Electronic supplementary materials *Mendeleev Commun.*, 2024, **34**, 525–527

Unsymmetrical cationic porphyrin that forms sedimentation-unstable complexes with nucleic acids

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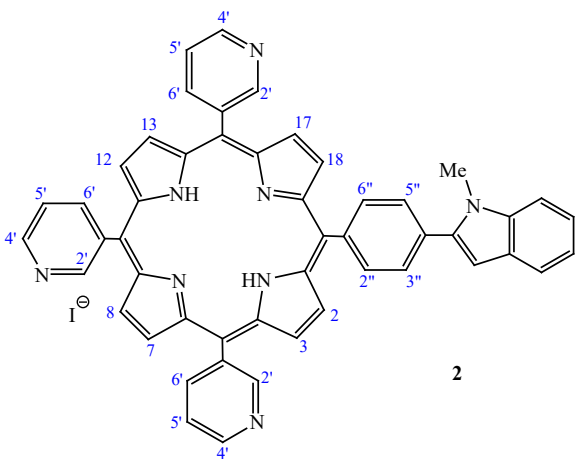

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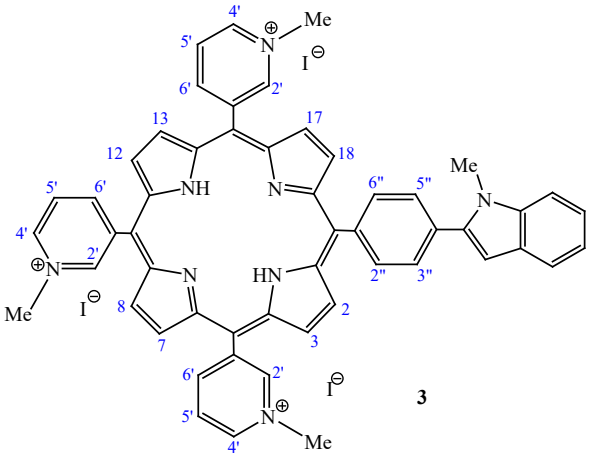

3

Atom numbering is given for NMR assignment.

5-[4-(1-Methylindol-2-yl)phenyl]-10,15,20-tri(pyridin-3-yl)porphyrin (2)

UV (CH_2Cl_2, λmax/nm (lgε)): 421 (5.98), 516 (4.12), 553 (3.83), 591 (3.99), 642 (3.56). Спектр ^{1}H NMR ($CDCl_3$), *δ*, ppm (*J*, Hz): 9.49 (s, 3H, $H^{2'}$, Py); 9.10 (d, 3H, $H^{6'}$, Py, *J* 5.5); 8.97 (d, 2H, $H^{8,12}$, *J* 4.5); 8.90 (s, 4H, $H^{3,7,13,17}$); 8.59 (d, 2H, $H^{2,18}$, *J* 4.5); 8.45 (d, 3H, $H^{4'}$, Py, *J* 5.5); 8.18 (d, 2H, $H^{2'',6''}$, Ph, *J* 6.0); 7.80–7.81 (m, 5H, $H^{5'}$, Py, $H^{3'',5''}$, Ph); 7.71 (d, 1H indole); 7.55 (d, 1H indole); 7.41 (t, 1H indole); 7.27 (t. 1H indole); 6.71 (s, 1H indole); 3.84 (s, 3H-CH_3 indole); -2.76 (s, 2H, NH). MS (MALDI-TOF), *m/z*: calculated for $C_{50}H_{34}N_{18}$ $[M]^+$ = 746.86; found=748.12.

5-[4-(1-Methylindol-2-yl)phenyl]-10,15,20-tris(1-methylpyridinium-3-yl)-porphyrin triiodide (3)

UV (water, λmax/nm (lgε)): 418 (6.01), 516 (4.13), 551 (4.43), 582 (4.59), 644 (4.62). ^{1}H NMR (DMSO-d_6), *δ*, ppm (*J*, Hz): 10.04 (m 6H $H^{3,7,8,12,13,17}$); 9.58 (m, 2H, $H^{2,18}$, *J* 4.4); 9.40 (m, 3H, $H^{6'}$, Py, *J* 5.4); 9.25 (m, 3H, $H^{2'}$, Py, *J* 5.4); 8.63-8.65 (m, 5H, $H^{5'}$, Py, $H^{3'',5''}$, Ph); 8.39 (m, 3H, $H^{4'}$, Py, *J* 5.5); 8.14 (d, 2H, $H^{2'',6''}$, Ph, *J* 5.9); 7.72 (d, 1H, indole); 7.67 (d, 1H, indole); 7.32 (t, 1H, indole); 7.18 (t, 1H, indole); 6.98 (s, 1H, indole); 4.69 (s, 9H, CH_3N, pyridyls); 4.11 (s, 3H-CH_3, indole); –3.02 (s, 2H, NH). MS (MALDI-TOF), *m/z*: calculated for $C_{53}H_{43}I_3N_8$ $[M]^+$ = 1172.69; found= 1172.68.

