Supporting information

J-dimers of phthalocyanine analogues: structural characterization and their use for determination of association constants between ligands and central cation.

Jiri Demuth,[a] Stefan Bednarik,[a] Radek Machan,[a] Ivan Mocak,[a] Tibor Malinsky,[a] Mona Abo El Dahabova,[a] Jakub Holcak,[a] Miroslav Miletin,[a] Jan Labuta,[b,c] Veronika Novakova,[a] Petr Zimcik[a*]

[a]Department of Pharmaceutical Chemistry and Pharmaceutical Analysis, Faculty of Pharmacy in Hradec Kralove, Charles University, Heyrovskeho 1203, Hradec Kralove, 50005. zimcik@faf.cuni.cz

[b]Institute of Organic Chemistry and Biochemistry (IOCB), Czech Academy of Sciences (CAS), Flemingovo nám. 2, 160 00 Prague, Czech Republic.

[c]Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.

Content

Binding models

For simplicity, we use the following notations in the sections below. AzaPc is denoted as host (H), i.e. AzaPc = H, and ligand (pyridine, piperidine, *N*-methylimidazol, triethylamine, etc.) is denoted as L.

General binding model used in this study

The binding interaction between two hosts (H) with subsequent formation of J-dimer (H_2) and host (H) and guest ligand (L) with the formation of HL complex is described by the following equilibrium Equations S1-S2.

$$H + H \overset{K_D}{\rightleftharpoons} H_2 \quad (S1)$$

$$H + L \overset{K_1}{\rightleftharpoons} HL \quad (S2)$$

Where K_D is the equilibrium dimerization binding constant for the formation of AzaPc J-dimer H_2, and K_1 is the equilibrium binding constant for the association between the monomeric AzaPc's central cation and the coordinating ligand describing the formation of HL complex.

While K_D and K_1 are step-wise binding constants that describe well-defined mechanisms, we can also define, for practical reasons, an apparent binding constant K_L, which is used in ligand-induced J-dimer disassembly experiments by the following equilibrium Equation S3.

$$H_2 + 2L \overset{K_L}{\rightleftharpoons} 2HL \quad (S3)$$

Then, the following formulas hold for binding constants and mass balances:

$$K_D = \frac{[H_2]}{[H]^2} \quad (S4)$$

$$K_1 = \frac{[HL]}{[H][L]} \quad (S5)$$

$$K_L = \frac{[HL]^2}{[H_2][L]^2} \quad (S6)$$

$$[H]_t = [H] + [HL] + 2[H_2] \quad (S7)$$

$$[L]_t = [L] + [HL] \quad (S8)$$

Where $[H]_t$ and $[L]_t$ are the total analytical concentrations of H and L, respectively. The square brackets "[ ]" denote the concentrations of indicated species.

Note that the combination of Equations S4-S6 shows that the apparent binding constant is a combination of step-wise constants with the following form, which can be conveniently used for the determination of K_L or K_1, depending on the formulation of the equations (in our case, the K_1 is primarily evaluated during the fitting procedures).

$$K_L = \frac{{K_1}^2}{K_D} \quad \Rightarrow \quad K_1 = \sqrt{K_D\, K_L} \quad (S9)$$

Expressing terms $[H_2]$ and [HL] from Equations S4 and S5, respectively, and substituting into Equations S7 and S8 yields the following formulas.

$$[\mathrm{H}]_\mathrm{t} = [\mathrm{H}] + K_1[\mathrm{H}][\mathrm{L}] + 2K_\mathrm{D}[\mathrm{H}]^2 \quad \text{(S10)}$$

$$[\mathrm{L}]_\mathrm{t} = [\mathrm{L}] + K_1[\mathrm{H}][\mathrm{L}] \quad \text{(S11)}$$

Expression of the term [L] from Equation S11 gives Equation S12.

$$[\mathrm{L}] = \frac{[\mathrm{L}]_\mathrm{t}}{1+K_1[\mathrm{H}]} \quad \text{(S12)}$$

Substitution of [L] from Equation S12 into Equation S10 yields (after some rearrangements) the formula for [H] in the form of a third-order algebraic equation (Equation S13).

$$2K_1K_\mathrm{D}[\mathrm{H}]^3 + (K_1 + 2K_\mathrm{D})[\mathrm{H}]^2 + (1 + K_1[\mathrm{L}]_\mathrm{t} - K_1[\mathrm{H}]_\mathrm{t})[\mathrm{H}] - [\mathrm{H}]_\mathrm{t} = 0 \quad \text{(S13)}$$

Solution of Equation S13 using a numerical bisection method in the interval $[\mathrm{H}]\in[0, [\mathrm{H}]_\mathrm{t}]$ yields the concentration of free AzaPc host [H]. The concentrations of other species, such as [L], [HL], and [H_2] can be obtained by subsequent evaluation of Equations S12, S5, and S4, respectively.

Temperature-induced disassembly of J-dimers

In order to determine K_D, we use equilibrium Equation S1 and corresponding Equations S4 and S7 (with [HL]=0). This model has an exact analytical solution in the form of Equations S14 and S15.

$$[\mathrm{H}] = \frac{-1+\sqrt{1+8K_\mathrm{D}[\mathrm{H}]_\mathrm{t}}}{4K_\mathrm{D}} \quad \text{(S14)}$$

$$[\mathrm{H_2}] = \frac{1+4K_\mathrm{D}[\mathrm{H}]_\mathrm{t}-\sqrt{1+8K_\mathrm{D}[\mathrm{H}]_\mathrm{t}}}{8K_\mathrm{D}} \quad \text{(S15)}$$

Then, the theoretical UV-vis (Equation S16) and fluorescence (Equation S17) binding curves are constructed as follows.

$$A = d(\varepsilon_\mathrm{H}[\mathrm{H}] + 2\varepsilon_{\mathrm{H2}}[\mathrm{H_2}]) \quad \text{(S16)}$$

$$F = p_\mathrm{H}[\mathrm{H}] + 2p_{\mathrm{H2}}[\mathrm{H_2}] \quad \text{(S17)}$$

Since we use a temperature-induced J-dimer disassembly experiment, the temperature-dependent expression for the K_D constant is used in the following form.

$$K_\mathrm{D} = e^{-\frac{\Delta H - T\Delta S}{RT}} \quad \text{(S18)}$$

Where *A* and *F* correspond to observed absorbance and fluorescence at a particular wavelength. The ε_H and ε_{H2} are molar extinction coefficients of H and H_2 species, respectively, and *d* is path length (in cm). The p_H and p_{H2} are proportionality constants for H and H_2 species, respectively. The ΔH and ΔS are the enthalpy and entropy of the dimerization process, respectively. *T* is the absolute temperature, and *R* is the gas constant.

The binding curves (Equations S16 and S17 together with input from Equations S14, S15, and S18) are fitted (using a non-linear least squares fitting procedure) to experimental data (with free parameters ΔH, ΔS, ε_H, ε_{H2}, $p_{H,}$ and p_{H2}). The value of the J-dimerization binding constant K_D at 23 °C (298.15 K) is determined by Equation S18 and further used in the following parts of the binding studies.

Ligand-induced disassembly of J-dimers at constant temperature (23 °C)

We use the solution of the general binding model described in section "General binding model …", i.e., we have access to [H], [L], [HL], and [H_2] concentrations through the procedure described in the "General binding model …" section. Then, the UV-vis (Equation S19), fluorescence (Equation S20), and NMR (Equation S21) binding isotherms for ligand-induced disassembly of J-dimers at constant temperature (23 °C) with known J-dimerization constant K_D have the following forms.

$$A = d(\varepsilon_{\mathrm{H}}[\mathrm{H}] + 2\varepsilon_{\mathrm{H2}}[\mathrm{H_2}] + \varepsilon_{\mathrm{HL}}[\mathrm{HL}]) \quad \text{(S19)}$$

$$F = p_{\mathrm{H}}[\mathrm{H}] + 2p_{\mathrm{H2}}[\mathrm{H_2}] + p_{\mathrm{HL}}[\mathrm{HL}] \quad \text{(S20)}$$

$$M_{\mathrm{H2}} = M_0 \cdot 2[\mathrm{H_2}]/[\mathrm{H}]_{\mathrm{t}} \quad \text{(S21)}$$

Where *A* and *F* correspond to observed absorbance and fluorescence at a particular wavelength. The ε_H, ε_{H2}, and ε_{HL} are molar extinction coefficients of H, H_2, and HL species, respectively, and *d* is path length (in cm). The p_H, p_{H2}, and p_{HL} are proportionality constants for H, H_2, and HL species, respectively. The M_{H2} is the magnetization corresponding to the AzaPc J-dimeric form, which is proportional to the fraction of J-dimer concentration in the solution with proportionality constant M_0.

The binding curves (Equations S19, S20, and S21, together with the known value of K_D and [H], [L], [HL], and [H_2] values obtained from the procedure described in "General binding model …" section) are fitted (using a non-linear least squares fitting procedure) to experimental data (with free parameters K_1, ε_H, ε_{H2}, ε_{HL}, p_H, p_{H2}, p_{HL}, and M_0). Through this process, we obtain the step-wise binding constant K_1 and the apparent binding constant binding constant K_L, which can be calculated using Equation S9.

HSQC experiment with **3Zn**

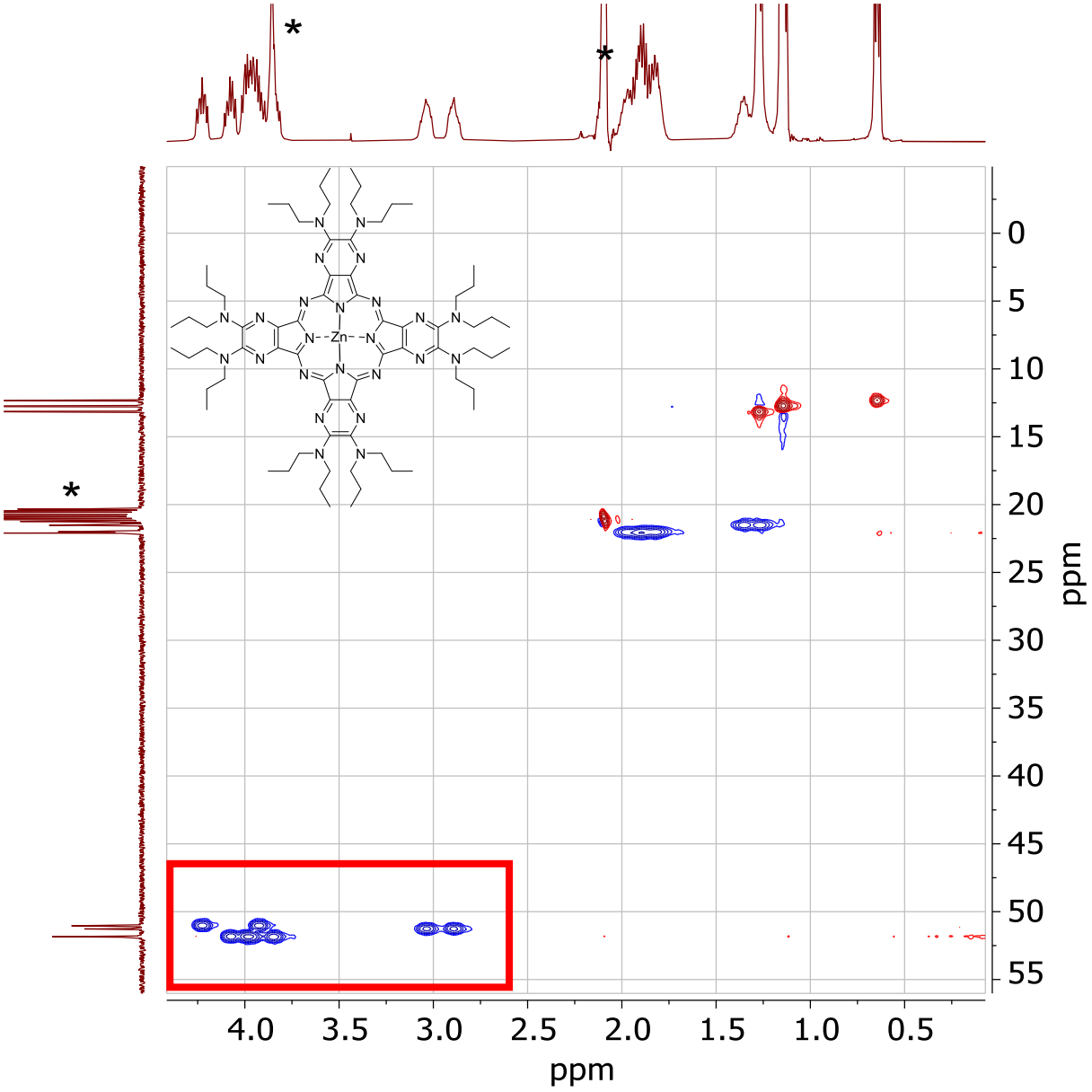

Figure S1. HSQC experiment of **3Zn** in toluene-d_8. Asterisk marks residual of solvents. Boxed area is zoomed and integrated in **Figure S2**.

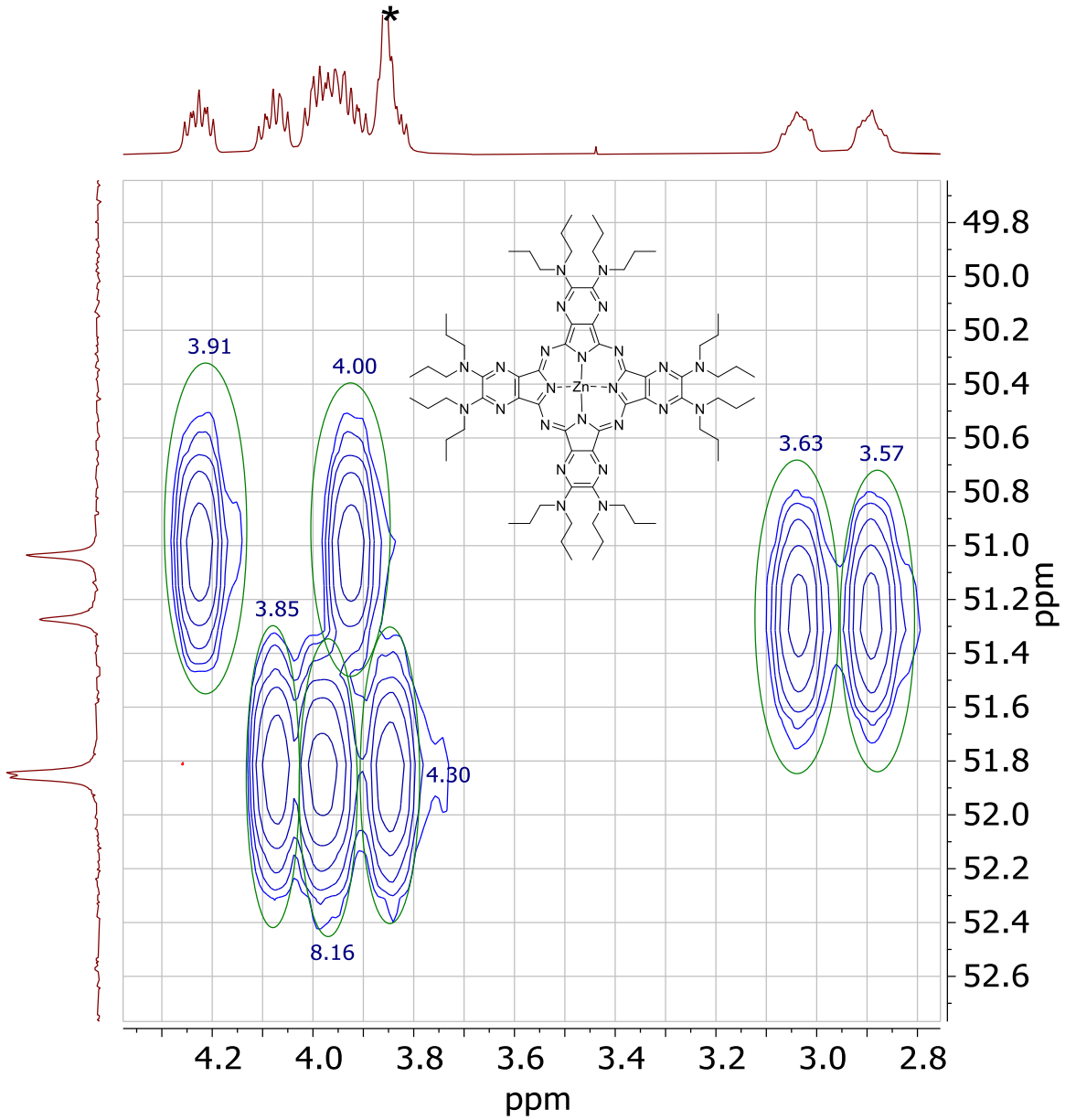

Figure S2. HSQC experiment of **3Zn** in toluene-d_8. Asterisk marks residual of solvents. Signals (integrated) belong to hydrogen on methylene groups next to amino nitrogen.

DOSY experiment with **3Zn**

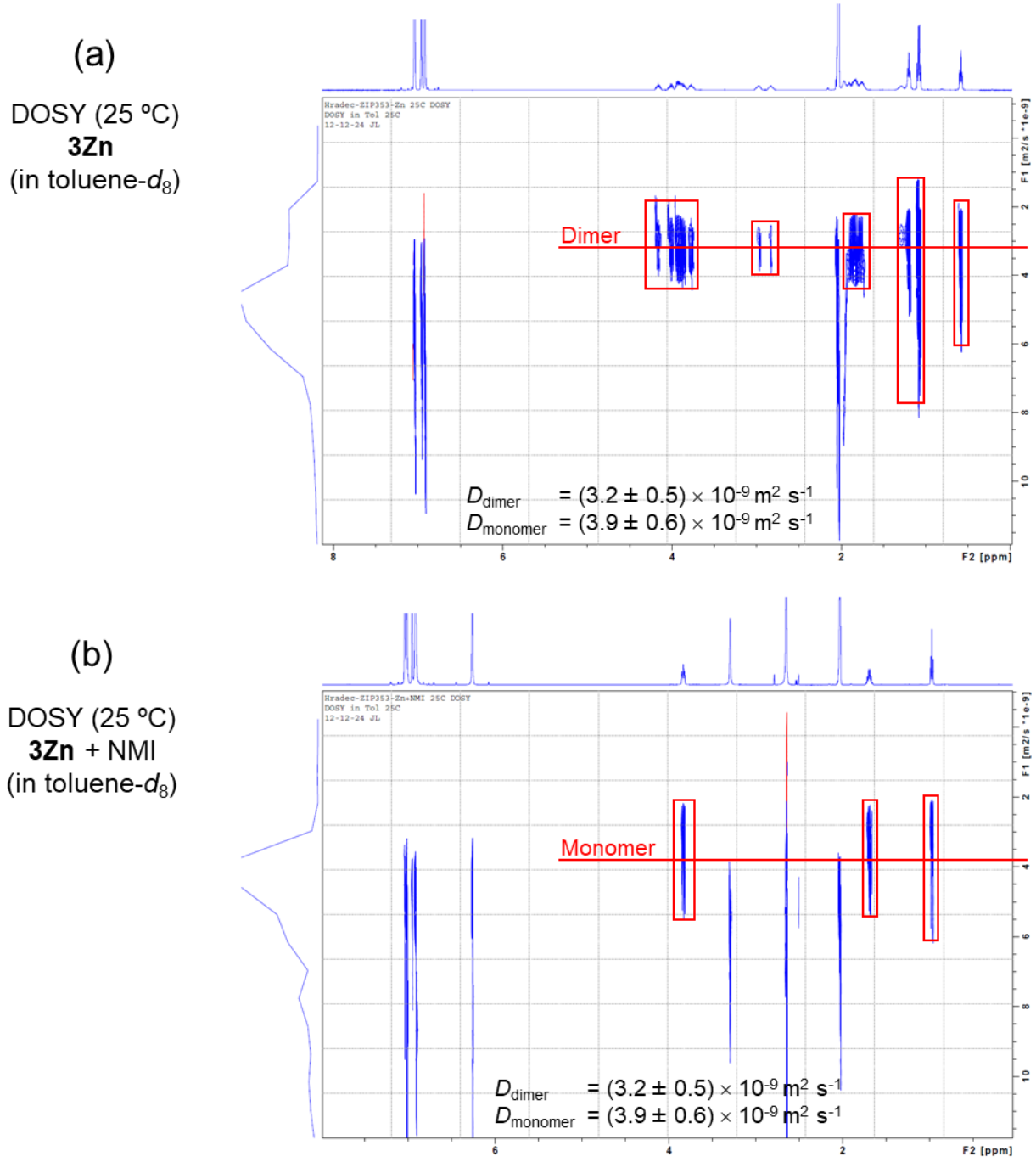

Figure S3. ^{1}H diffusion ordered spectroscopy (DOSY) spectrum (500 MHz) of **3Zn** (2.2 mM, toluene-d_8) at 25 °C: (a) in the absence of NMI and (b) in the presence of NMI (5 equiv.). DOSY signals of monomer ($D_{monomer}$ = (3.9 ± 0.6)×10^{-9} m^2 s^{-1}) and dimer (D_{dimer} = (3.2 ± 0.5)× 10^{-9} m^2 s^{-1}) are denoted by red rectangles.

Fluorescence spectra in toluene

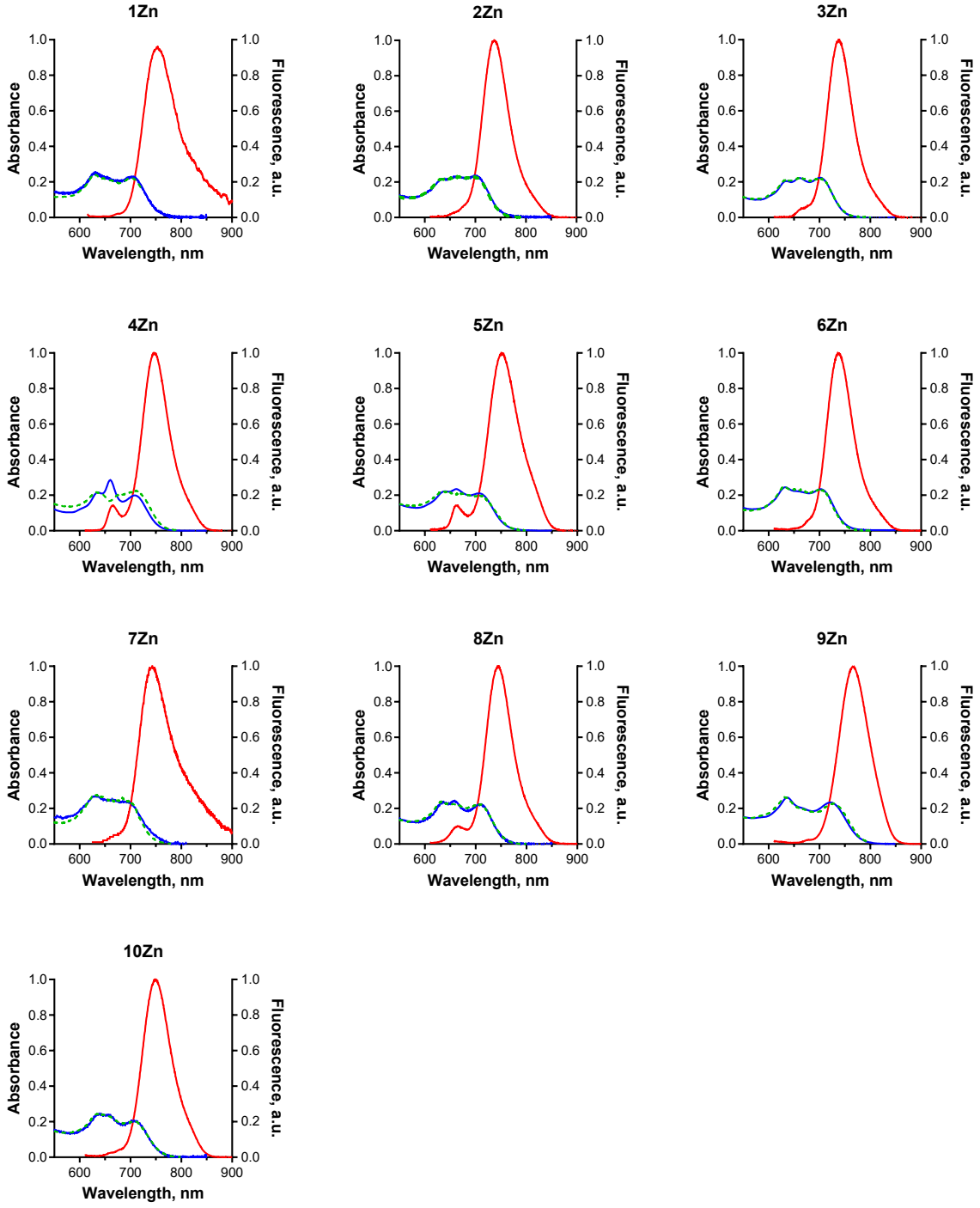

Figure S4. Absorption (blue), emission (red, λ_{ex} = 588 nm) and excitation (green, dashed, λ_{em} = 820 nm) spectra of compounds **1Zn**-**10Zn** in toluene (c = 2 μM). Emission spectra were normalized to 1.0, excitation spectra were normalized to have the same value as in the absorption spectra in Q-band.

