## Supplementary materials

# Unusual 'Turn-on' Ratiometric Response of Fluorescent Porphyrin-Pyrene Dyads to the Nitroaromatic Compounds

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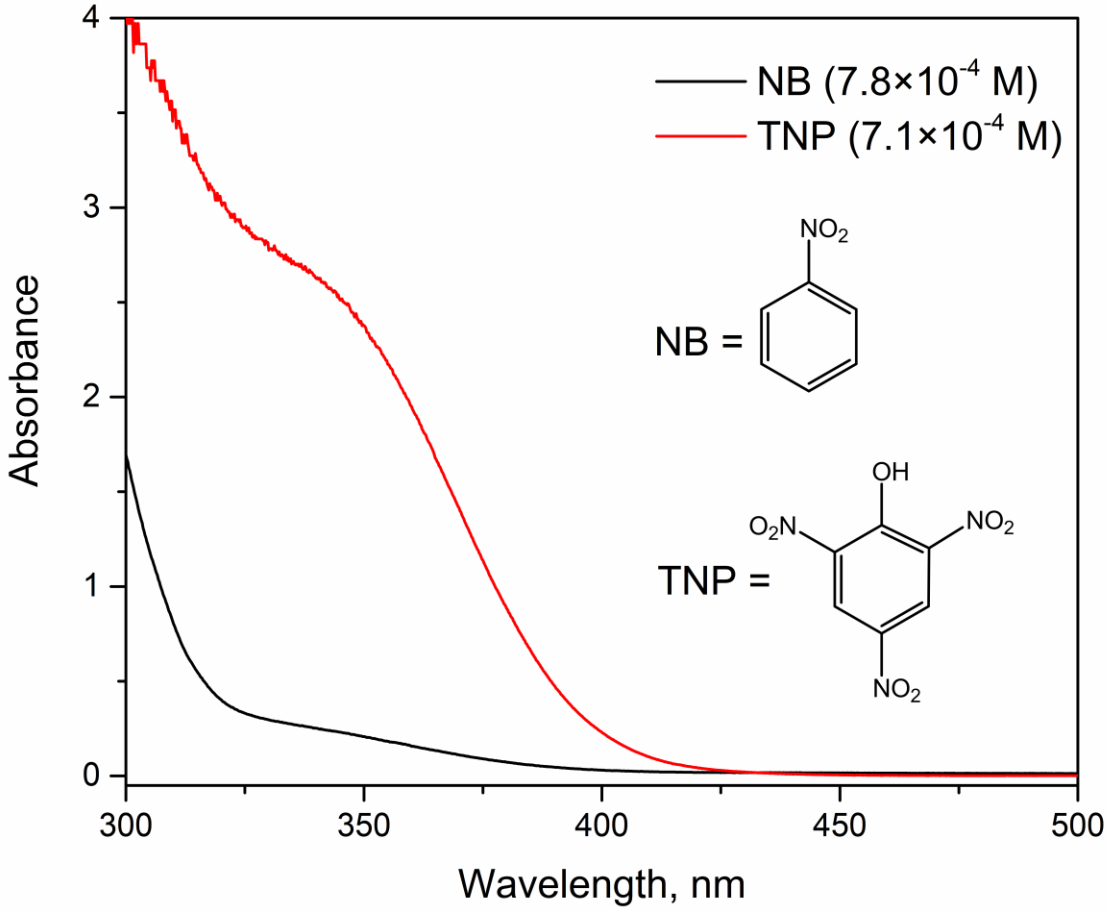
**1. The UV-vis spectra of NB and TNP solutions in toluene.**




**Fugure S1.** The UV-vis spectra of NB (7.8×10−4 M) and TNP (7.1×10−4 M) solutions in toluene.

**2. The elimination of artefacts from the fluorescence spectra.**

To eliminate the artefacts, we register so called "fluorescence spectrum" of blank toluene in the cuvette under the same instrumental conditions and at the same excitation wavelengths as for the dyads. Then, we subtract this "spectrum" containing information on the Rayleigh scattering and the 2nd order of diffraction from the fluorescence spectrum of the dyad. An example of this calculation for **$H_2$PIP** fluorescence spectrum process is shown in Figure S2.

