

Coordination-Induced Spin-State-Switch (CISSS) in water

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I. Analytical equipment

NMR Spectroscopy

NMR spectra were measured in deuterated solvents (Deutero). The degree of deuteration is given in parentheses. ^1H NMR-spectra in reference to the following signals.

acetone- d_6 (99.8 %): $\delta = 2.0549$ ppm (quintet)

chloroform- d (99.8 %): $\delta = 7.2600$ ppm (s)

methanol- d_4 (99.8 %): $\delta = 3.3500$ ppm (quintet)

water- d_2 (99.9 %): $\delta = 4.7900$ ppm (s)

Reference for all ^{19}F -NMR-spectra is trichloro fluoromethane to the frequency of which the spectrometer is calibrated. Fluorine atoms are labeled as *o*-F, *m*-F und *p*-F (*ortho*-, *meta*- und *para*-fluorine) according to their position in the aromatic system.

The signal multiplicities are abbreviated as follows.

s: singlet, d: doublet, t: triplet, q: quartet, quint: quintet, m: multiplet, br: broad signal

Measurements were performed with a Bruker DRX 500 (^1H NMR: 500 MHz, ^{19}F NMR: 470 MHz) and a Bruker AV 600 (^1H NMR: 600 MHz)

IR spectroscopy

Infrared spectra were measured on a Perkin-Elmer 1600 Series FT-IR spectrometer with a A531-G Golden-Gate-Diamond-ATR-unit. Signals were abbreviated with w, m, s and vs for weak, medium, strong and very strong intensities. Broad signals are additionally labeled with br.

UV-Vis spectroscopy

The UV-Vis spectra were measured on a Lambda 14 spectrometer (Perkin-Elmer) with a (Büchi) thermostat. Quartz cuvettes of 1 cm and 1 mm optical path length were used.

Elemental analysis

The amount of carbon, hydrogen and nitrogen in a compound was determined with a CHNSO-Elementaranalysator Euro EA 3000 Series by co. Euro Vector. The dendronized porphyrins were not examined by this method because of the low amount of obtained substance.

Mass spectrometry

The high resolution (HR) mass spectra were measured with an APEX 3 FT-ICR with a 7.05 T magnet by co. Bruker Daltonics. Electron impact (EI) and chemical ionisation (CI) mass spectra were measured with a MAT 8230 by co. Finnigan.

Chromatography stationary phases

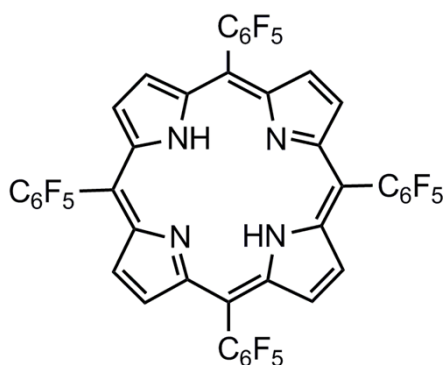
For column chromatography purifications silica gel (Merck, particle size 0.040-0.063 mm) was used. R_f values were determined by thin layer chromatography on Polygeram® Sil G/UV₂₅₄ (Macherey-Nagel, 0.2 mm particle size).

II. Syntheses

II.1 Synthesis of *meso*-tetrakis(pentafluorophenyl)porphyrin (1)

Freshly distilled pyrrole (700 μ L, 10.1 mmol), pentafluoro benzaldehyde (1.91 g, 9.72 mmol) and boron trifluoride diethyl etherate (150 μ L, 1.19 mmol) were stirred in dichloromethane (400 mL) for 40 h under nitrogen atmosphere at 37 $^{\circ}$ C. After addition of *p*-chloranil (1.90 g, 7.73 mmol) stirring at 37 $^{\circ}$ C was continued for 3 h. The solvent was removed under reduced pressure. The black crude product was purified by column chromatography (hexane/chloroform = 3:2, R_f = 0.45).

Yield: 870 mg (0.89 mmol, 37 %, Lit.: 25 %) ¹



¹H NMR (500 MHz, 300 K, CDCl₃): δ = 8.92 (s, 8H, *H*-Ar), -2.91 (s, 2H, *N*-*H*) ppm.

¹⁹F NMR (470 MHz, 300 K, CDCl₃) δ = -136.50 (dd, ³*J* = 23.4 Hz, ⁵*J* = 8.4 Hz, *o*-F), -151.21 (t, ³*J* = 20.7 Hz, *p*-F), -161.32 (td, ³*J* = 22.3 Hz, ⁵*J* = 8.4 Hz, *m*-F) ppm.

MS (EI, 70 eV): *m/z* (%) = 974 (100) [M]⁺, 955 (12) [M-F]⁺, 487 (33) [M]²⁺, 478 (4) [M-F]²⁺.

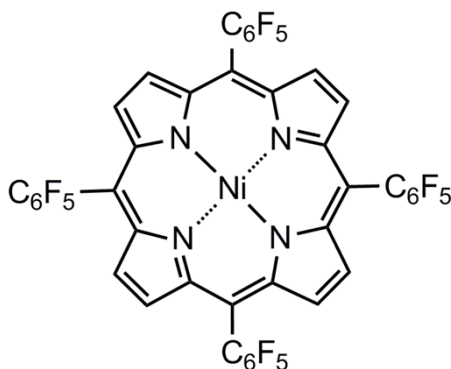
MS (CI, isobutane): *m/z* (%) = 975 (100) [M+H]⁺.

EA: (C ₄₄ H ₁₀ F ₂₀ N ₄)	C / %	H / %	N / %
found:	54.10	0.94	5.65
calc.:	54.23	1.03	5.75

II.2 Synthesis of *meso*-tetrakis(pentafluorophenyl)nickel(II)porphyrin (2)

Porphyrin **1** (503 mg, 0.516 mmol) and nickel(II)acetylacetonate (1.33 g, 5.15 mmol) were stirred under reflux for 4 d in toluene (100 mL). The solvent was removed under reduced pressure and the crude product was purified by column chromatography (chloroform, $R_f = 0.78$).

Yield: 518 mg (0.502 mmol, 97 %)



$^1\text{H NMR}$ (500 MHz, 300 K, CDCl_3): $\delta = 8.79$ (s, 8H, *H*-Ar) ppm.

$^{19}\text{F NMR}$ (470 MHz, 300 K, CDCl_3) $\delta = -136.62$ (dd, $^3J = 23.0$ Hz, $^5J = 8.4$ Hz, *o*-F), -151.29 (t, $^3J = 21.0$ Hz, *p*-F), -161.32 (td, $^3J = 22.0$ Hz, $^5J = 8.4$ Hz, *m*-F) ppm.

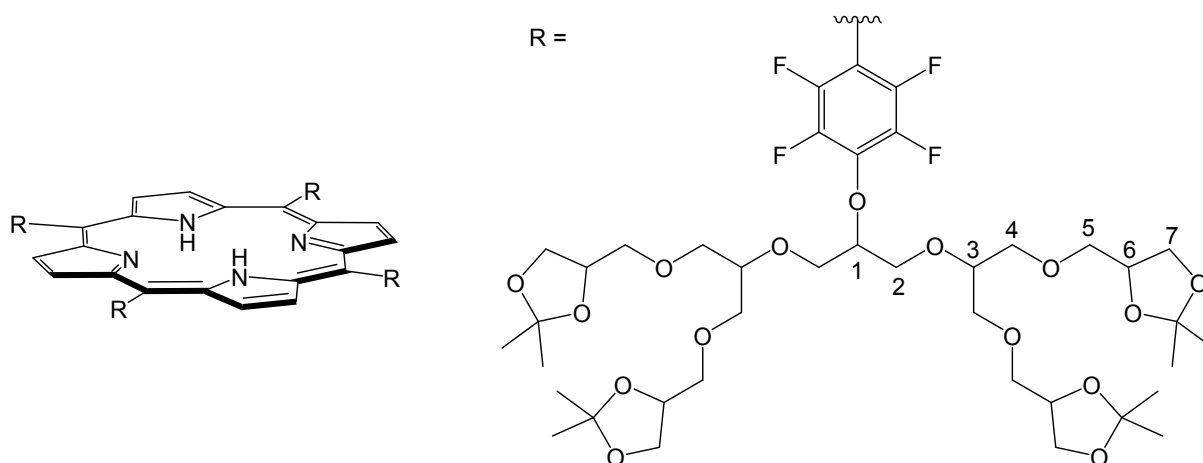
MS (EI, 70 eV): m/z (%) = 1030 (100) $[\text{M}]^+$, 1011 (9) $[\text{M}-\text{F}]^+$, 515 (29) $[\text{M}]^{2+}$.

EA: ($\text{C}_{44}\text{H}_8\text{F}_{20}\text{N}_4\text{Ni}$)	C / %	H / %	N / %
found:	50.90	0.85	5.26
calc.:	51.25	0.78	5.69

II.3 Synthesis of glycerol functionalised porphyrin 5

Sodium hydride (15 mg, 375 μmol) (60 % dispersion in mineral oil) was suspended in dry tetrahydrofuran (5 mL) under nitrogen atmosphere. [G2.0]-OH (83.4 mg, 120 μmol) was dissolved in tetrahydrofuran (3 mL) and slowly added to the sodium hydride suspension. The suspension was stirred for 50 min. TPPF₂₀ (**1**) (19.5 mg, 20 μmol) was added and stirring was continued for 7 d. The reaction was quenched with water and diethyl ether (200 mL) was added. The organic layer was washed with 200 mL of 0.1 M hydrochloric acid and dried over magnesium sulphate. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane / methanol = 98 : 2, R_f = 0.06). The product was obtained as a red, viscous oil.

Yield: 26.2 mg (7.12 μmol , 36 %)



FT-IR (layer): ν = 2986 (m), 2873 (m), 1696 (w), 1649 (w), 1494 (s), 1479 (s), 1430 (m), 1370 (s), 1255 (s), 1212 (s), 1144 (s), 1050 (vs), 983 (vs), 921 (s), 841 (s), 806 (m), 773 (m), 757 (s), 727 (w), 636 (w), 516 (m), 463 (m), 416 (m) cm^{-1} .