Absorption and emission spectra from temperature experiments

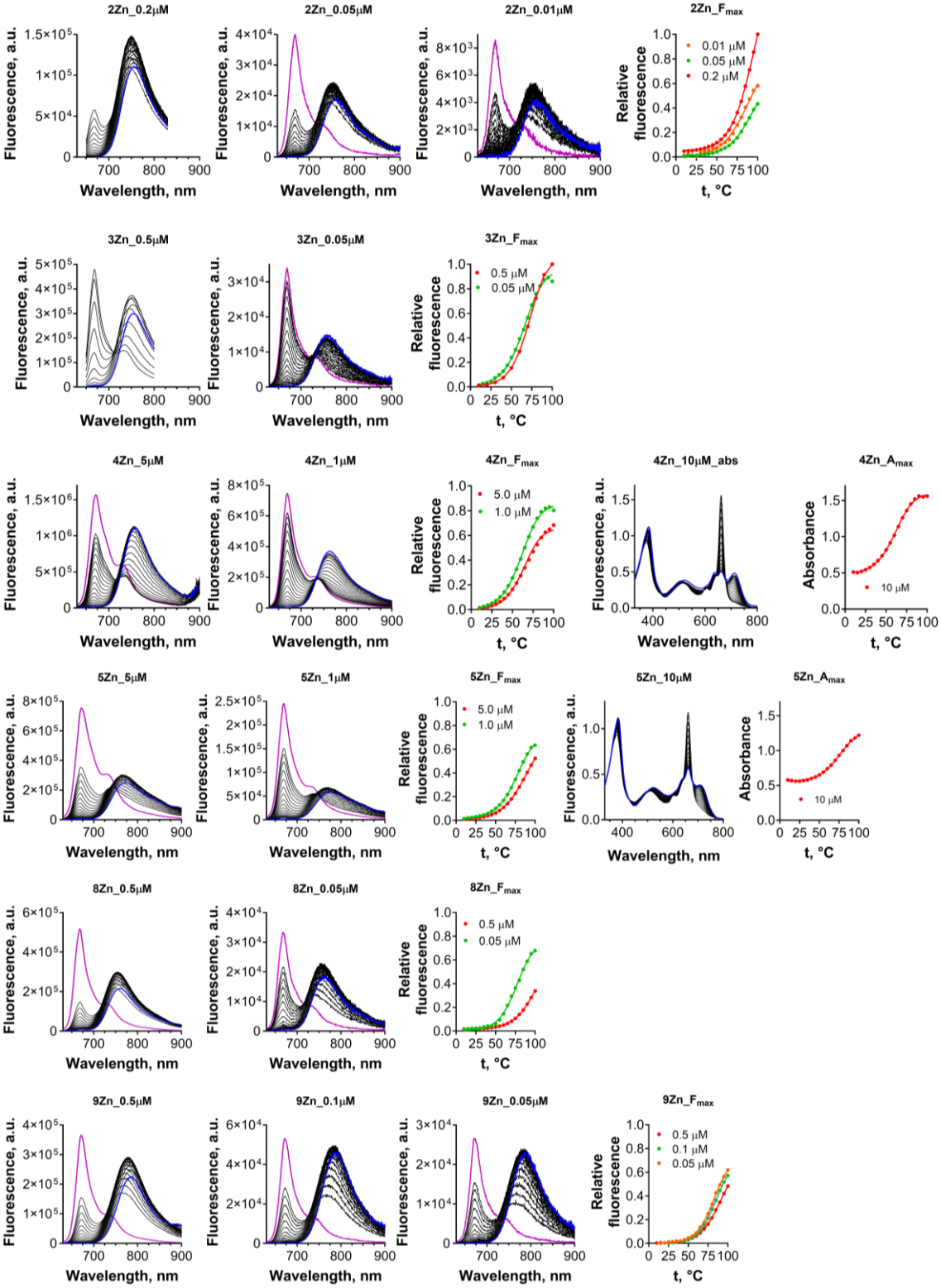

Figure S5. Changes in emission or absorption spectra of AzaPcs in toluene as a function of temperature (blue line belongs to starting spectrum at 10°C). After reaching 100°C, pyridine (25 mL of pyridine (0.12 M)) was also added to assure full monomerization (purple line) and was considered as maximum fluorescence of monomer. In plot graphs, dots always show experimental data and curves represent fits of the binding model.

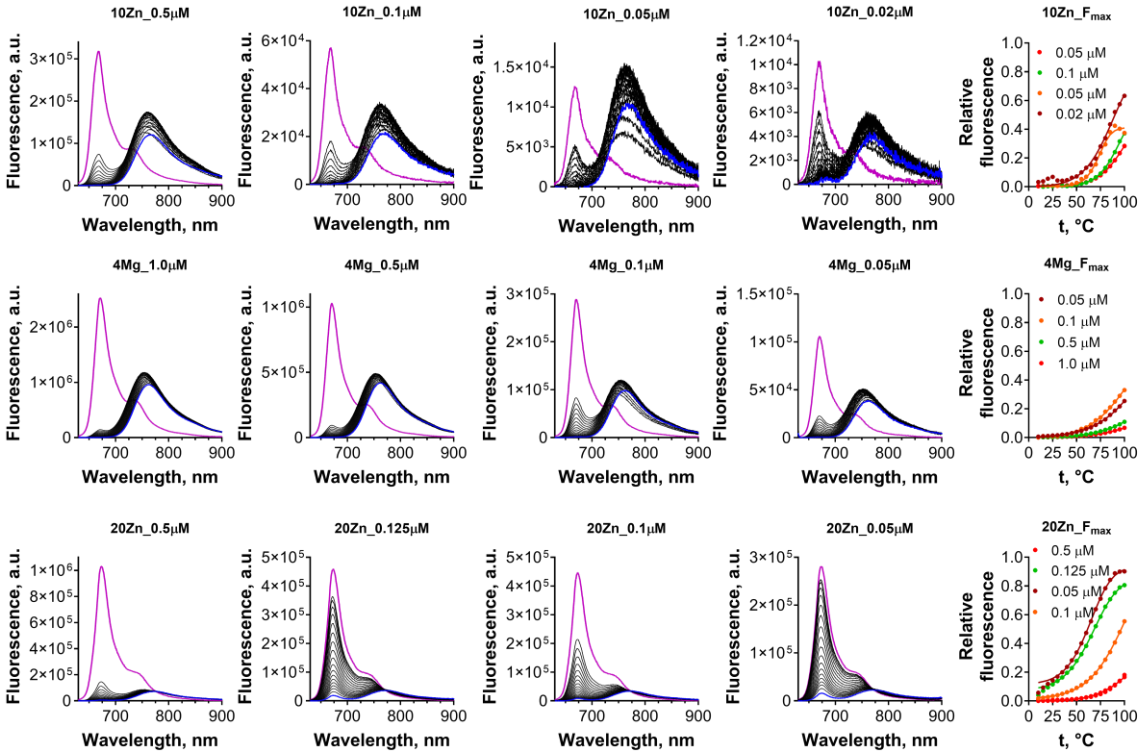

Figure S6. Changes in emission spectra of AzaPcs in toluene as a function of temperature (blue line belongs to starting spectrum at 10°C). After reaching 100°C, pyridine (25 mL of pyridine (0.12 M)) was also added to assure full monomerization (purple line) and was considered as maximum fluorescence of monomer. In plot graphs, dots always show experimental data and curves represent fits of the binding model.

Absorption and emission spectra from titrations

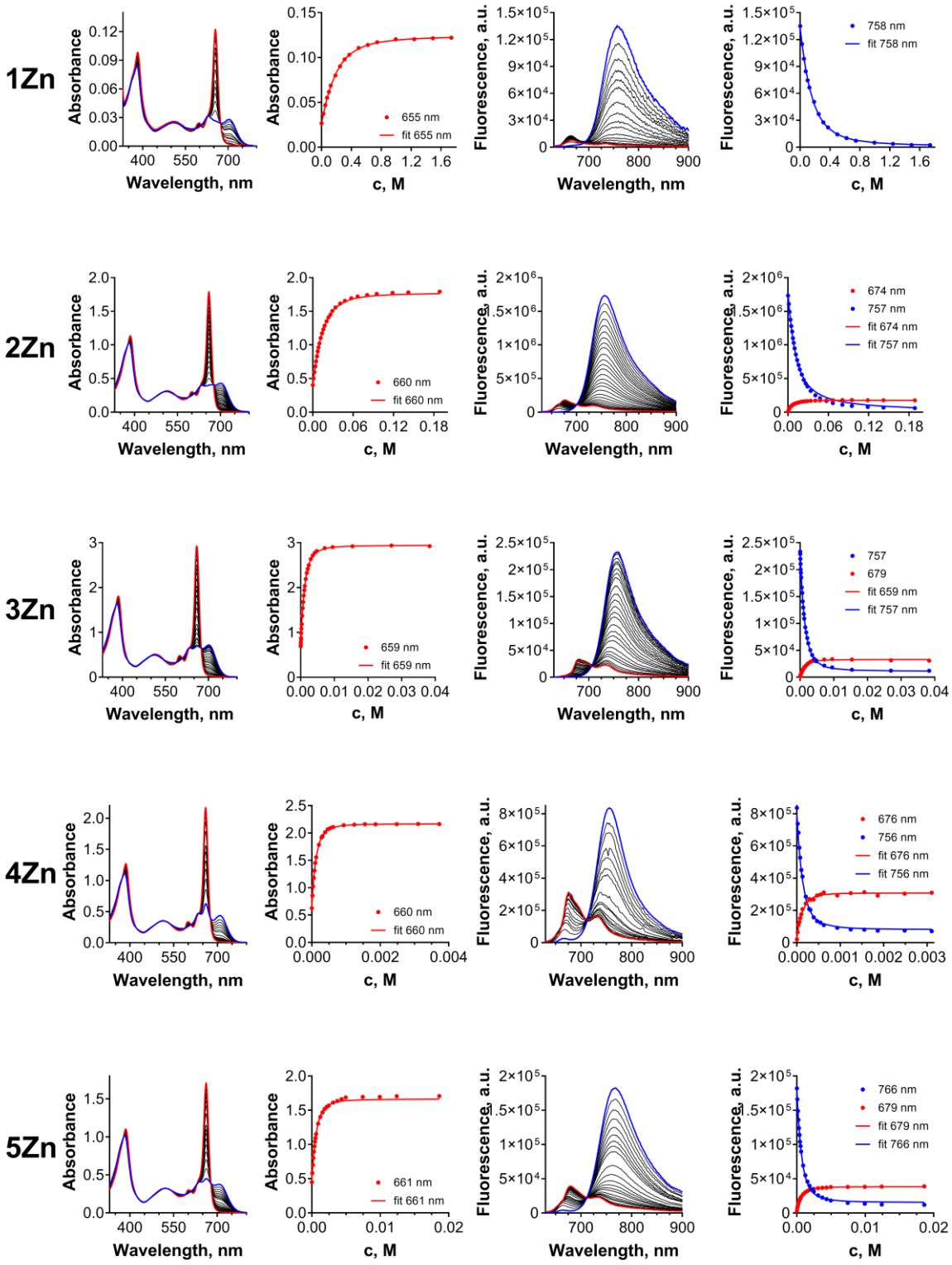

Figure S7. Titration of AzaPcs **1Zn**-**5Zn** in toluene by addition of pyridine. In plot graphs, dots always show experimental data and curves show mathematical fit. Concentration of AzaPc solutions was 1 µM for **1Zn**; 10 µM for **2Zn**, **4Zn** and **5Zn**; 15 µM for **3Zn**. In plot graphs, dots always show experimental data and curves represent fits of the binding model.

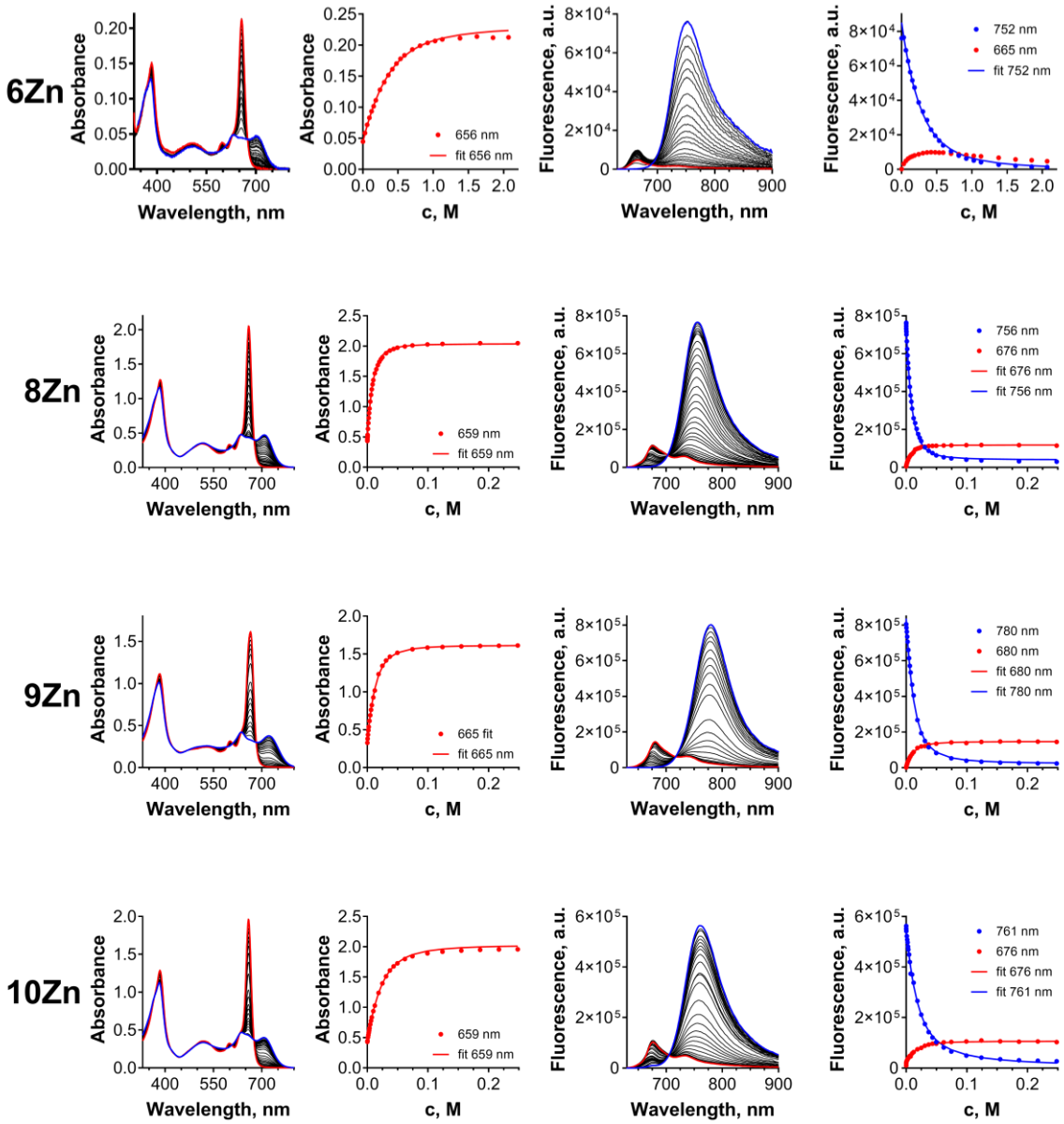

Figure S8. Titration of AzaPcs **5Zn**, **6Zn**, **8**-**10Zn** in toluene by addition of pyridine. In plot graphs, dots always show experimental data and curves show mathematical fit. Concentration of AzaPc solutions was 1 µM for **6Zn**; 10 µM for **5Zn**, **8-10Zn**. In plot graphs, dots always show experimental data and curves represent fits of the binding model.

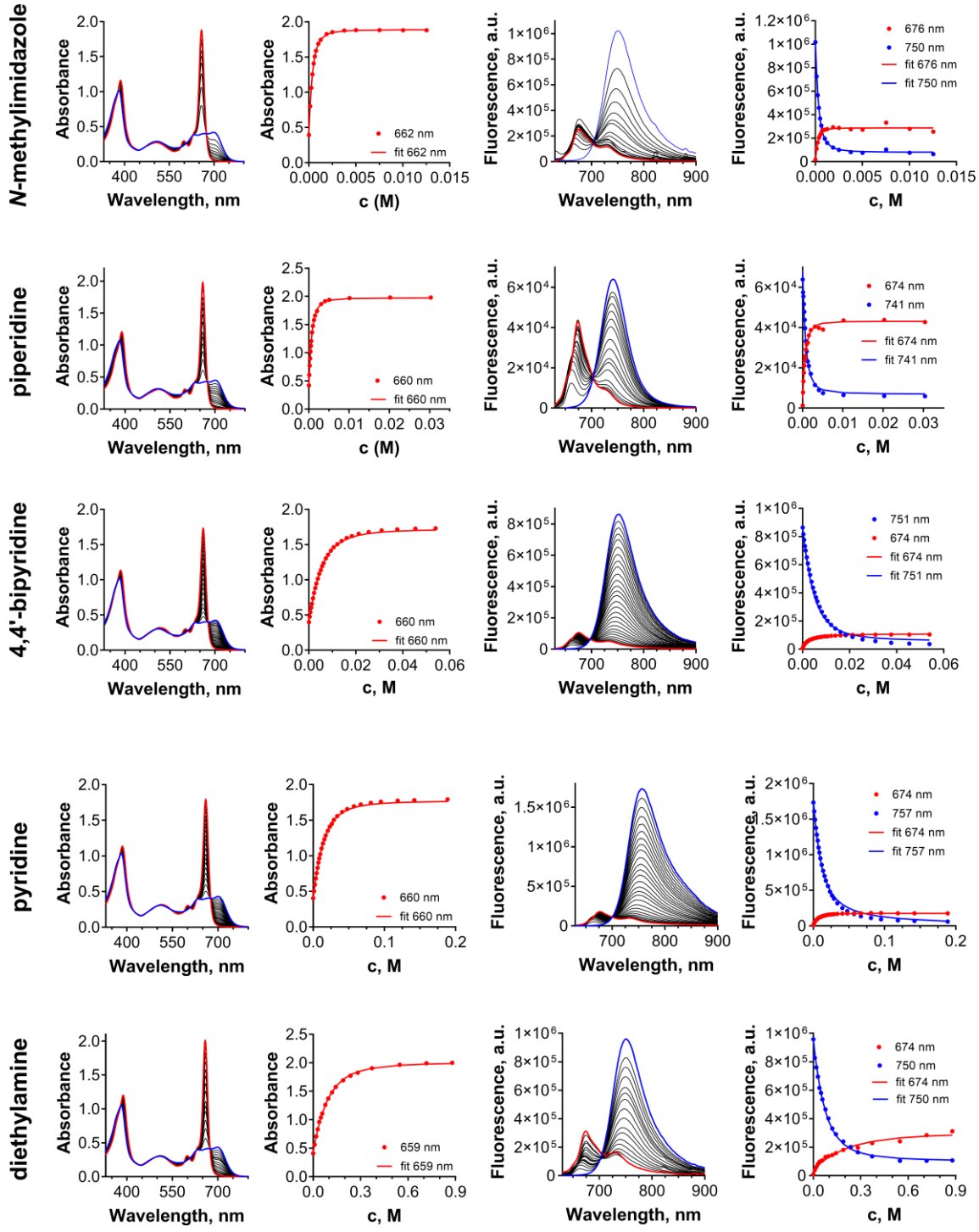

Figure S9. Titration of AzaPc **2Zn** (10 μM) in toluene by addition of different ligands. In plot graphs, dots always show experimental data and curves represent fits of the binding model.

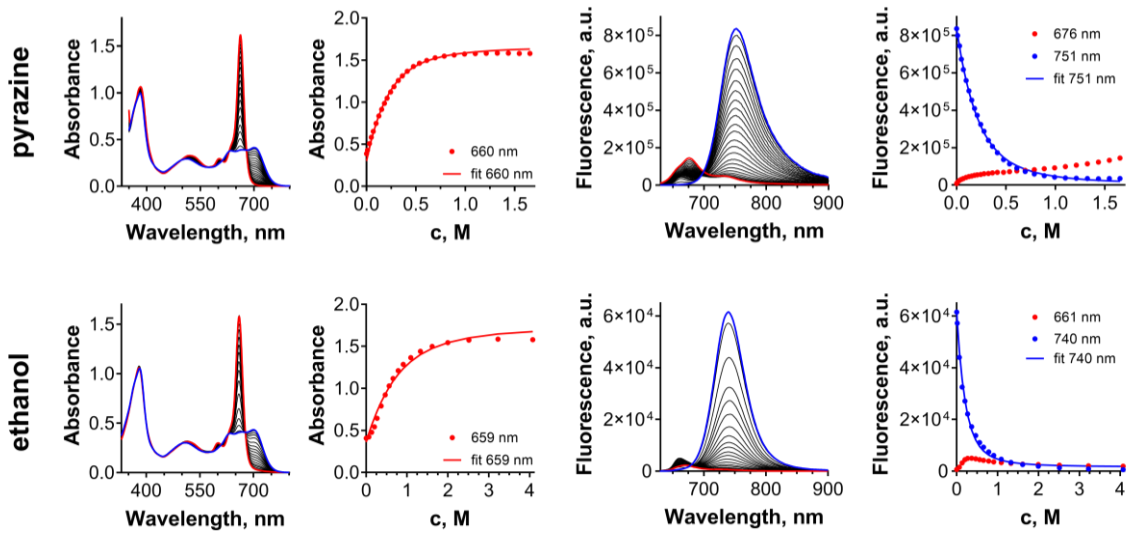

Figure S10. Titration of AzaPc **2Zn** (10 µM) in toluene by addition of different ligands. In plot graphs, dots always show experimental data and curves represent fits of the binding model.

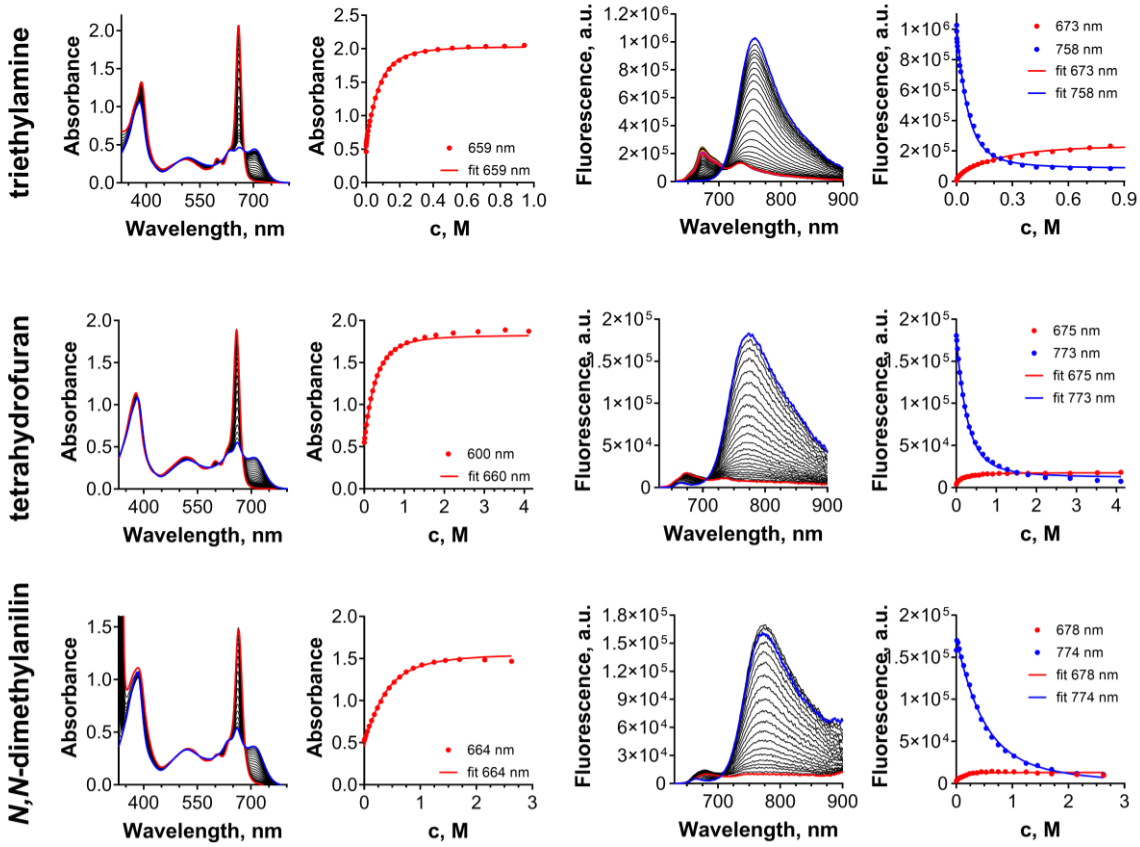

Figure S11. Titration of AzaPcs (10 µM) in toluene by addition of different ligands. In plot graphs, dots always show experimental data and curves show mathematical fit. AzaPc **3Zn** was used for triethylamine and AzaPc **5Zn** was used for tetrahydrofuran and *N,N*-dimethylaniline. In plot graphs, dots always show experimental data and curves represent fits of the binding model.

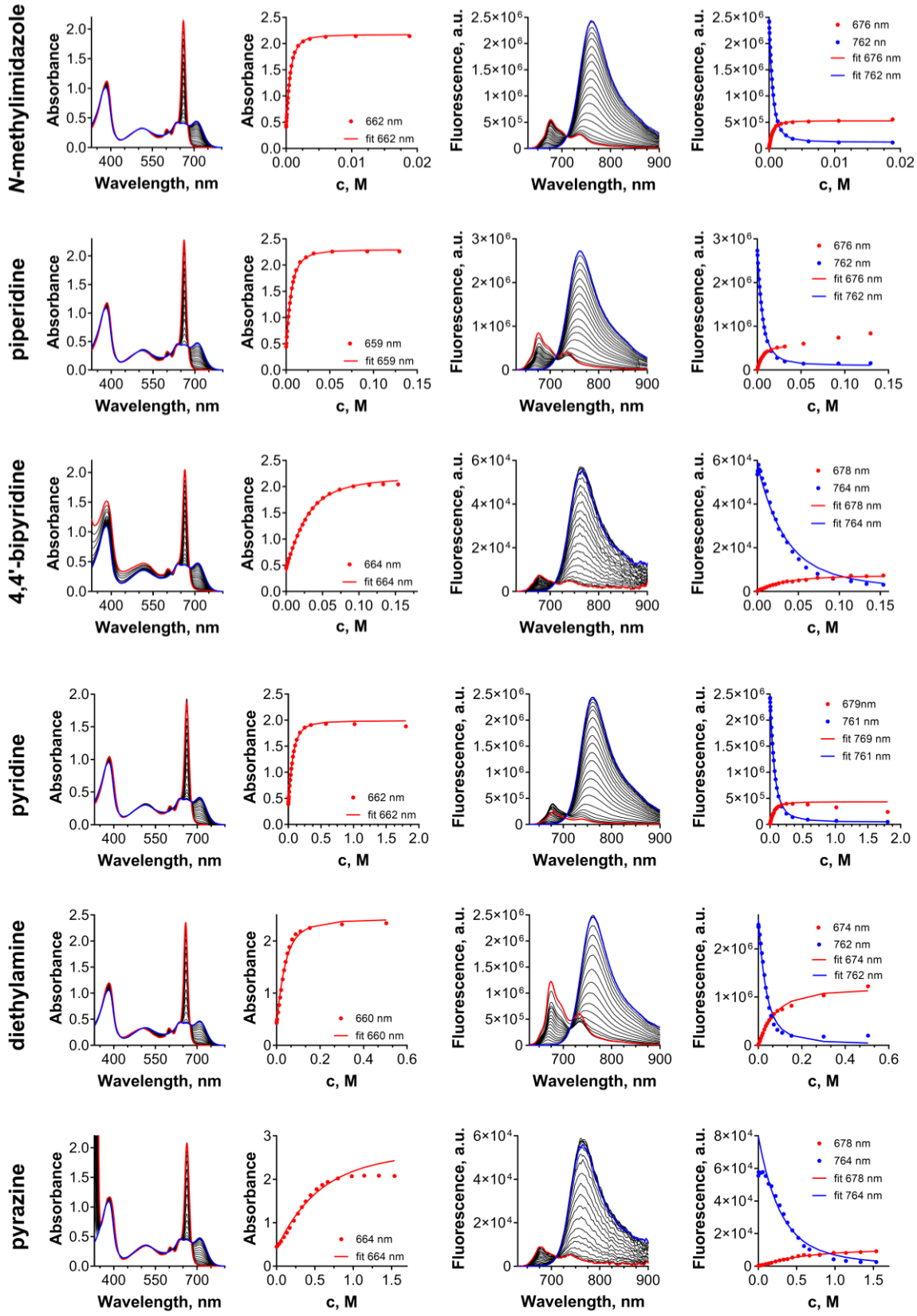

Figure S12. Titration of AzaPc **4Mg** (10 μM) in toluene by addition of different ligands. In plot graphs, dots always show experimental data and curves represent fits of the binding model.