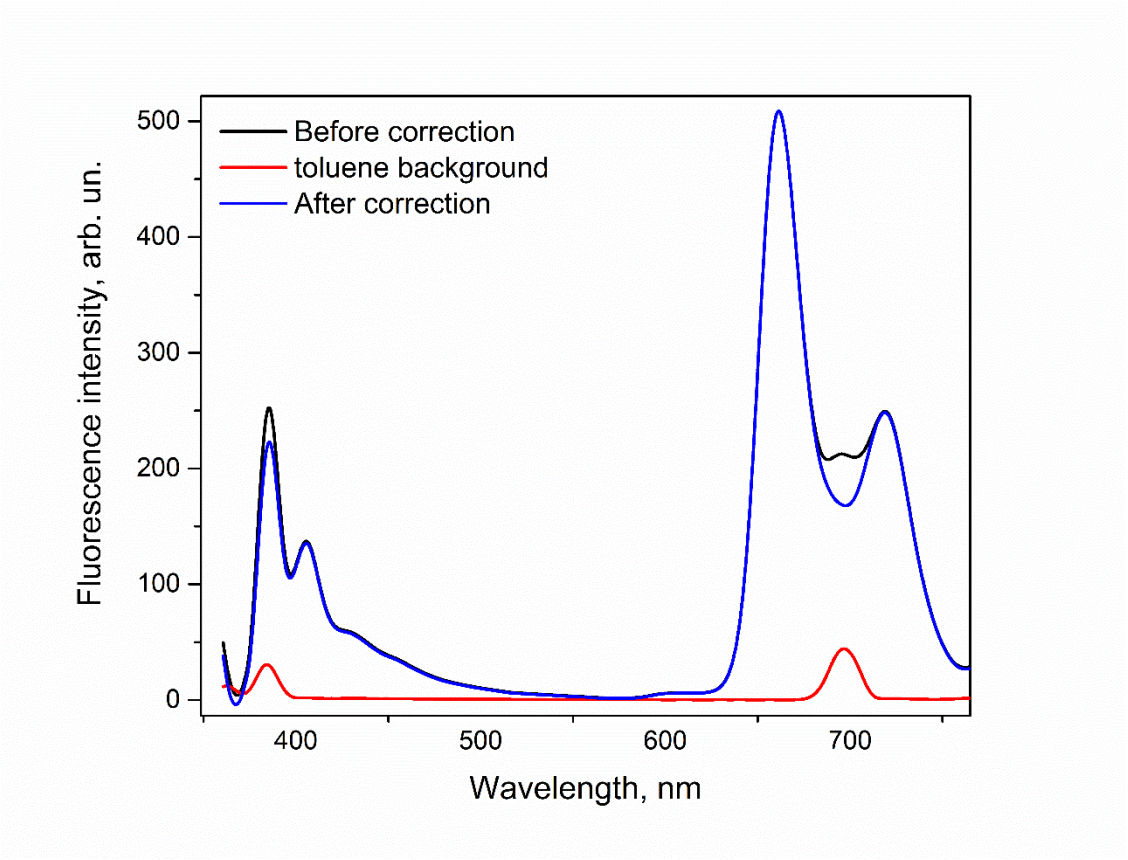



**Figure S2.** The fluorescence spectrum of toluene solution of H2PIP (7.6×10−7 M) before correction (the black curve) and after correction (the blue curve) by the subtraction of the toluene background with Rayleigh scattering and the 2nd order diffraction artefact from the 346 nm excitation light.

**3. The UV-vis absorbance and fluorescence spectra of TPP solution in toluene.**

For demonstration purposes, we have chosen tetraphenylporphyrin (**TPP**) as a porphyrin model. As it known, porphyrins can absorb light in the near UV-region [1]. Therefore, one can see that excitation at 346 nm leads to **TPP** luminescence which intensity is ca 3.5 times weaker than the **TPP** one generated by the IV Q-band excitation. Note: a small peak at ca. 692 nm on the red curve is the 2nd order diffraction artefact from the 346 nm excitation light