¹H NMR (600 MHz, acetone- d_6 , 300 K): δ = 9.29 (s, 8H, *H*-Ar), 5.04-4.97 (m, 4H, *H*-1), 4.32-4.25 (m, 16H, *H*-6), 4.23-4.17 (m, 16H, *H*-2), 4.09-4.03 (m, 16H, *H_a*-7), 3.89-3.84 (m, 8H, *H*-3), 3.83-3.48 (m, 80H, *H*-4, *H*-5, *H_b*-7), 1.37-1.26 (m, 96H, *CH*₃), -2.85 (s, 2H, *H*-N) ppm.

¹⁹F NMR (470 MHz, acetone- d_6 , 300 K): δ = -141.9 (m, 8F, *o*-F), -157.1 (m, 8F, *m*-F) ppm.

MS (HR): m/z (calc.) = 1227.533 (1227.543) [*M*+3*H*]³⁺

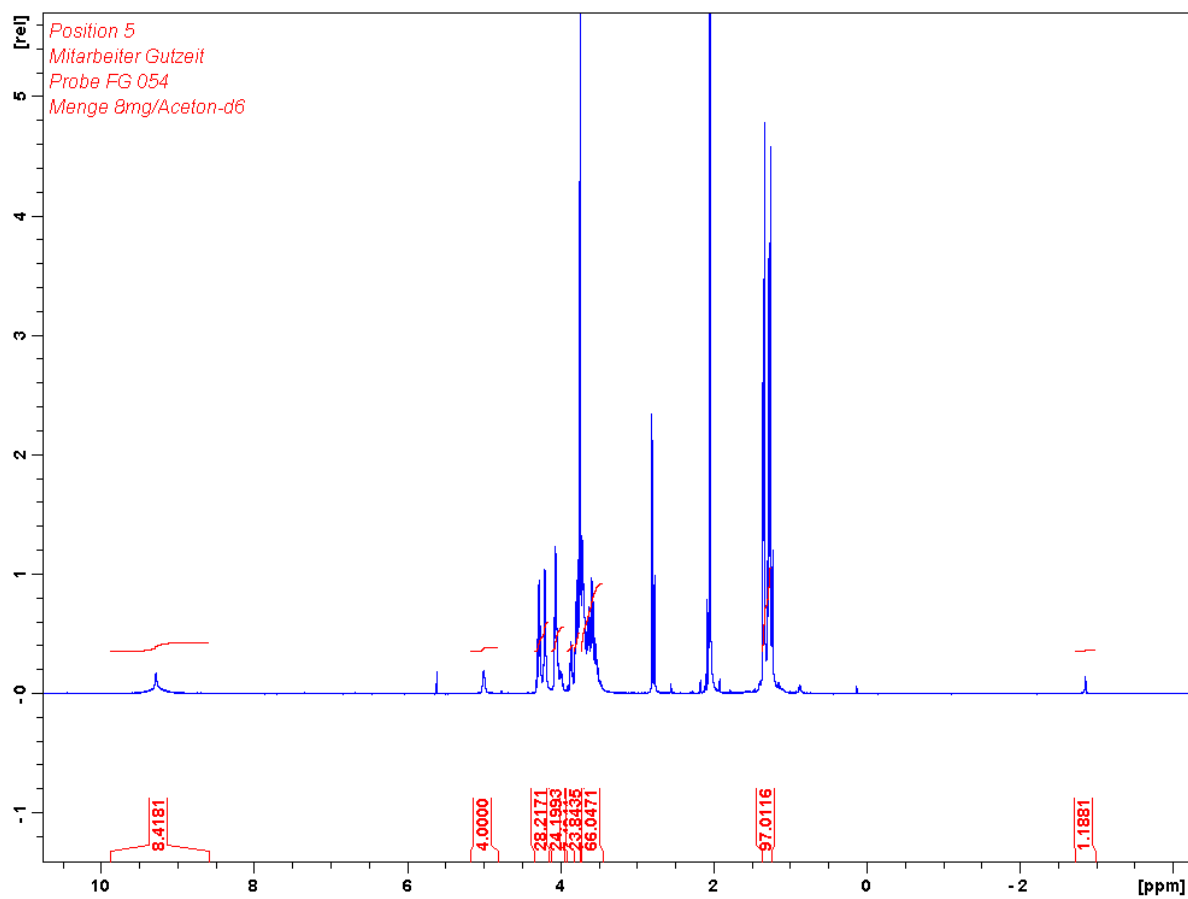


Fig S1 ^1H NMR spectrum of **5** in acetone- d_6 .

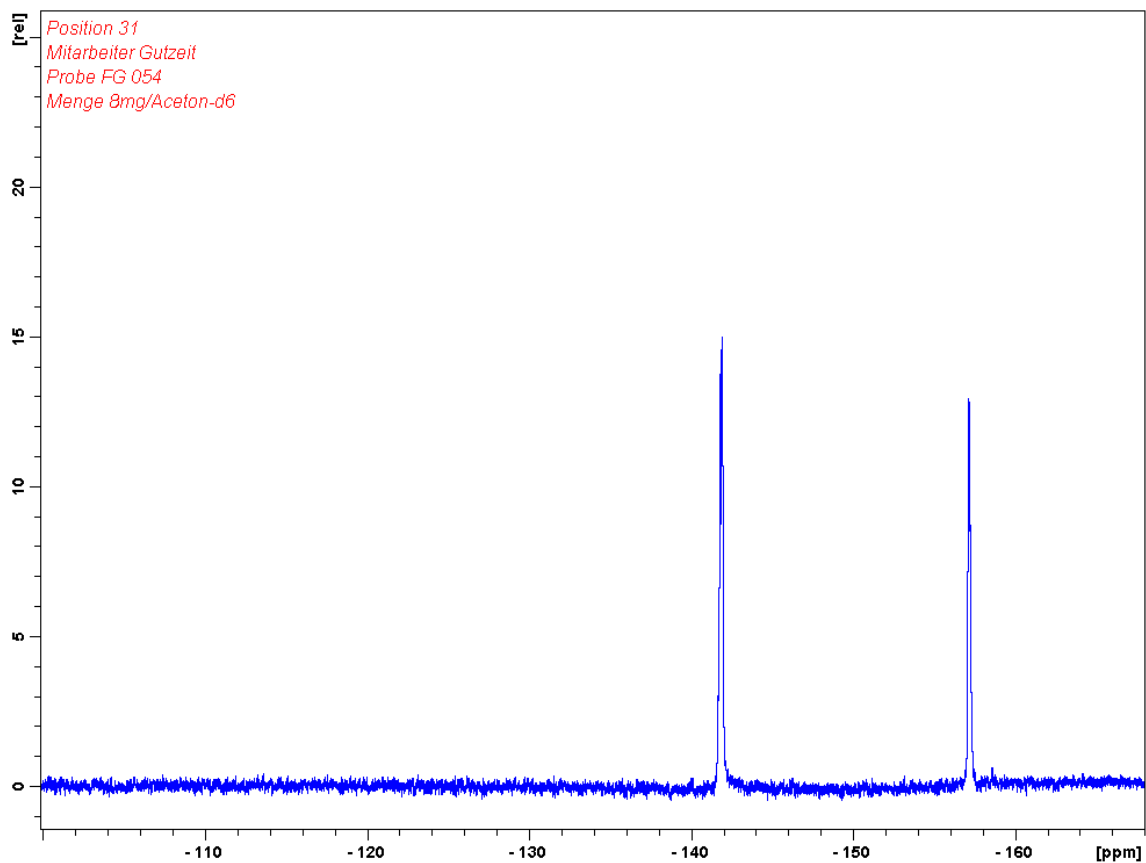
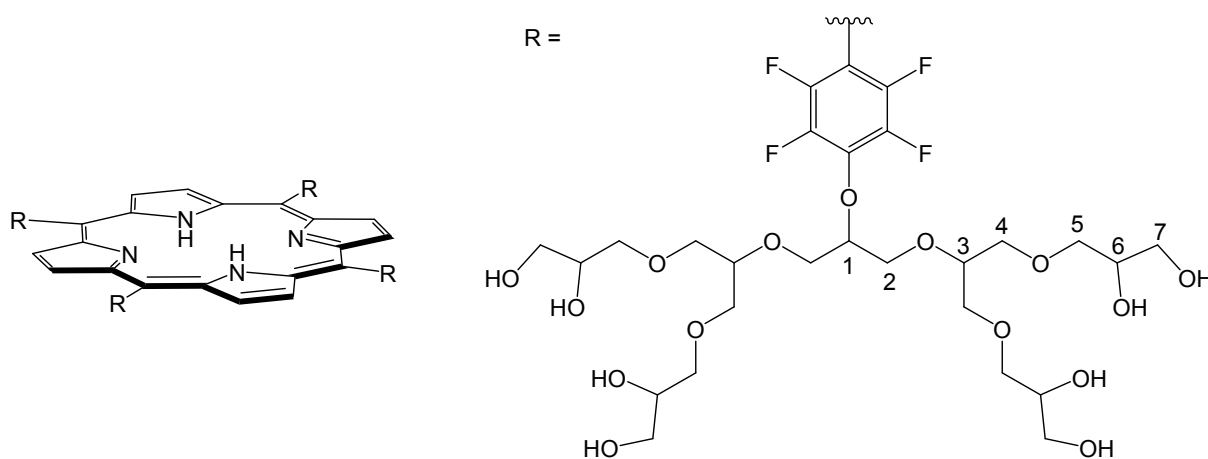


Fig S2 ^{19}F NMR spectrum of **5** in acetone- d_6 .

II.4 Synthesis of glycerol functionalised porphyrin 3

Acetal protected porphyrin **5** (17.3 mg, 4.7 μmol) was dissolved in a mixture of 0.3 mL of acetic acid, 1 mL of methanol and 0.5 mL of water and stirred for 4 d at 40 $^{\circ}\text{C}$. The solvent was removed under reduced pressure. The product was obtained as a red, viscous oil.