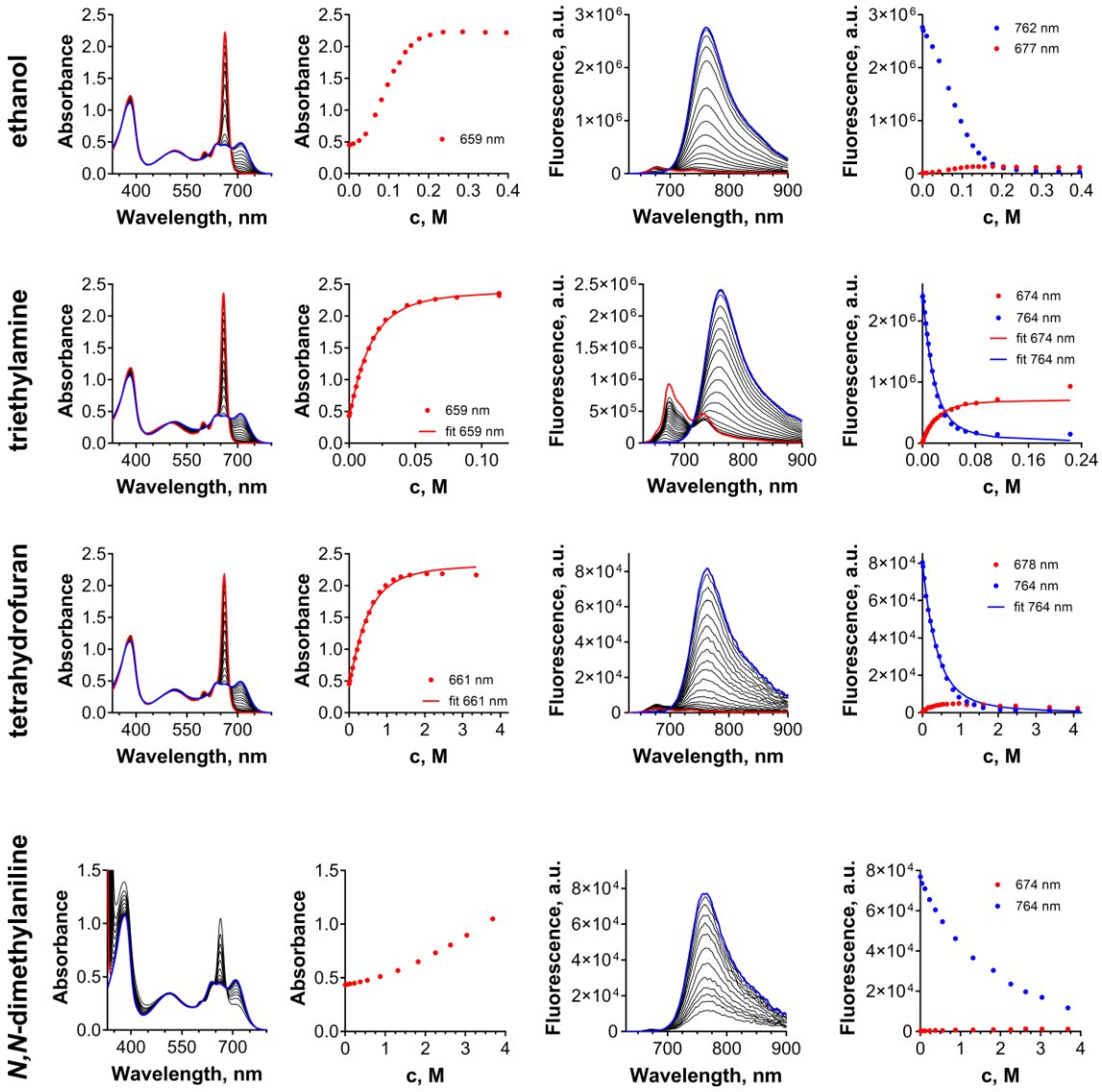

Figure S13. Titration of AzaPc **4Mg** in toluene by addition of different ligands. In plot graphs, dots always show experimental data and curves represent fits of the binding model.

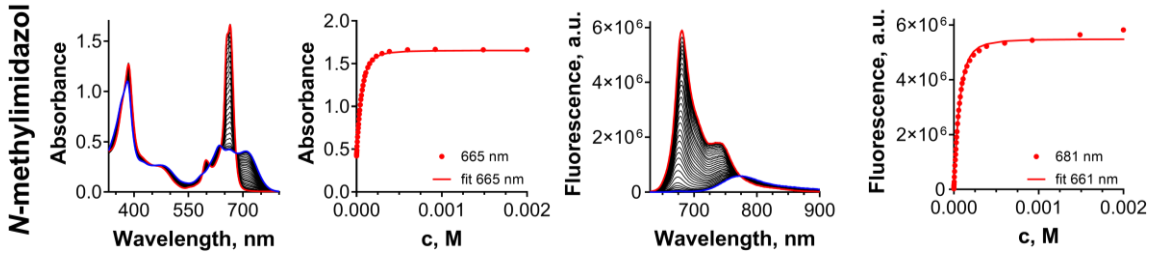

Figure S14. Titration of AzaPc **20Zn** (10 μM) in toluene by addition of *N*-methylimidazole. In plot graphs, dots always show experimental data and curves represent fits of the binding model.

Absorption and emission spectra from negative control

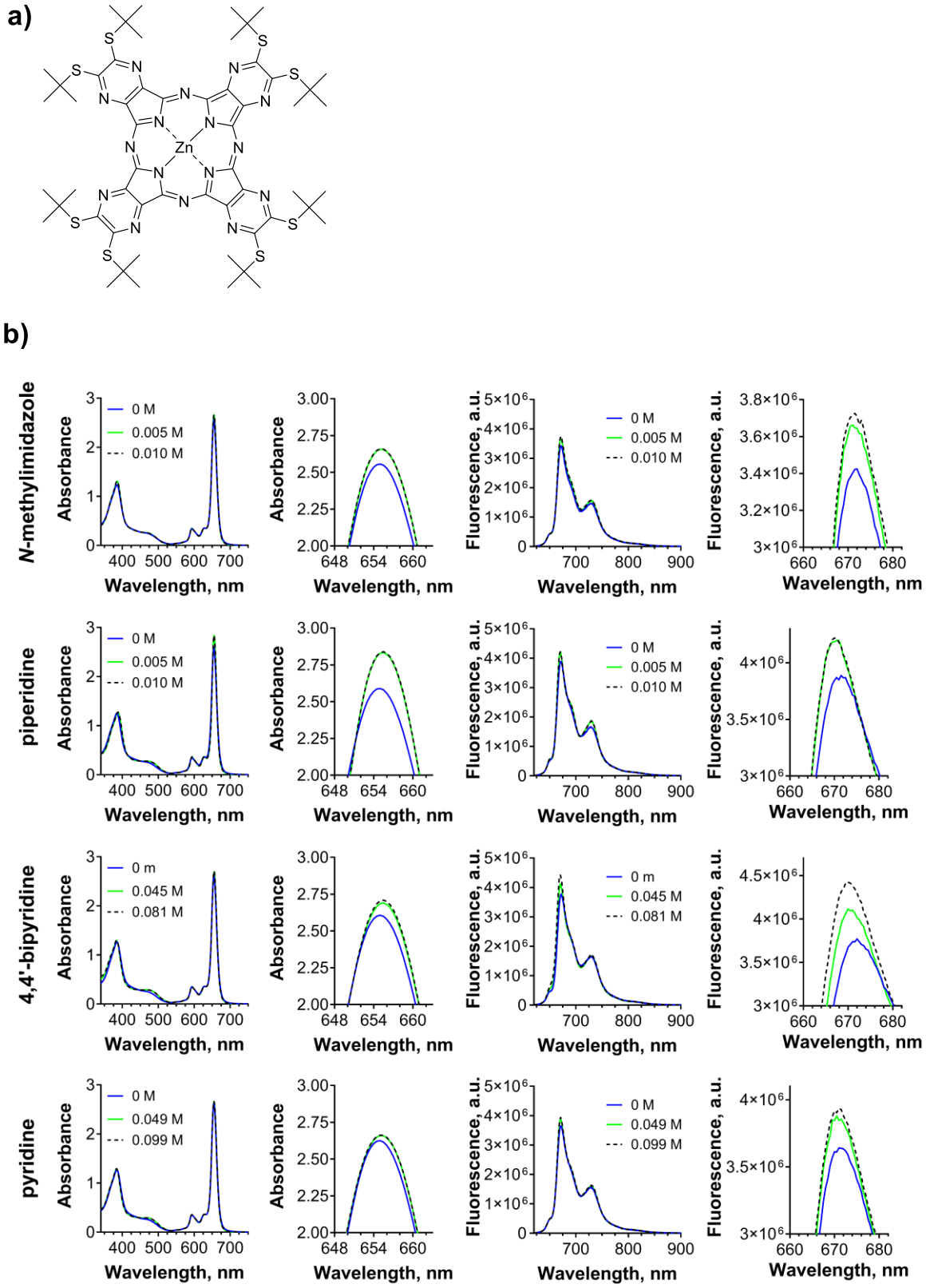

Figure S15. (a) Structure of 2,3,9,10,16,17,23,24-octakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyaninato zinc(II), and (b) its titration of toluene solution (10 µM) by addition of different ligands.

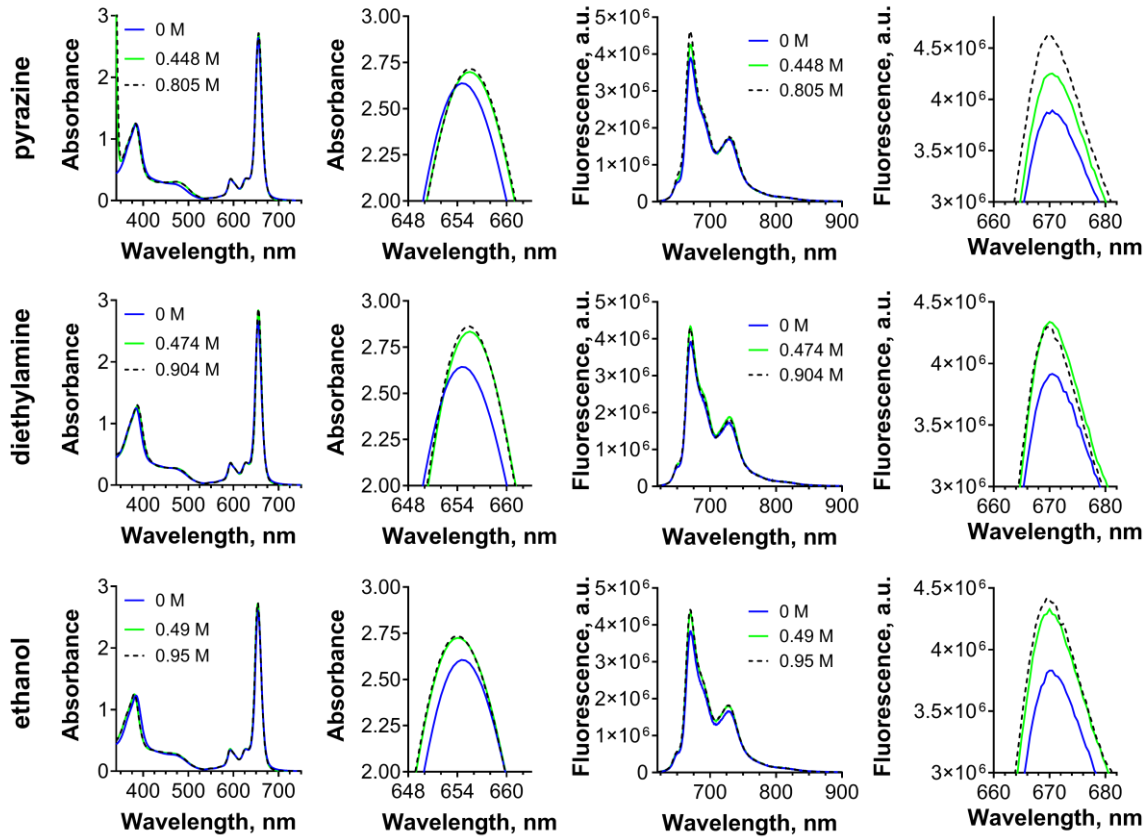

Figure S16. Titration of 2,3,9,10,16,17,23,24-octakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyaninato zinc(II) in toluene (10 μM) by addition of different ligands.

Association constants from literature

Table S1. Literature reported association constants K_1 between ZnPc or zinc(II)naphthalocyanine (ZnNc) and pyridine or NMI ligands. For detailed structures, the reader is referred to the original documents.

Type of ZnPc	Modification of ligand	Solvent	K_1 for pyridine, M^{-1}	K_1 for NMI, M^{-1}	Ref.
Dialkylamino AzaPcs	-	Toluene	1.54×10^5	5.82×10^6	This work
20Zn	-	Toluene	6.05×10^4	9.73×10^6	This work
$(BuO)_8ZnPc$	-	Toluene	-	2.85×10^5	[1]
$(t\text{Bu})_4ZnPc$	-	Toluene	6.1×10^3	-	[2]
$(t\text{Bu})_4ZnPc$	AzaBODIPY	*o*-dichlorobenzene	7.8×10^4	1.3×10^5	[3]
$(t\text{Bu})_4ZnNc$	AzaBODIPY	*o*-dichlorobenzene	2.2×10^4	2.3×10^5	[3]
$(C_7H_{15}O)_4ZnPc$	SubPc(3-OPy)	DMF	6.1×10^3	-	[4]
$(C_7H_{15}O)_4ZnPc$	SubPc(4-OPy)	DMF	3.1×10^3	-	[4]
$(t\text{Bu})_4ZnPc$	C_{60}	n.a.	4.8×10^3	-	[5]
$(t\text{Bu})_4ZnPc$	AuPorphyrin	*o*-dichlorobenzene	2.94×10^4	-	[6]
$(RSO_2)_8ZnPc$	Corrole	$CDCl_3$	$>10^6$	-	[7]

NMR Spectra

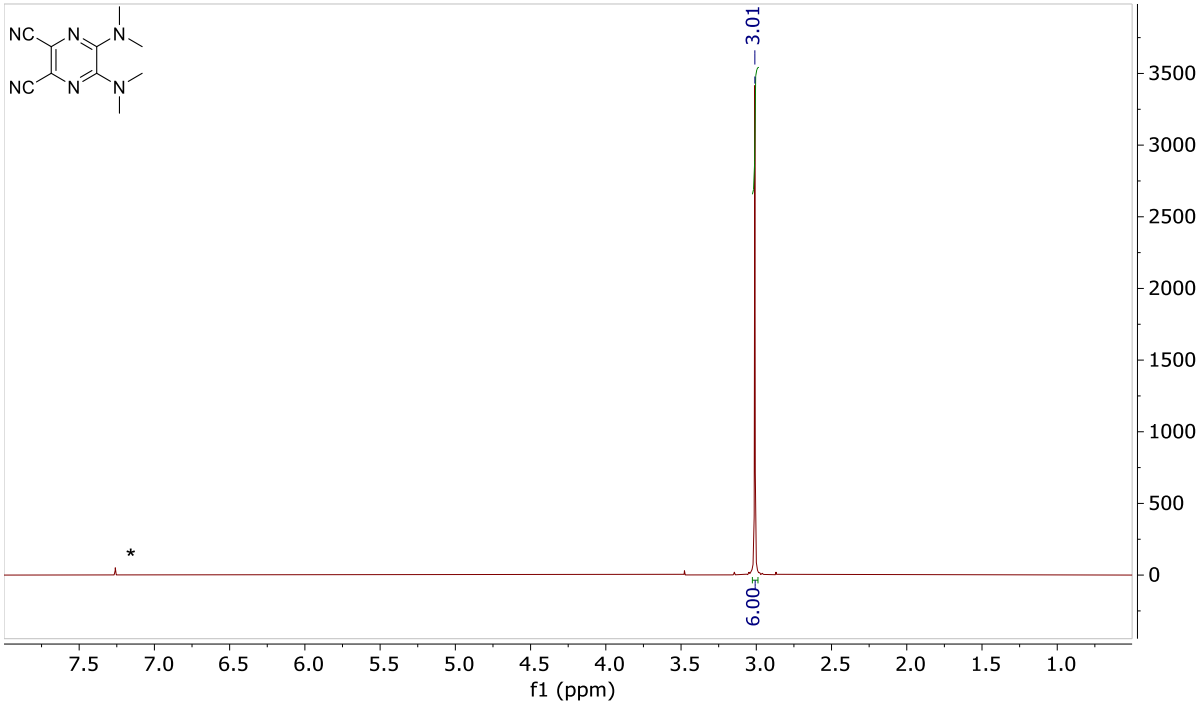

Figure S17. ^{1}H NMR (500 MHz, $CDCl_3$) of **12**. Asterisk marks residual of solvents.

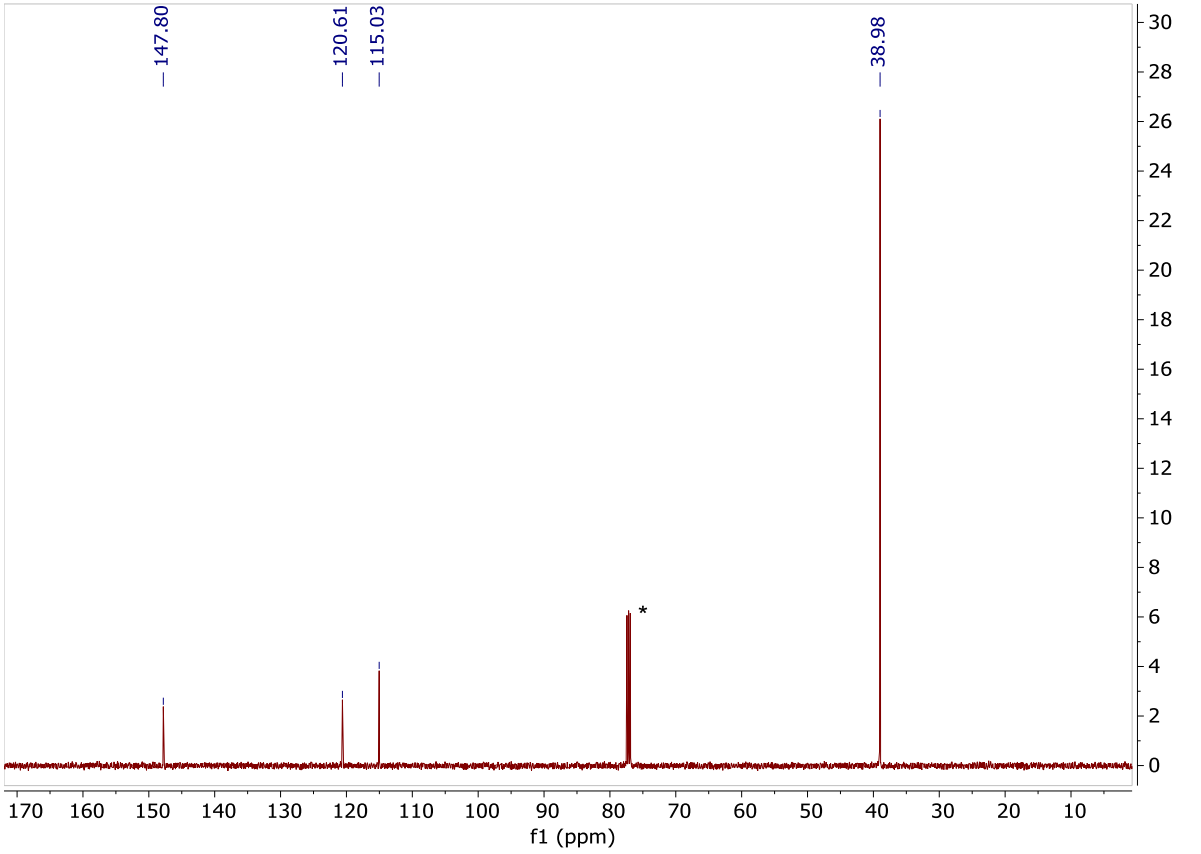

Figure S18. ^{13}C NMR (126 MHz, $CDCl_3$) of **12**. Asterisk marks residual of solvents.

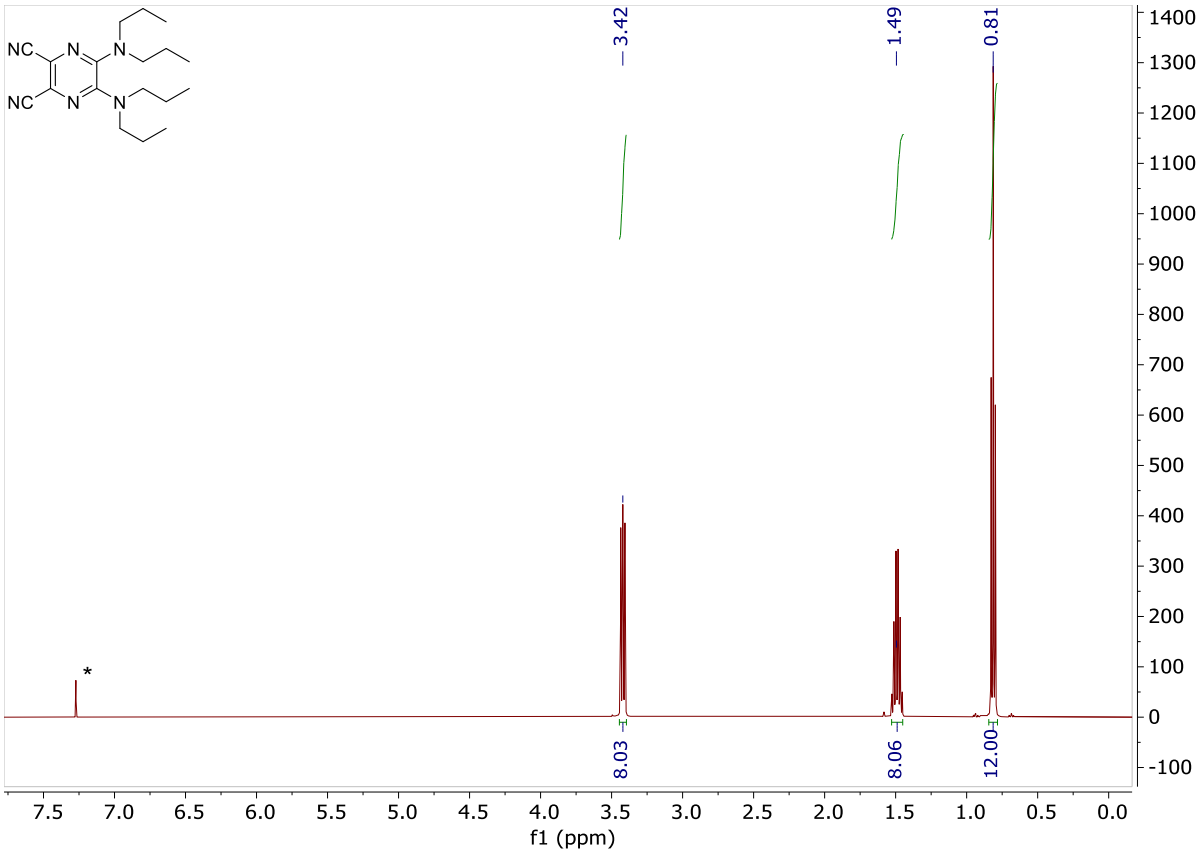

Figure S19. ^{1}H NMR (500 MHz, $CDCl_3$) of **13**. Asterisk marks residual of solvents.