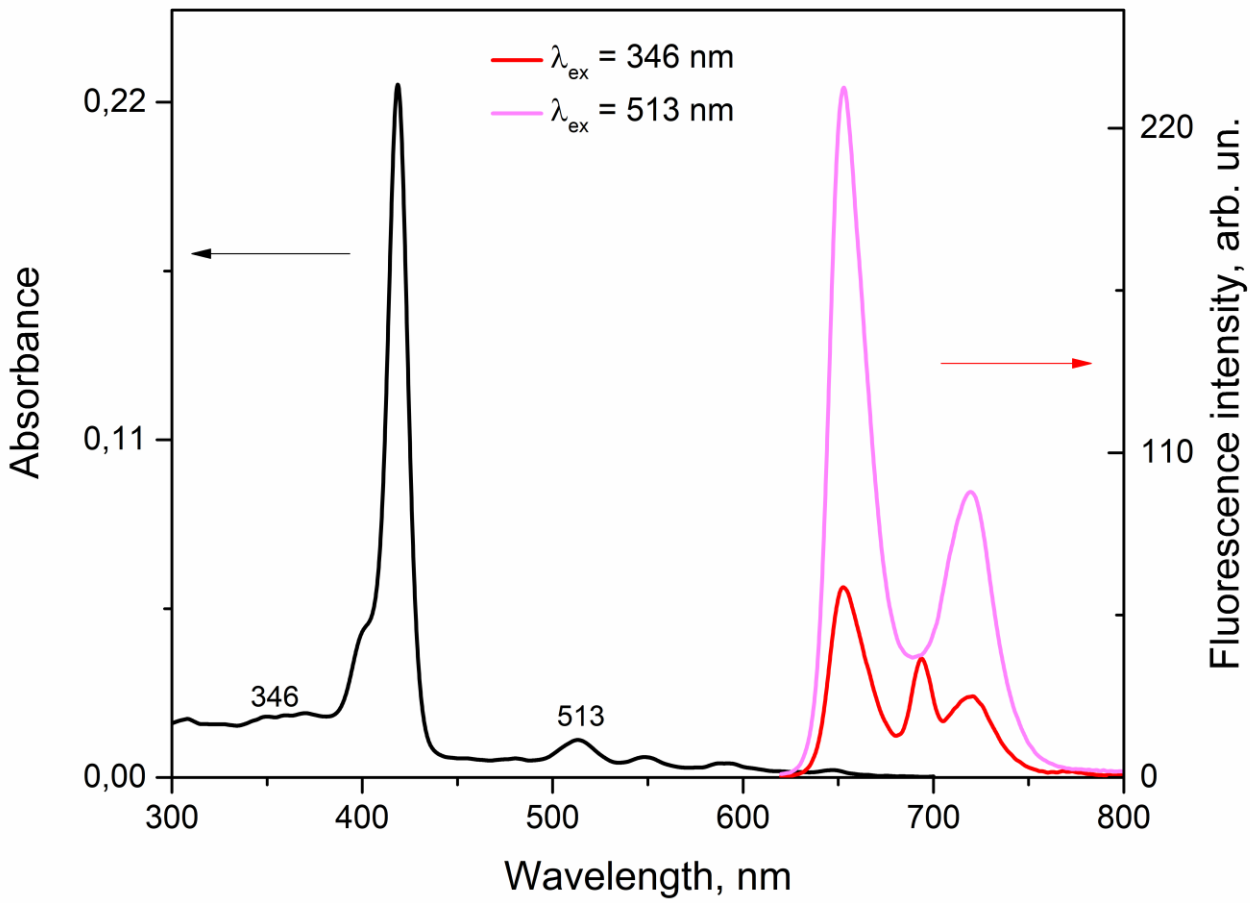



**Figure S3.** The UV-vis absorbance and fluorescence spectra of TPP (5.8×10−7 M) solution in toluene. Note: a small peak at ca. 692 nm on the red curve is the 2nd order diffraction artefact from the 346 nm excitation light.