Yield: 16.4 mg (4.73 μmol , quant.)



FT-IR (layer): $\nu = 3321$ (br, m), 2873 (m), 1650 (w), 1493 (s), 1478 (s), 1429 (m), 1401 (m), 1352 (m), 1250 (m), 1045 (vs), 981 (vs), 909 (s), 866 (m), 807 (m), 772 (m), 756 (s), 571 (m) cm^{-1} .

^1H NMR (500 MHz, methanol- d_4 , 300 K): $\delta = 9.47$ -8.91 (m, br, 8H, H -Ar), 5.03 (q, $^3J = 4.7$ Hz, 4H, H -1) 4.27-4.08 (m, 16H, H -2), 3.96-3.46 (m, 120H, H -3, H -4, H -5, H -6, H -7) ppm.

HN- and HO-protons are not found because of deuterium exchange.

^{19}F NMR (470 MHz, methanol- d_4 , 300 K): $\delta = -142.1$ (m, 8F, o -F), -157.7 (m, 8F, m -F) ppm.

UV-Vis (MeOH): λ_{max} ($\lg \epsilon$) = 409 (5.4333), 504 (4.2900), 581 (3.7672) nm.

UV-Vis (H_2O): λ_{max} ($\lg \epsilon$) = 419 (5.3973), 509 (4.2509), 582 (3.7672) nm.

MS (HR): m/z (calc.) = 1014.044 (1014.043) $[\text{M}+3\text{H}]^{3+}$

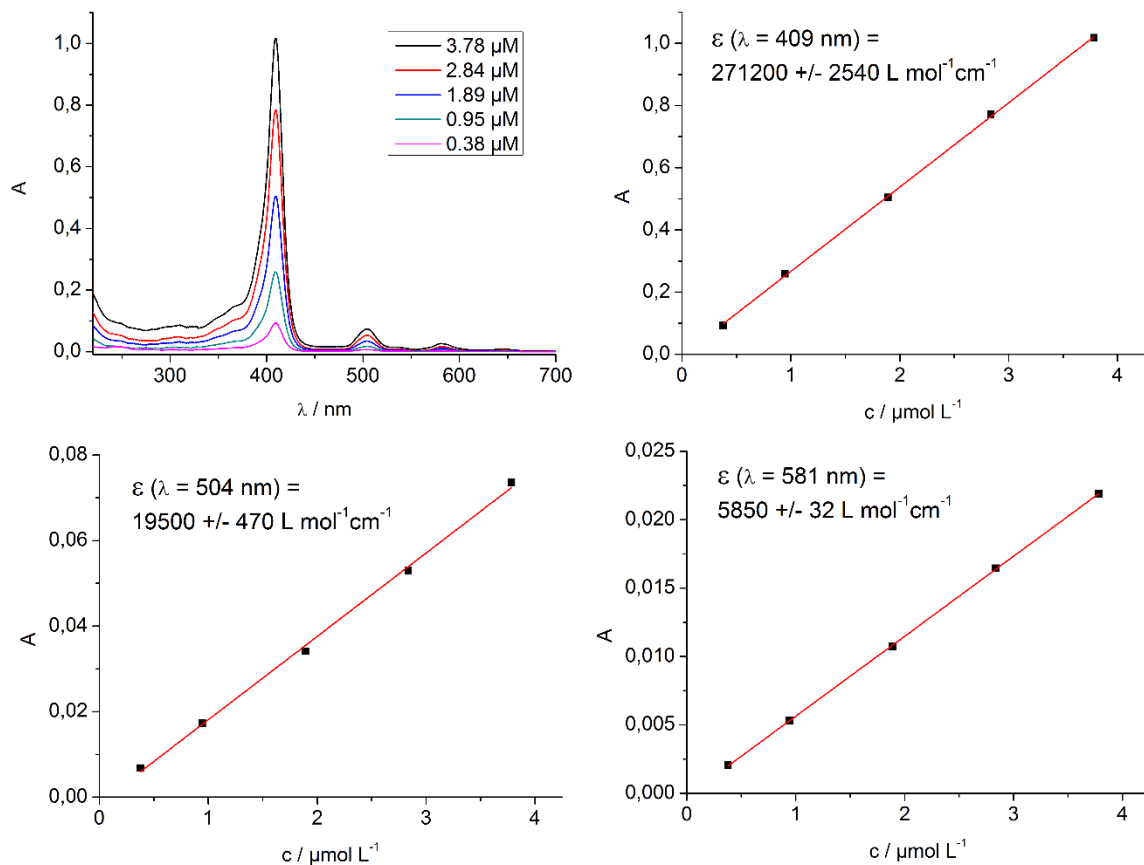


Fig S3 UV-Vis spectra (top left) and extinction coefficients of **3** in methanol.

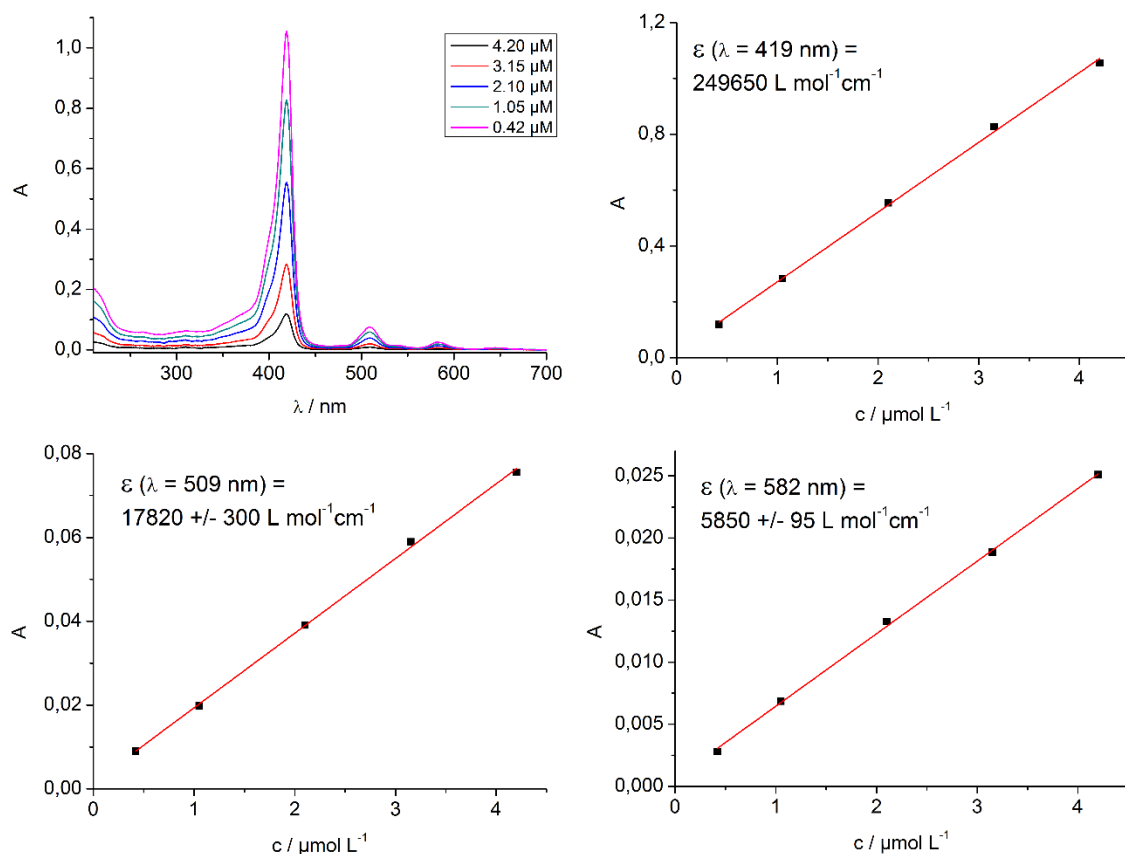


Fig S4 UV-vis spectra (top left) and extinction coefficients of **3** in water.

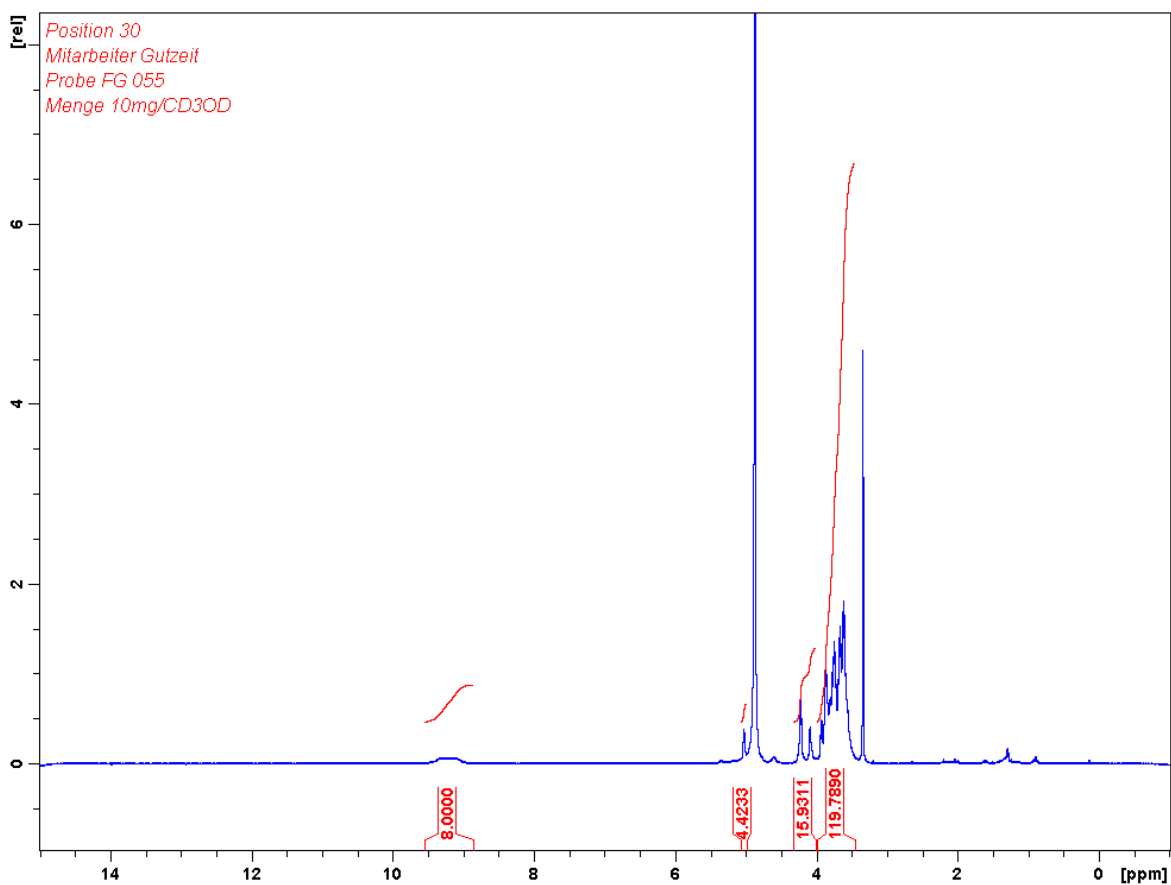


Fig S5 ^1H NMR spectrum of **3** in methanol- d_4 .