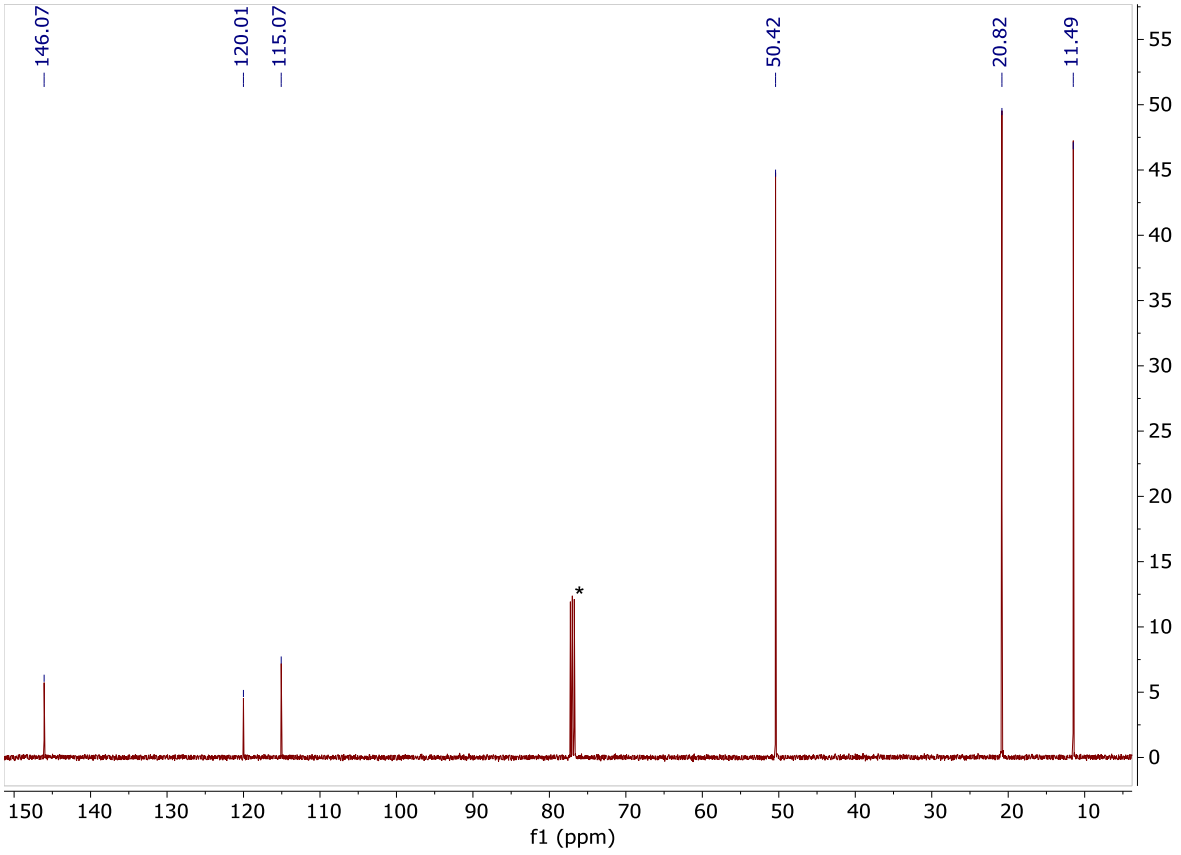

Fig S20. ^{13}C NMR (126 MHz, $CDCl_3$) of **13**. Asterisk marks residual of solvents.

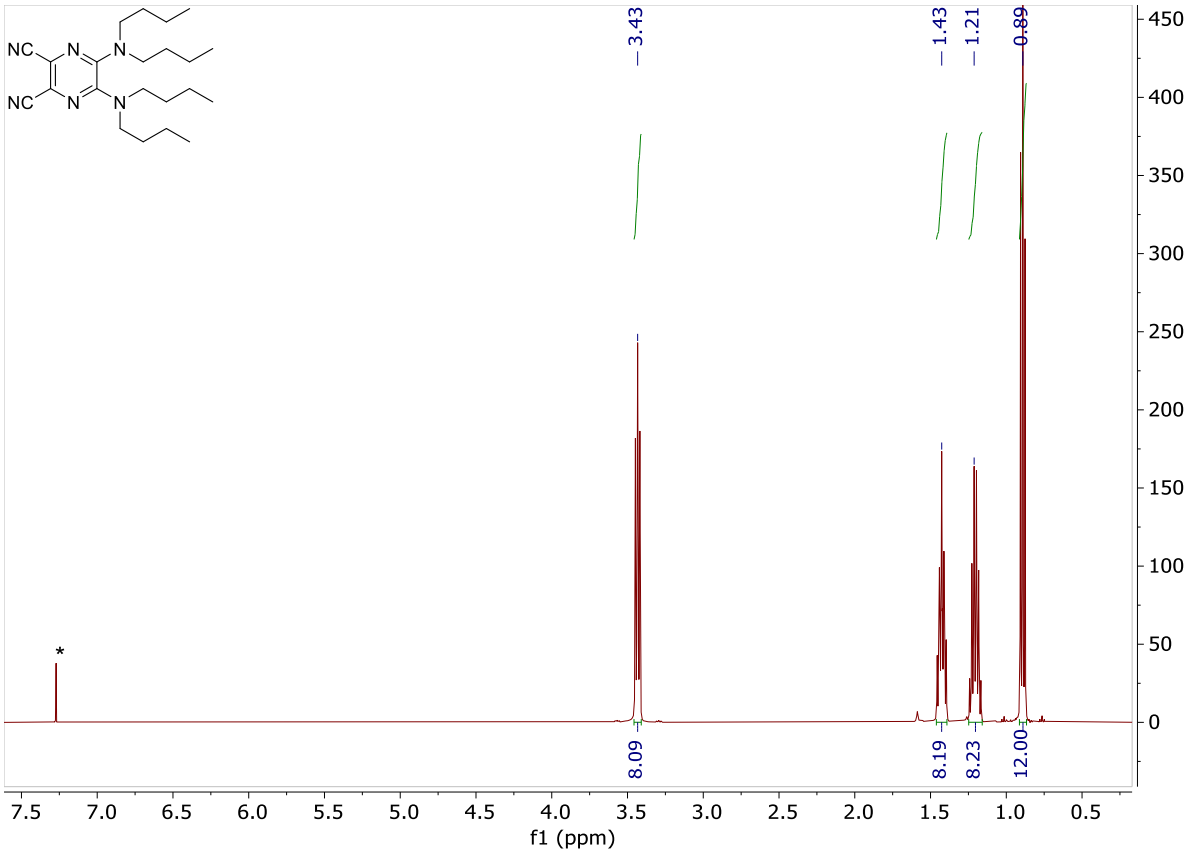

Fig S21. ^{1}H NMR (500 MHz, $CDCl_3$) of **14**. Asterisk marks residual of solvents.

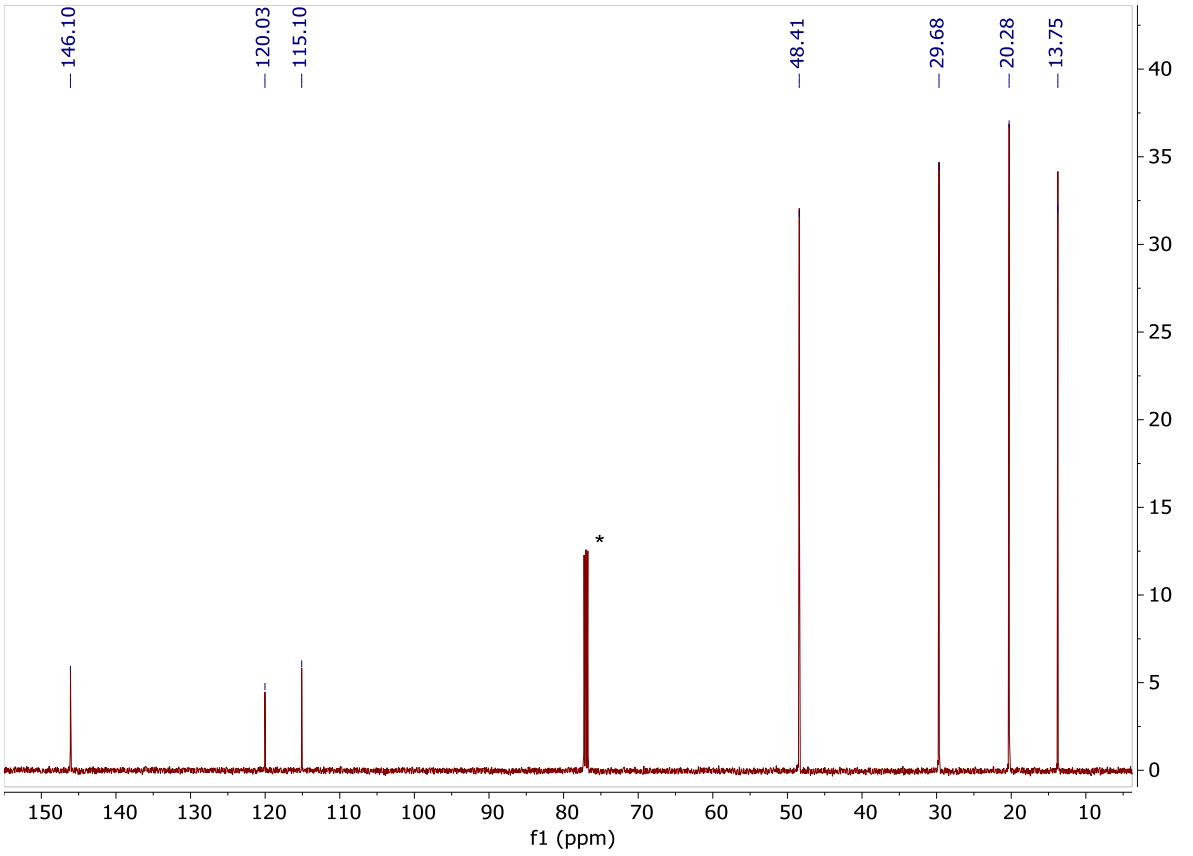

Fig S22. ^{13}C NMR (126 MHz, $CDCl_3$) of **14**. Asterisk marks residual of solvents.

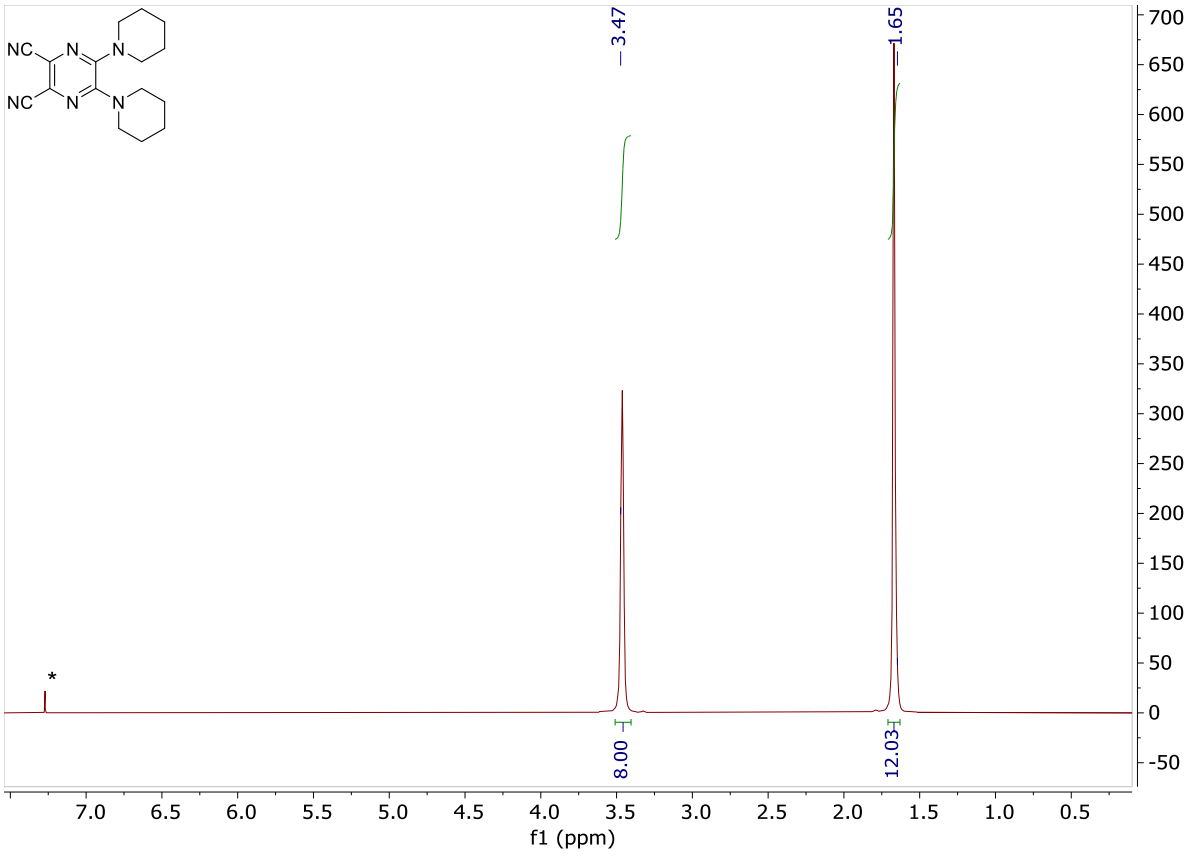

Fig S23. ^{1}H NMR (500 MHz, $CDCl_3$) of **15**. Asterisk marks residual of solvents.

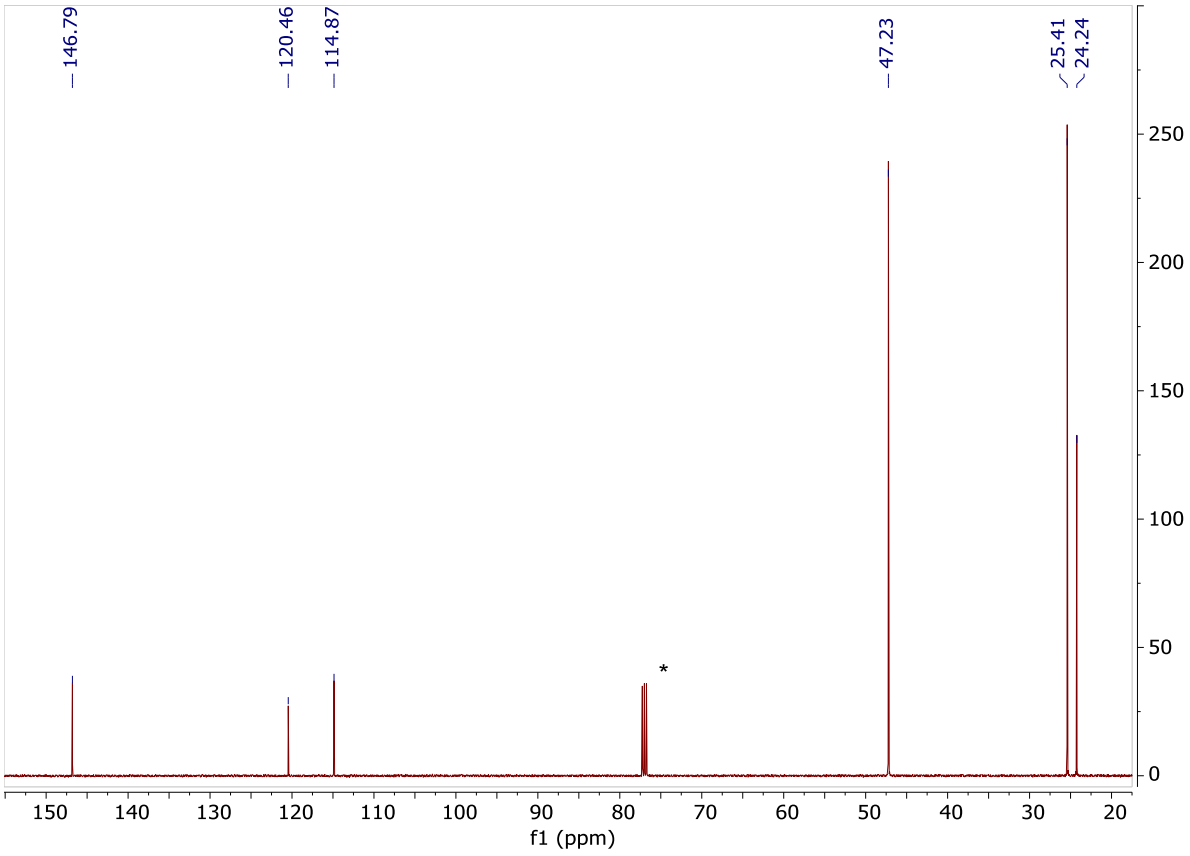

Fig S24. ^{13}C NMR (126 MHz, $CDCl_3$) of **15**. Asterisk marks residual of solvents.

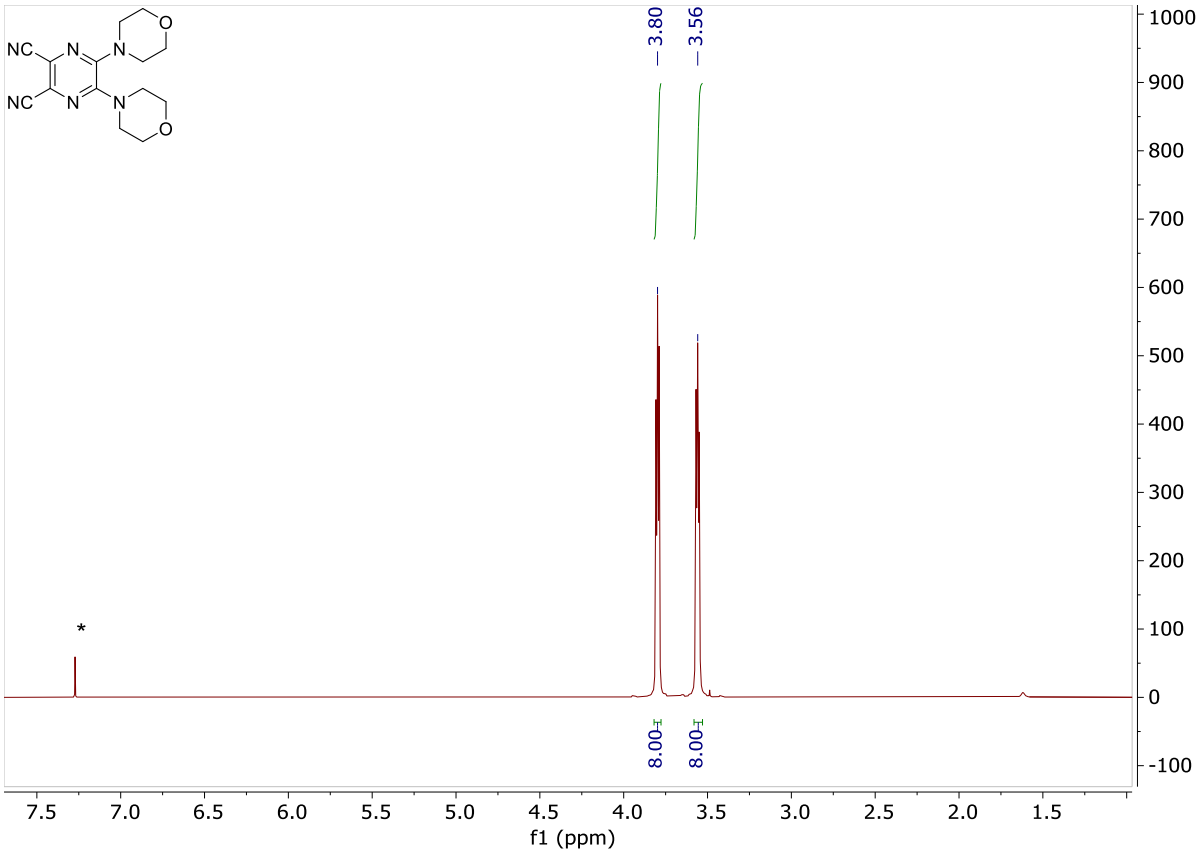

Fig S25. ^{1}H NMR (500 MHz, $CDCl_3$) of **16**. Asterisk marks residual of solvents.

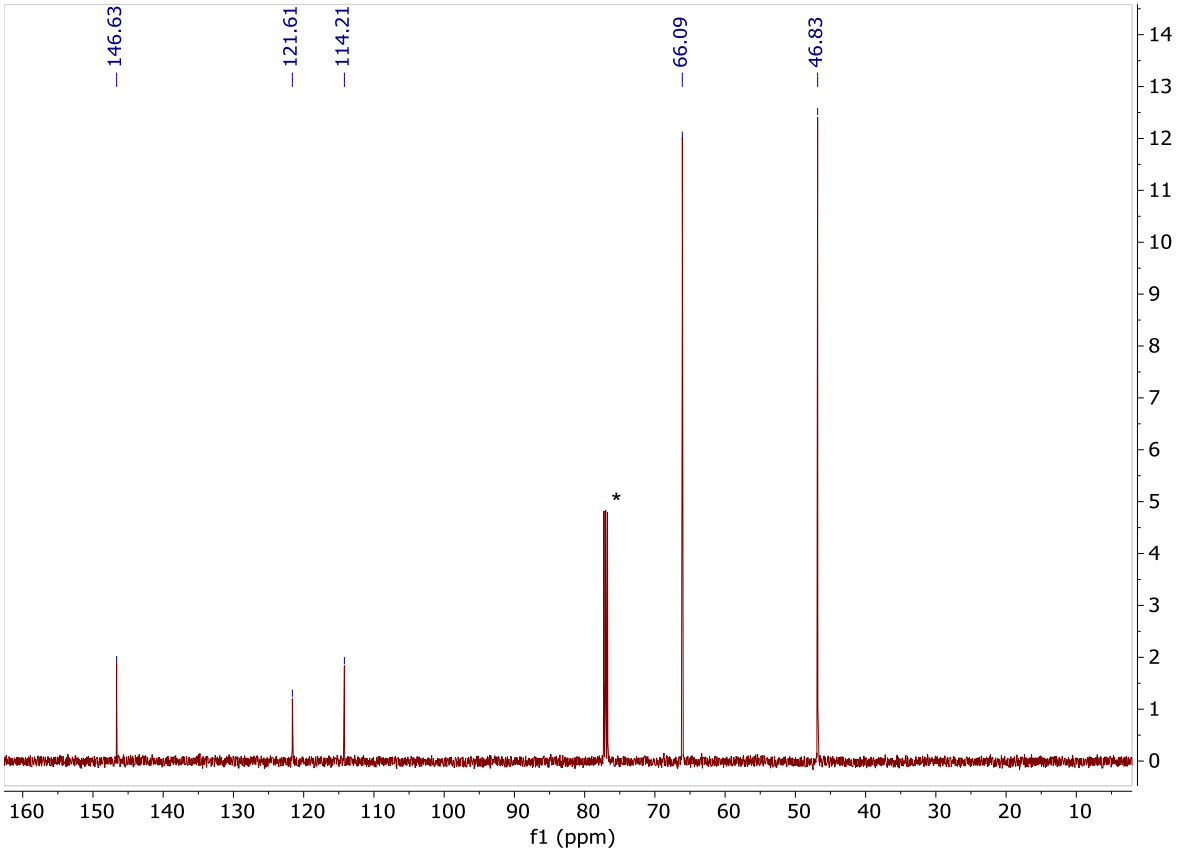

Fig S26. ^{13}C NMR (126 MHz, $CDCl_3$) of **16**. Asterisk marks residual of solvents.

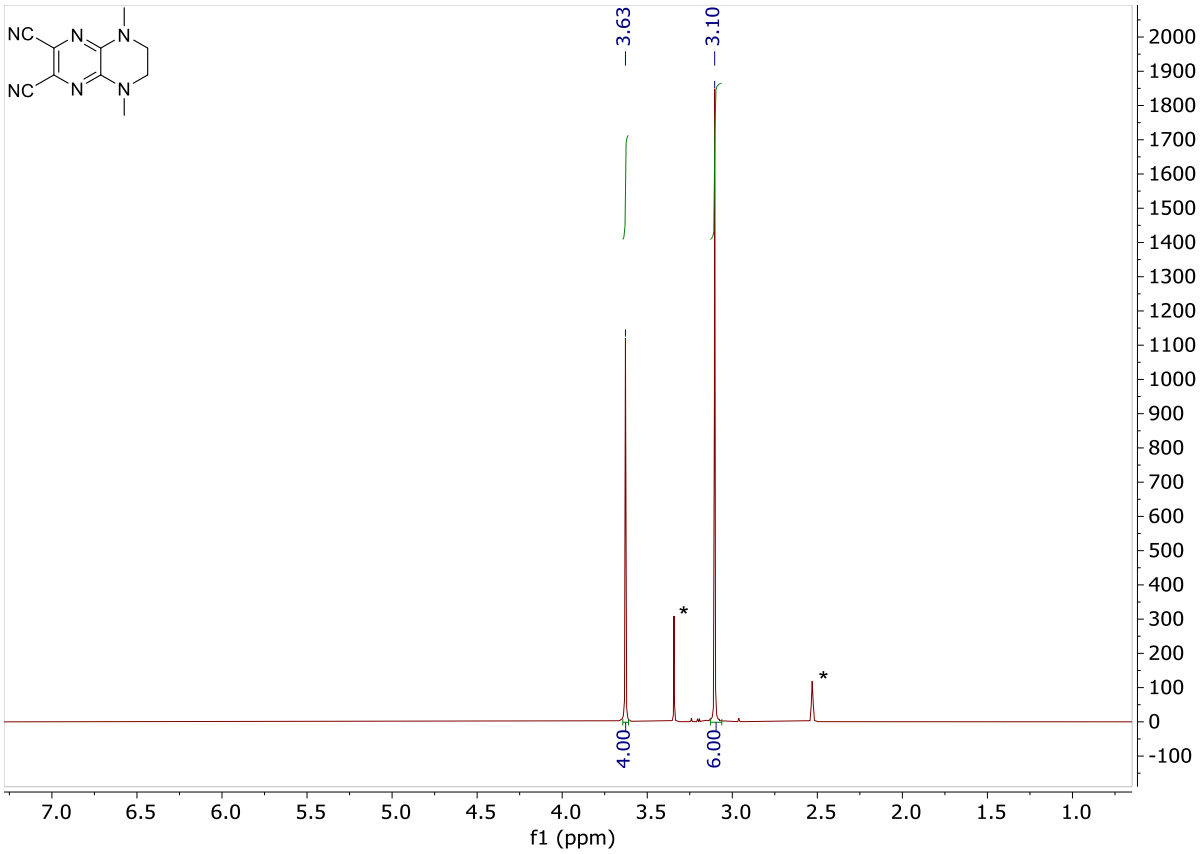

Fig S27. ^{1}H NMR (500 MHz, DMSO-d_6) of **17**. Asterisk marks residual of solvents.

