Supramolecular assembly of phosphonate-substituted porphyrins in Langmuir layers and Langmuir-Schäfer films: structural studies and selective sensing of pyridine

Elizaveta V. Ermakova[†,*], *Vladimir V. Arslanov*[†], *Yann Bretonnière*[ɬ], *Carine Michel*[ɬ], *Alla Bessmertnykh-Lemeune*[ɬ,*].

[†]Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky Pr. 31-4, Moscow 119071, Russia.
[ɬ]Laboratoire de Chimie, UMR 5182, CNRS, ENS de Lyon, 46 allée d'Italie, CEDEX, 69364 Lyon, France

Supporting information

Table of Contents:

1. UV–vis and fluorescence spectroscopies studies

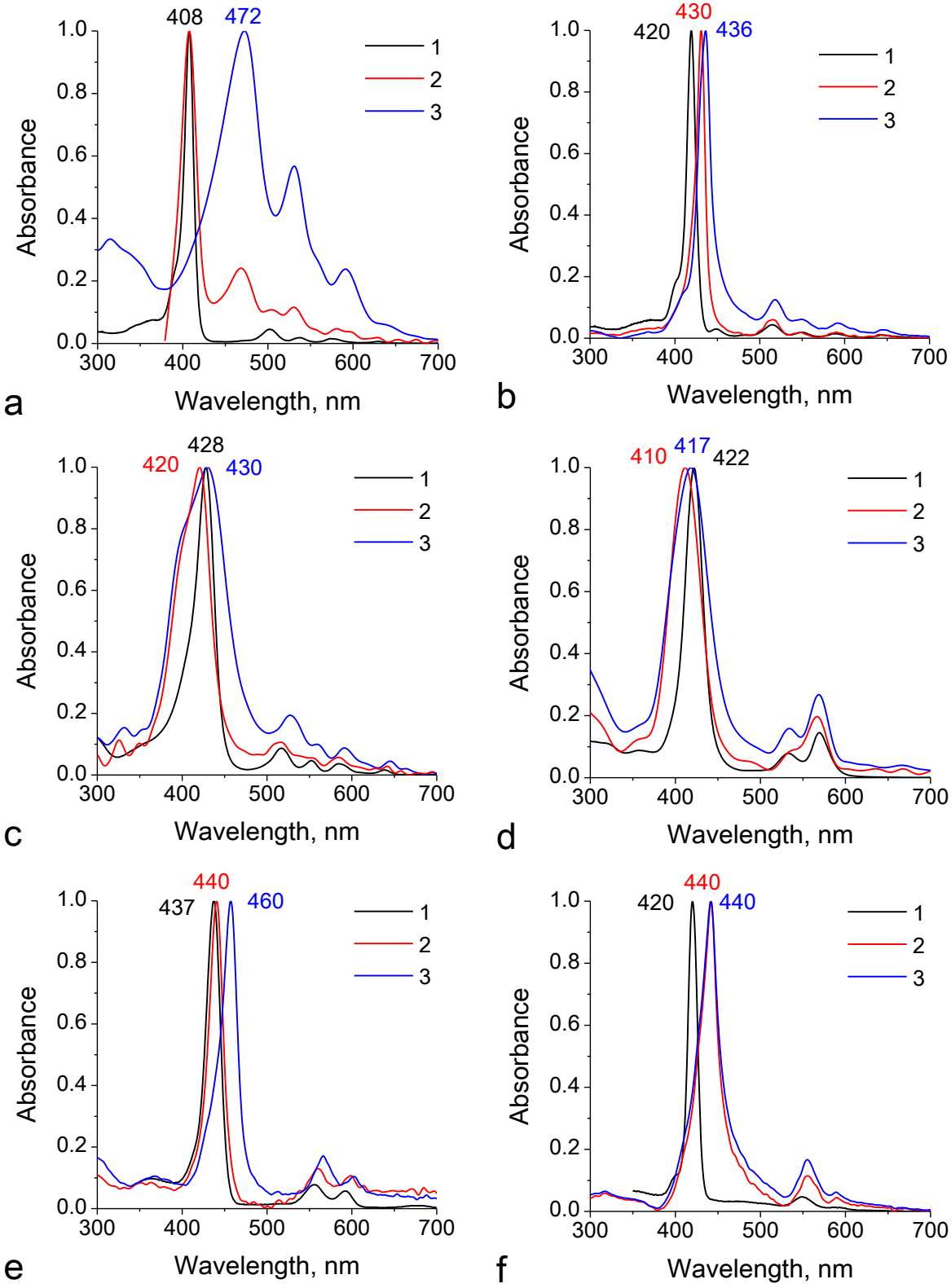


Figure S1. Normalized [0;1] UV–vis spectra of H_2DPPP (a), H_2TPPP (b) and H_2OPPP (c), NiOPPP (d), ZnOPPP (e), ZnTPP (f) in chloroform solution (*1*), monolayer on the deionized water at surface pressure 0 (*2*) and 35 (*3*, a), 18 (*3*, b), 22 (*3*, c), 35 (*3*, d), 30 (*3*, e), 24 (*3*, f), 27 (*3*, g) mN m^{-1}.