**4. The UV-vis titration of ZnPIP solution (7.3×10$^{-7}$ M) with NB (0–250 eq) in toluene.**

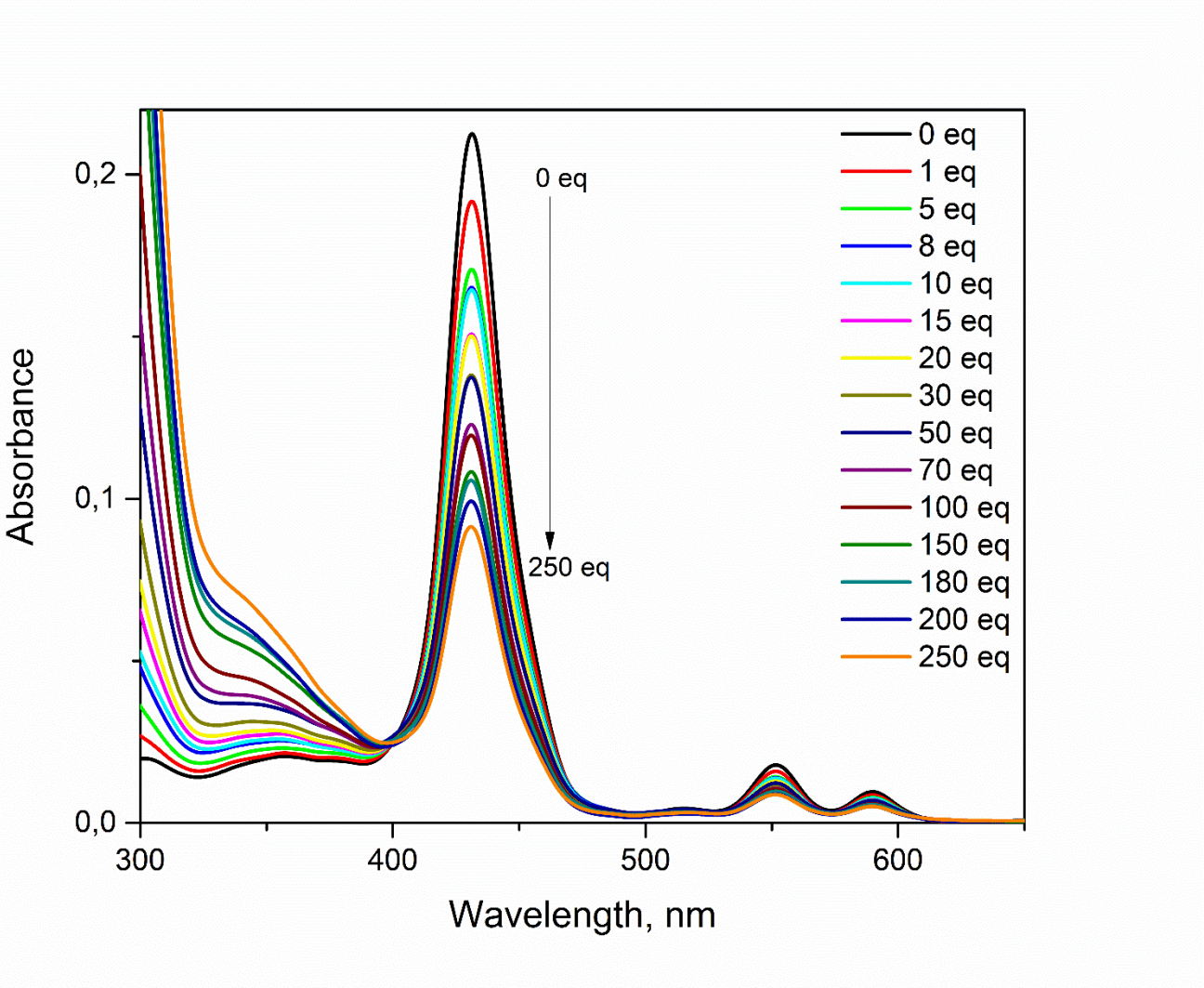



**Figure S4.** The UV-vis titration of ZnPIP solution (7.3×10−7 M) with NB (0–250 eq) in toluene.

**5. Calculation of association constants**

To estimate the associate constants $K_a$, we have studied Pall Thordarson's extensive review [2] and used Bandfit, an online program developed by his group — http://supramolecular.org. The Bandfit program is based on accurate equations of complex formation derived in terms of binding constants and mass balances.

On the basis of the **D-D** values and concentrations of the added NAC (Figure S5a,b), we have calculated that in the case of **ZnPIP** titration with **NB,** $K_a$ equals to $2.9\times10^5$ $M^{-1}$ and in the case of **ZnPIP** titration with **TNP**, $K_a$ is found to be $7.5\times10^4$ $M^{-1}$.