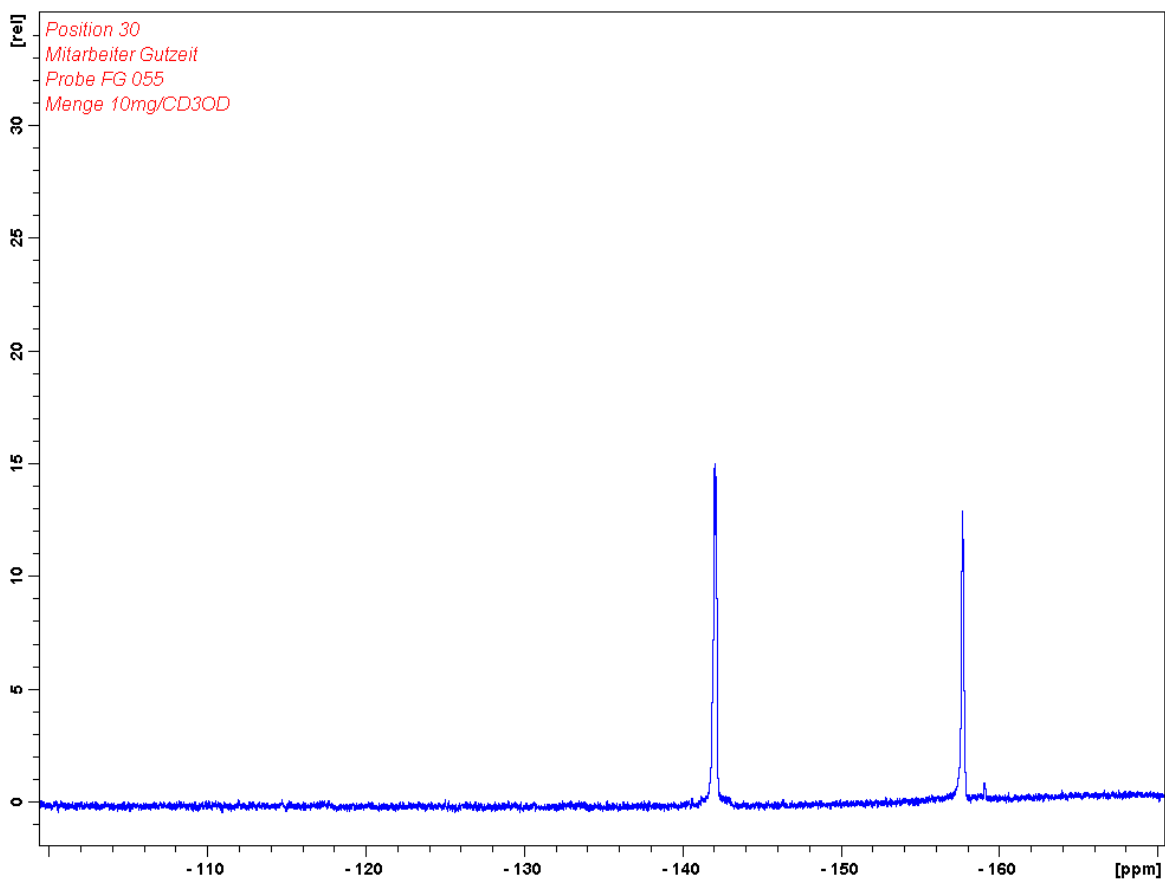
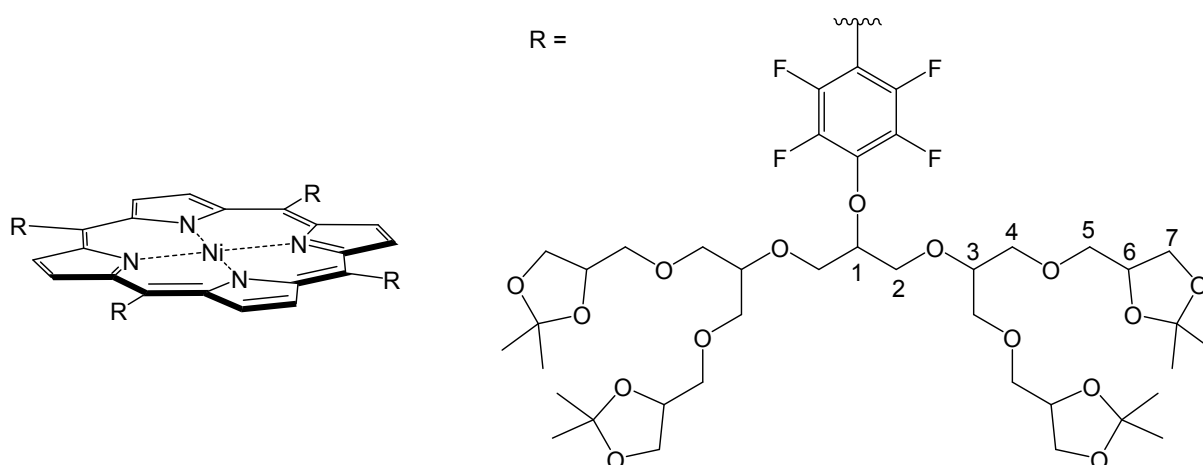


Fig S6 ^{19}F NMR spectrum of **3** in methanol- d_4 .

II.5 Synthesis of glycerol functionalised Ni-porphyrin 6

Sodium hydride (15 mg, 375 μmol) (60 % dispersion in mineral oil) was suspended in 5 mL of dry tetrahydrofuran under nitrogen atmosphere. [G2.0]-OH (85.7 mg, 123 μmol) was dissolved in 3 mL of tetrahydrofuran and slowly added to the sodium hydride suspension. The suspension was stirred for 1 h. Ni-TPPF₂₀ (**2**) (21.1 mg, 20.5 μmol) was added and the mixture was stirred for 5 d. The reaction was quenched with water and added to 100 mL of diethyl ether. The organic layer was washed with 100 mL of 0.1 M hydrochloric acid and dried over magnesium sulphate. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane / methanol = 97 : 3, R_f = 0.1). The product was obtained as a red, viscous oil.

Yield: 60.1 mg (16.1 μmol , 79 %)



FT-IR (layer): ν = 2987 (m), 2876 (m), 1650 (w), 1490 (s), 1427 (w), 1370 (m), 1258 (m), 1214 (m), 1147 (s), 1080 (vs), 984 (s), 947 (s), 842 (m), 763 (m), 667 (w), 514 (w), 463 (w) cm^{-1} .

¹H NMR (600 MHz, acetone- d_6 , 300 K): δ = 9.17 (s, 8H, *H*-Ar), 4.99-4.92 (m, 4H, *H*-1), 4.30-4.24 (m, 16H, *H*-6), 4.20-4.15 (m, 16H, *H*-2), 4.07-4.02 (m, 16H, *H*_a-7), 3.85-3.81 (m, 8H, *H*-3), 3.80-3.51 (m, 80H, *H*-4, *H*-5, *H*_b-7), 1.35-1.25 (m, 96H, *CH*₃) ppm.

¹⁹F NMR (470 MHz, acetone- d_6 , 300 K): δ = -141.9 (m, 8F, *o*-F), -157.0 (m, 8F, *m*-F) ppm.