2. Fitting of *in situ* UV–vis spectra of H_2DPPP and H_2OPPP monolayers

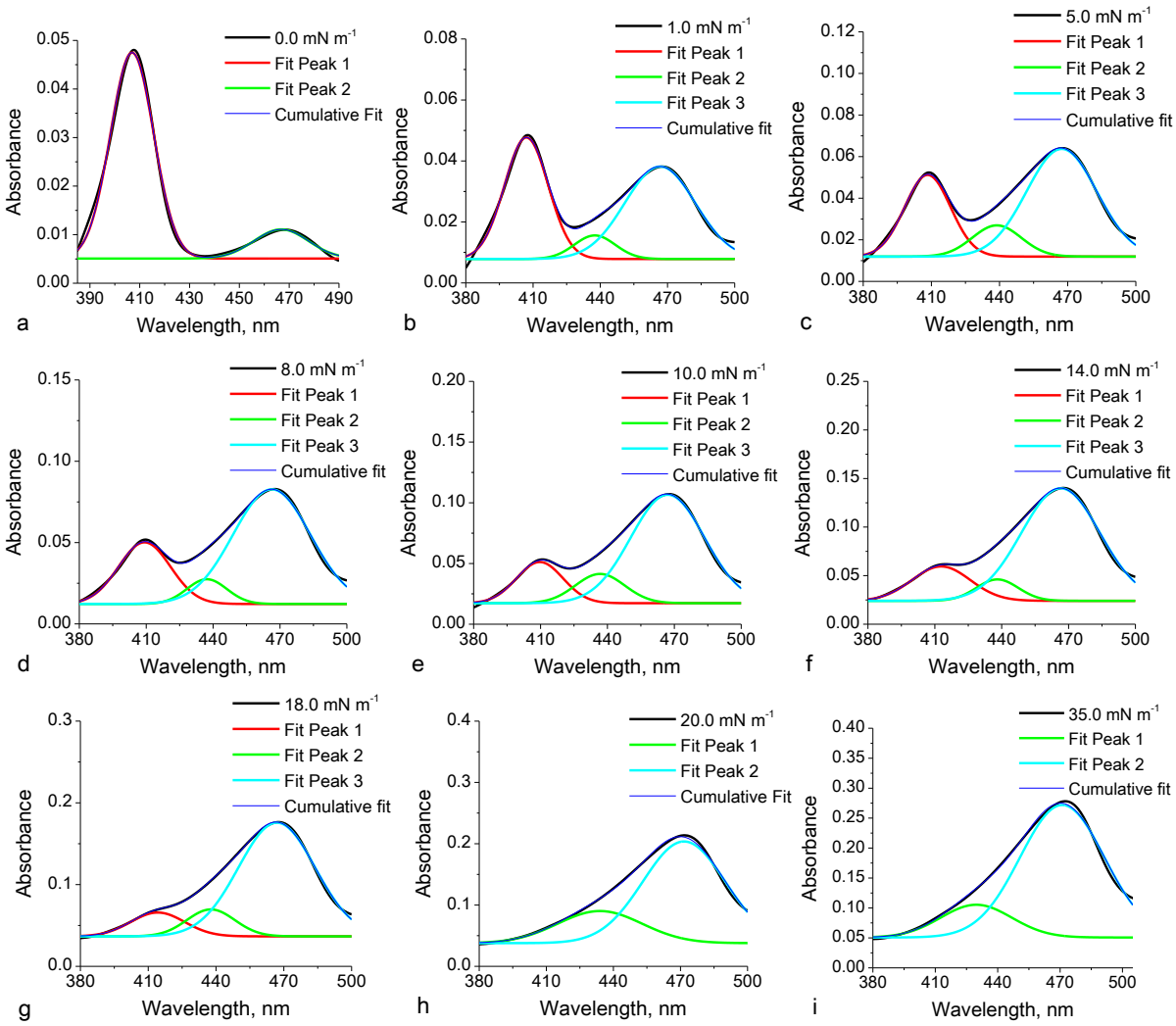
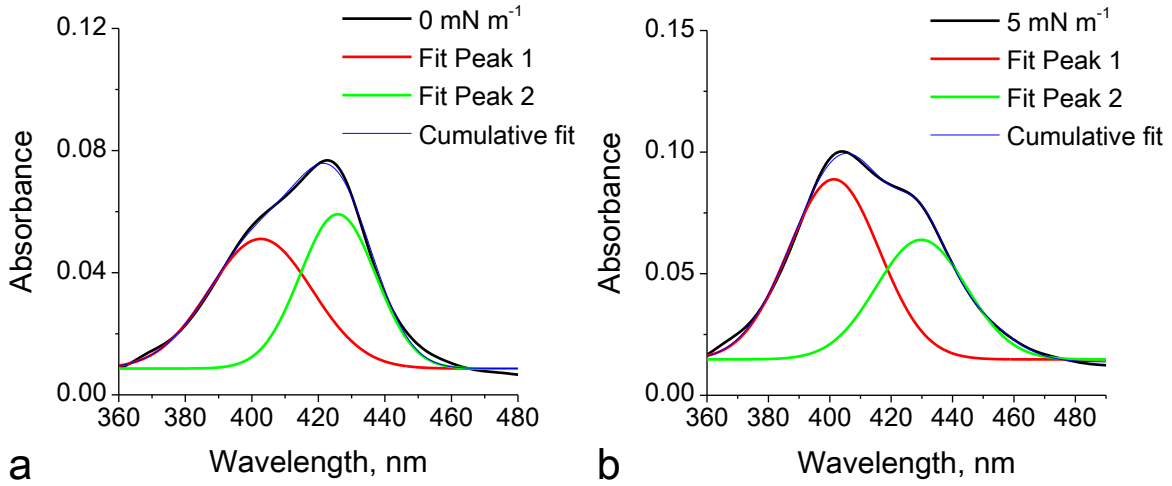


Figure S2. *In situ* UV-vis spectra of H_2DPPP monolayer and their multipeak Gaussian fitting.



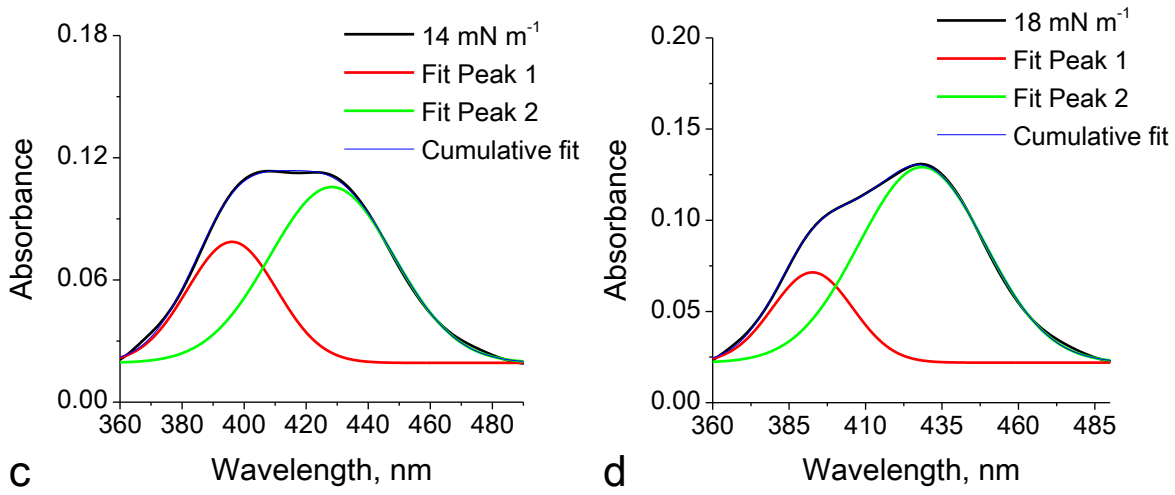


Figure S3. *In situ* UV–vis spectra of H_2OPPP monolayer and their multipeak Gaussian fitting.

3. Monolayers of H_2DPPP, H_2TPPP and H_2OPPP at the air–water interface

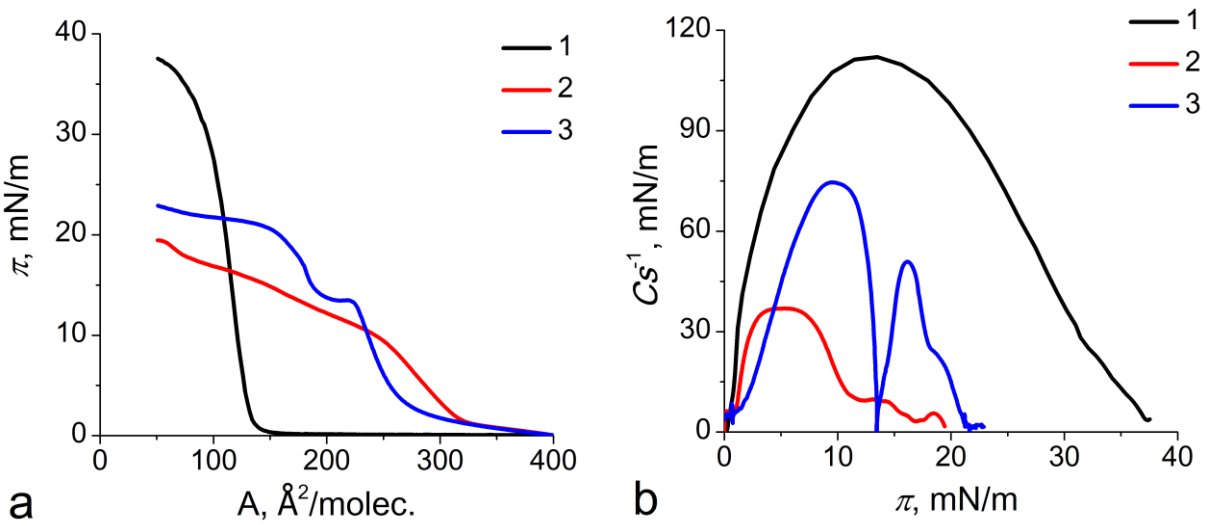


Figure S4. (a) Surface pressure–area isotherms and (b) compressibility modulus Cs^{-1} *vs.* surface pressure plots for the H_2DPPP (*1*), H_2TPPP (*2*) and H_2OPPP (*3*) monolayers on the water surface.