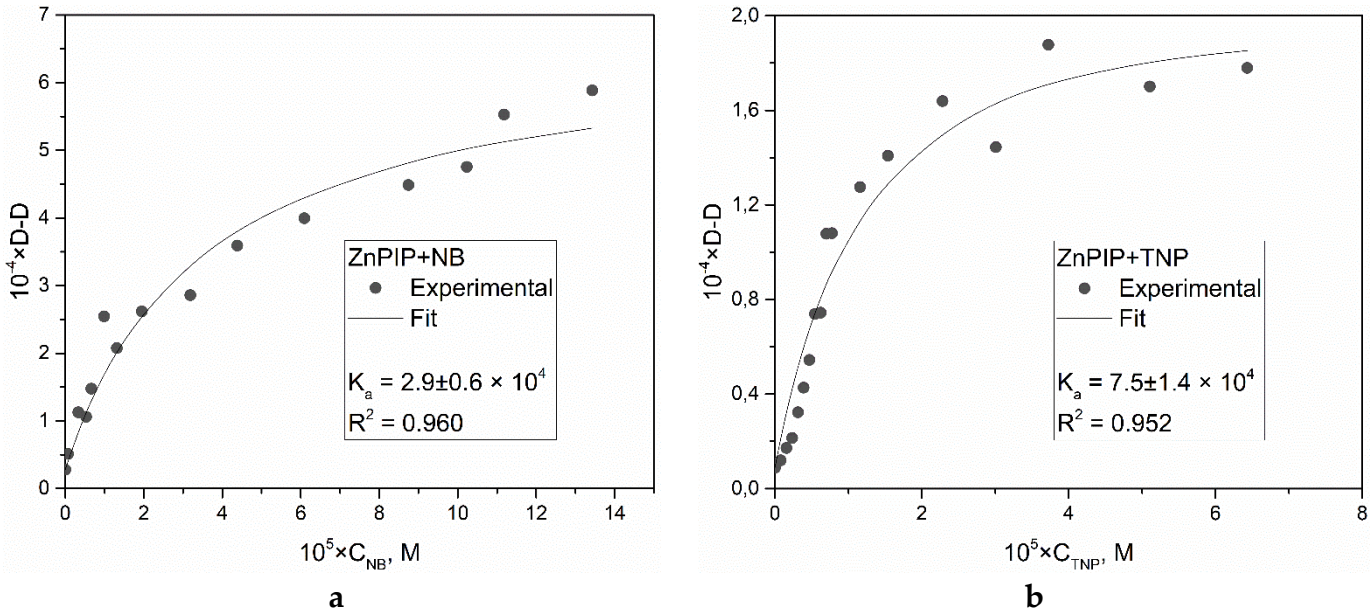



**Figure S5.** The Ka calculation plot for ZnPIP under (**a**) NB addition and (**b**) TNP addition.

**6. The UV-vis titration of ZnPIP solution (7.9×10⁻⁷ M) with TNP (0–194 eq) in toluene.**

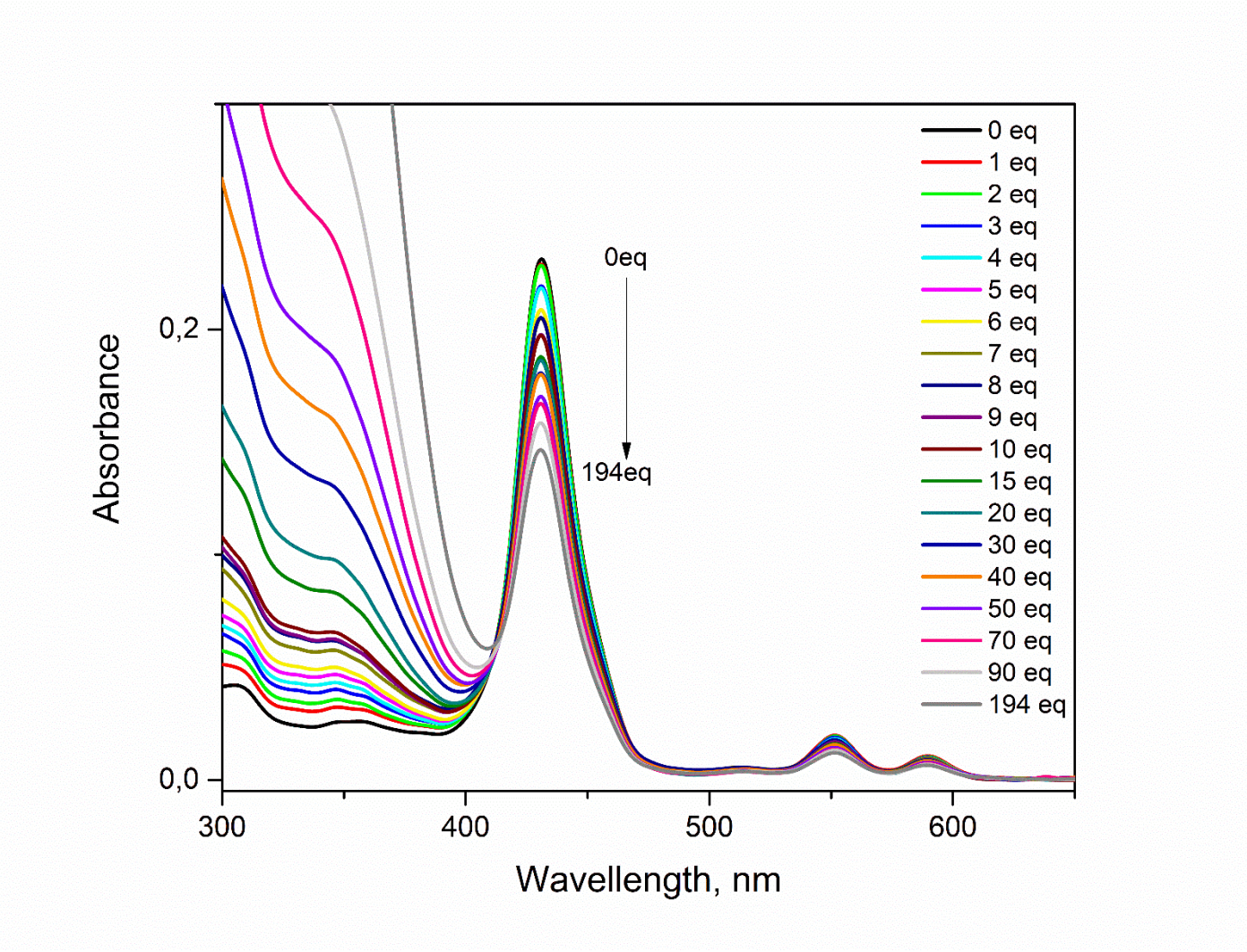



**Figure S6.** The UV-vis titration of ZnPIP solution (7.9×10–7 M) with TNP (0–194 eq) in toluene.

**7. The fluorescence titration of ZnPIP ($7.9\times10^{-7}$ M) with TNP (0–194 eq) under the direct A excitation (550 nm) in toluene.**