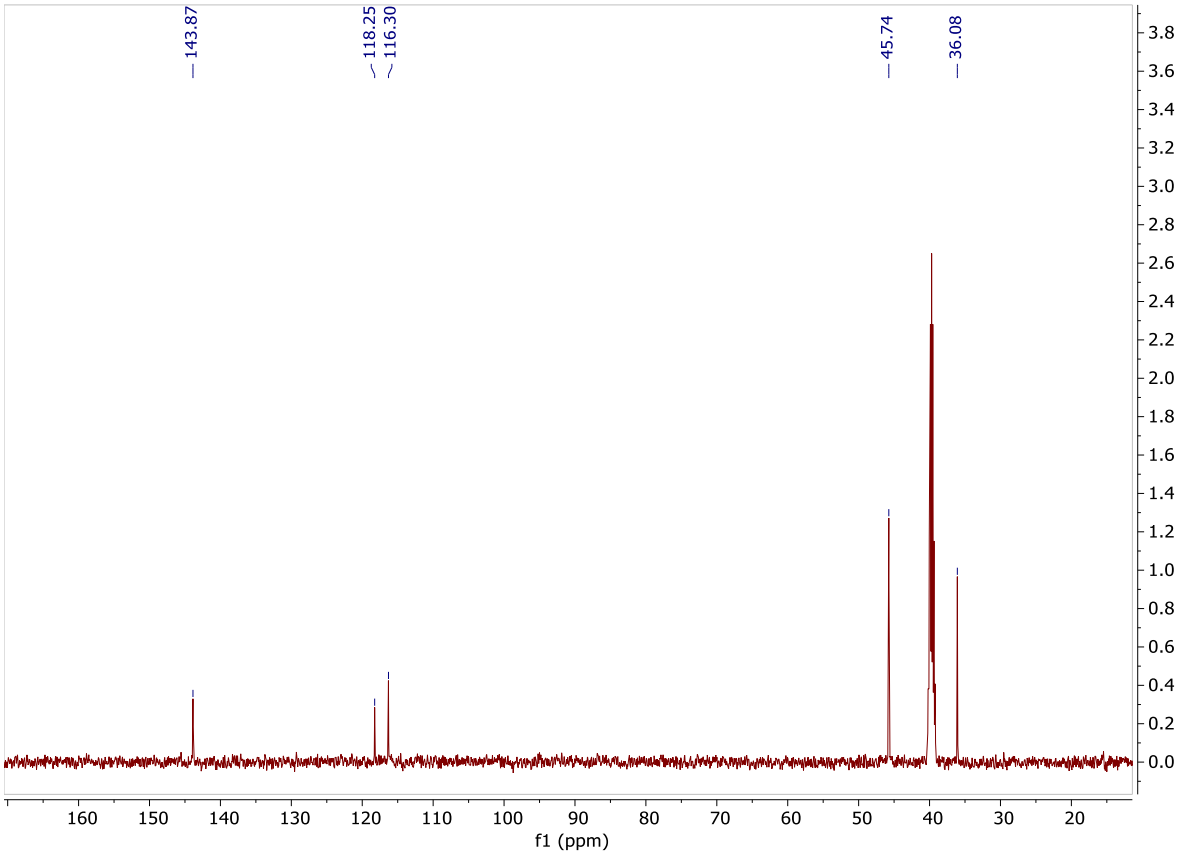

Fig S28. ^{13}C NMR (126 MHz, DMSO-d_6)of **17**. Asterisk marks residual of solvents.

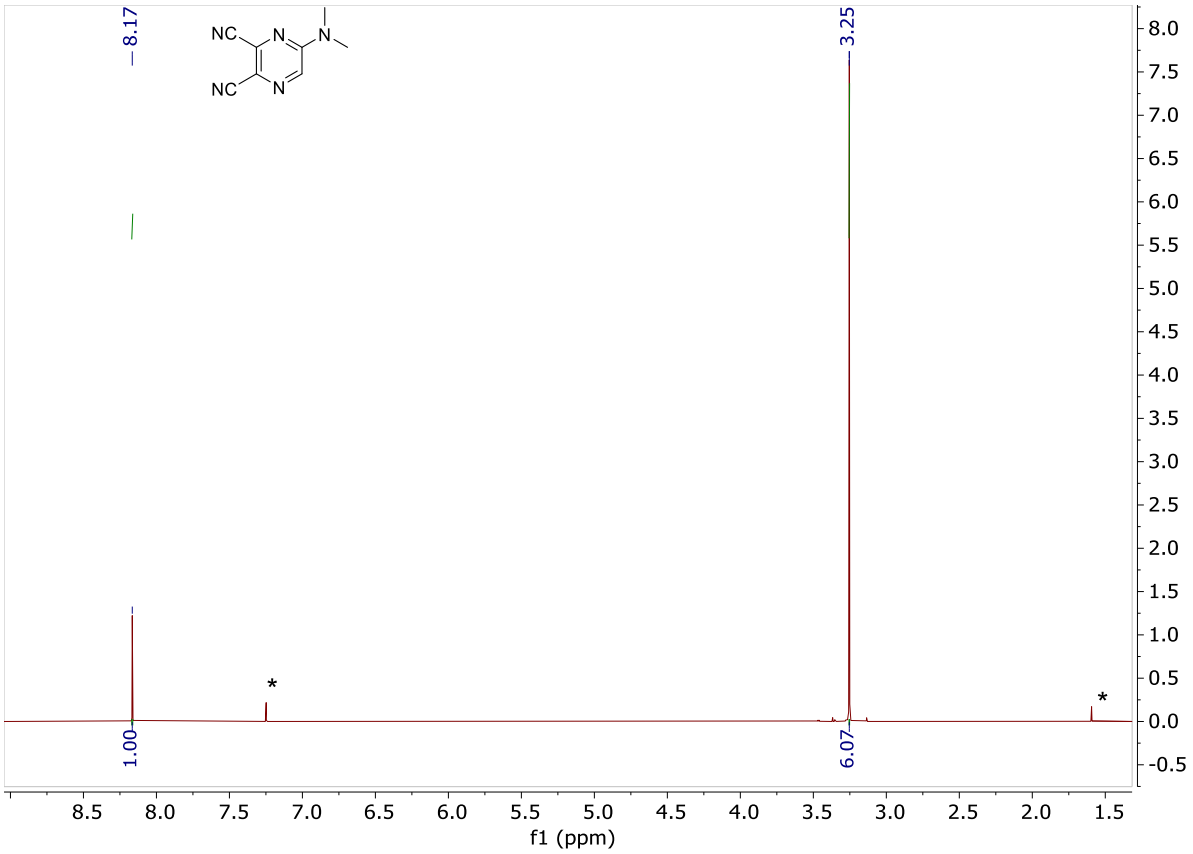

Fig S29. ^{1}H NMR (600 MHz, $CDCl_3$) of **19**. Asterisk marks residual of solvents.

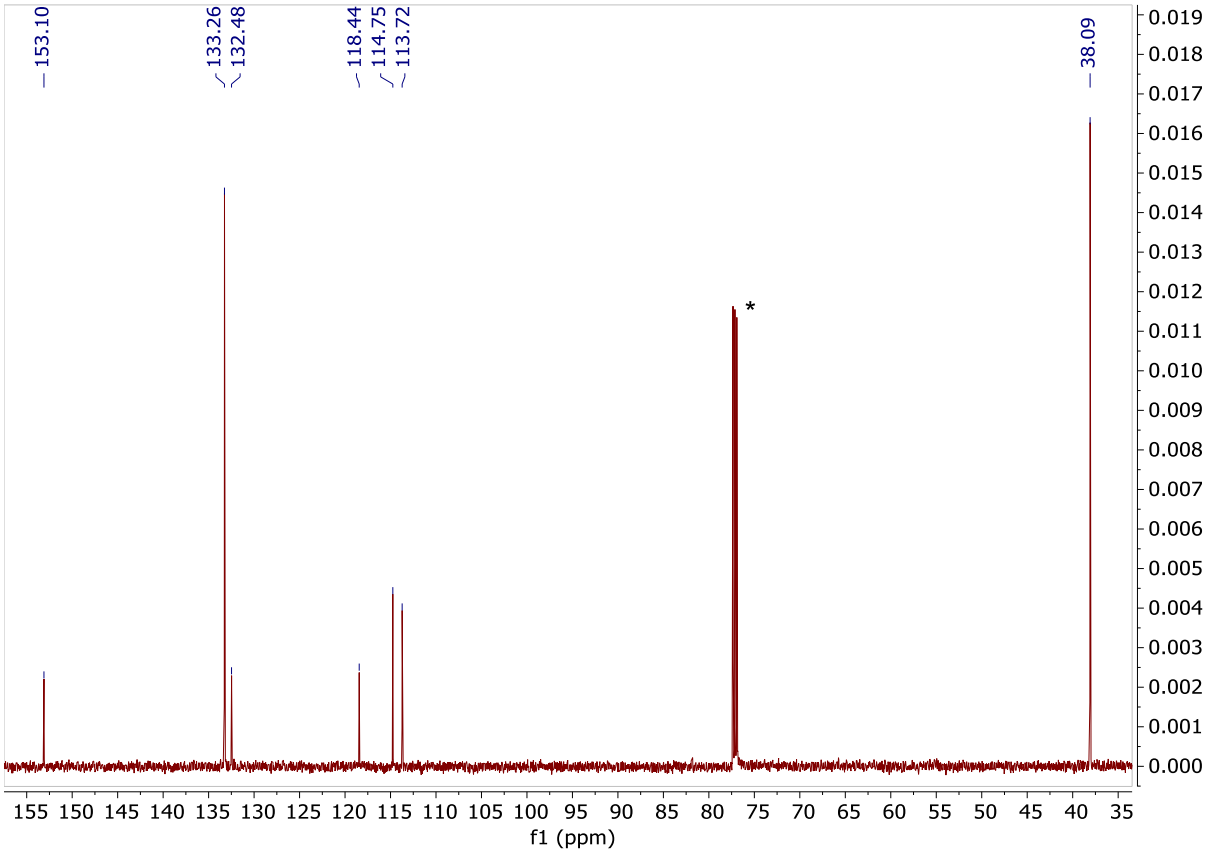

Fig S30. ^{13}C NMR (150 MHz, $CDCl_3$) of **19**. Asterisk marks residual of solvents.

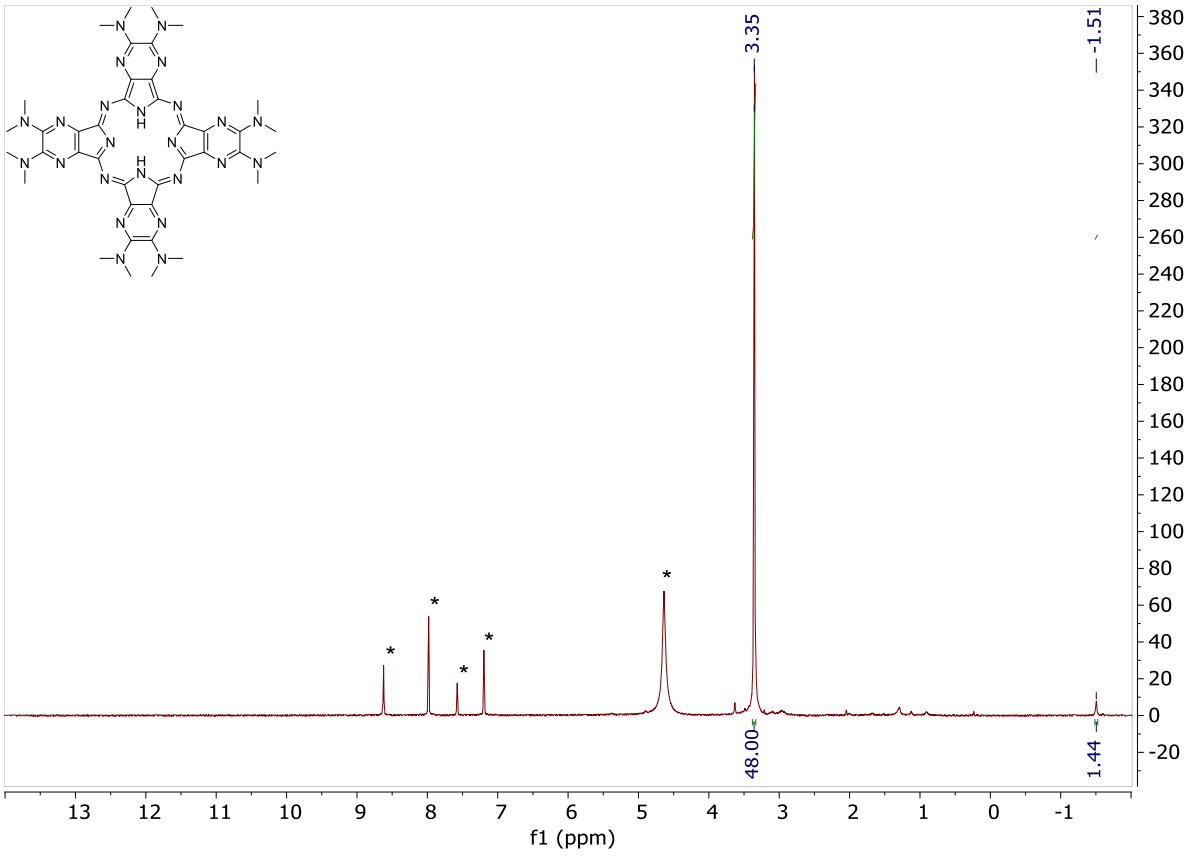

Fig S31. ^{1}H NMR (500 MHz, $CDCl_3$/pyridin-d_5 (3 : 1)) of **1H2**. Asterisk marks residual of solvents.

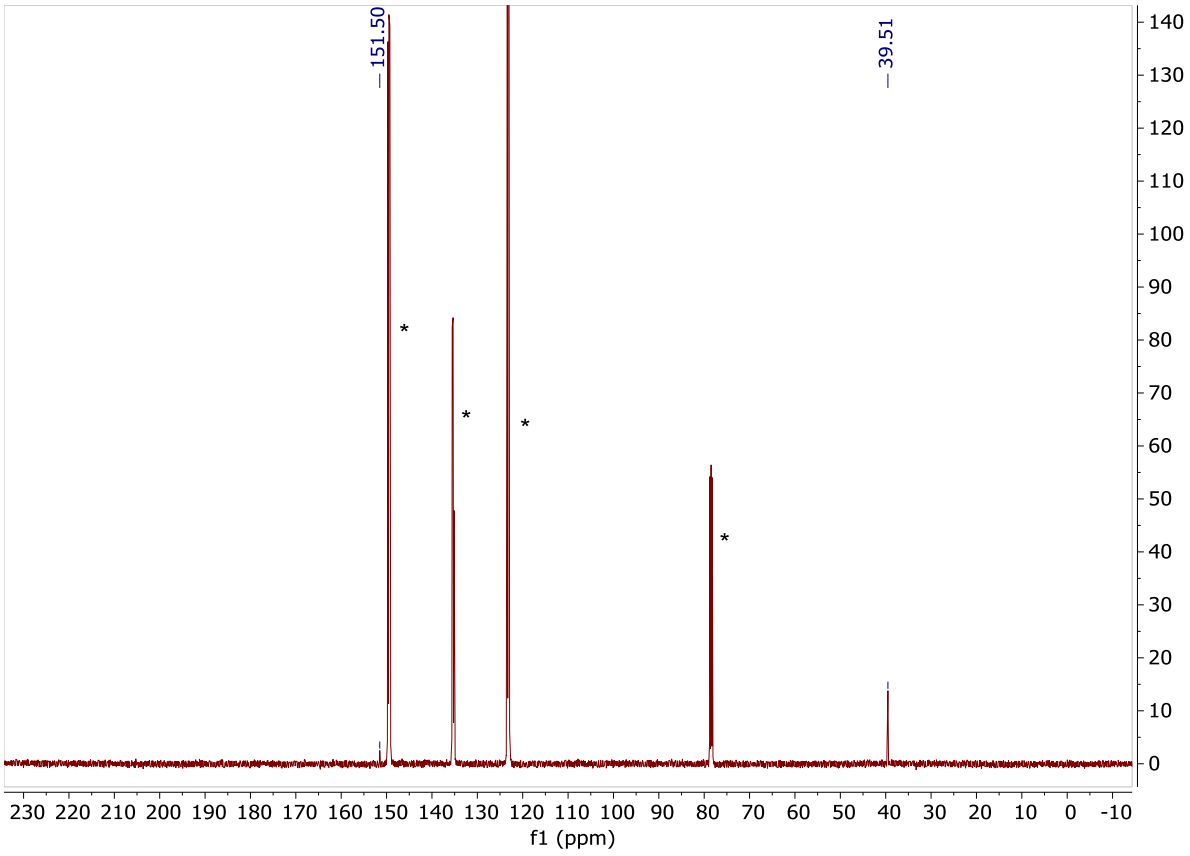

Fig S32. ^{13}C NMR (126 MHz, $CDCl_3$/pyridin-d_5 (3 : 1)) of **1H2**. Asterisk marks residual of solvents.

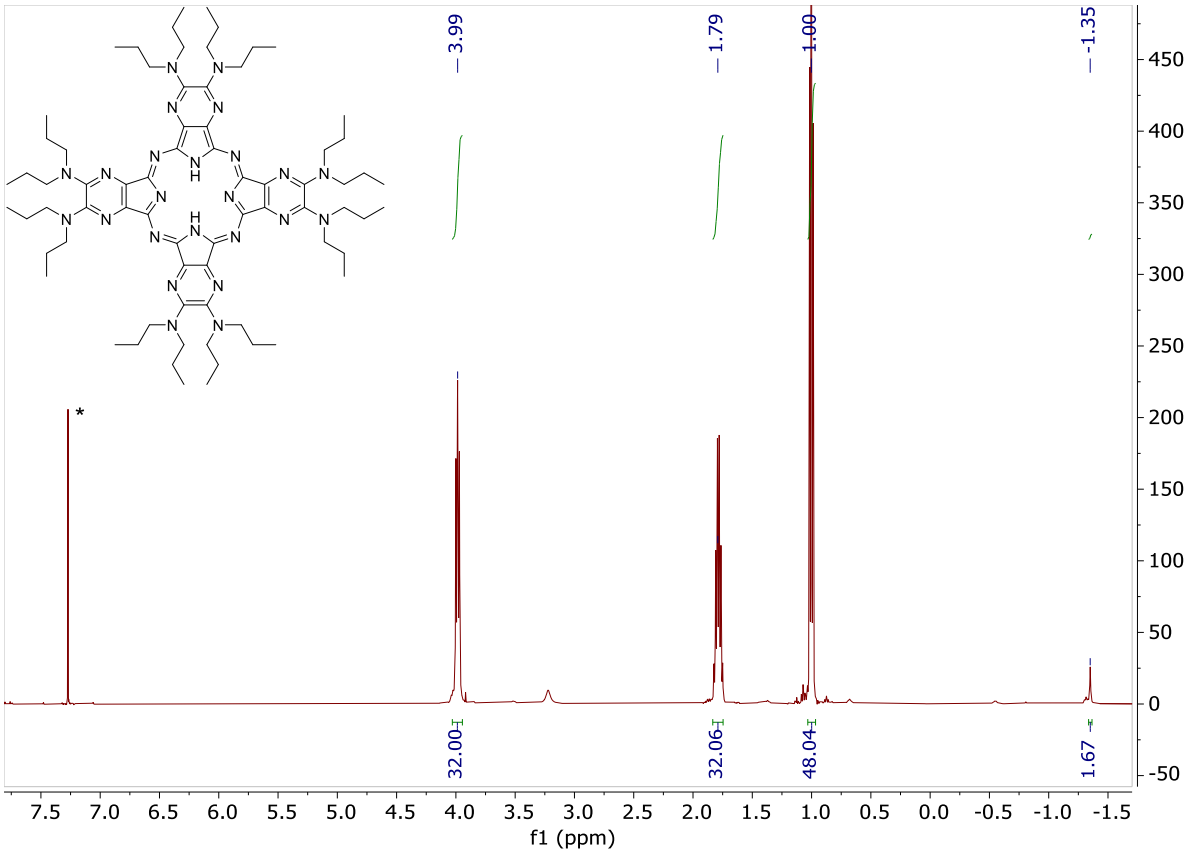

Fig S33. ^{1}H NMR (500 MHz, $CDCl_3$) of **3H2**. Asterisk marks residual of solvents.

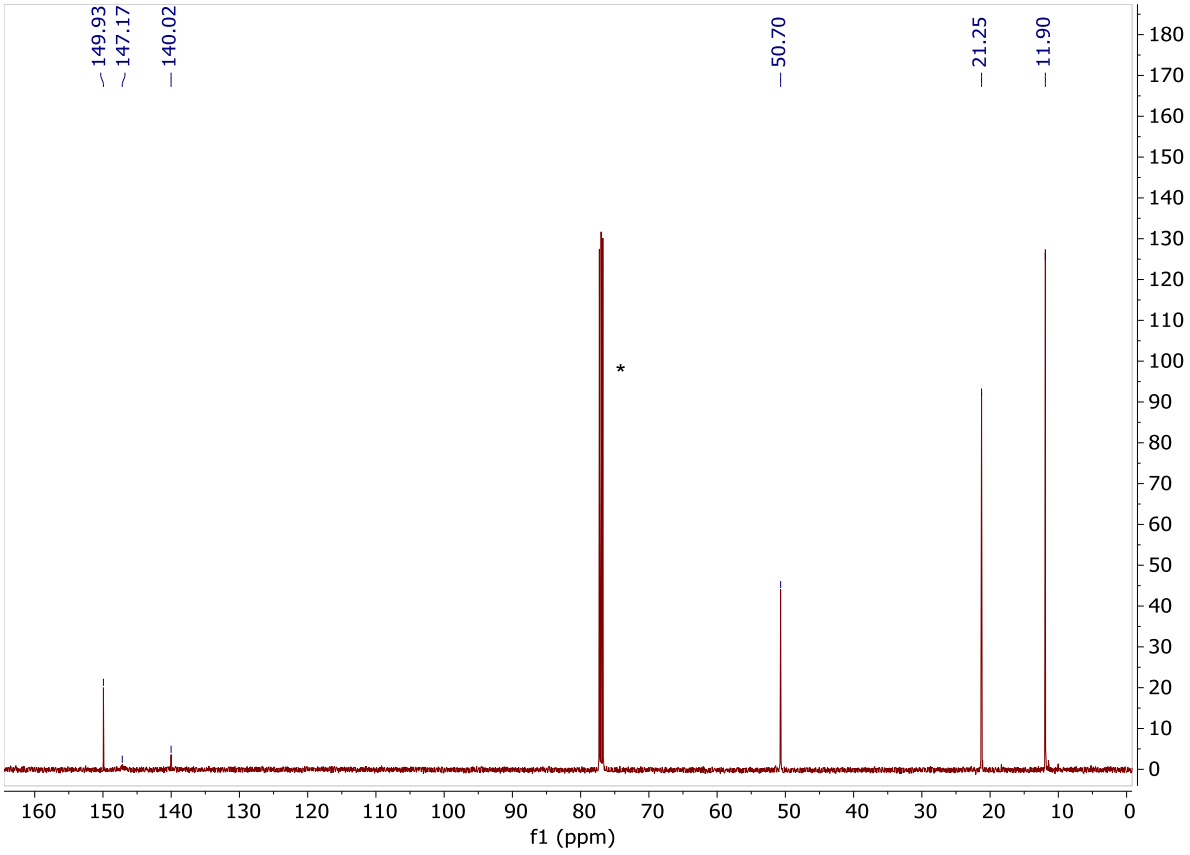

Fig S34. ^{13}C NMR (126 MHz, $CDCl_3$) of **3H2**. Asterisk marks residual of solvents.

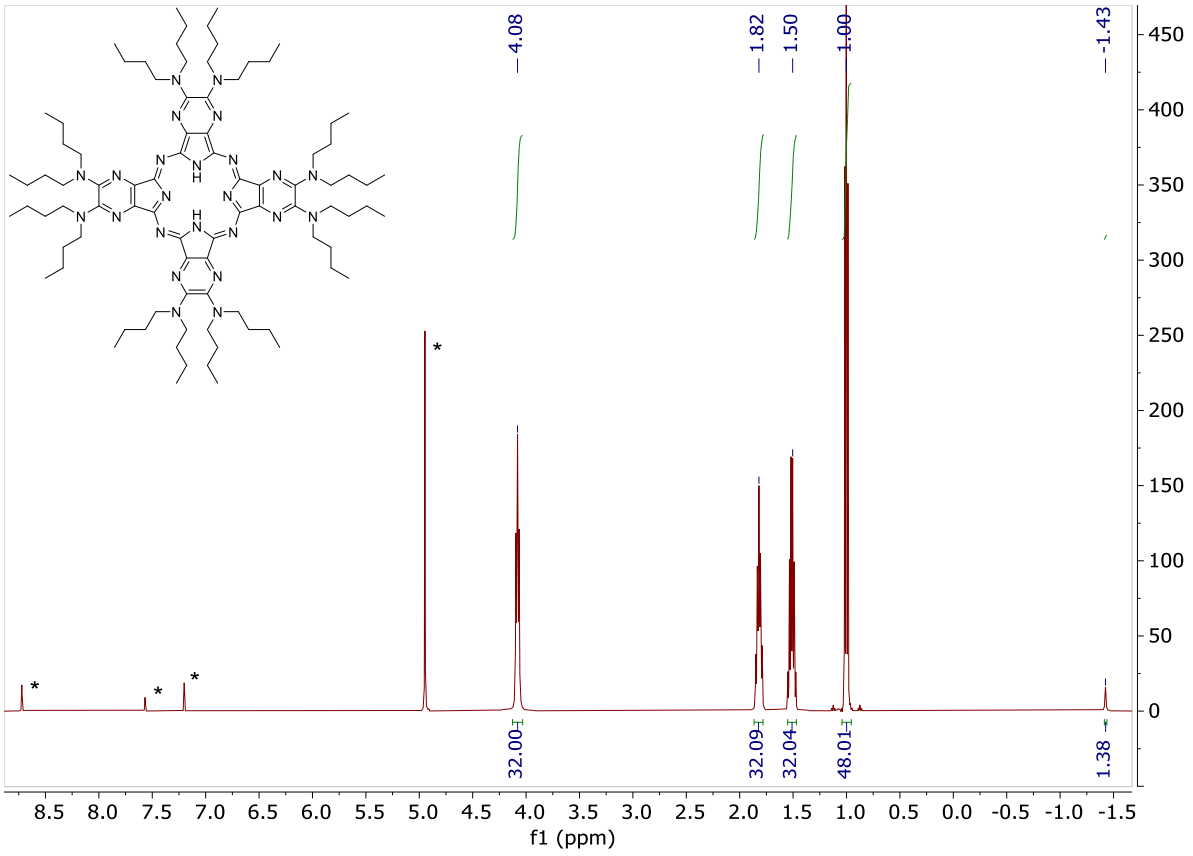

Fig S35. ^{1}H NMR (500 MHz, pyridin-d_5) of **4H2.** Asterisk marks residual of solvents.

