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# Synthesis of 5,10,15,20-tetra[6'-nitro-1,3,3-trimethylspiro(indolino-2,2'-2*H*-chromen-5-yl)]porphyrin and its metal complexes

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## *Experimental*

Thin-layer chromatography was performed on $60F_{254}$ neutral aluminum oxide plates (Merck, Germany) in dichloromethane; the spots were detected under the action of UV light (254 nm) on the plate. Preparative column adsorption chromatography was performed using Brockmann IV grade alumina (Reanal, Hungary). The spectroscopic studies were performed at $25^0$C. The $^1$H NMR spectra were measured on a Bruker DPX-300 spectrometer (Germany) with an operating frequency of 300 MHz in deuterochloroform. Chemical shifts (ppm) were measured to within 0.01 ppm with reference to deuterochloroform as an internal standard ($\delta$ 7.26 ppm). The spin-spin interaction constants J (Hz) were measured to within 0.1 Hz. The mass spectra were measured on a Bruker Ultraflex TOF/TOF MALDI spectrometer (Germany). The electronic spectra of test solutions in chloroform were measured in quartz cells with an optical path length of 10 mm on a Shimadzu UV-1700 spectrophotometer (Japan). The test samples were irradiated with continuous light from Vilber Lourmat VL-6.LC 6W lamps (France) at 254 and 365 nm.

*5,10,15,20-Tetra[6'-nitro-1,3,3-trimethylspiro(indolino-2,2'-2*H*-chromen-5-yl)]porphyrin* **3.** A reaction mixture of 175 μl (2.53 mmol) of pyrrole **2**, 2 ml of methanol and 876 mg (2.50 mmol) of 6'-nitro-1,3,3-trimethyl-5-formylspiro(indolino-2,2'-2*H*-chromene) **1** in 250 ml of chloroform was purged with argon for 20 min at room temperature. Then, 0.1 ml of boron trifluoride etherate was added to the reaction mass, and the mixture was stirred for 1.5 h; thereafter, the mixture was heated to boiling for 25 min, and 0.483 mg (3.76 mmol) of *p*-chloranil was added; the contents were additionally heated for 40 min with intense stirring. The solvent was removed in a vacuum, and the target porphyrin was separated by flash chromatography on aluminum oxide using elution with chloroform. The yield of product **3** was

270 mg (0.17 mmol) (27%). $R_f$ 0.73. UV-VIS [($CHCl_3$); $\lambda_{max}$, nm (lg $\varepsilon$)]: 242 (4.59), 268 (4.60), 347 (4.43), 436 (5.04), 525 (3.91), 570 (3.93), 661 (3.72). $^1$H NMR ($CDCl_3$, $\delta$/ppm, $J$/Hz): 9.03 (8H, m β-H), 8.11 (16H, m, Ar-H), 7.04 (12H, m, Ar–H, 4'–H), 6.09 (4H, d, J 10.4, 3'–H), 3.05 (12H, s, 1–$CH_3$), 1.49 (24H, s, 3–$CH_3$), -2.56 (2H, m, NH). Mass spectrum [m/z]: 1591 ($M^+$).

*Zn complex of 5,10,15,20-tetra[6'-nitro-1,3,3-trimethylspiro(indolino-2,2'-2*H*-chromen-5-yl)]porphyrin* **4.** A solution of 20 mg of zinc acetate in 3 ml of methanol was added to a solution of 20 mg (0.013 mmol) of compound **3** in 10 ml of chloroform. The mixture was boiled with stirring on a magnetic stirrer for 30 min. The reaction mixture was cooled to room temperature and poured into 50 ml of distilled water. The product was extracted with dichloromethane in a separatory funnel; the extracts were dried with anhydrous sodium sulfate, and the solvent was removed in a vacuum. Flash chromatography on aluminum oxide with chloroform as an eluent was used to purify the product. The yield of compound **4** was 16 mg (0.01 mmol) (77%). $R_f$ 0.6. UV-VIS [($CHCl_3$), $\lambda_{max}$, nm]: 239, 266, 309, 345, 437, 557, 600. $^1$H NMR ($CDCl_3$, $\delta$/ppm, $J$/Hz): 9.12 (8H, m, β-H), 8.07 (16H, m, Ar-H), 7.06 (12H, m, Ar–H, 4'–H), 6.03 (4H, d, J 10.4, 3'–H), 3.15 (12H, s, 1–$CH_3$), 1.62 (12H, s, 3b–$CH_3$), 1.59 (12H, s, 3a–$CH_3$). Mass spectrum [*m/z*]: 1654 ($M^+$).