MS (HR): m/z (calc.) = 1246.173 (1227.178) [*M*+3*H*]³⁺

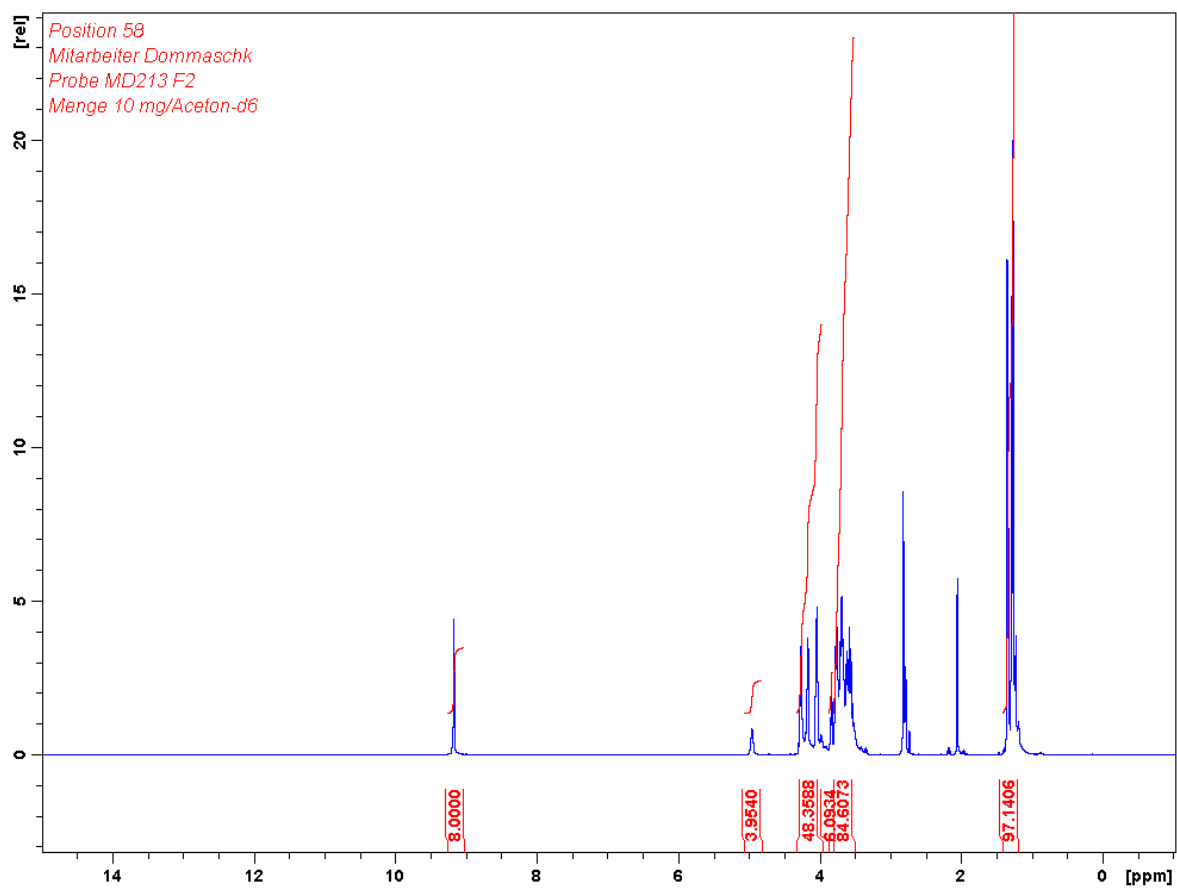


Fig S7 ^1H NMR spectrum of **6** in acetone- d_6 .

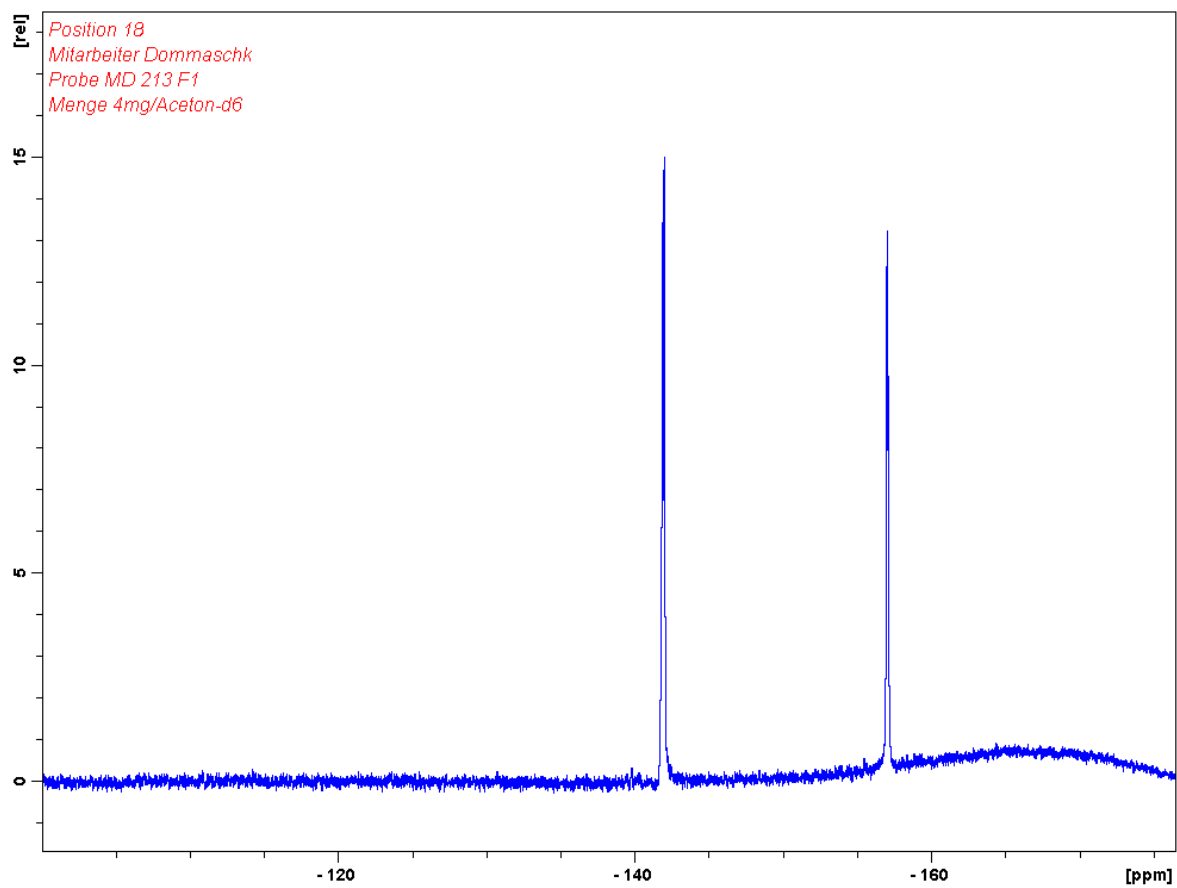
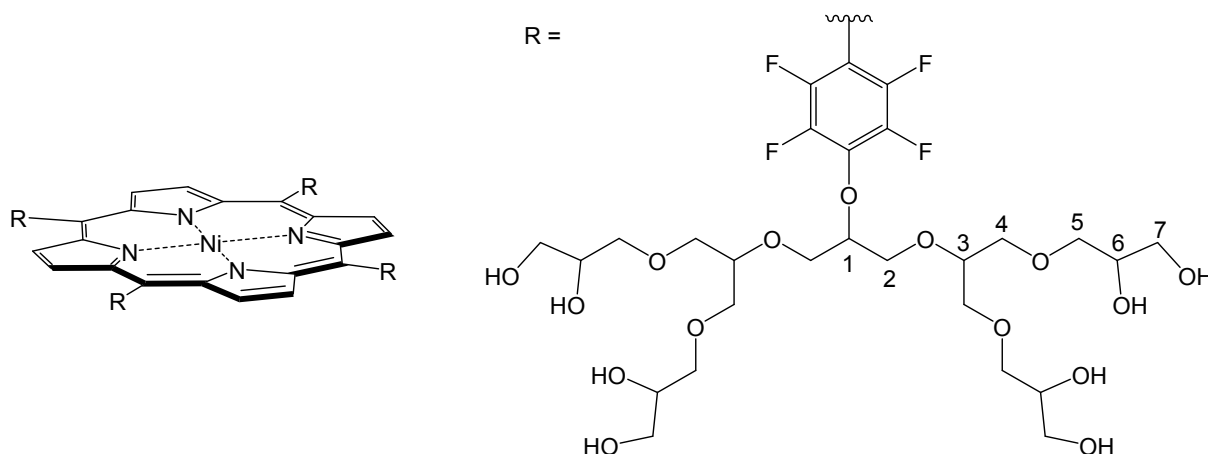


Fig S8 ^{19}F NMR spectrum of **6** in acetone- d_6 .

II.6 Synthesis of glycerol functionalised Ni-porphyrin 4

Acetal protected porphyrin **6** (60.1 mg, 16.1 μmol) was dissolved in a mixture of 1.00 mL of acetic acid, 2 mL of methanol and 1.00 mL of water and stirred for 4 d at 40 °C. The solvent was removed under reduced pressure. The product was obtained as a red, viscous oil.

Yield: 49.8 mg (16.1 μmol , quant.)



FT-IR (layer): $\nu = 3368$ (br, m), 2921 (s), 1648 (m), 1484 (s), 1347 (m), 1070 (vs), 980 (vs), 945 (s), 854 (m), 762 (s), 705 (m), 617 (s), 543 (s), 487 (s), 442 (vs), 420 (vs), 411 (s) cm^{-1} .

^1H NMR (500 MHz, methanol- d_4 , 300 K): $\delta = 9.58$ (s, 8H, $H\text{-Ar}$), 4.95 (p, $^3J = 4.7$ Hz, 4H, $H\text{-1}$), 4.20-4.05 (m, 16H, $H\text{-2}$), 3.88-3.43 (m, 120H, $H\text{-3}$, $H\text{-4}$, $H\text{-5}$, $H\text{-6}$, $H\text{-7}$) ppm.