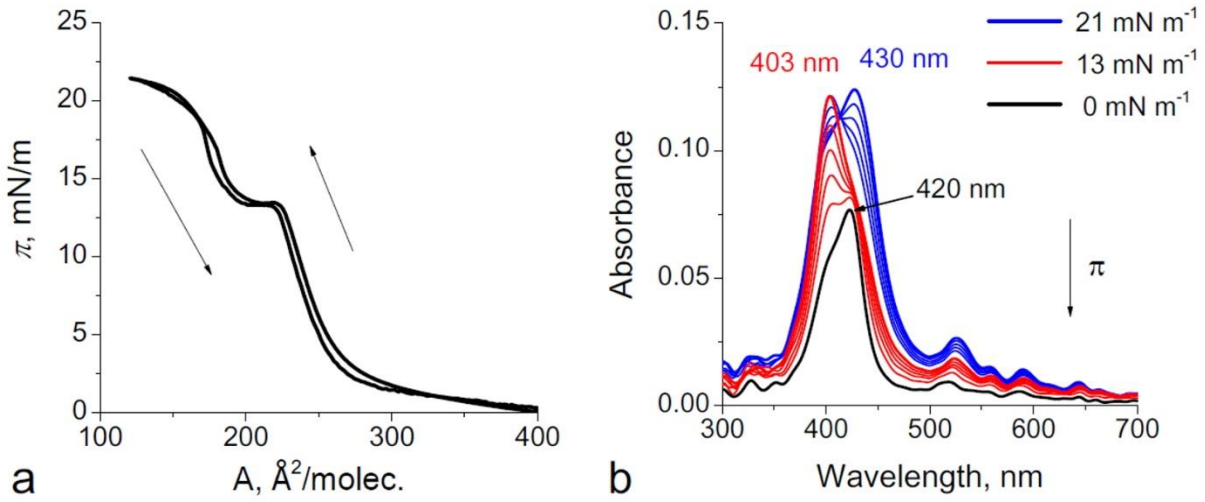


Figure S5. (a) Compression–expansion cycles for porphyrin H_2OPPP. (b) *In situ* UV–vis spectra of the H_2OPPP monolayer recorded during the monolayer expansion.

4. LS and drop-cast films of H_2OPPP

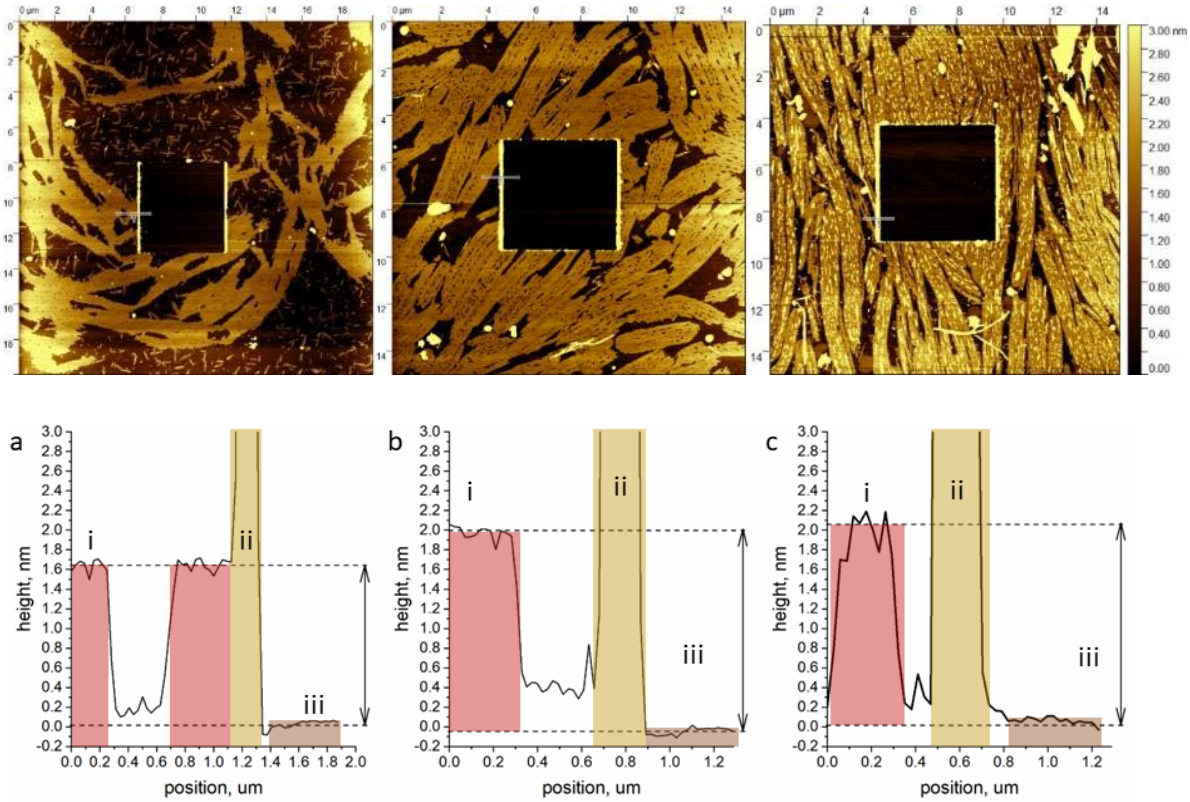


Figure S6. AFM images obtained after 'scratching' the samples in contact mode to reveal bare mica. Top, from left to right: LS film of H_2OPPP transferred onto mica at 5, 14, and 18 mN m^{-1}. Bottom: corresponding height profiles obtained along the scratched surface line for samples transferred at (a) 5, (b) 14, and (c) 18 mN m^{-1}. Colored regions on the height profiles correspond to (i) observed porphyrin domains, (ii) film material piled up after 'scratching', and (iii) bare mica surface.

