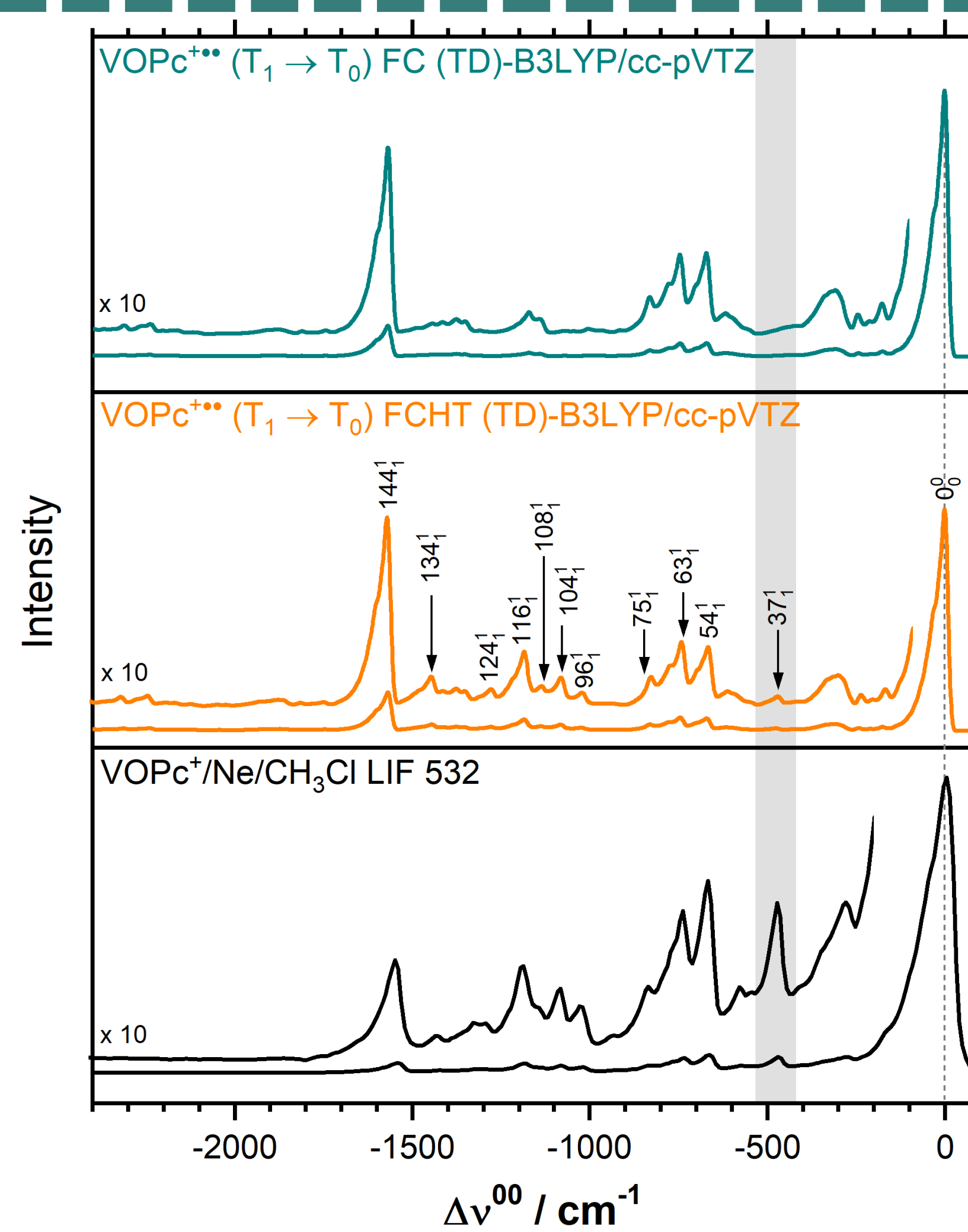


Fig 5. LIF spectrum of VOPc<sup>••+</sup> isolated in solid Ne (532 nm excitation) at 5 K in comparison with Franck-Condon (FC) and Franck-Condon/Herzberg-Teller (FC/HT) TD-B3LYP/cc-pVDZ predictions. The spectra are plotted with respect to the 0-0 band origin at 11923 cm<sup>-1</sup>. The gray shaded area indicates the region with the significant deviation between the theory and experiment. **The VOPc<sup>••+</sup> can be unambiguously identified.**