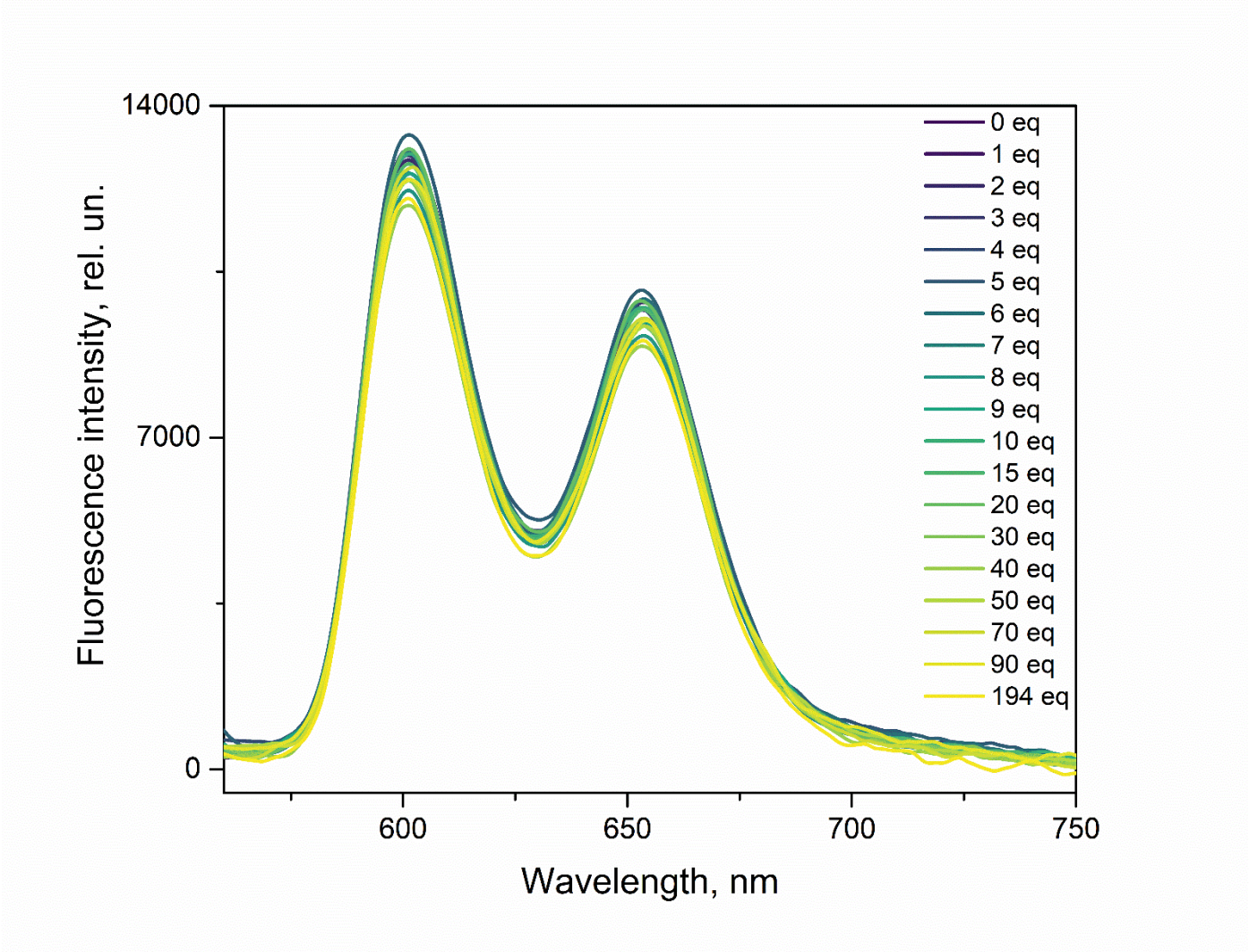



**Figure S7. The fluorescence titration of ZnPIP (7.9×10–7 M) with TNP (0–194 eq) under the direct A excitation (550 nm) in toluene.**

**8. The difference in the luminescence behaviour of the D moiety in ZnPIP and porphyrin-absent model**

2-(1-pyrenyl) benzimidazole **BIP** was used to model the **D** moiety without the porphyrin macrocycle.

It is clearly seen (0) that the intensity of **BIP** fluorescence is several orders of magnitude larger than that of **ZnPIP**. Such differences in the radiative relaxation of their excited states indicate that in the studied dyads, besides the fluorescence, **D** relaxes through a number of non-radiative pathways.