*Cu complex of 5,10,15,20-tetra[6'-nitro-1,3,3-trimethylspiro(indolino-2,2'-2*H*-chromen-5-yl)]porphyrin* **5.** A mixture of 20 mg (0.013 mmol) of compound **3** and 20 mg of copper chloride in 10 ml of DMF was heated at 80°C and stirred with a magnetic stirrer for 1 h. The reaction mixture was cooled to room temperature and poured into a 10% solution of sodium chloride. The precipitate formed was filtered off and washed with water. The product was purified by flash chromatography on aluminum oxide; chloroform was an eluent. The yield of compound **5** was 17 mg (0.01 mmol) (82%). $R_f$ 0.75. UV-VIS [($CHCl_3$), $\lambda_{max}$, nm]: 240, 266, 307, 344, 432, 547, 587. $^1$H NMR ($CDCl_3$, $\delta$/ppm, $J$/Hz): 8.99 (8H, m, β-H), 8.10 (16H, m, Ar-H), 7.02 (12H, m, Ar–H, 4'–H), 6.19 (4H, d, J 10.4, 3’–H), 3.15 (12H, s, 1–$CH_3$), 1.37 (12H, s, 3b–$CH_3$),1.33 (12H, s, 3a–$CH_3$). Mass spectrum [*m/z*]: 1652 ($M^+$).

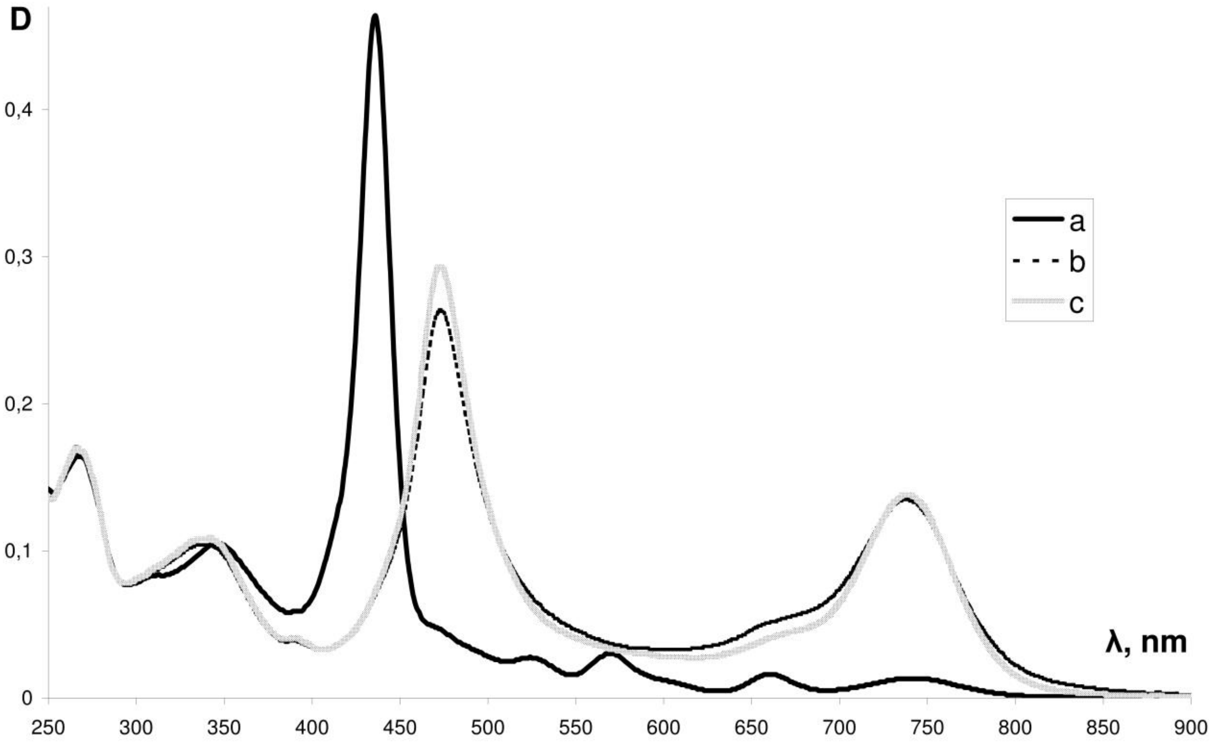

**Figure S1** Absorption spectra of compound **3** (c ≈ $10^{-5}$ M) in chloroform at $25^0$C: (a) initial solution, (b) upon UV-254 illumination and (c) upon the subsequent storage in the dark for 3 min.