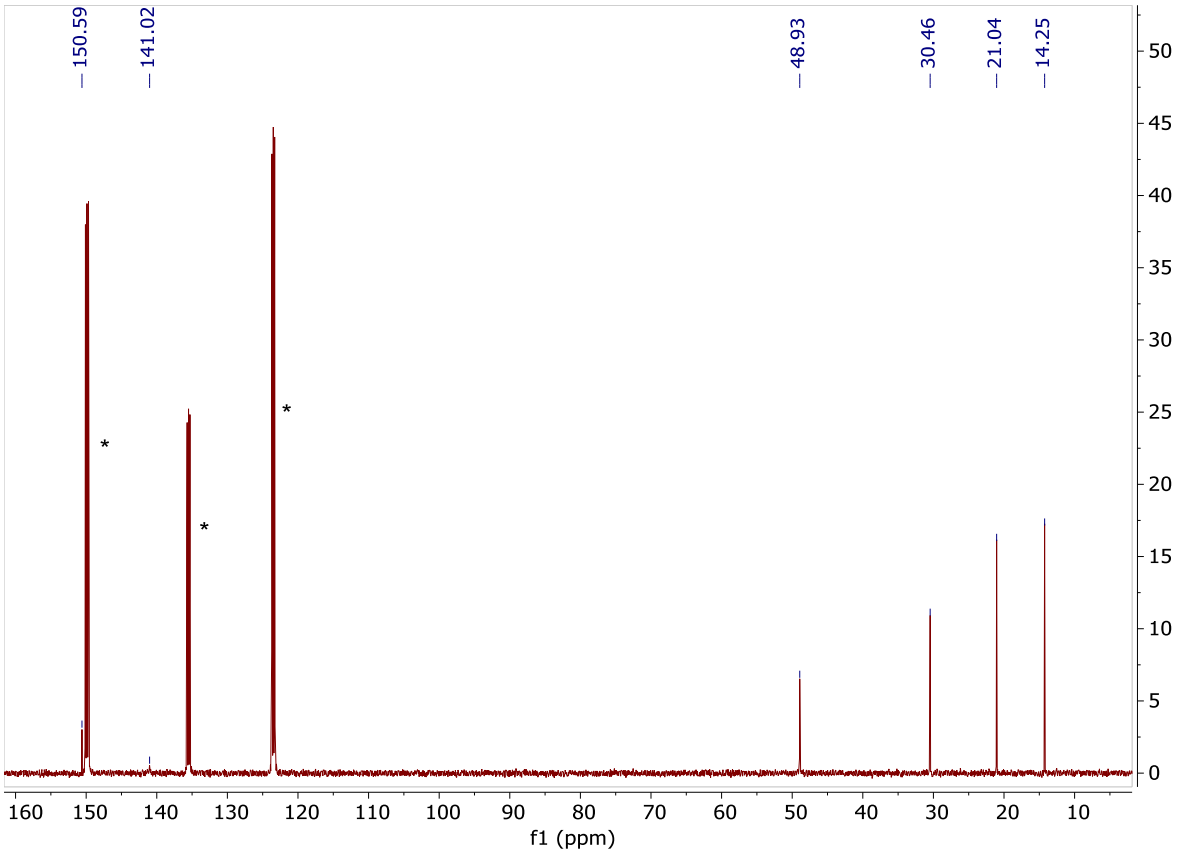

Fig S36. ^{13}C NMR (126 MHz, pyridin-d_5)of **4H2**. Asterisk marks residual of solvents.

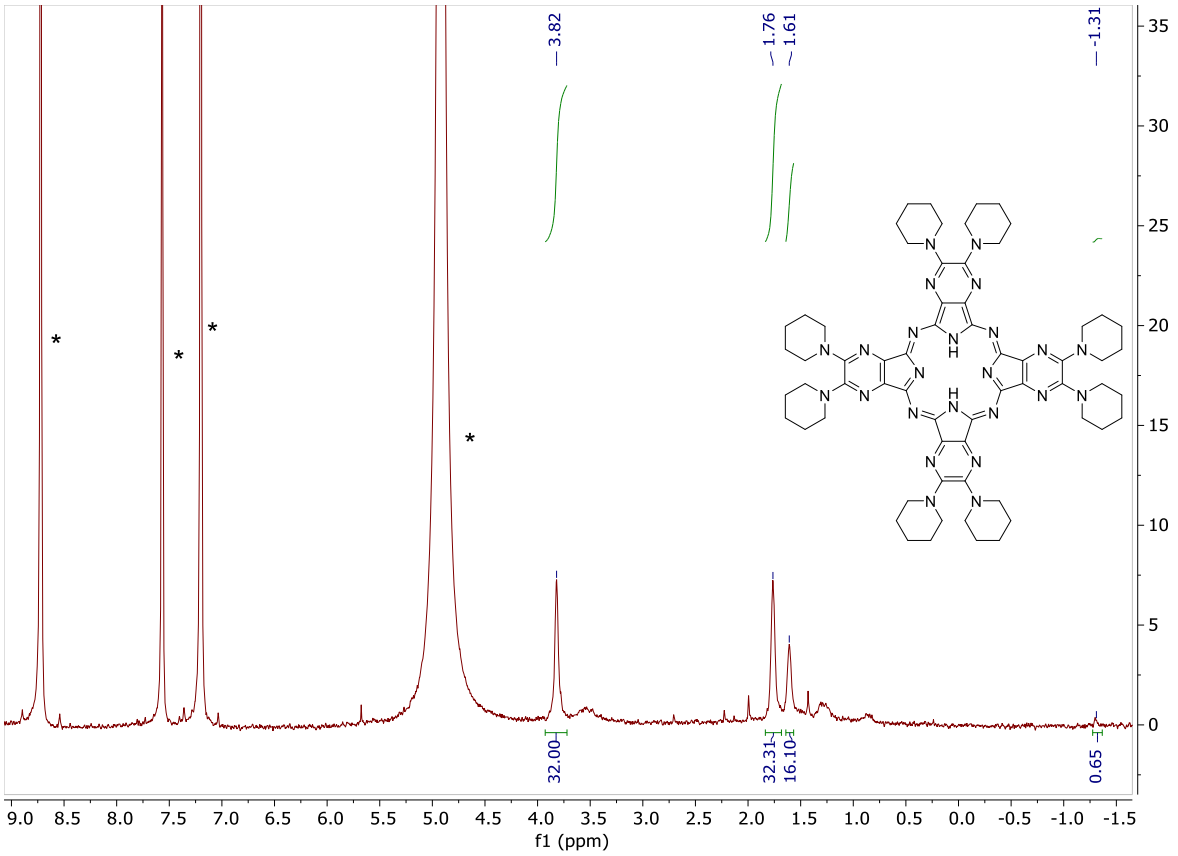

Fig S37. ^{1}H NMR (500 MHz, pyridin-d_5) of **6H2**. Asterisk marks residual of solvents.

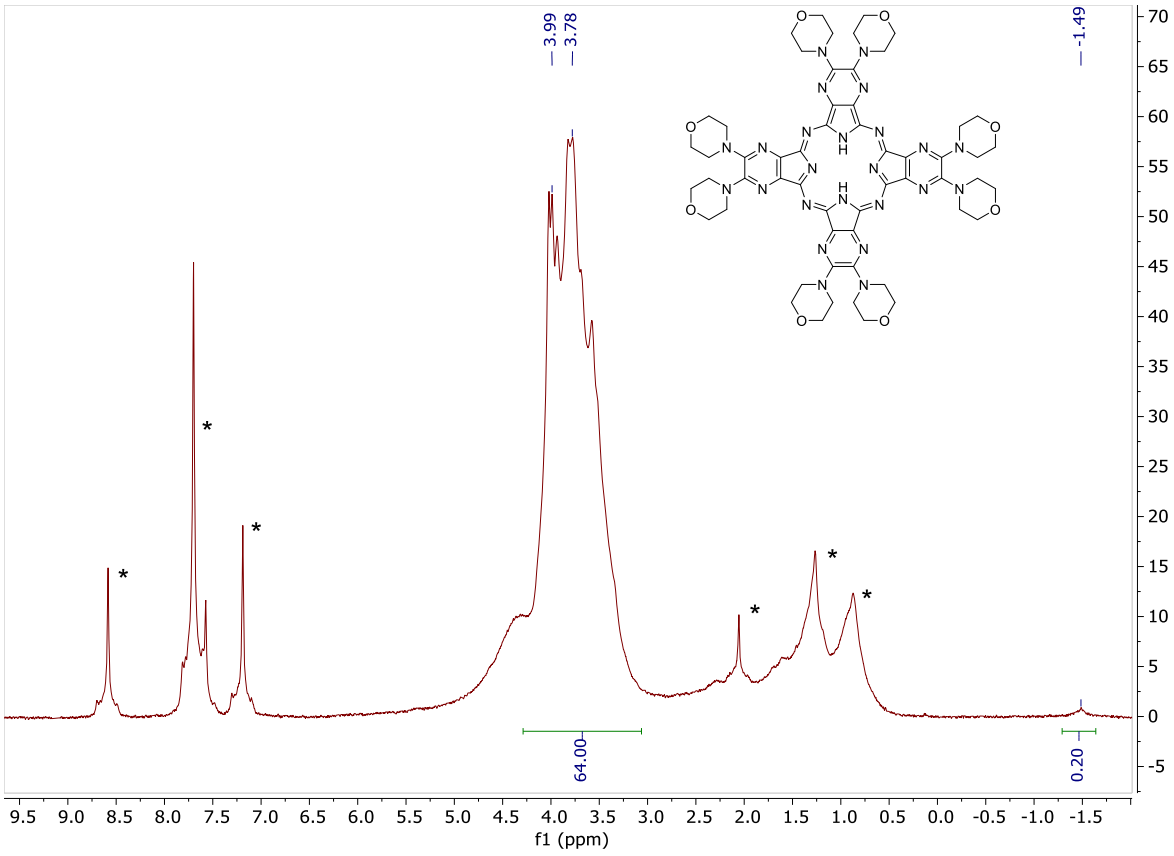

Fig S38. ^{1}H NMR (500 MHz, $CDCl_3$/pyridin-d_5 (2 : 1)) of **7H2**. Asterisk marks residual of solvents.

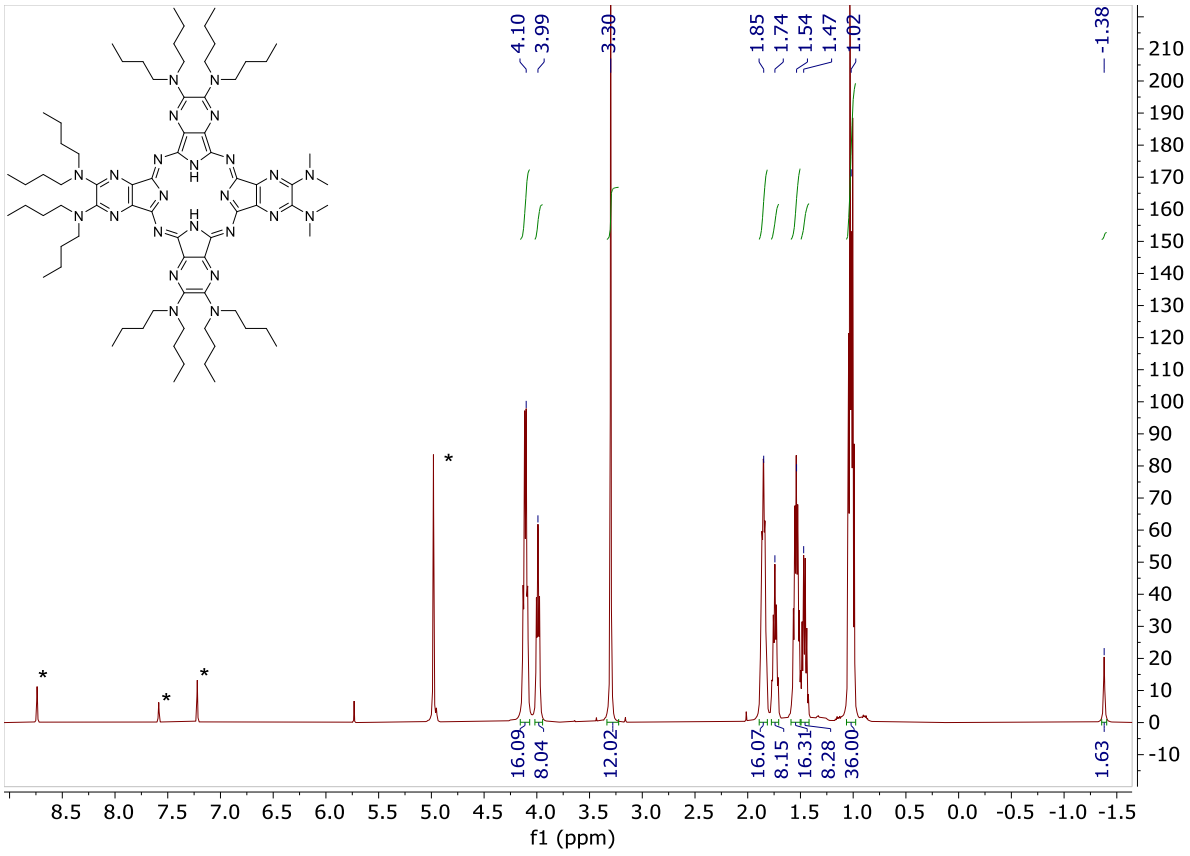

Fig S39. ^{1}H NMR (500 MHz, pyridin-d_5) of **8H2**. Asterisk marks residual of solvents.

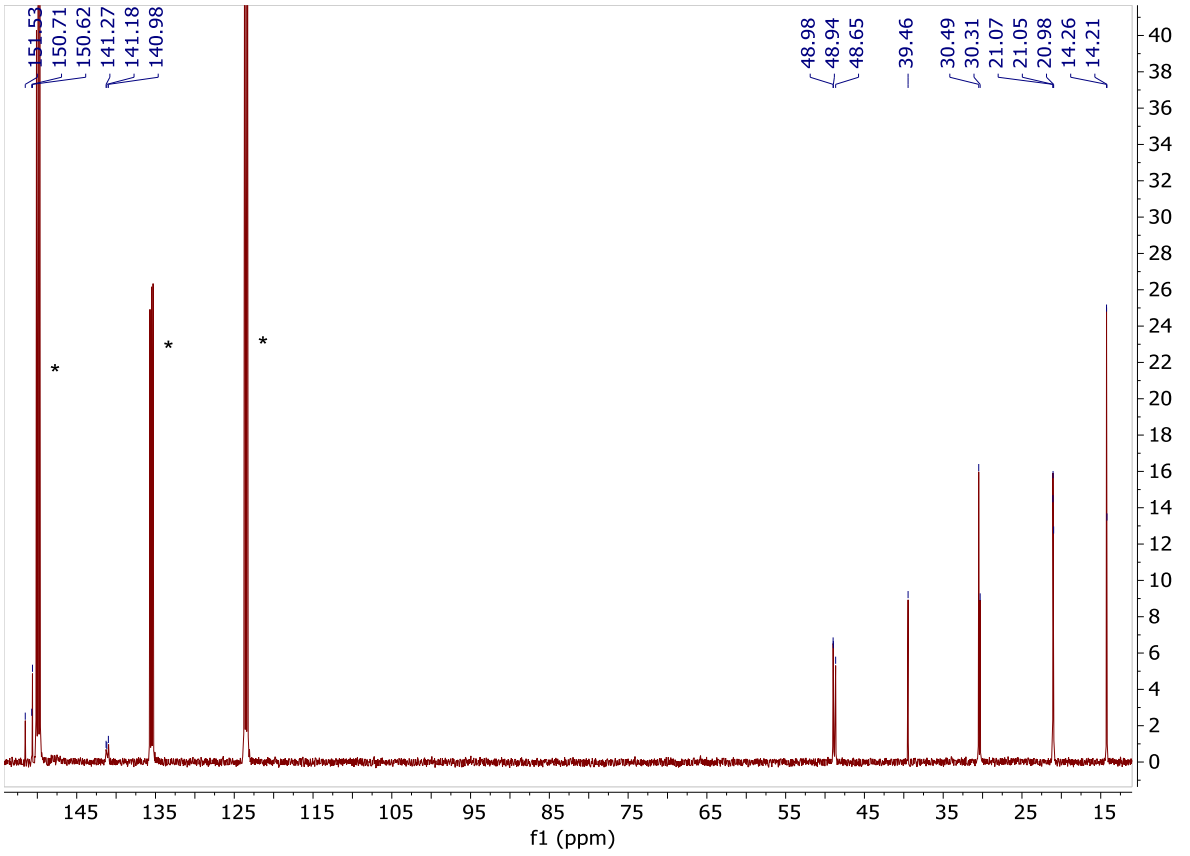

Fig S40. ^{13}C NMR (126 MHz, pyridin-d_5) of **8H2**. Asterisk marks residual of solvents.

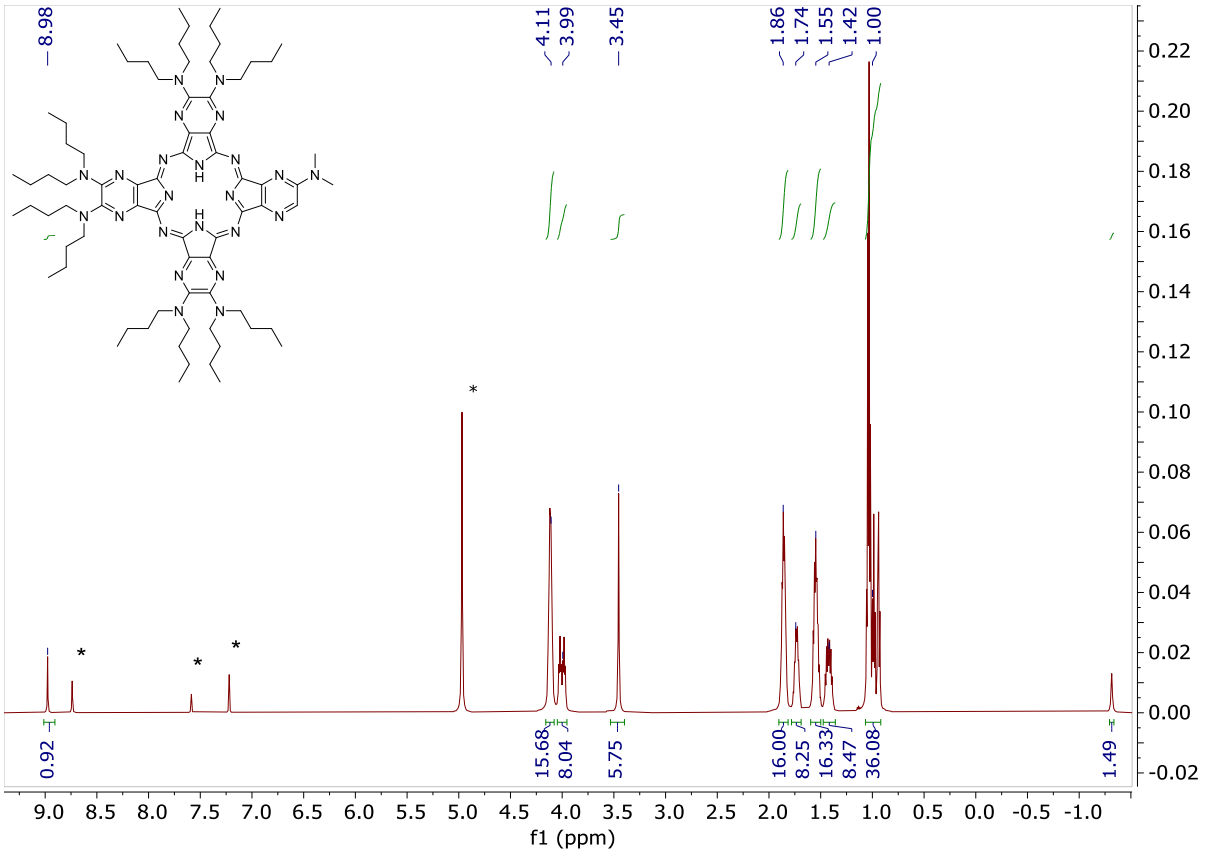

Fig S41. ^{1}H NMR (600 MHz, pyridin-d_5) of **9H2**. Asterisk marks residual of solvents.

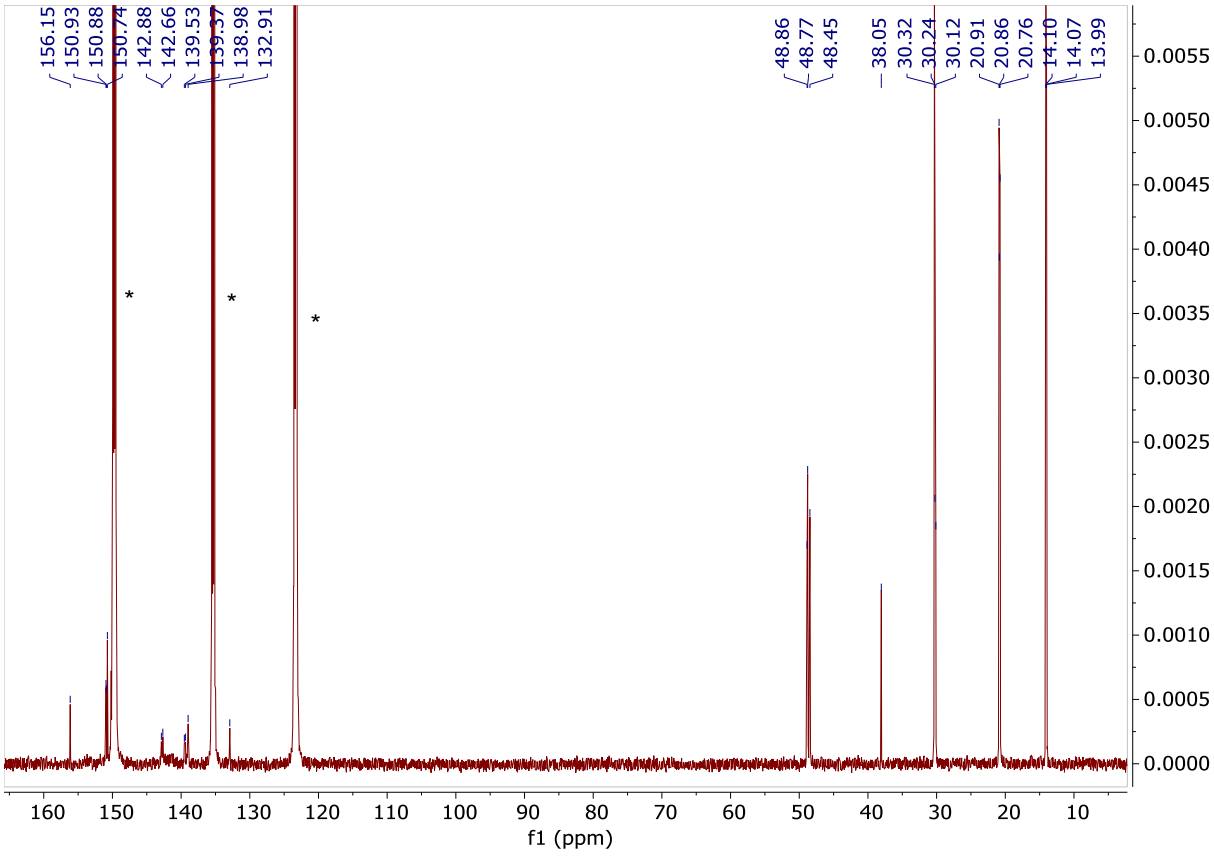

Fig S42. ^{13}C NMR (150 MHz, pyridin-d_5) of **9H2**. Asterisk marks residual of solvents.

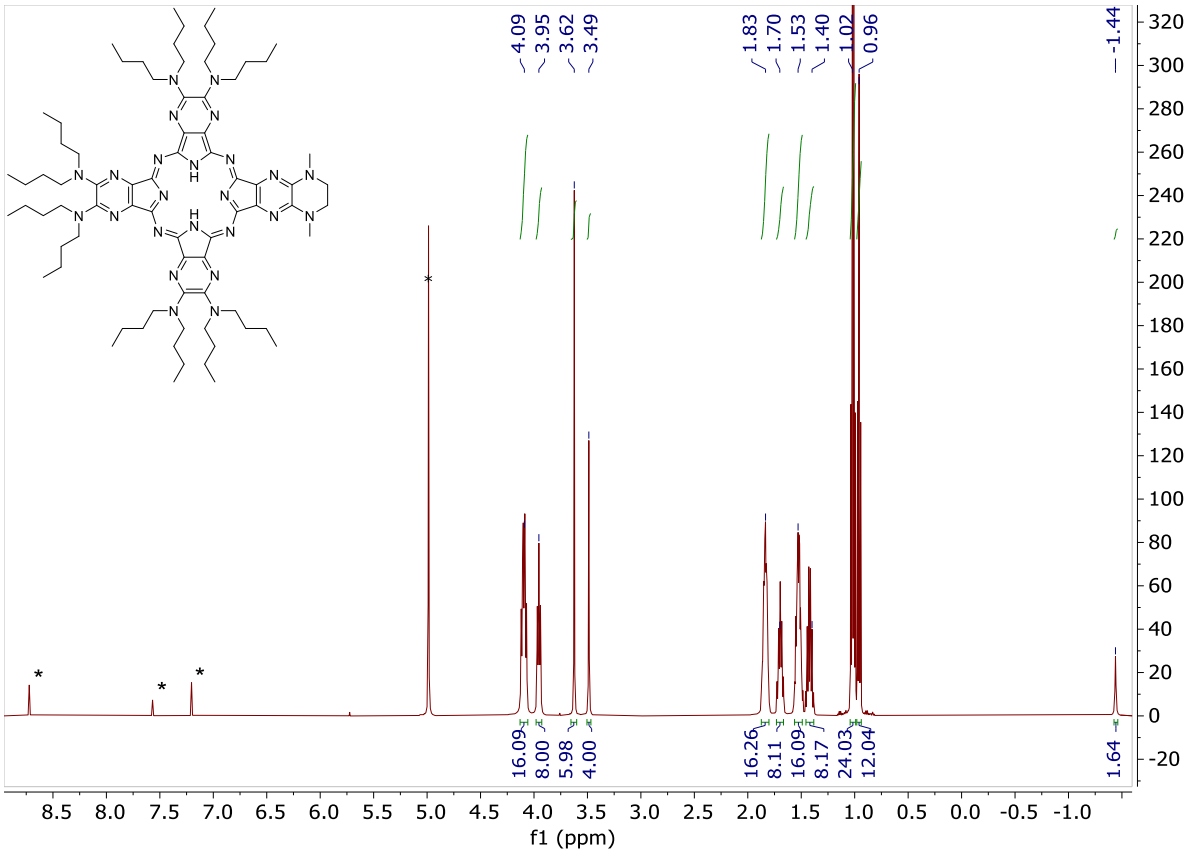

Fig S43. ^{1}H NMR (500 MHz, pyridin-d_5) of **10H2**. Asterisk marks residual of solvents.