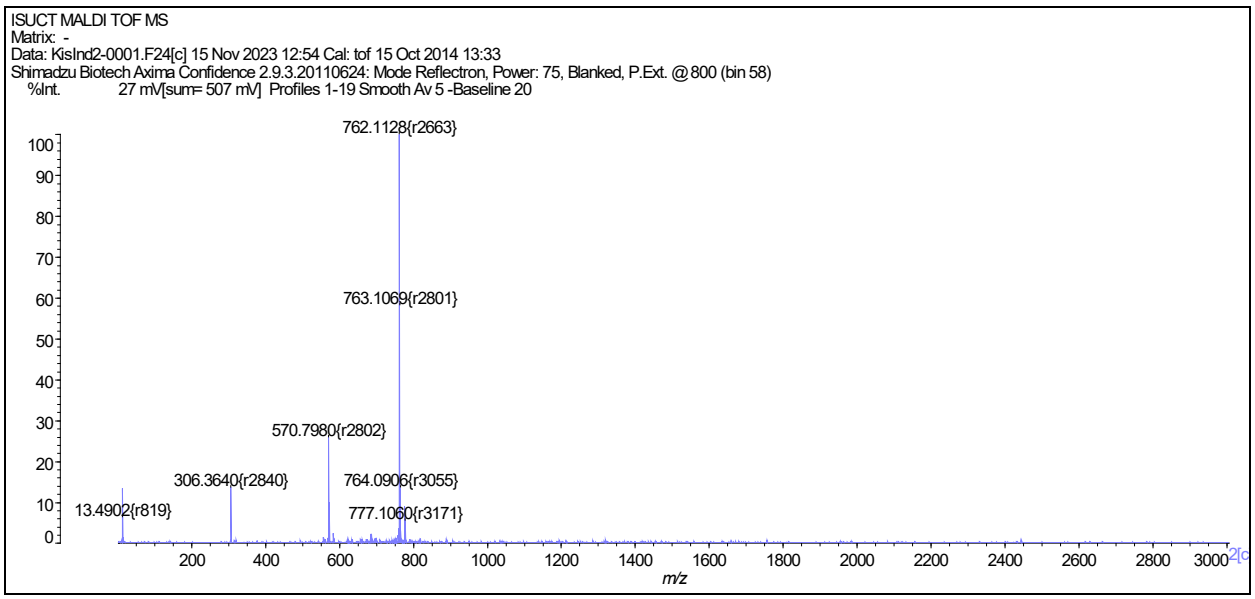

Figure S1. MALDI mass spectrum of 5-[4-(1-methylindol-2-yl)phenyl]-10,15,20-tris(1-methyl-pyridinium-3-yl)porphyrin triiodide