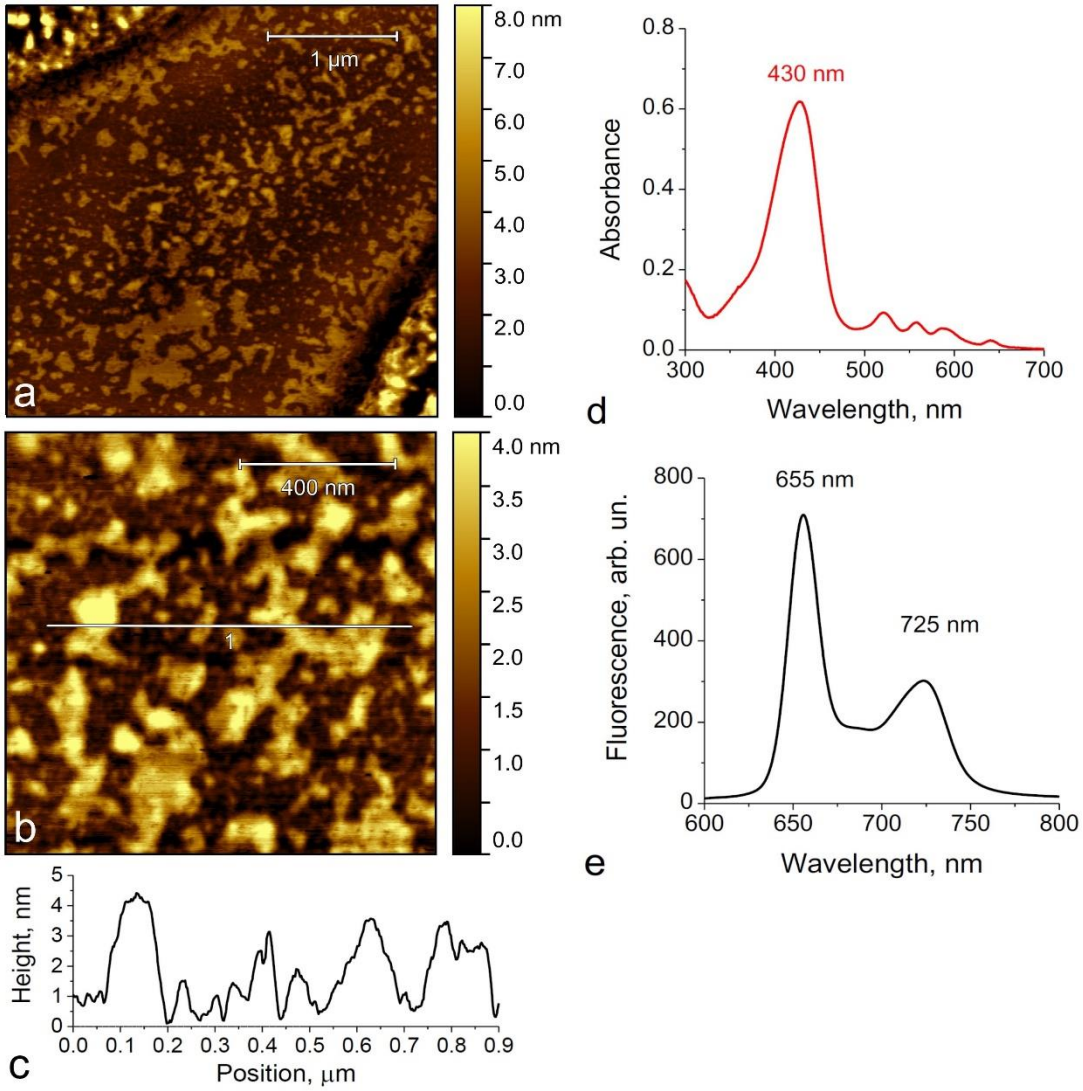


Figure S7. (a, b) AFM images of drop-cast film of H_2OPPP deposited onto a mica substrate and (c) corresponding height profile. UV–vis (d) and fluorescence (e) spectra of drop-cast film of H_2OPPP deposited onto a quartz substrate (λ_{ex} = 420 nm).

5. Acidochromism studies of H_2DPPP, H_2TPPP and H_2OPPP in chloroform solution

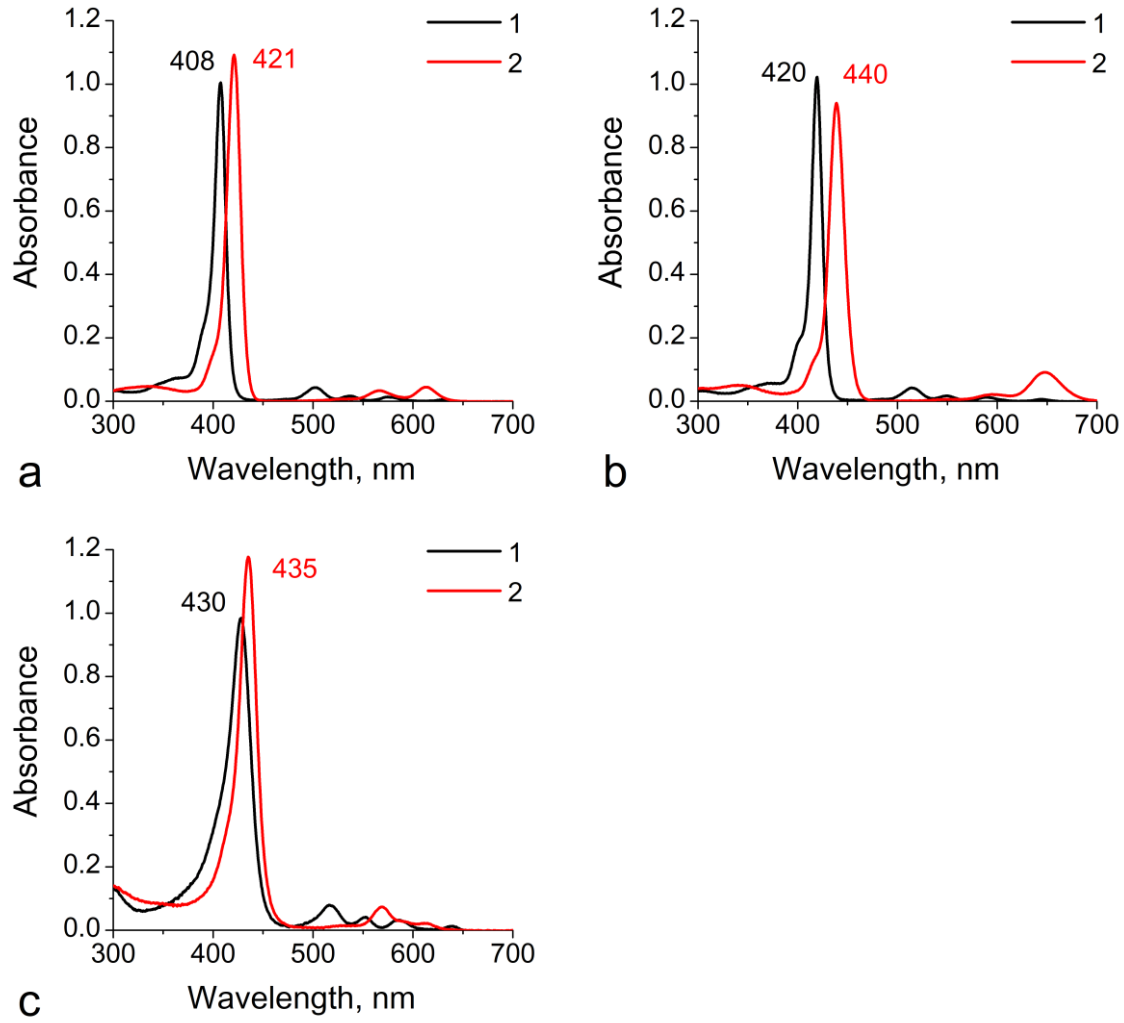
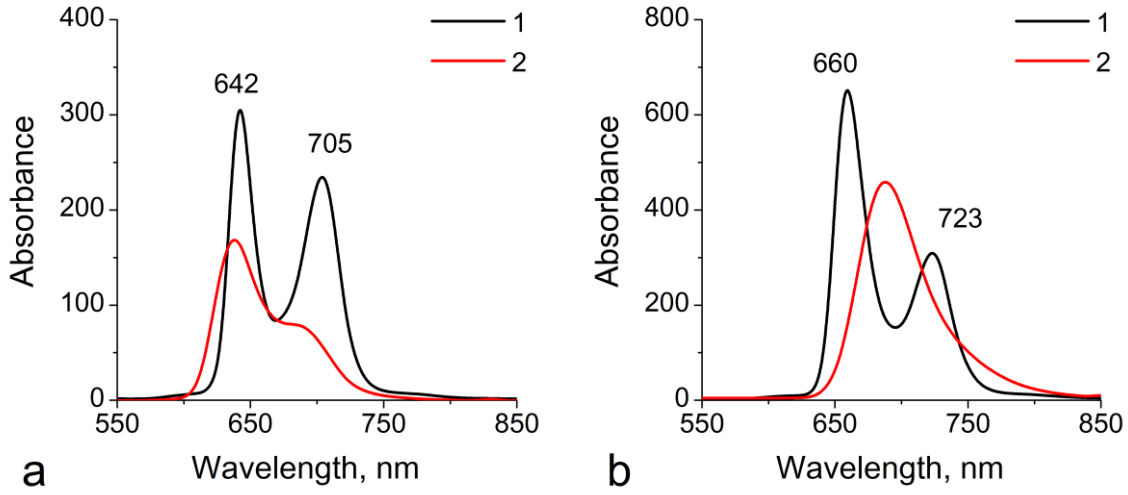


Figure S8. UV–vis spectra of H_2DPPP (a), H_2TPPP (b) and H_2OPPP (c) in chloroform solution (*1*) upon addition of TFA (*2*).