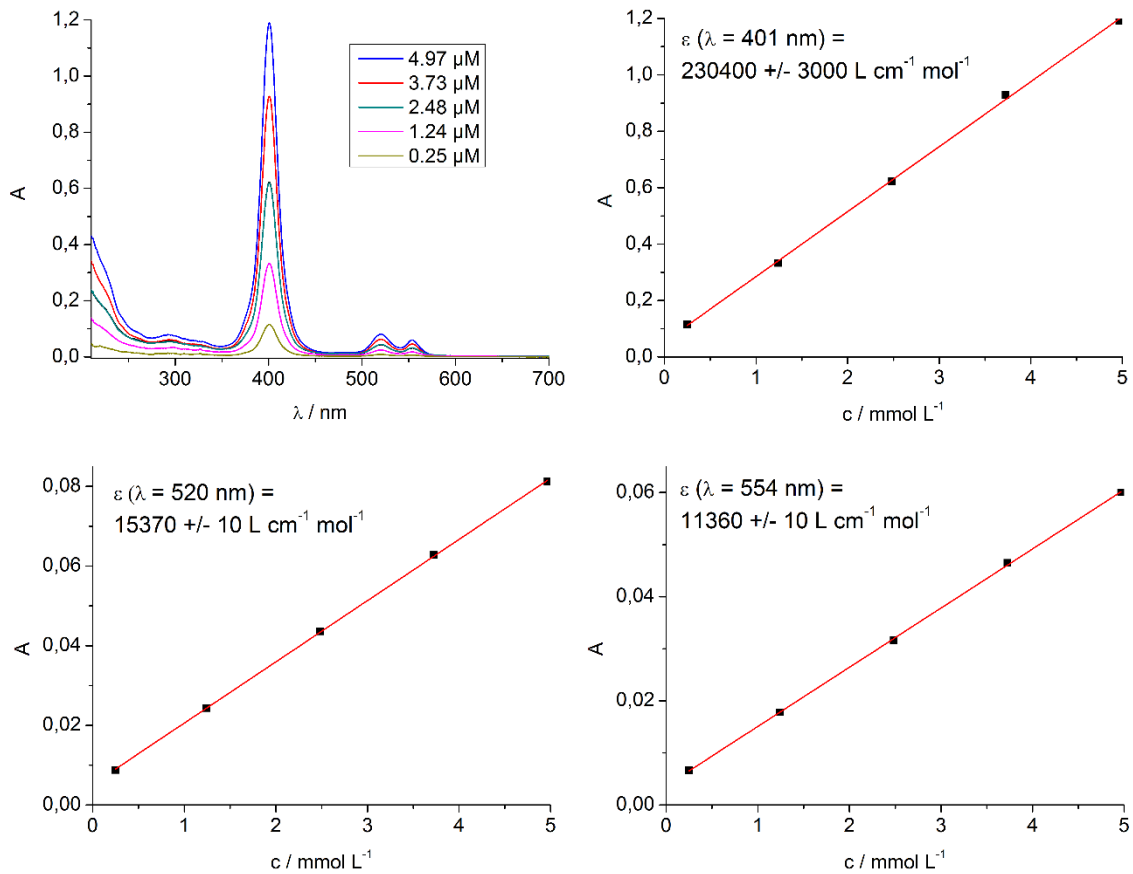
HO-protons are not found because of deuterium exchange.

^{19}F NMR (470 MHz, methanol- d_4 , 300 K): $\delta = -142.2$ (m, 8F, $o\text{-F}$), -157.7 (m, 8F, $m\text{-F}$) ppm.

UV-Vis (MeOH): λ_{max} ($\lg \epsilon$) = 401 (5.3625), 520 (4.1867), 554 (4.0554) nm.

UV-Vis (H_2O): λ_{max} ($\lg \epsilon$) = 409 (5.2483), 524 (4.1824), 559 (4.0013) nm.

MS (HR): m/z (calc.) = The mass peak is not found due to high fragmentation during electrospray ionisation.



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g S9 UV-vis spectra (top left) and extinction coefficients of **4** in methanol.

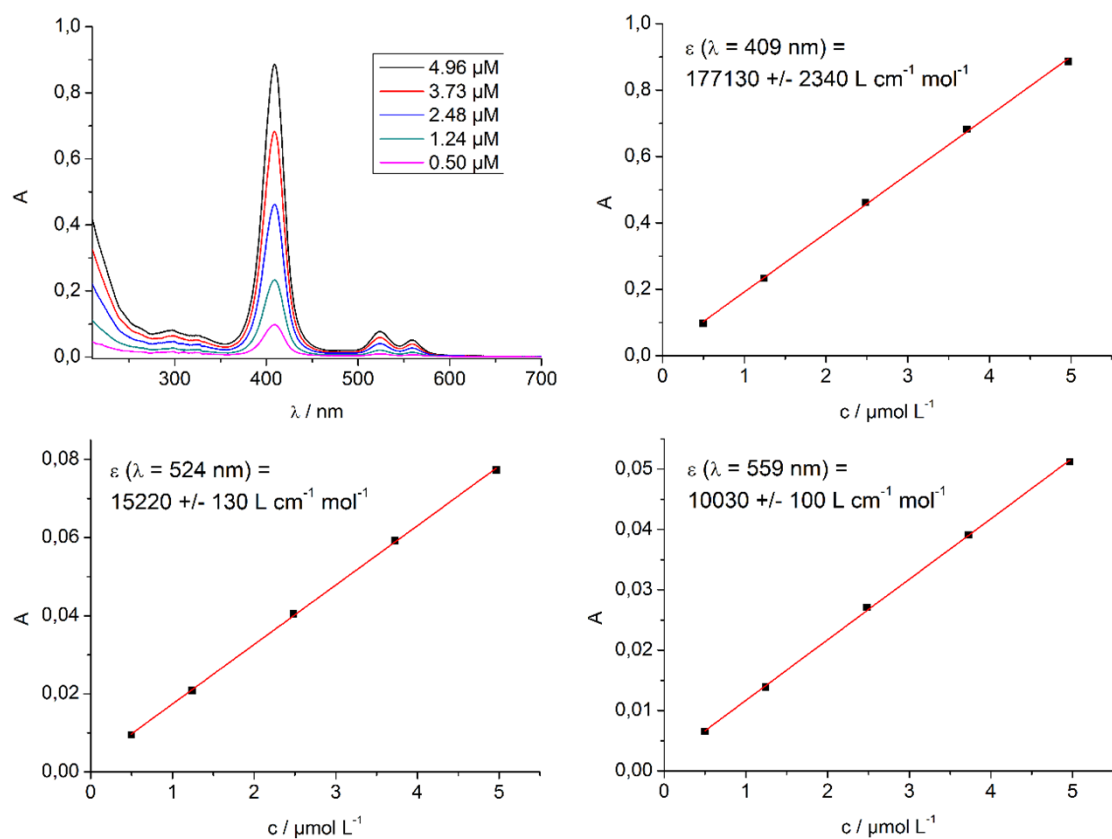


Fig S10 UV-vis spectra (top left) and extinction coefficients of **4** in water.

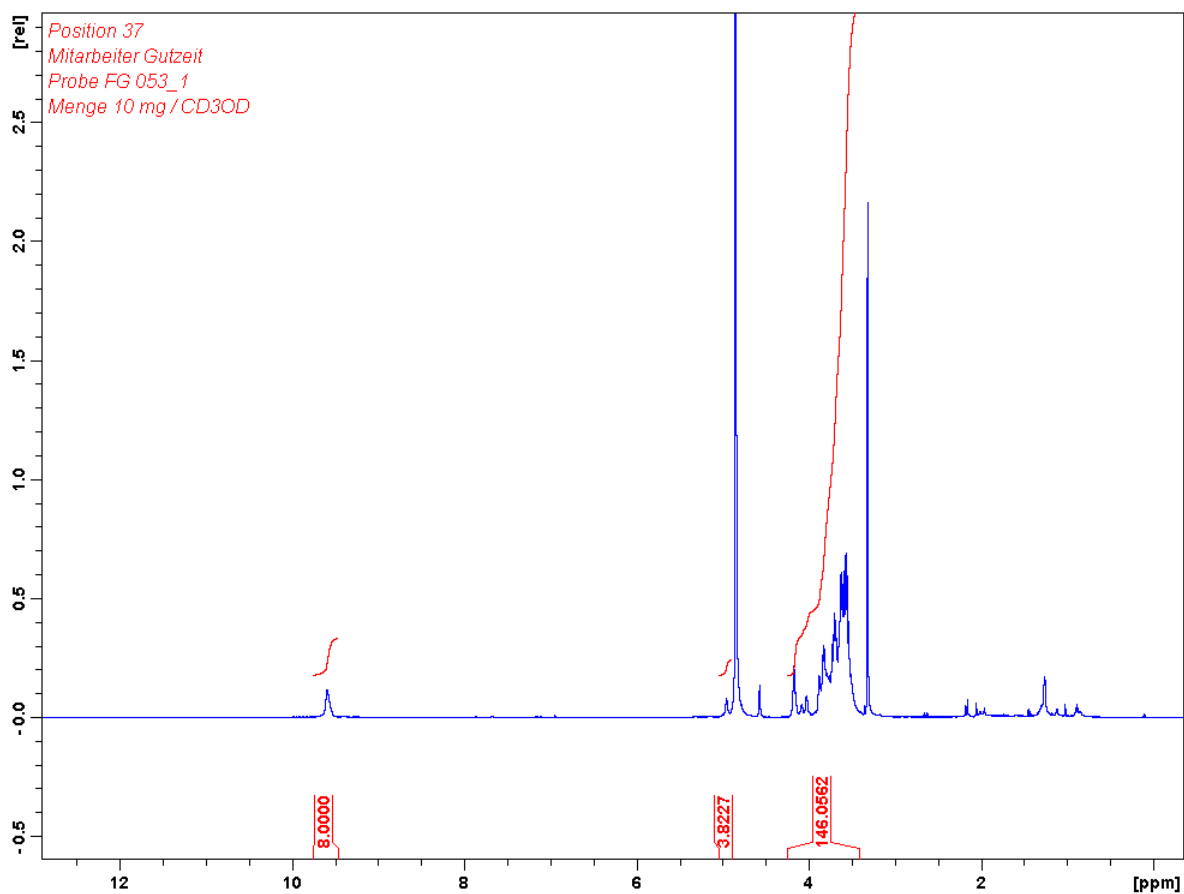


Fig S11 ^1H NMR spectrum of **4** in methanol- d_4 .