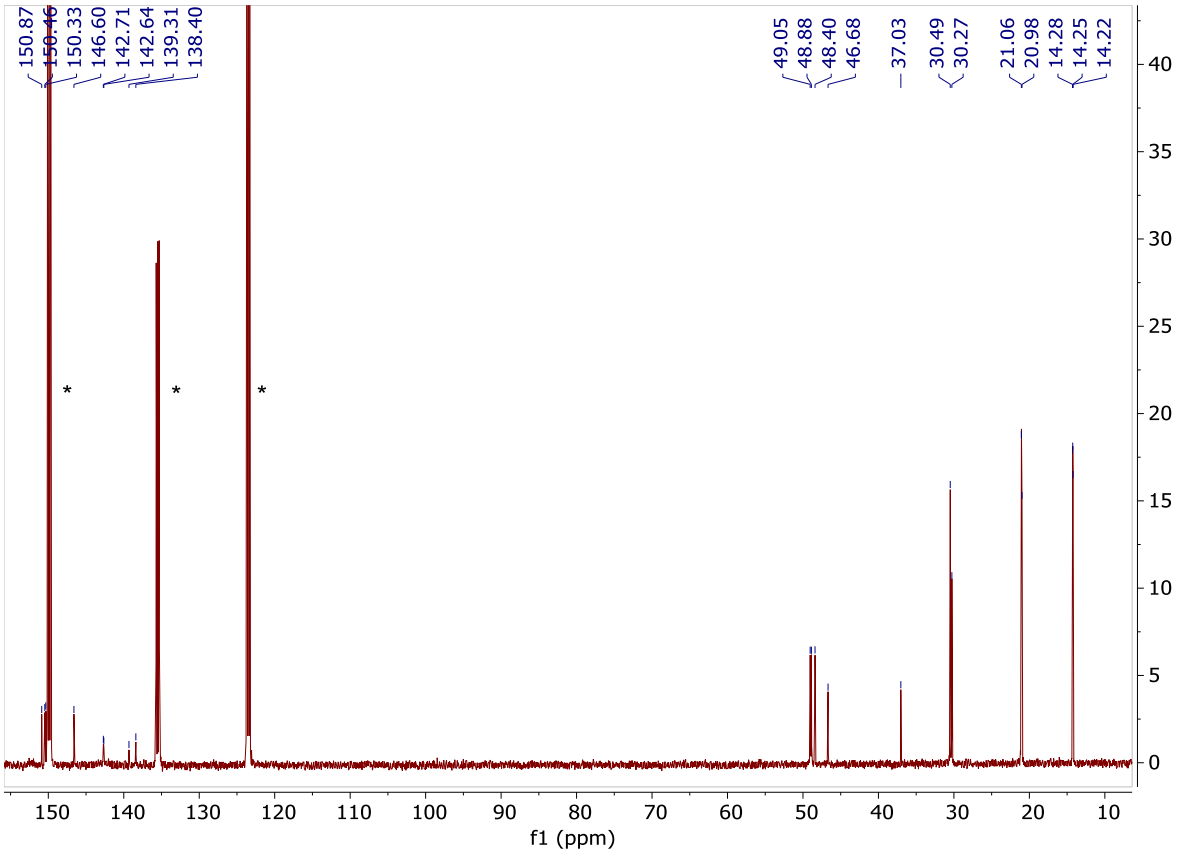

Fig S44. ^{13}C NMR (126 MHz, pyridin-d_5) of **10H2**. Asterisk marks residual of solvents.

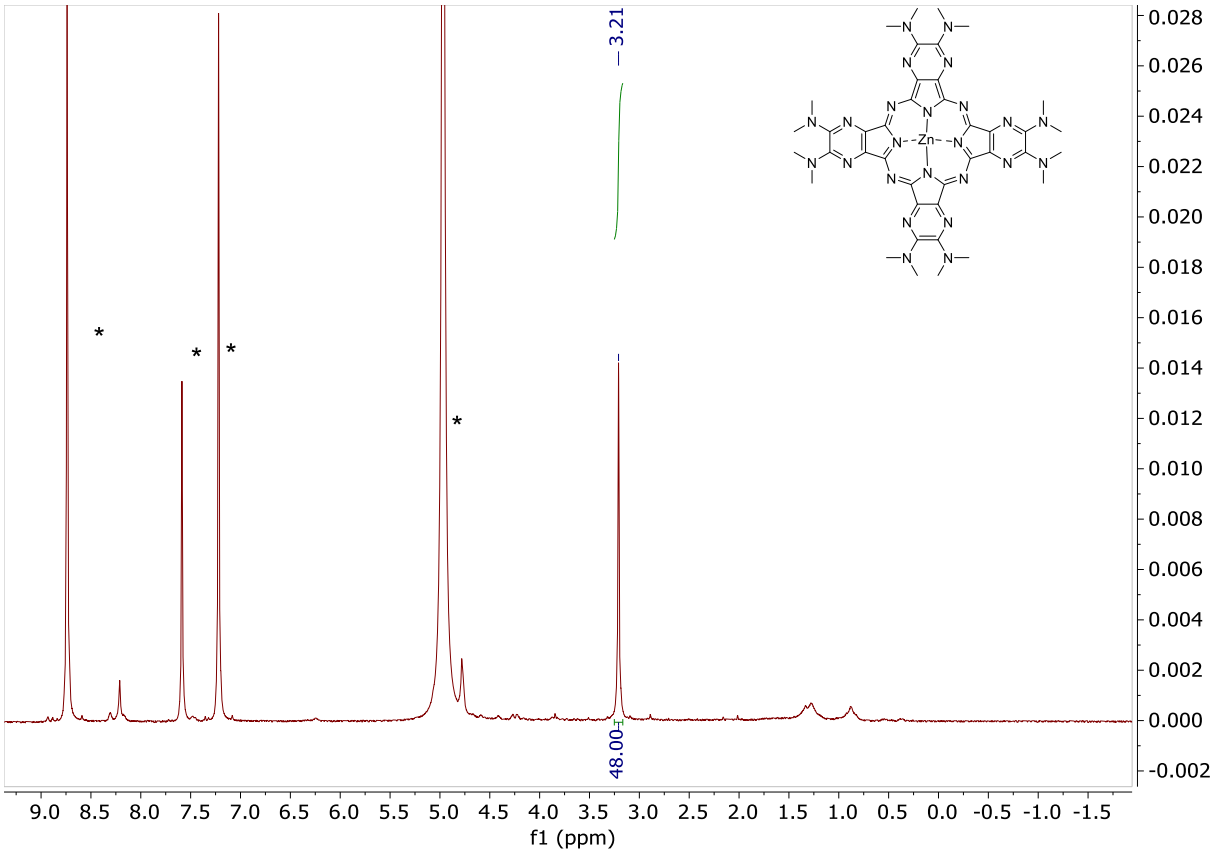

Fig S45. ^{1}H NMR (600 MHz, pyridin-d_5) of **1Zn**. Asterisk marks residual of solvents.

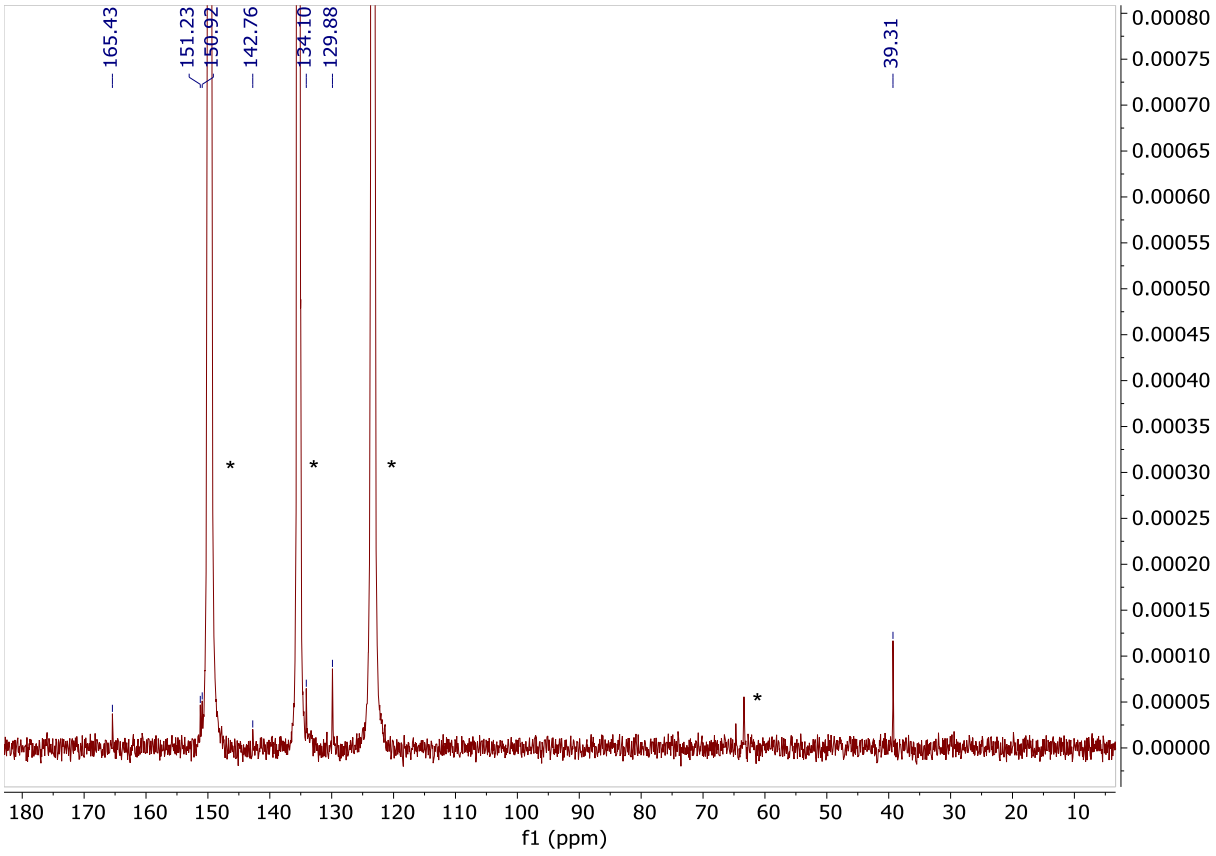

Fig S46. ^{13}C NMR (150 MHz, pyridin-d_5) of **1Zn**. Asterisk marks residual of solvents.

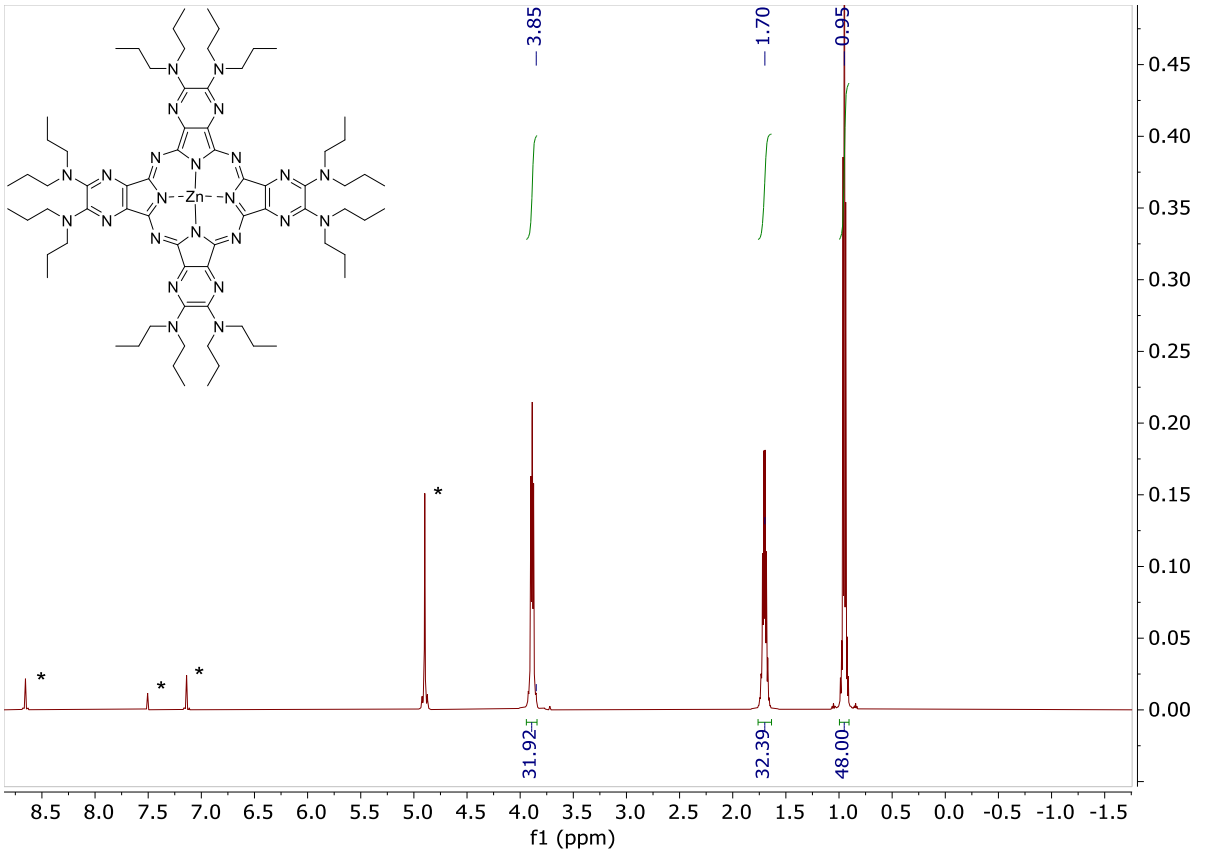

Fig S47. ^{1}H NMR (600 MHz, pyridin-d_5) of **3Zn**. Asterisk marks residual of solvents.

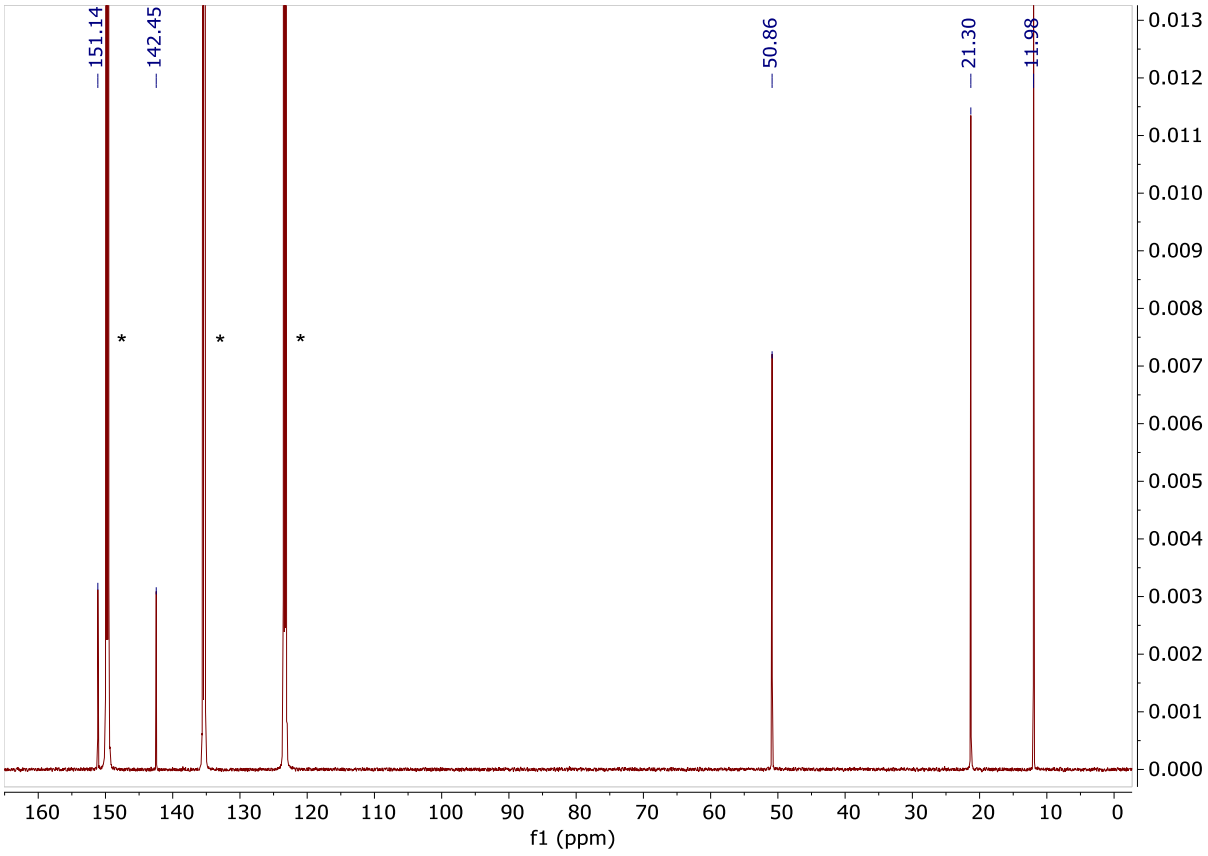

Fig S48. ^{13}C NMR (150 MHz, pyridin-d_5) of **3Zn**. Asterisk marks residual of solvents.

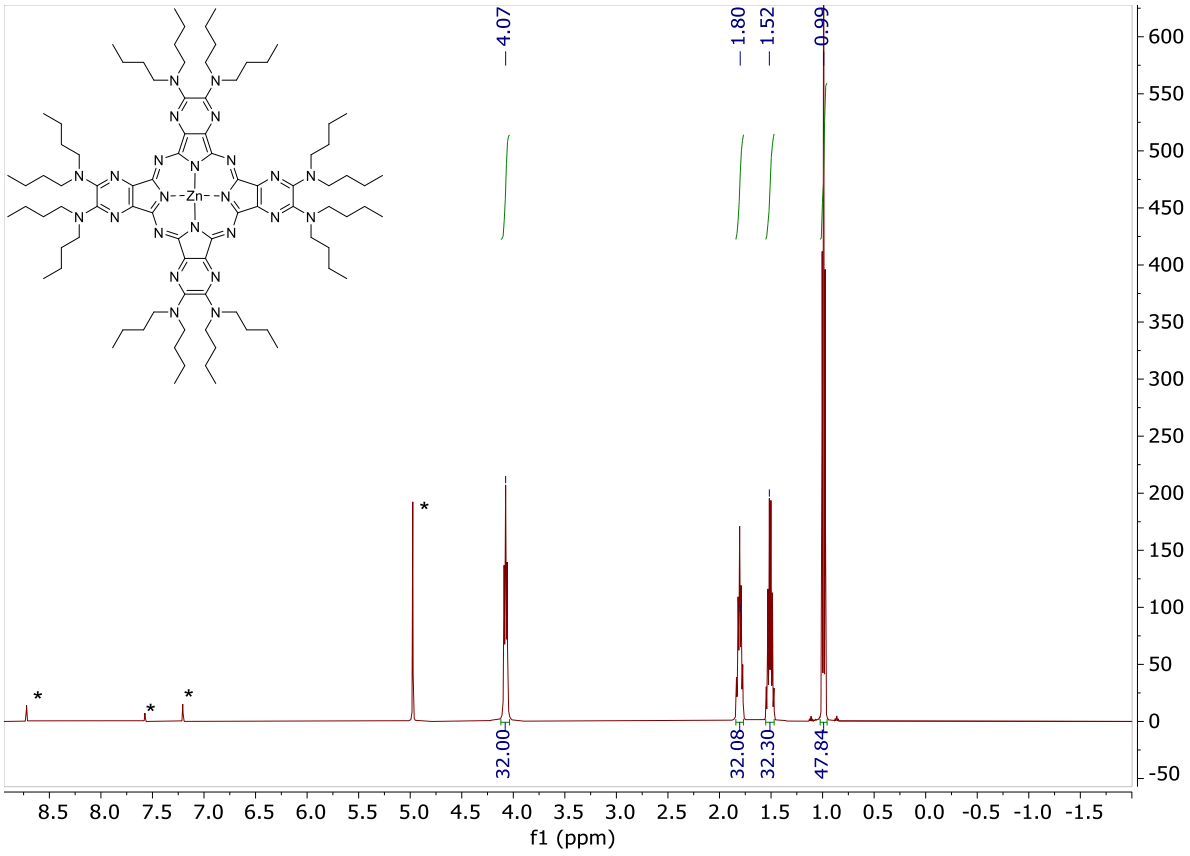

Fig S49. ^{1}H NMR (500 MHz, pyridin-d_5) of **4Zn**. Asterisk marks residual of solvents.

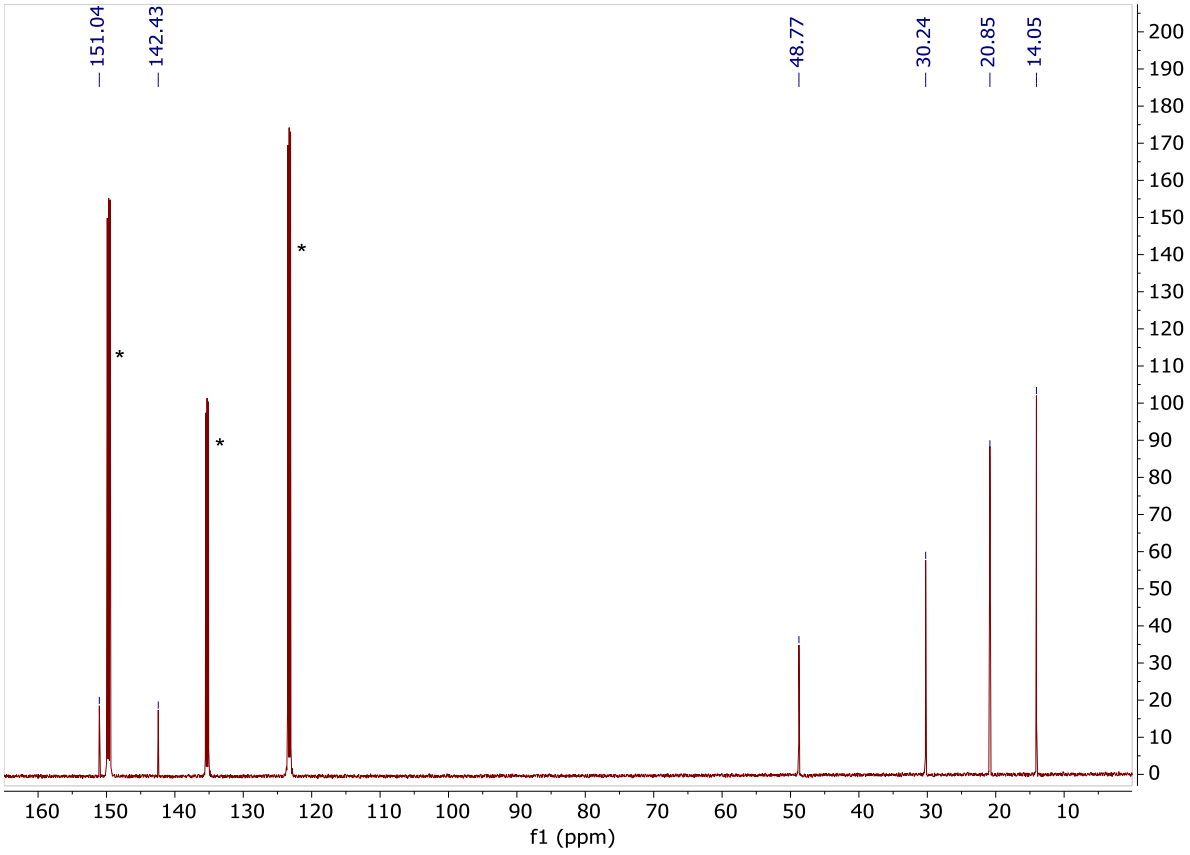

Fig S50. ^{13}C NMR (126 MHz, pyridin-d_5) of **4Zn**. Asterisk marks residual of solvents.