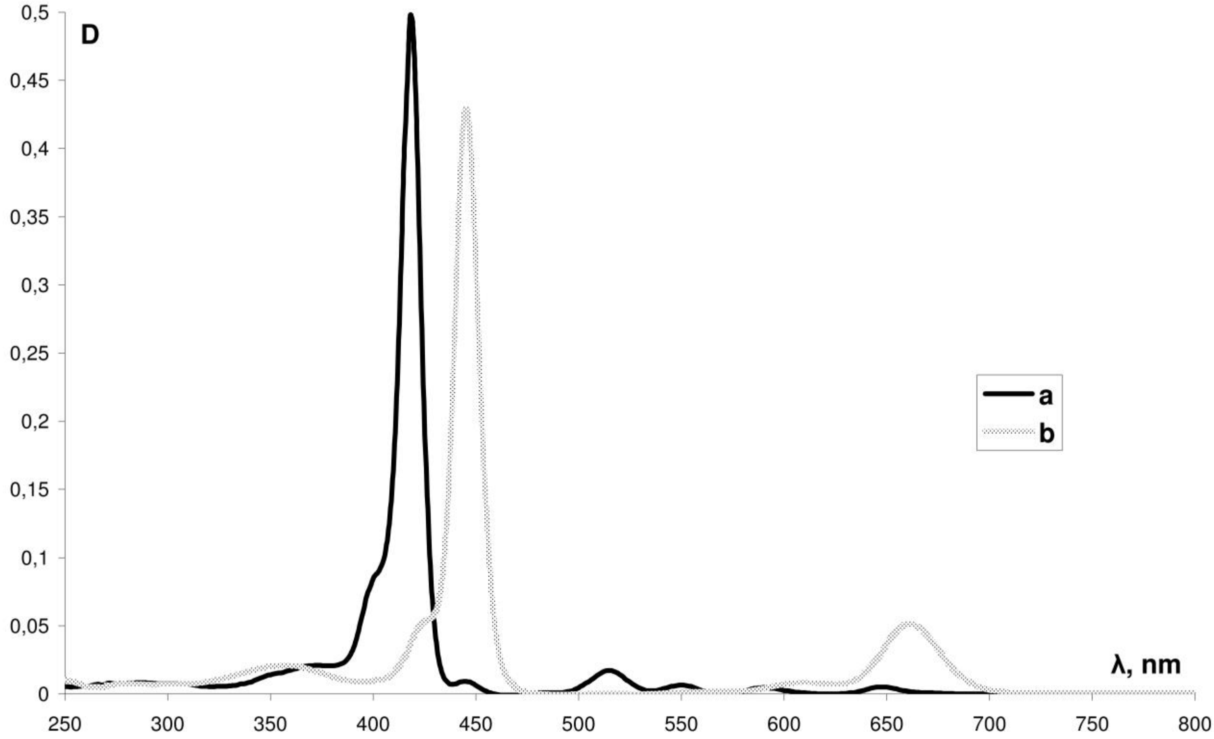

**Figure S2** Absorption spectra of TPP (c ≈ $10^{-5}$ M) in chloroform at $25^0$C: (a) initial solution and (b) upon UV-254 illumination.