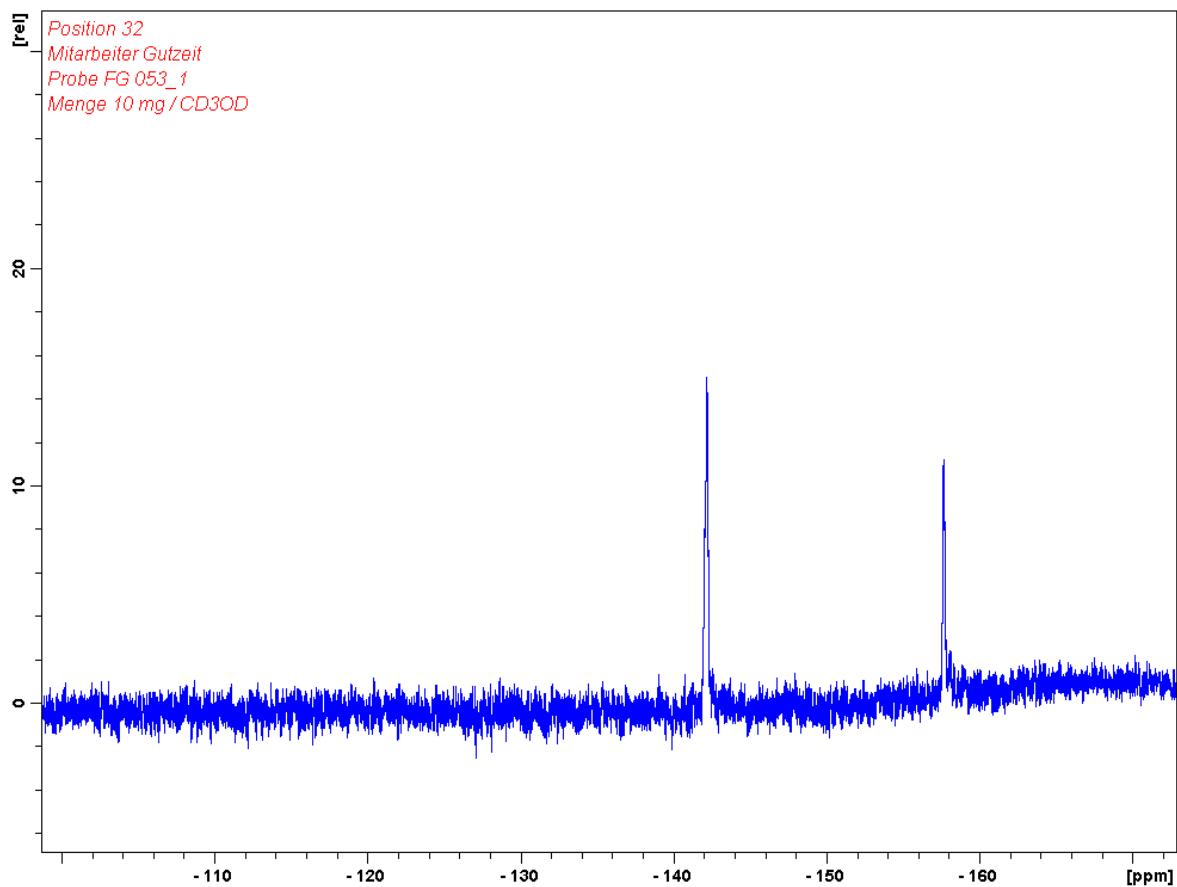


Fig S12 ^{19}F NMR spectrum of **4** in methanol- d_4 .

Tab S1 Overview of absorption maxima and extinction coefficients of water soluble glycerol substituted porphyrins **12** and **14**.

Compound (solvent)	λ_{max} (ϵ) / nm (L cm ⁻¹ mol ⁻¹)		
3 (MeOH)	409 (271200)	504 (19500)	581 (5850)
3 (H ₂ O)	419 (249650)	509 (17820)	582 (5850)
4 (MeOH)	401 (230400)	520 (15370)	554 (11360)
4 (H ₂ O)	409 (177130)	524 (15220)	559 (10030)

III. UV-vis titration

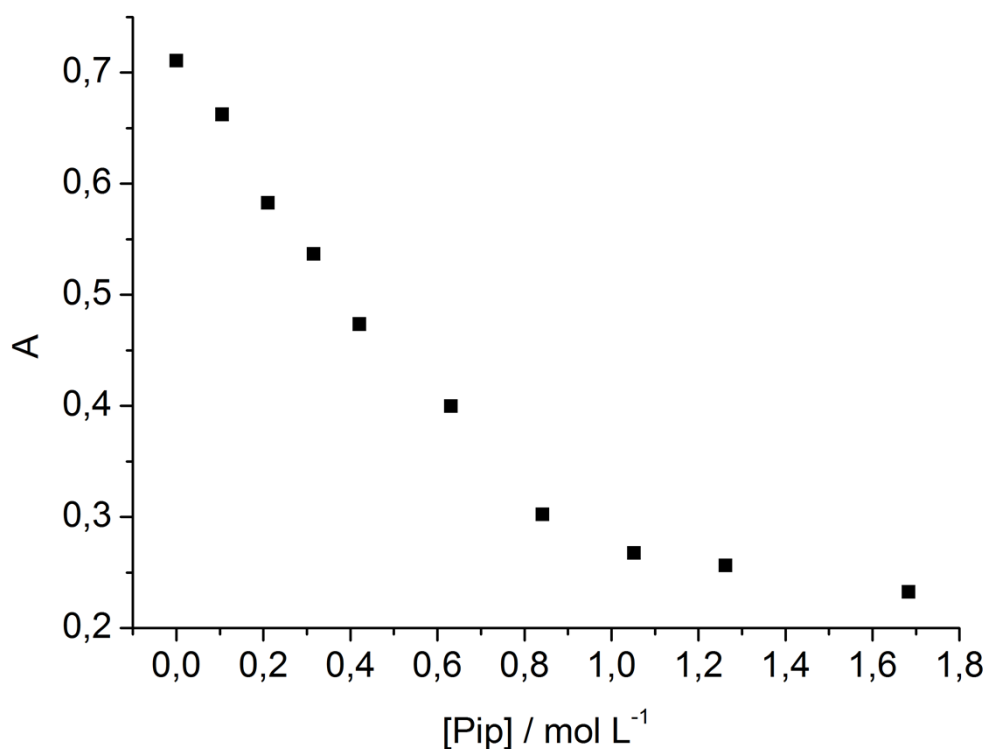


Fig S13 UV-Vis titration of Ni-porphyrin **4** with piperidine. The concentration of the aqueous solution of the porphyrin was $4.05 \mu\text{mol L}^{-1}$.

At least two complex formation reactions have to be considered (Fig. S14):

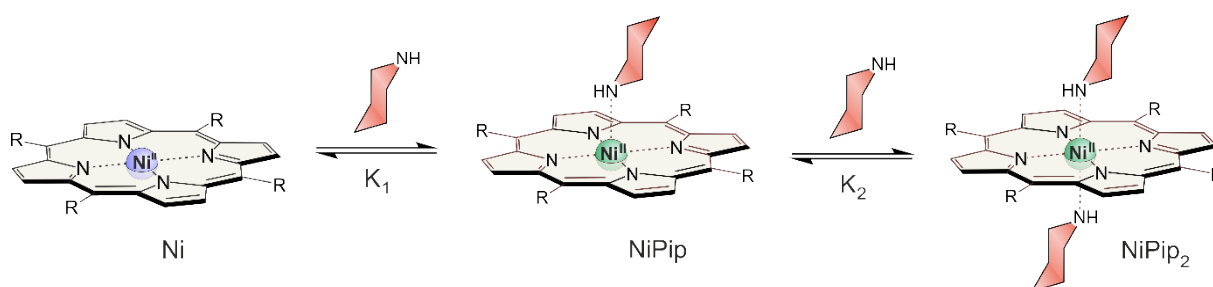


Fig S14 Formation of the square pyramidal and the square bipyramidal complexes upon titration with piperidine.

Formation of square pyramidal paramagnetic complex:
$$K_1 = \frac{[\text{NiPip}]}{[\text{Ni}][\text{Pip}]} = 0.481 \quad (\text{eq 1})$$

Formation of square bipyramidal paramagnetic complex:
$$K_2 = \frac{[\text{NiPip}_2]}{[\text{NiPip}][\text{Pip}]} = 14.662 \quad (\text{eq 2})$$

The paramagnetic complexes NiPip and NiPip₂ cannot be observed separately. Assuming their absorption wavelengths and extinction coefficients are almost equal, the overall concentration of paramagnetic Ni-complexes (NiPip and NiPip₂) and diamagnetic Ni-complex (Ni) can be estimated from the decreasing absorption at 409 nm by nonlinear fitting (SSQ = 0.005).² Piperidine is a strong base (pK_a = 11.12). For the calculation of K₁ and K₂ the concentration of the free base ([Pip]_{eff}) was considered using the formula for strong bases:

$$[Pip]_{eff} = [Pip] - [PipH^+] = [Pip] - \left(-\frac{K_B}{2} + \sqrt{\frac{K_B^2}{4} + K_B c_0} \right) \quad (\text{eq 3})$$

Tab. S2 Results of the titration series.

[Pip] mol L ⁻¹	[Pip] _{eff} mol L ⁻¹	A (409 nm)	[Ni] mol L ⁻¹	[NiPip] mol L ⁻¹	[NiPip ₂] mol L ⁻¹
0.000	0.000	0.71064	4.050E-06	0.000E+00	0.000E+00
0.105	0.086	0.66223	3.704E-06	1.531E-07	1.930E-07
0.210	0.183	0.58275	3.059E-06	2.690E-07	7.215E-07
0.316	0.282	0.53681	2.389E-06	3.237E-07	1.337E-06
0.421	0.382	0.47362	1.833E-06	3.362E-07	1.881E-06
0.631	0.583	0.39976	1.102E-06	3.088E-07	2.640E-06
0.842	0.786	0.30235	7.066E-07	2.670E-07	3.076E-06
1.052	0.990	0.26764	4.833E-07	2.300E-07	3.337E-06
1.262	1.194	0.25638	3.484E-07	2.000E-07	3.502E-06
1.683	1.604	0.2325	2.034E-07	1.569E-07	3.690E-06

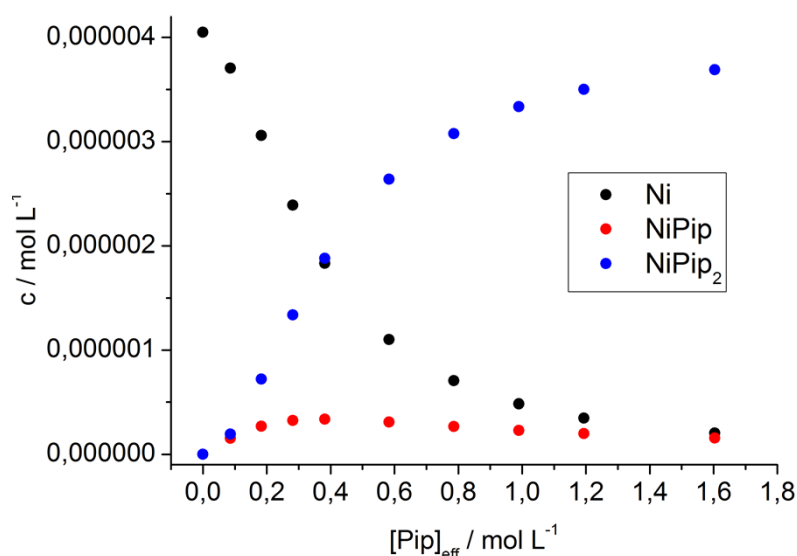


Fig S15 Concentrations of the complexes Ni, NiPip and NiPip₂ as a function of added piperidine in the titration experiment.