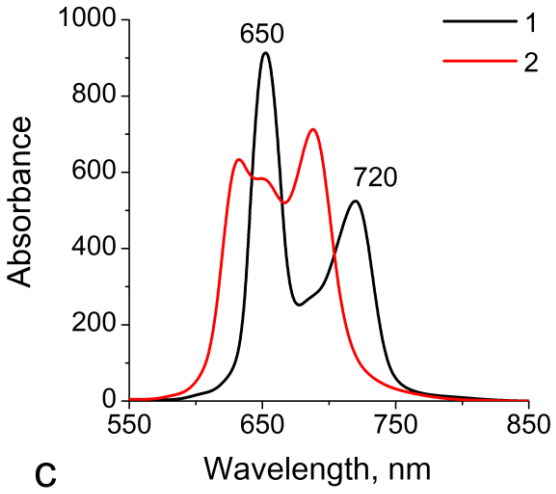


Figure S9. Fluorescence spectra of H_2DPPP (a), H_2TPPP (b) and H_2OPPP (c) in chloroform solution (*1*) upon addition of TFA (*2*) (λ_{ex} = 410, 420 and 430 nm).

6. Monolayers of NiOPPP and ZnOPPP at the air–water interface

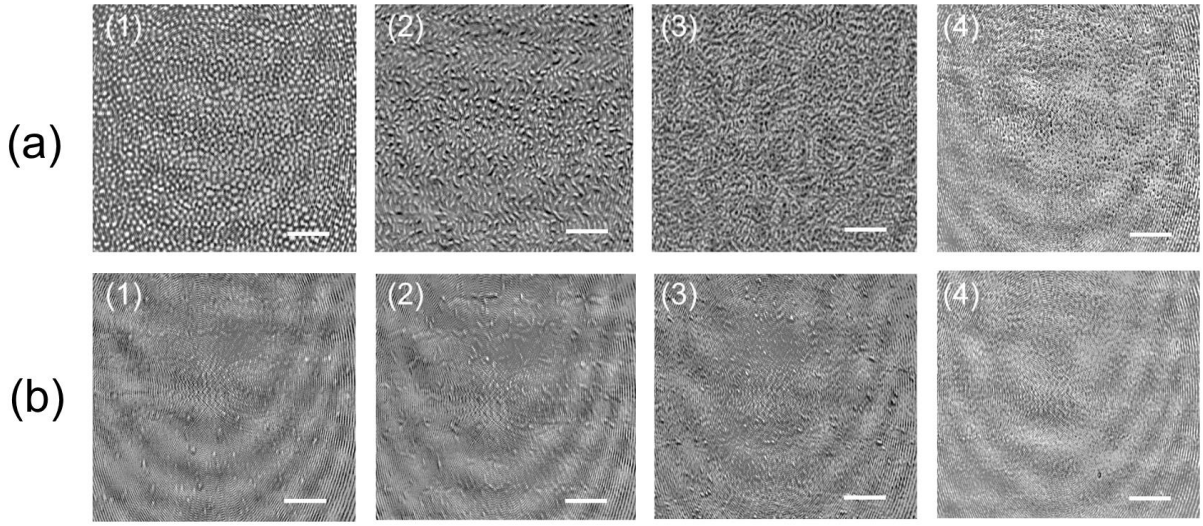


Figure S10. BAM images of the NiOPPP (a) and ZnOPPP (b) monolayers on the aqueous subphase at surface pressure 5 (*1*), 14 (*2*), 18 (*3*) and 22 (*4*) mN m^{-1}. The scale bar represents 40 μm.

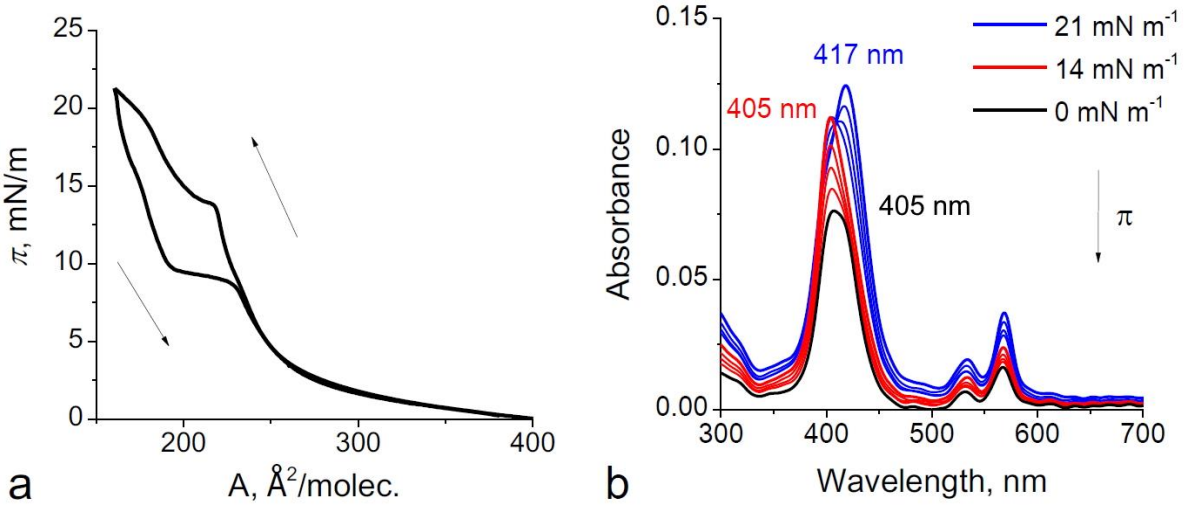


Figure S11. (a) Compression–expansion cycles for porphyrin NiOPPP. (b) *In situ* UV–vis spectra of the NiOPPP monolayer recorded during the monolayer expansion.

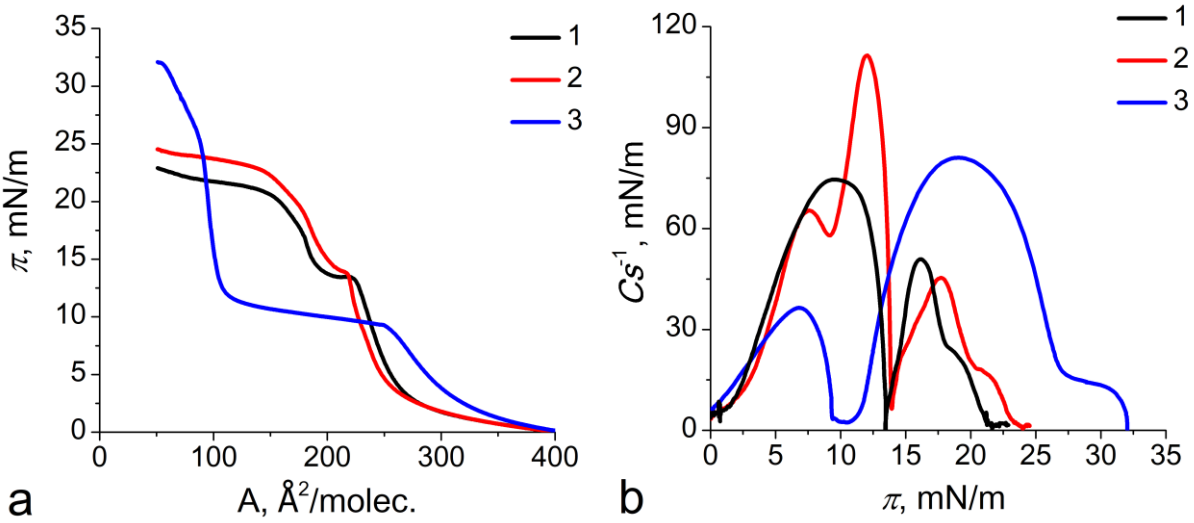


Figure S12. (a) Surface pressure–area isotherms and (b) compressibility modulus Cs^{-1} *vs.* surface pressure plots for the H_2OPPP (*1*), NiOPPP (*2*) and ZnOPPP (*3*) monolayers on the water surface.