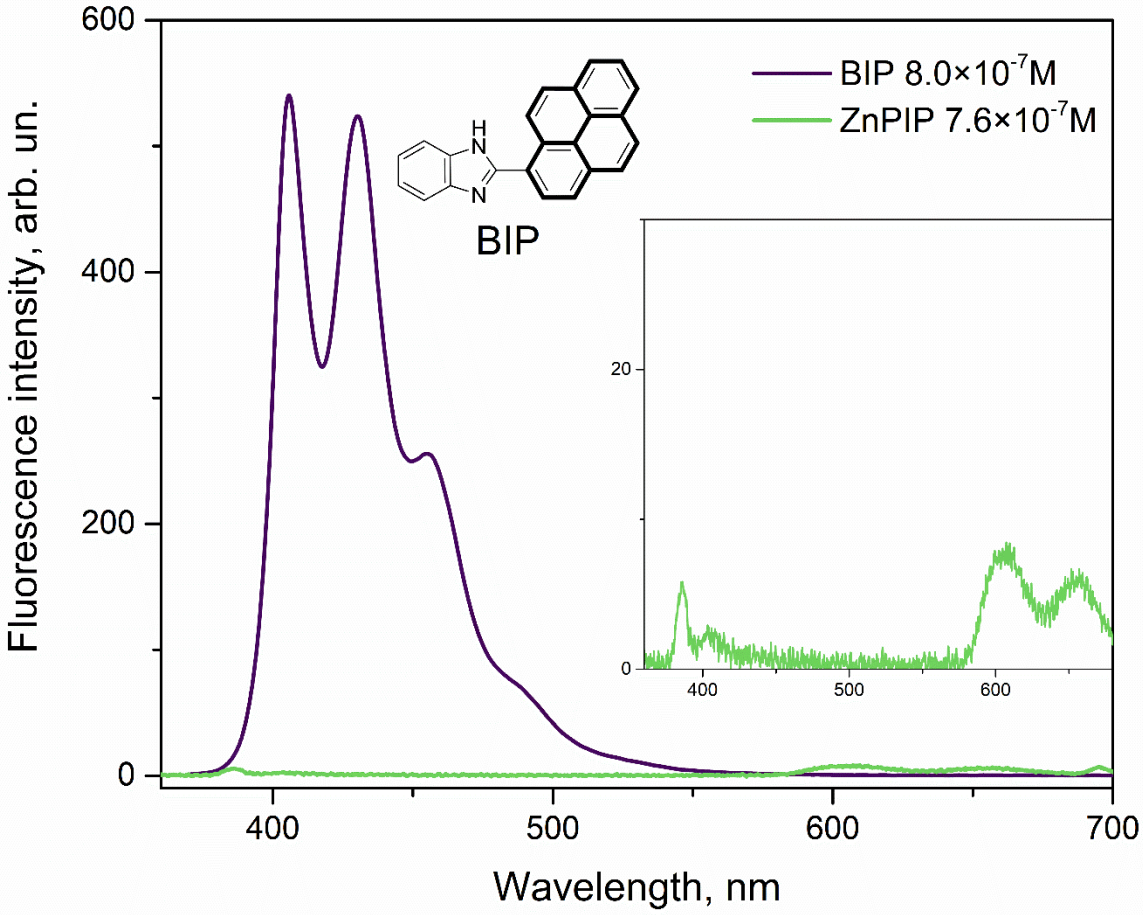



**Figure S8.** The comparison of BIP (8.0×10−7 M) and ZnPIP (7.6 ×10−7 M) solutions in toluene fluorescence spectra toluene (λex = 346 nm) under the same experimental conditions. In the inset: the zoomed ZnPIP spectrum.

**9. The spectral characterization of ZnPIP immobilized in the PMMA matrix**

The fluorescence spectrum of the obtained solid film demonstrates a similar **ZnPIP** behaviour as that described for a viscous solvent — the area of **D** fluorescence intensifies relatively to the **A** emission intensity; however, no new **D** peak in the region of 460–500 nm arises.