The values for K_1 and K_2 are small compared to the corresponding association constants in organic solution obtained by similar experiments.³⁻⁵ The ligand seems to be drastically decreased in its donor strength because of hydrogen bonding.

IV. Aggregation investigation

The glycerol functionalised porphyrins **3** and **4** do not exhibit aggregation or excimer formation which is probably due to the large steric hindrance of the polyols. Solutions of **3** and **4** perfectly follow the Lambert-Beer law up to a concentration of 50 μM (Fig. S16).

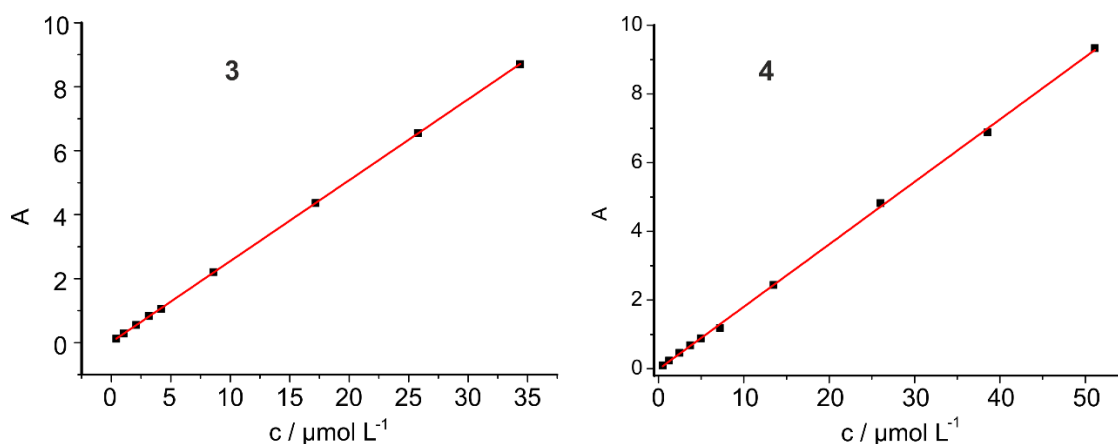


Fig. S16 Absorption of solutions of **3** ($\lambda = 419 \text{ nm}$) and **4** ($\lambda = 409 \text{ nm}$) in water as a function of molar concentration perfectly follows the Lambert-Beer law up to a concentration of 35 or 50 μM .

To investigate the aggregation of **3** and **4** at higher concentrations, NMR spectra at different concentrations were measured (Fig S17).

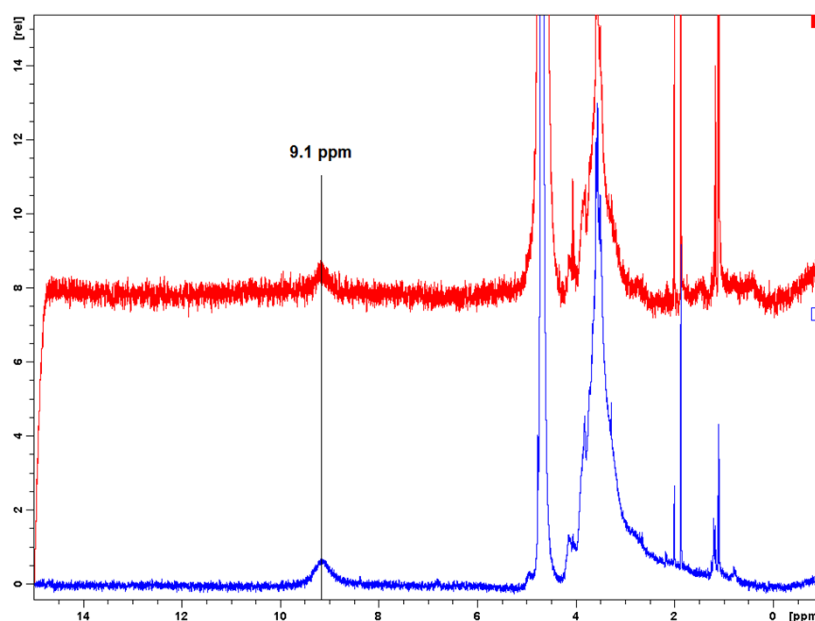


Fig S17 ^1H NMR spectra of 0.8 mM (blue) and 0.08 mM (red) solutions of water soluble porphyrin **4**. The signal of pyrrole protons do not exhibit a downfield shift or broadening at higher concentrations which proves that there is no aggregation.

V. Relaxation time experiments

Longitudinal relaxation times (T_1) were measured in water using an inversion recovery spin echo sequence (2D, TE/TR=6.3/3000 ms, 24 inversion times (TI 50 - 2000 ms), spatial resolution $300 \times 300 \mu\text{m}^2$, slice thickness $700 \mu\text{m}$) at a 7 T MRI spectrometer (ClinScan 70/30 USR, Bruker Biospin, Germany). Relaxation follows first order exponential decay:

$$I(t) = I_0 + P e^{\left(-\frac{t}{T_1}\right)} \quad (\text{eq 4})$$

$I(t)$: Intensity

I_0 : Intensity after 180° pulse

P : Pre-exponential factor

T_1 : Relaxation time

To determine the effect of the coordination induced spin state switch (CISSS) on the relaxation time four samples were investigated:

1. 2 mM solution of **4**
2. Water
3. Water + piperidine (20 %)
4. 2 mM solution of **4** + piperidine (20 %)

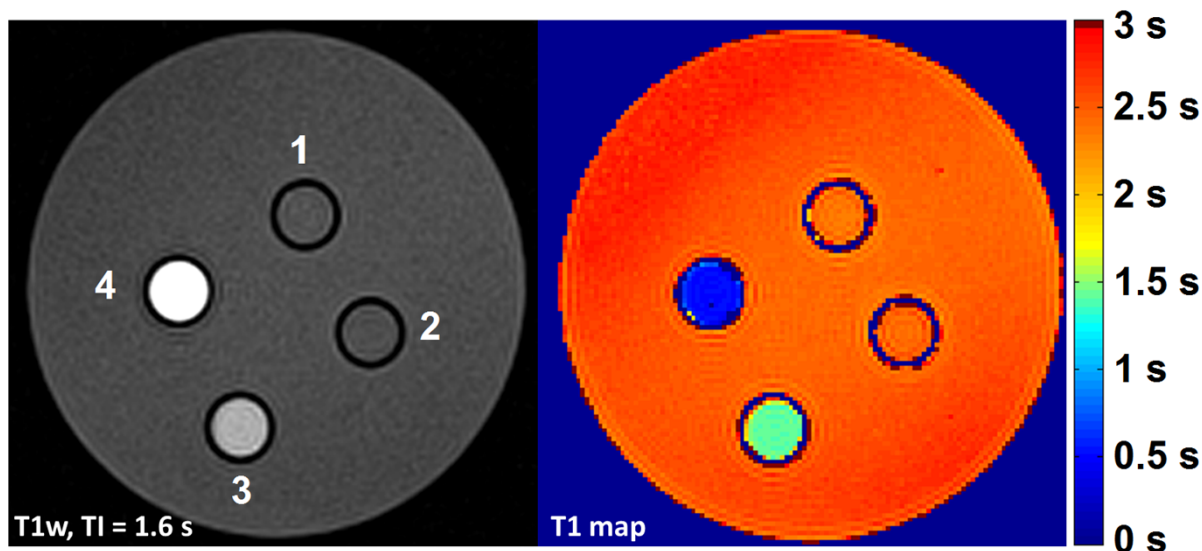


Fig S18 MR images of 1. **14** (2 mM in water), 2. Water, 3. Water + 20 % piperidine and 4. **14** (2 mM in water + 20 % piperidine).

Tab. S3 Relaxation times (T_1) and relaxation rates (T_1^{-1}) of the observed samples. Times and errors were determined from MR images (Fig. 7).

Samples	T_1 / ms	T_1^{-1} / s ⁻¹
1. 2 mM solution of 4	2350 +/- 38	0.426
2. Water	2410 +/- 45	0.415
3. Water + piperidine (20 %)	1415 +/- 13	0.707
4. 2 mM solution of 4 + piperidine (20 %)	510 +/- 13	1.961

From the relaxation time of the 2 mM solution **4**·Pip₂ the relaxivity is estimated to be 0.627 mM⁻¹s⁻¹ (eq 5)

$$T_1^{-1} = T_s^{-1} + R_1[c] \quad (\text{eq 5})$$

T_1^{-1} : relaxation rate (1,961 s⁻¹)

T_s^{-1} : relaxation rate of solution without paramagnetic substance (0,707 s⁻¹)

R_1 : T_1 relaxivity / (mmol)⁻¹s⁻¹ or mM⁻¹s⁻¹

$[c]$: concentration of paramagnetic substance (2 mmol)

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