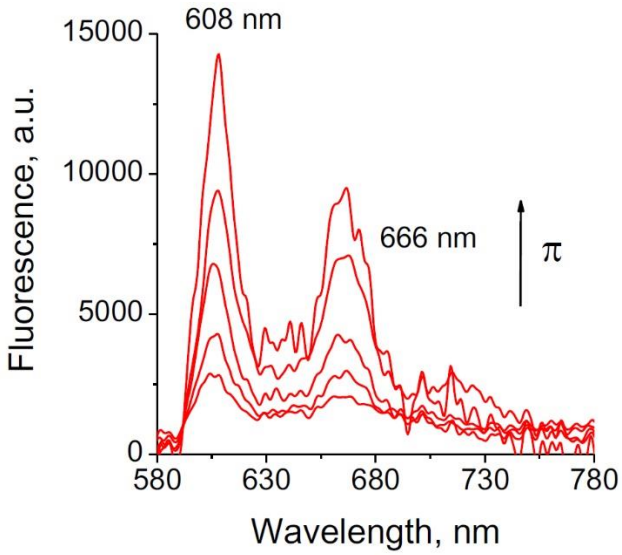


Figure S13. *In situ* fluorescence spectra ZnOPPP monolayer on the deionized water surface. *In situ* fluorescence spectra are recorded during the monolayer compression (λ_{ex} = 440 nm).

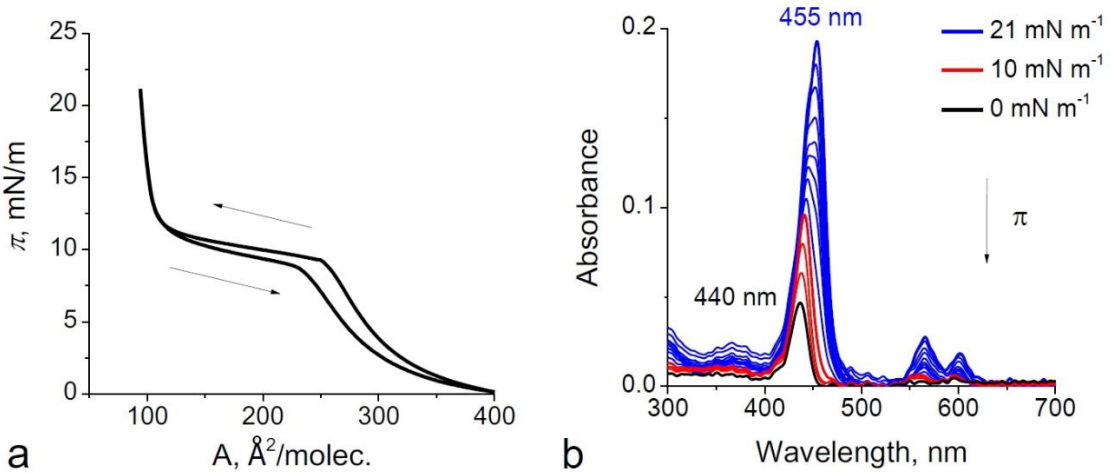


Figure S14. (a) Compression–expansion cycles for porphyrin ZnOPPP. (b) *In situ* UV–vis spectra of the ZnOPPP monolayer recorded during the monolayer expansion.

7. LS films of NiOPPP and ZnOPPP

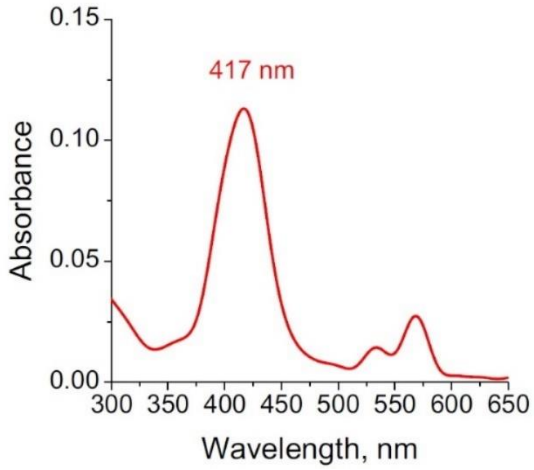


Figure S15. UV–vis spectra of one-layer LS film NiOPPP deposited onto a PVC substrate at a surface pressure of 18 mN m^{-1}.

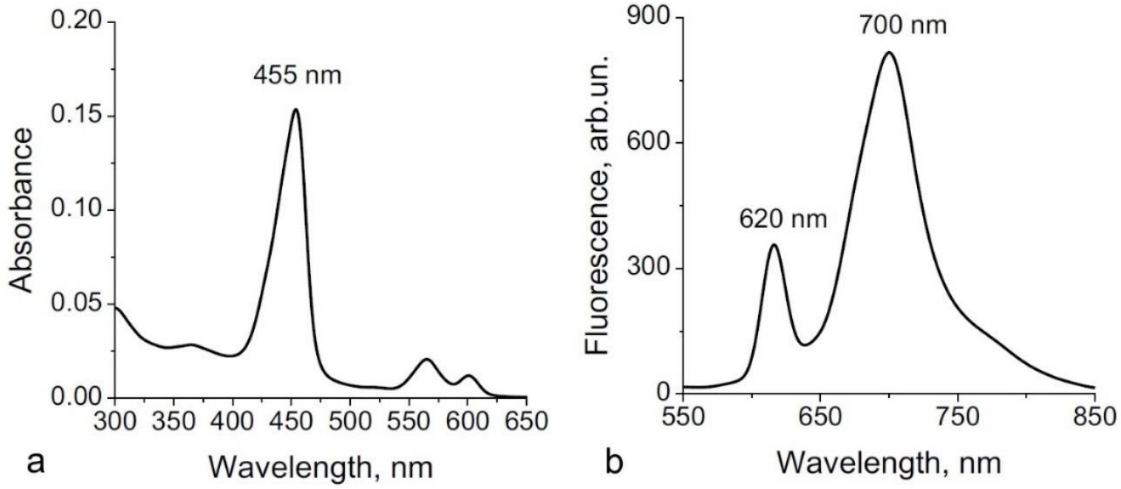


Figure S16. UV–vis (a) and fluorescence (b) spectra of one-layer LS film of ZnOPPP deposited onto a PVC substrate at a surface pressure of 18 mN m^{-1}, (λ_{ex} = 440 nm).

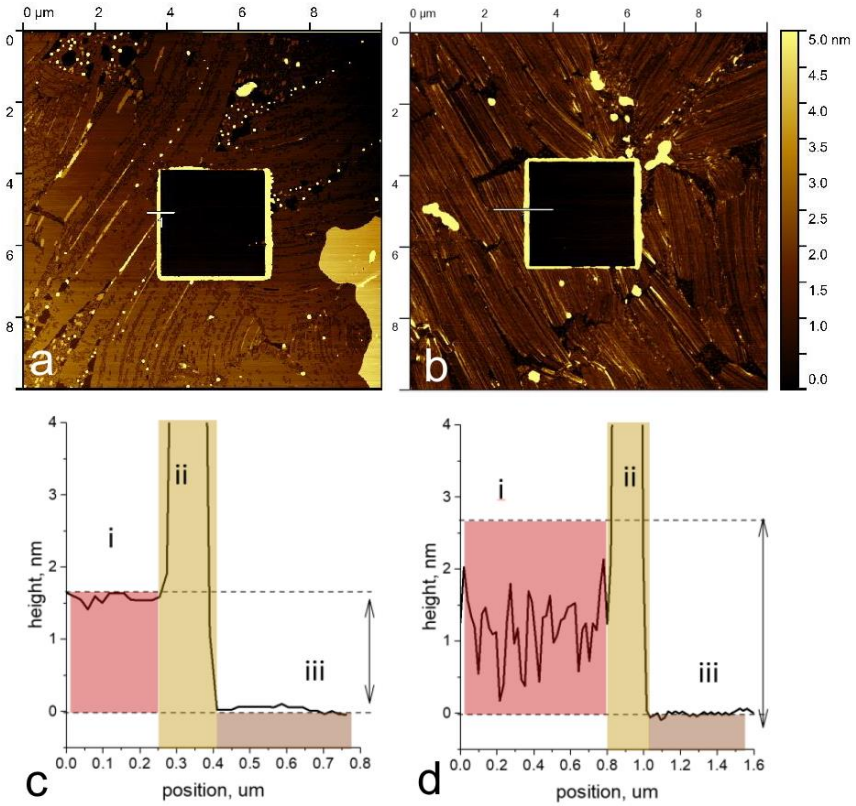


Figure S17. AFM images obtained after 'scratching' the samples in contact mode to reveal bare mica: one-layer LS films of NiOPPP (a) and ZnOPPP (b) transferred onto mica substrates at a surface pressure of 18 mN m^{-1}. (c, d) Corresponding height profiles obtained along the scratched surface line for samples transferred. Colored regions on the height profiles correspond to (i) observed porphyrin domains, (ii) film material piled up after 'scratching', and (iii) bare mica surface.