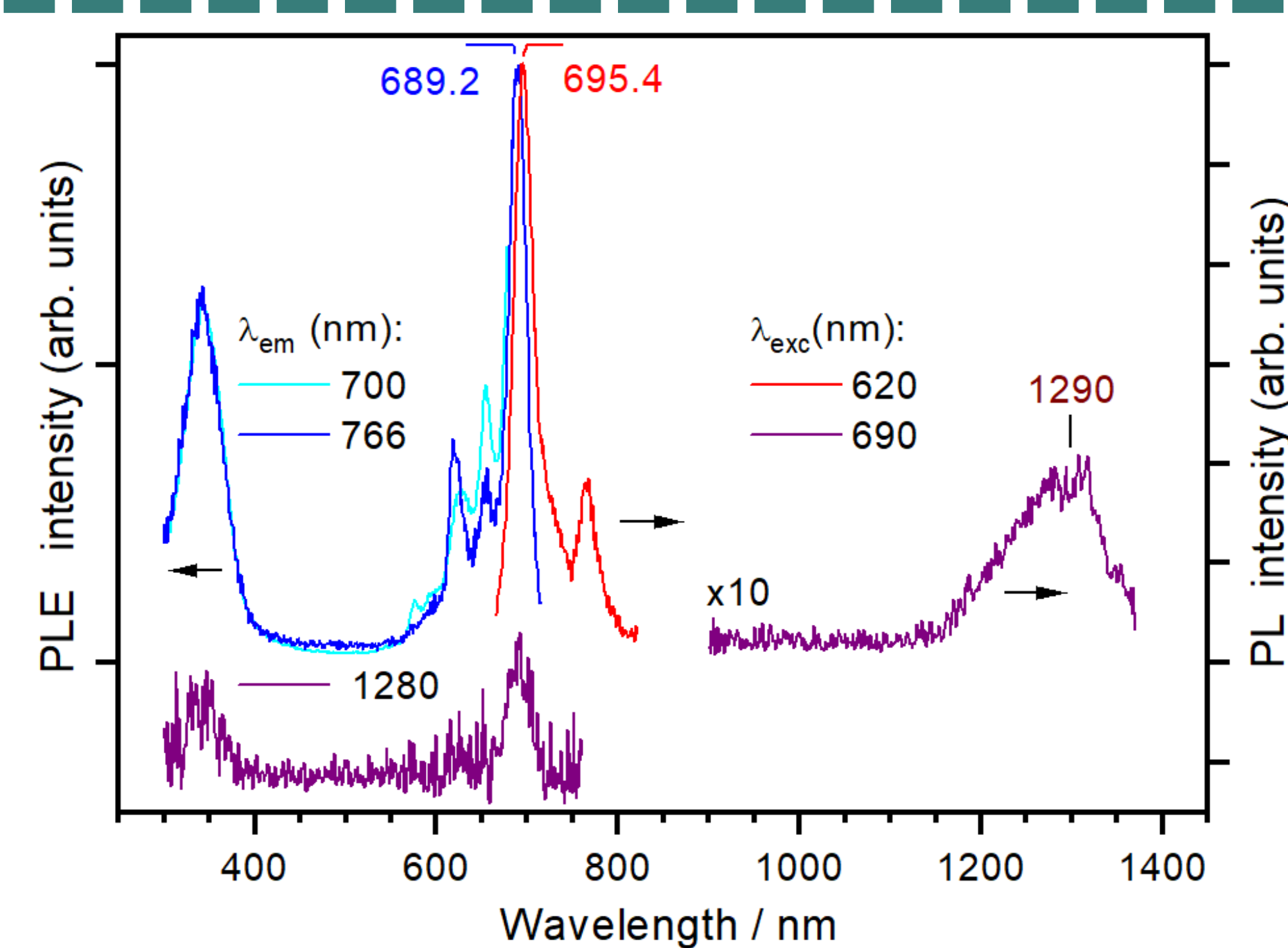


Fig 6. Photoluminescence emission (PL) and excitation (PLE) spectra of VOPc dissolved in dichloromethane (~10<sup>-6</sup> M) at room temperature. The respective excitation and emission wavelengths are indicated. **The emission of VOPc<sup>•</sup> is very weak**, particularly in the NIR region, and was correspondingly recorded using large monochromator slits (5-10 nm) and long acquisition times (up to 1 h). The visible and NIR emission spectra are presented on the same intensity scale. The NIR excitation spectrum is vertically shifted for clarity.