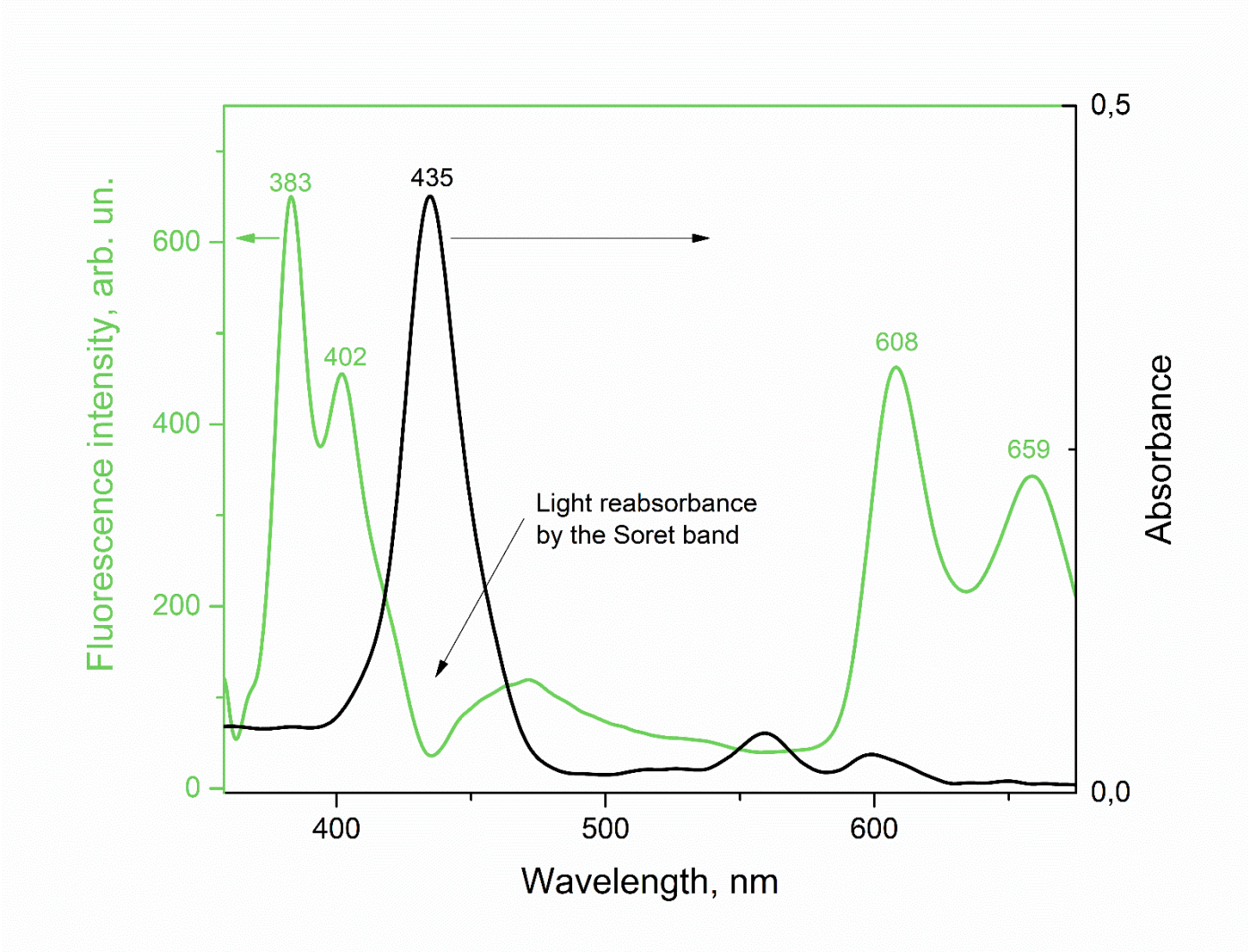



**Figure S9.** The fluorescence (the green curve) and UV-vis absorbance (the black curve) spectra of 'ZnPIP in PMMA' solid film under $\lambda$ex = 346 nm.

**10. The UV-Vis and fluorescence ($\lambda_{ex}$ = 346 nm) titration of ZnPIP solution ($7.5\times10^{-7}$ M) with $C_6F_6$ in toluene**

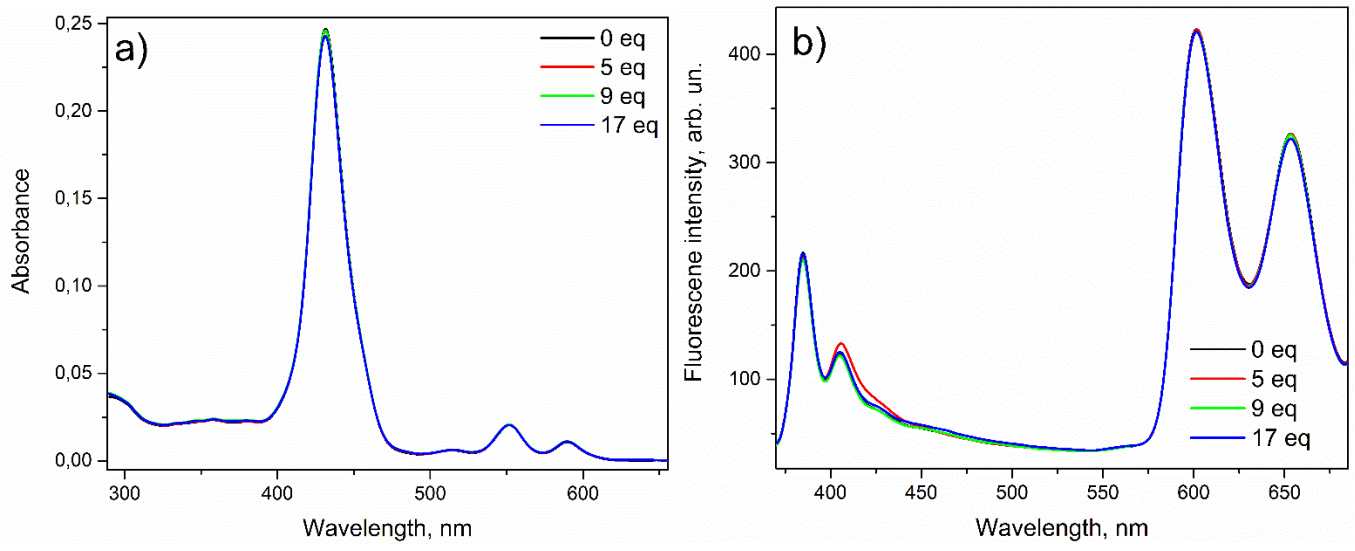


**Figure S10.** The UV-Vis and fluorescence ($\lambda$ex = 346 nm) titration of ZnPIP solution (7.5×10-7 M) with C6F6 in toluene.

**References.**


1. Edwards, L.; Dolphin, D.H.; Gouterman, M.; Adler, A.D. Porphyrins XVII. Vapor Absorption Spectra and Redox Reactions: Tetraphenylporphins and Porphin. J. Mol. Spectrosc. 1971, 38, 16–32. https://doi.org/10.1016/0022-2852(71)90090-7.
2. Thordarson, P. Determining Association Constants from Titration Experiments in Supramolecular Chemistry. *Chem. Soc. Rev.* **2011**, *40*, 1305–1323, doi:10.1039/C0CS00062K.