8. Monolayer and LS film of ZnTPP

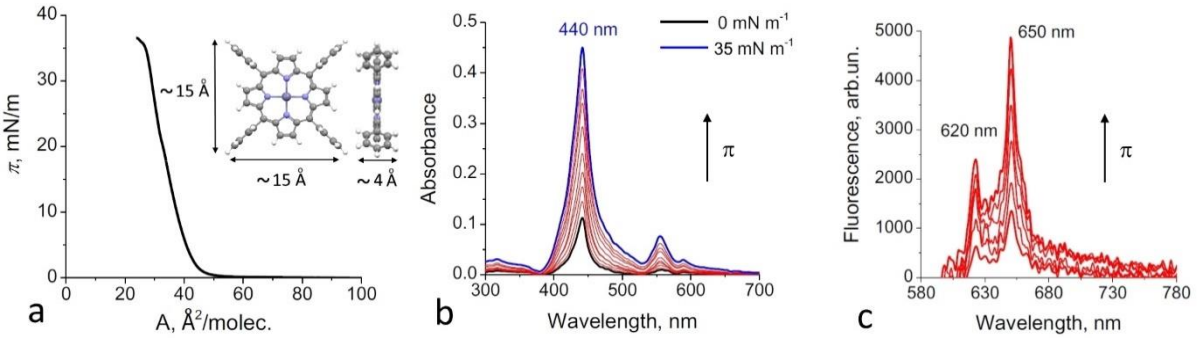


Figure S18. Surface pressure *vs* area isotherm (a), *in situ* UV–vis (b) and fluorescence spectra (c) of ZnTPP monolayer on the deionized water surface. Insets: Spacefill model of ZnTPP (a) molecule optimized by the semi-empirical PM6 method. *In situ* UV–vis and fluorescence spectra are recorded during the monolayer compression (λ_{ex} = 440 nm).

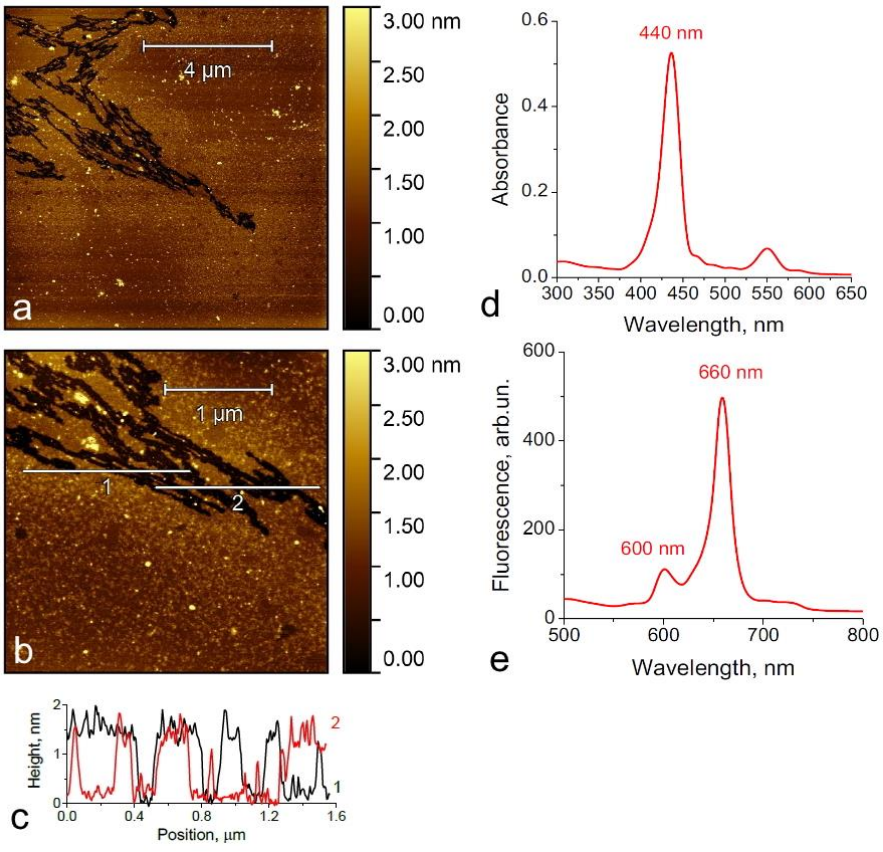


Figure S19. (a, b) AFM images of one-layer LS films of ZnTPP deposited onto a mica substrate at 18 mN m^{-1} from the deionized water surface and (c) corresponding height profiles. UV–vis (d) and fluorescence (e) spectra of one-layer LS film of ZnOPPP deposited onto a PVC substrate at a surface pressure of 18 mN m^{-1}, (λ_{ex} = 440 nm).