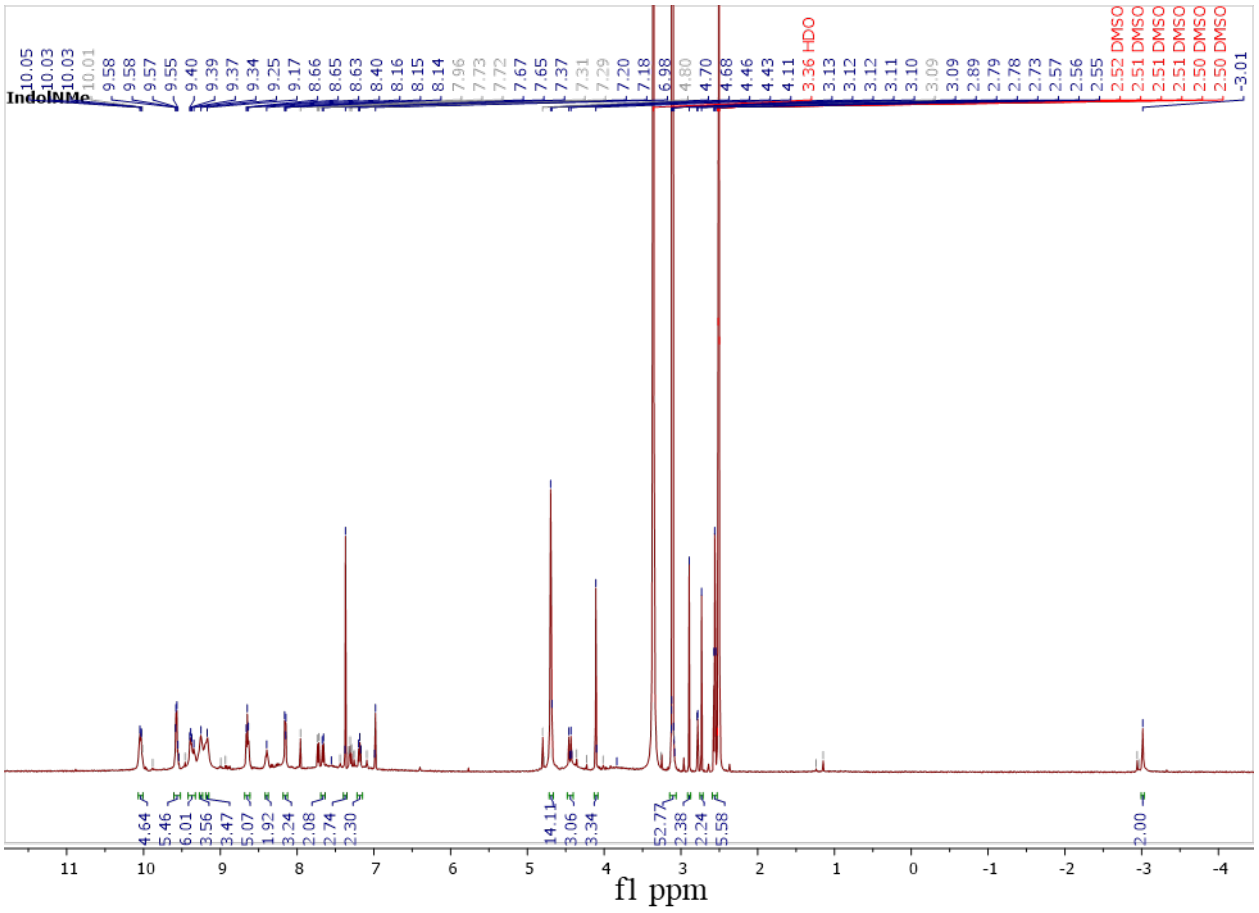

Figure S2 ^{1}H NMR spectrum of 5-[4-(1-methylindol-2-yl)phenyl]-10,15,20-tris(1-methyl-pyridinium-3-yl)porphyrin triiodide

Electronic absorption spectra of compounds **2,3** were recorded on a Hitachi U2001 UV/VIS spectrophotometer (Japan) at room temperature in the range of λ 200–1000 nm. ^{1}H NMR spectra were recorded on a Bruker Avance-500 instrument (USA). Solvent signals were used as internal standards. MALDI-TOF mass spectra of positive ions were recorded on a Shimandzu AXIMA Confidence time-of-flight mass spectrometer with matrix-associated laser desorption (Japan) and on a Bruker Daltonics Ultraflex instrument (USA).

ssDNA, ctDNA were bought in Acros Organics. Oligonucleotide poly[d(GC)2] was synthesized by Synthol (Moscow, Russia). The DNA concentrations were determined spectrophotometrically using molar extinction coefficients: ε262 nm = 6600 cm^{-1} M^{-1}, ε254 nm = 8400 cm^{-1} M^{-1}. UV-VIS absorption and fluorescence spectra were recorded using an AvaSpec-2048 double channel spectrophotometer (Avantes BV, Netherlands) at 25°C in 1 cm quartz cuvettes.

The time-resolved fluorescence measurements were carried out by means of a high-performance fluorescence lifetime and steady state spectrometer FluoTime 300 (PicoQuant, Germany) with a laser 450 nm as an excitation source. The instrument response function (IRF) of the system was measured with the stray light signal of a dilute colloidal silica suspension (LUDOX®). The fluorescence decay curves were measured and the fluorescence lifetimes were obtained by deconvolution of the decay curves using the EasyTau 2 software package (PicoQuant, Germany).

Particle size was determined by dynamic light scattering (DLS) using a Zetasizer Nano ZS analyzer (Malvern Instruments, Malvern, UK). The measurements were carried out at 25°C in the backscattering mode, angle 173 deg, laser wavelength 633 nm. Each sample was measured three times and the average was taken.

The rheological measurements of the samples were performed using a MCR Evolution - 302e (Anton Paar GmbH, Graz, Austria) rotational rheometer, equipped with a cone-plate measuring cell (the cone diameter is 50 mm and the cone to plate angle is 1°), using the Reocompas software. The temperatures were 25°C.