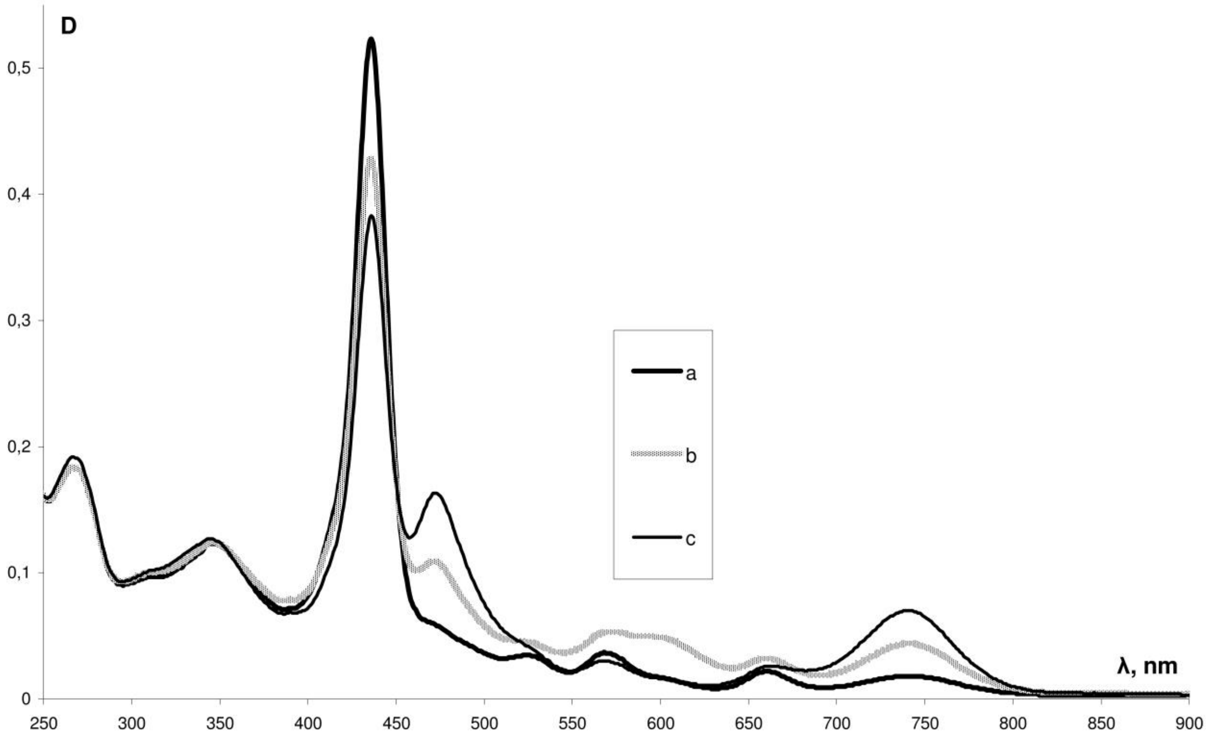

**Figure S3** Absorption spectra of compound **3** (c ≈ $10^{-5}$ M) in chloroform at 25$^{0}$C: (a) initial solution, (b) upon UV-365 illumination and (c) upon the subsequent storage in the dark for 10 min.

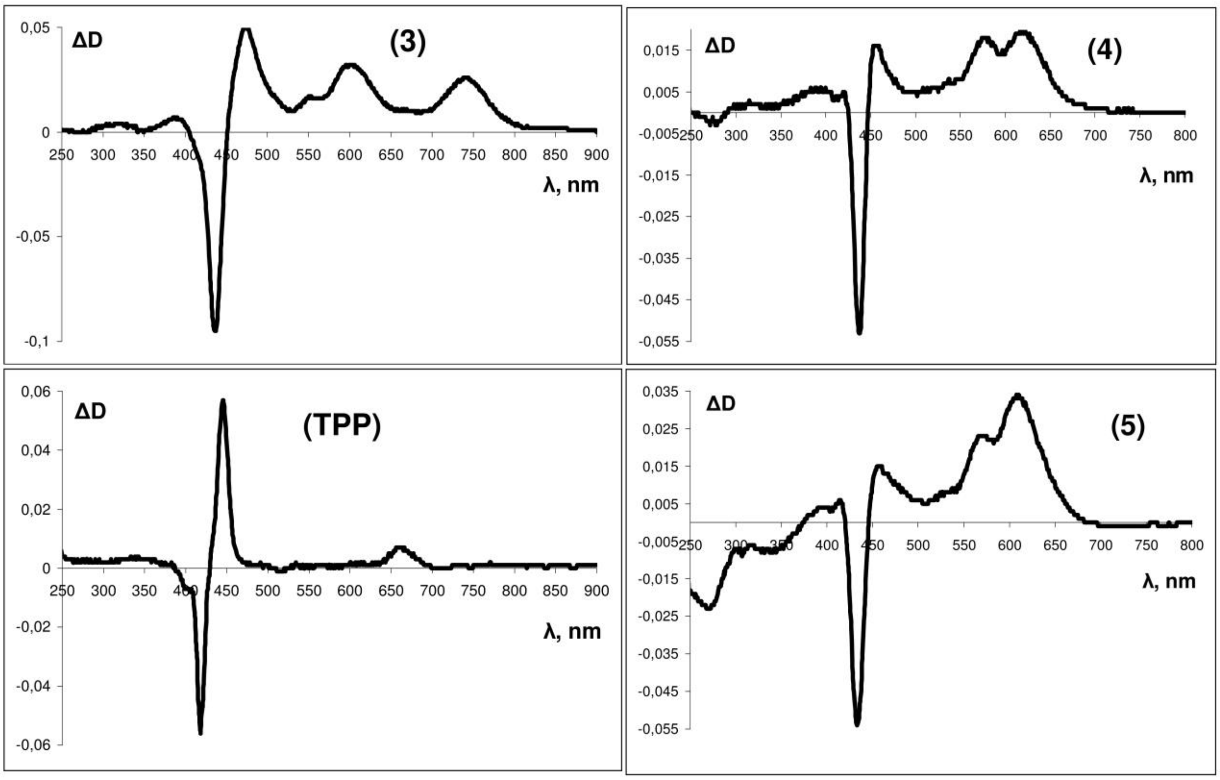

**Figure S4** Optical absorption difference curves of porphyrin solutions in an initial state and upon UV illumination at 365 nm.