9. UV–vis and fluorescence spectroscopies studies of ZnOPPP and ZnTPP in chloroform solutions in presence of amines

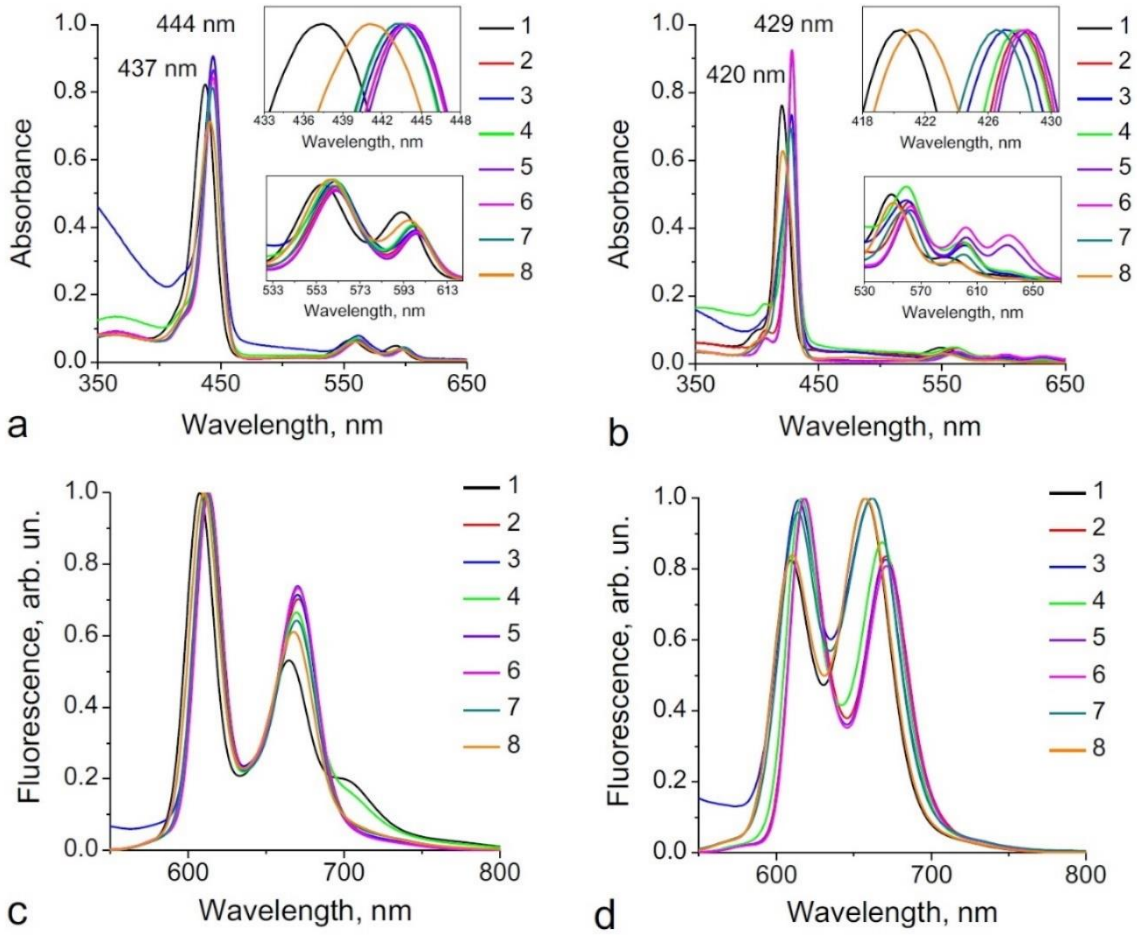


Figure S20. UV–vis (a, b) and fluorescence (c, d) spectra (λ_{ex} = 440 nm) of ZnOPPP (a, c, *1*) and ZnTPP (b, d, *1*) chloroform solutions (6.25 μM) in presence of pyridine (*2*), triethylamine (*3*), aniline (*4*), diethylamine (*5*), benzylamine (*6*), trimethylpyridine (*7*), diisopropylamine (*8*) (5 μL of each amine was added into porphyrin solutions).

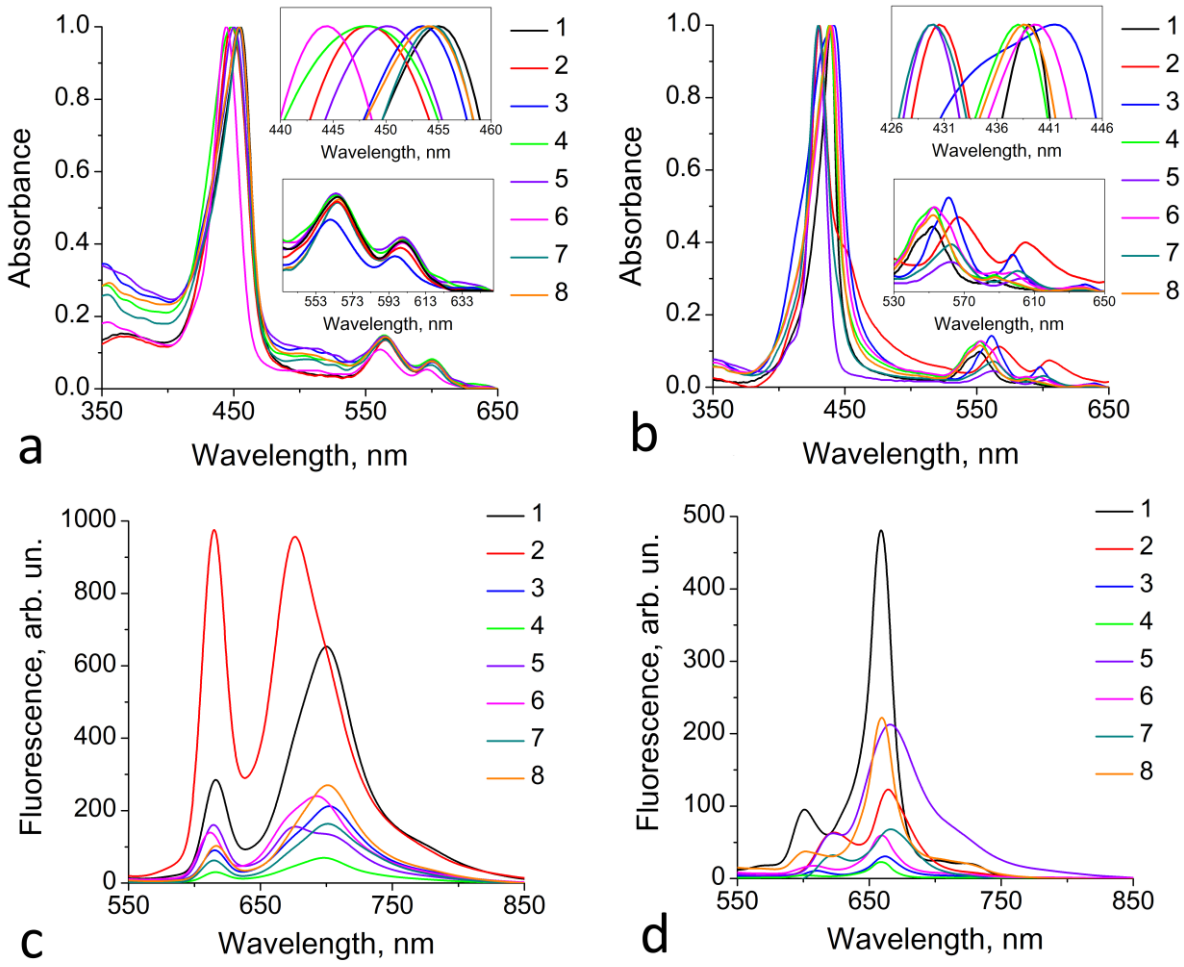


Figure S21. Normalized UV–vis (a, b) and fluorescence (c, d) spectra (λ_{ex} = 440 nm) of one-layer LS films of ZnOPPP (a, c, *1*) and ZnTPP (b, d, *1*) deposited onto a PVC at 18 mN m^{-1} from the deionized water and treated by pyridine (*2*), triethylamine (*3*), aniline (*4*), diethylamine (*5*), benzylamine (*6*), 2,4,6-trimethylpyridine (*7*), diisopropylamine (*8*) vapors for 1 min.

10. Quantum yield measurements for ZnOPPP LS film

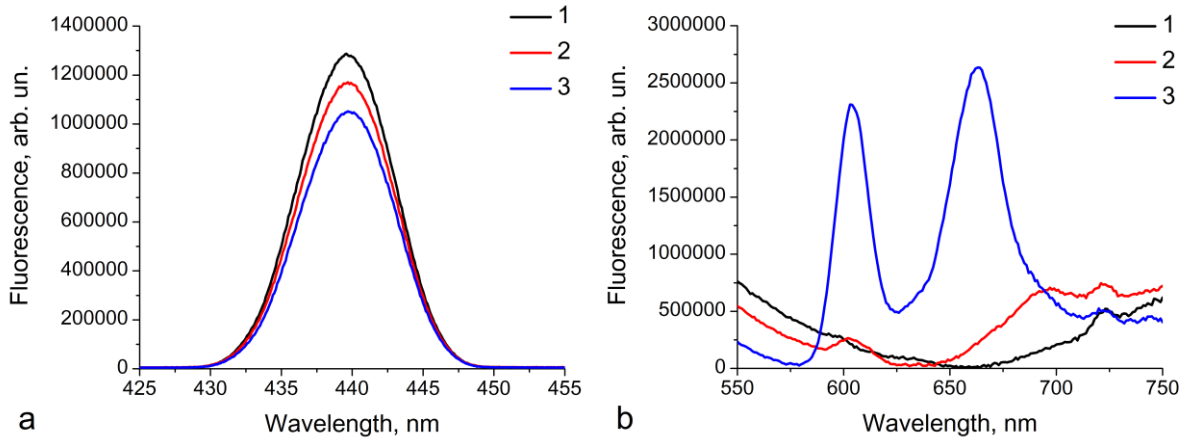


Figure S22. Fluorescence spectra (λ_{ex} = 440 nm) of laser excitation beam (a) and samples (b): PVC substrate (*1*), one-layer ZnOPPP LS films before (*2*) and after treatment by pyridine vapor for 60 s (*3*).