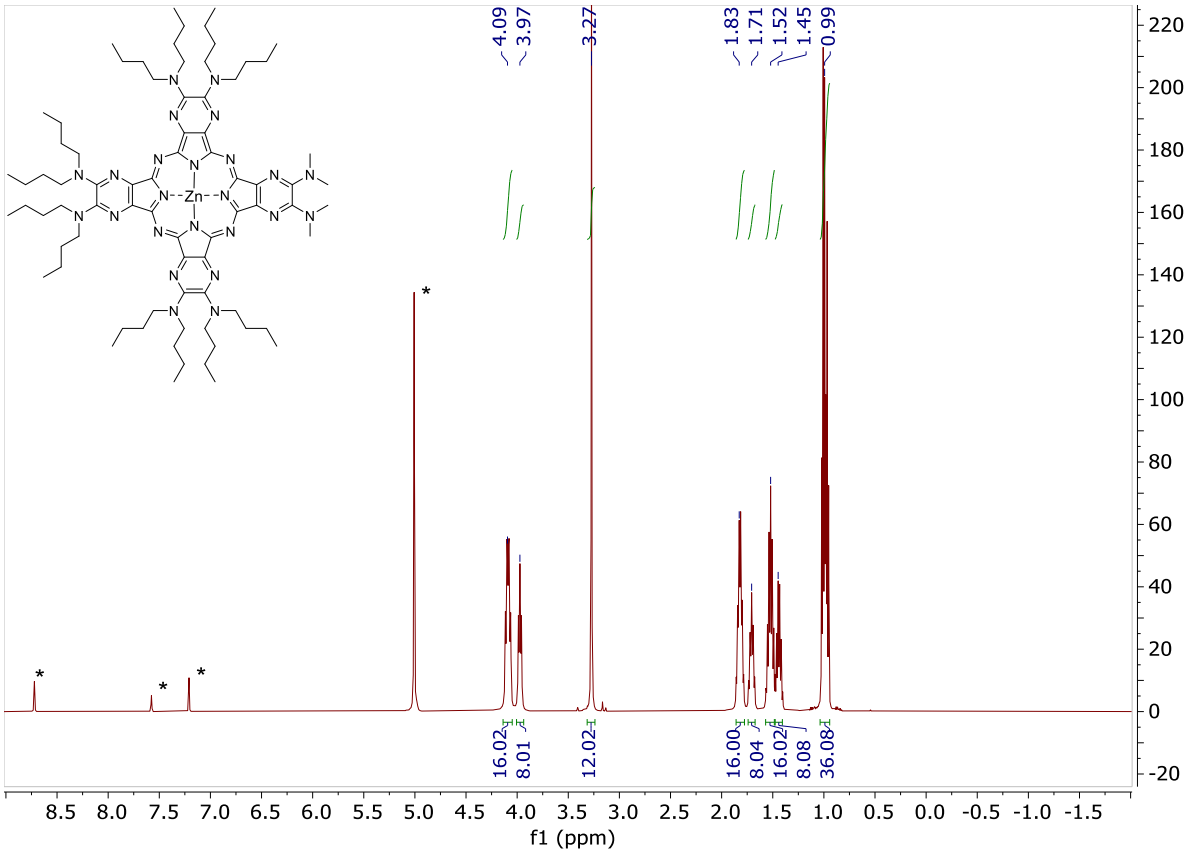

Fig S51. ^{1}H NMR (500 MHz, pyridin-d_5) of **8Zn**. Asterisk marks residual of solvents.

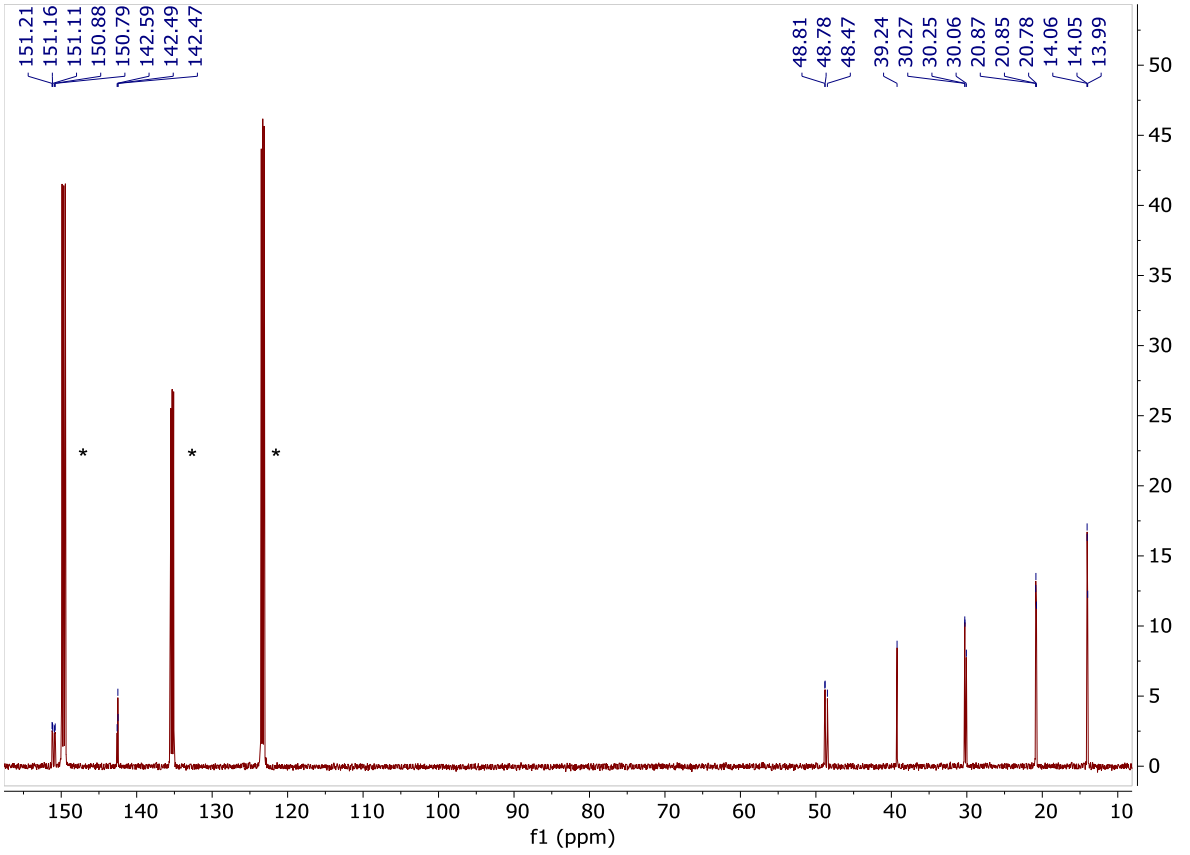

Fig S52. ^{13}C NMR (126 MHz, pyridin-d_5) of **8Zn**. Asterisk marks residual of solvents.

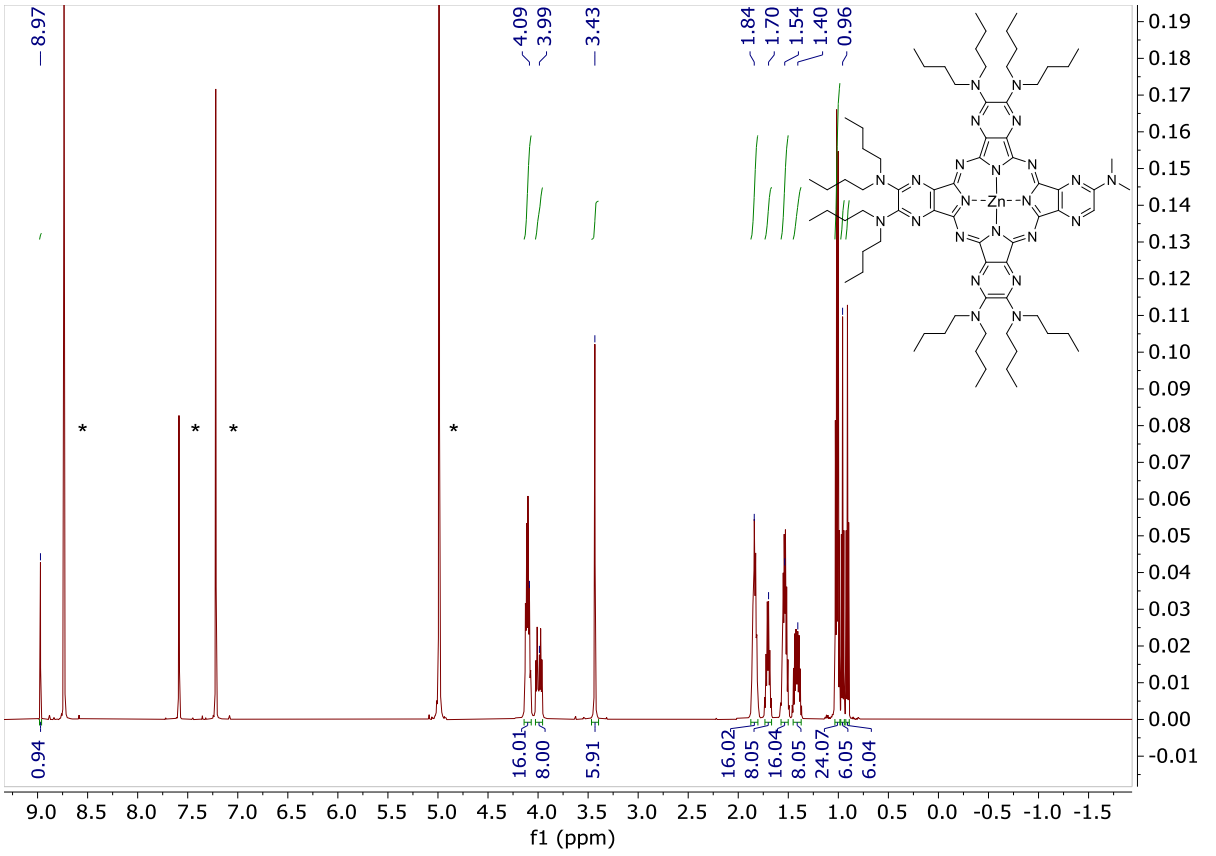

Fig S53. ^{1}H NMR (600 MHz, pyridin-d_5) of **9Zn**. Asterisk marks residual of solvents.

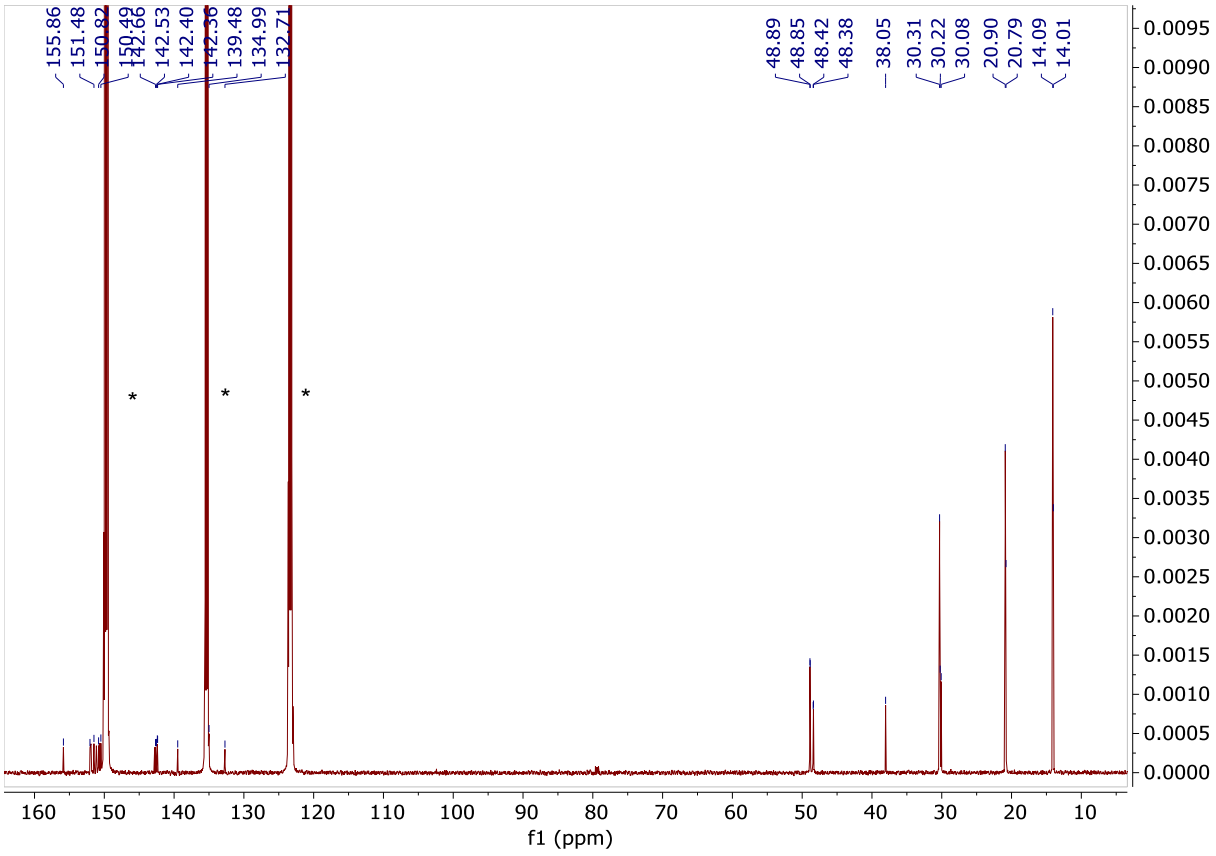

Fig S54. ^{13}C NMR (150 MHz, pyridin-d_5) of **9Zn**. Asterisk marks residual of solvents.

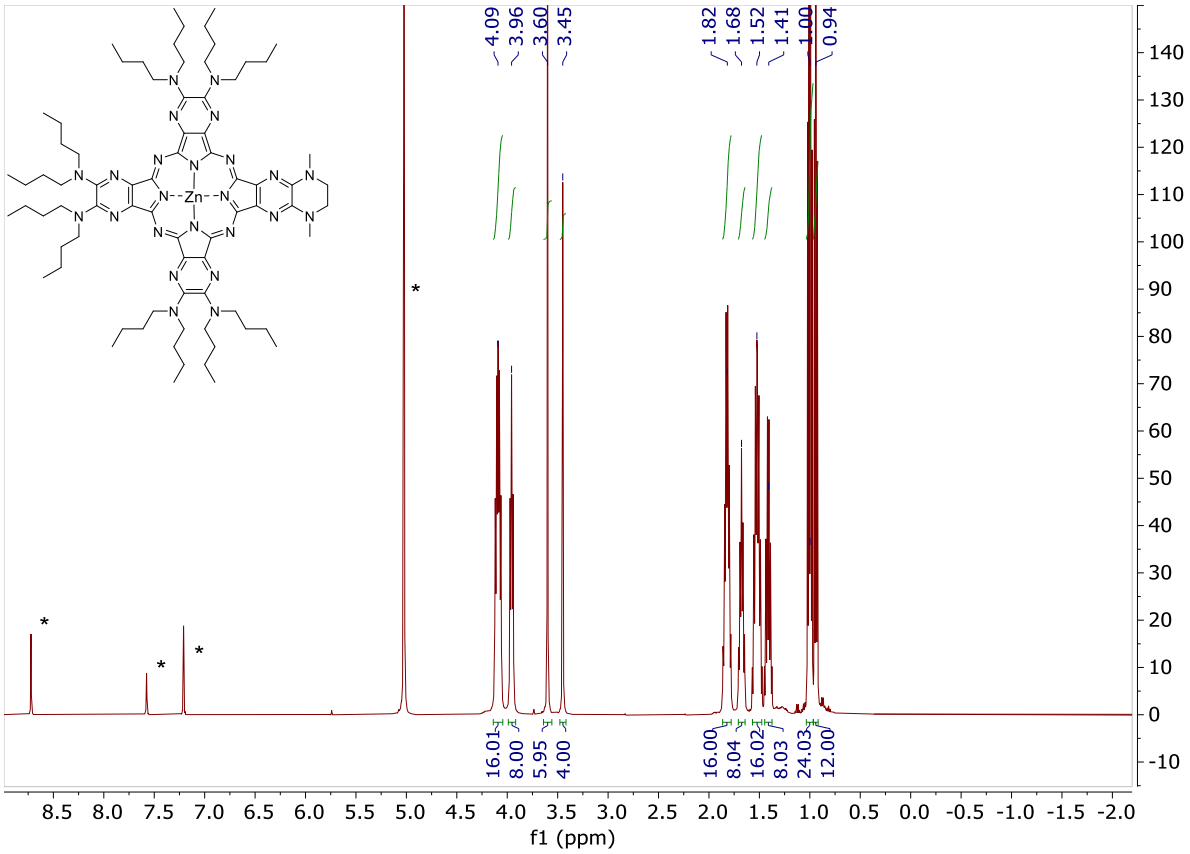

Fig S55. ^{1}H NMR (500 MHz, pyridin-d_5) of **10Zn**. Asterisk marks residual of solvents.

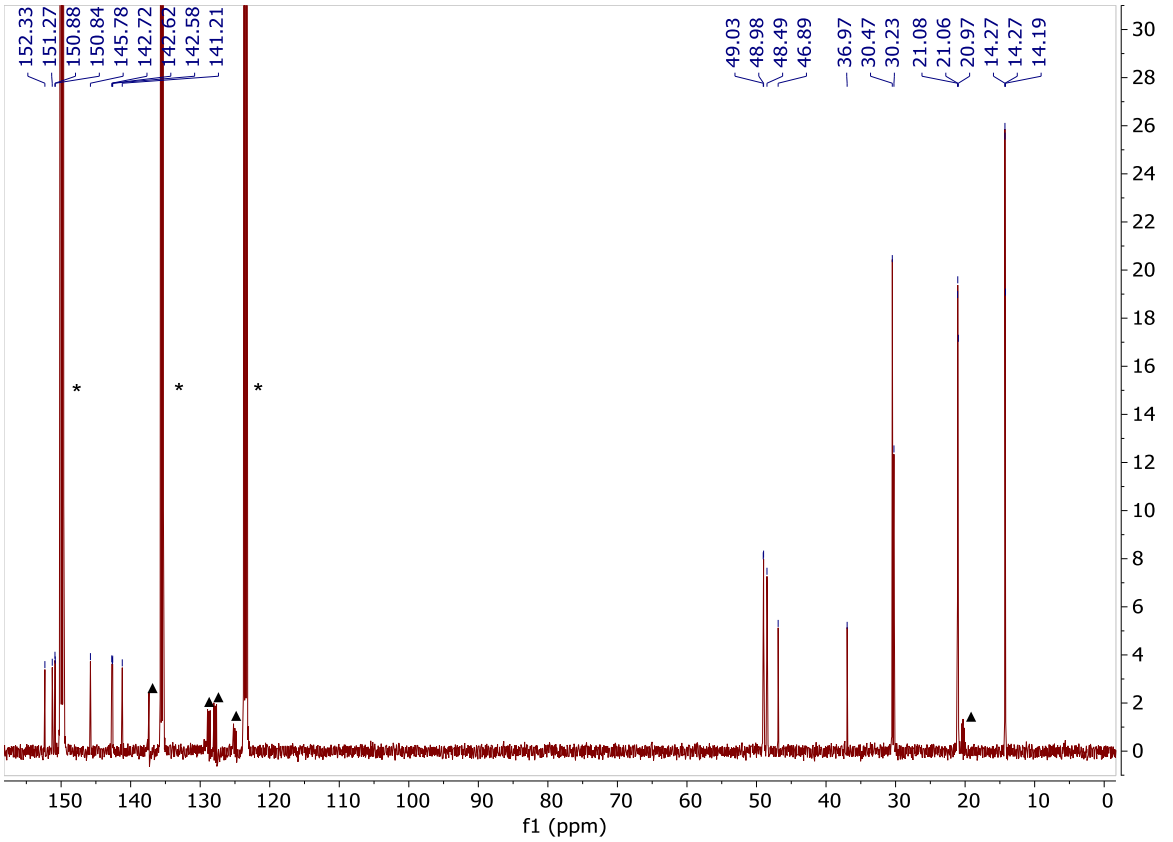

Fig S56. ^{13}C NMR (126 MHz, pyridin-d_5) of **10Zn**. Asterisk marks residual of solvents. Triangles mark residual toluene.

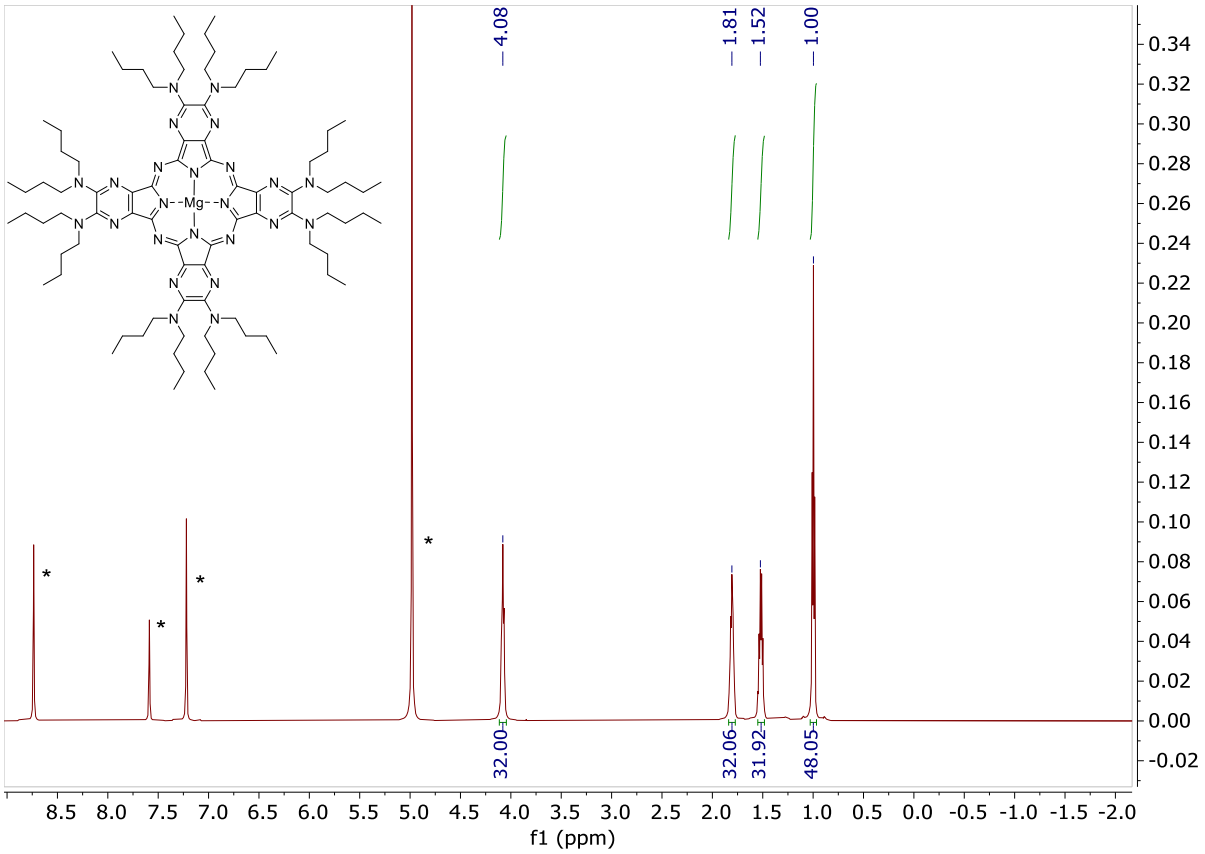

Fig S57. ^{1}H NMR (600 MHz, pyridin-d_5) of **4Mg**. Asterisk marks residual of solvents.

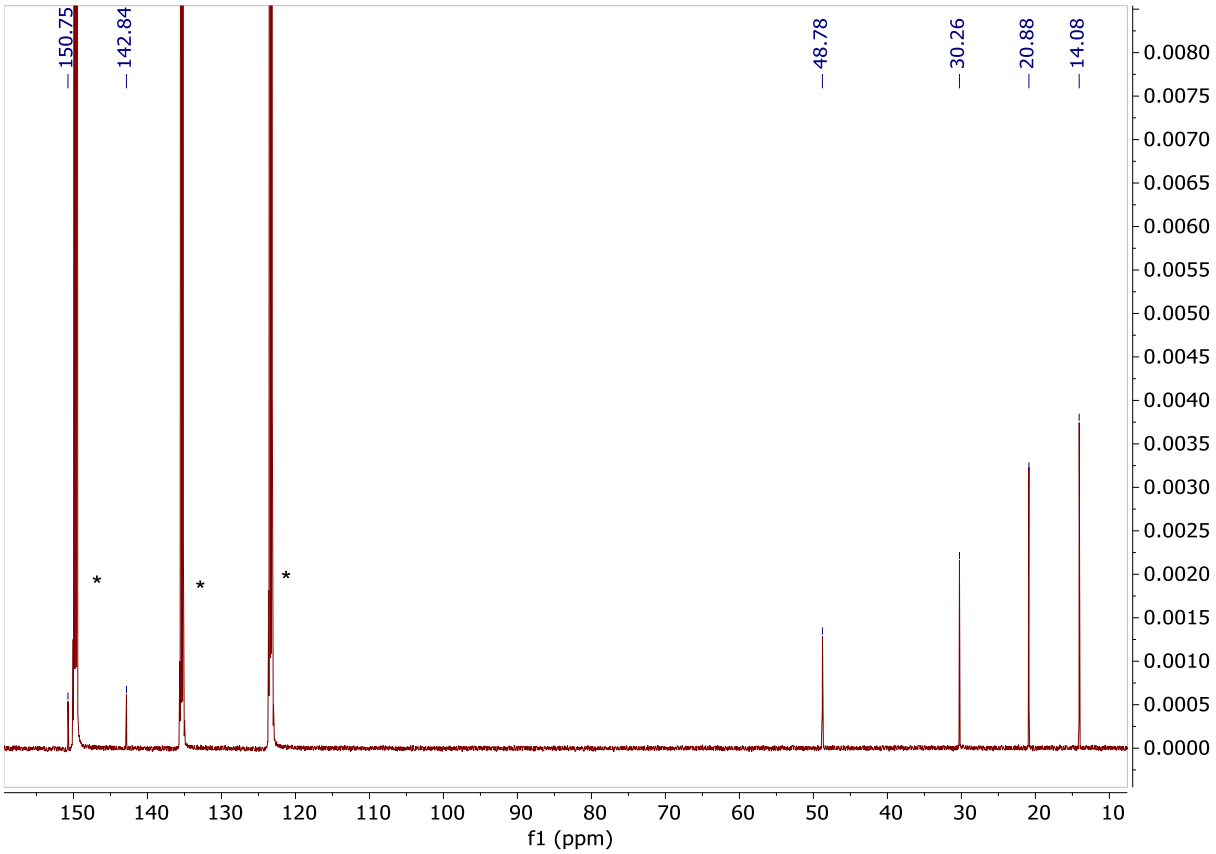

Fig S58. ^{13}C NMR (150 MHz, pyridin-d_5) of **4Mg** in pyridine-d_5. Asterisk marks residual of solvents.

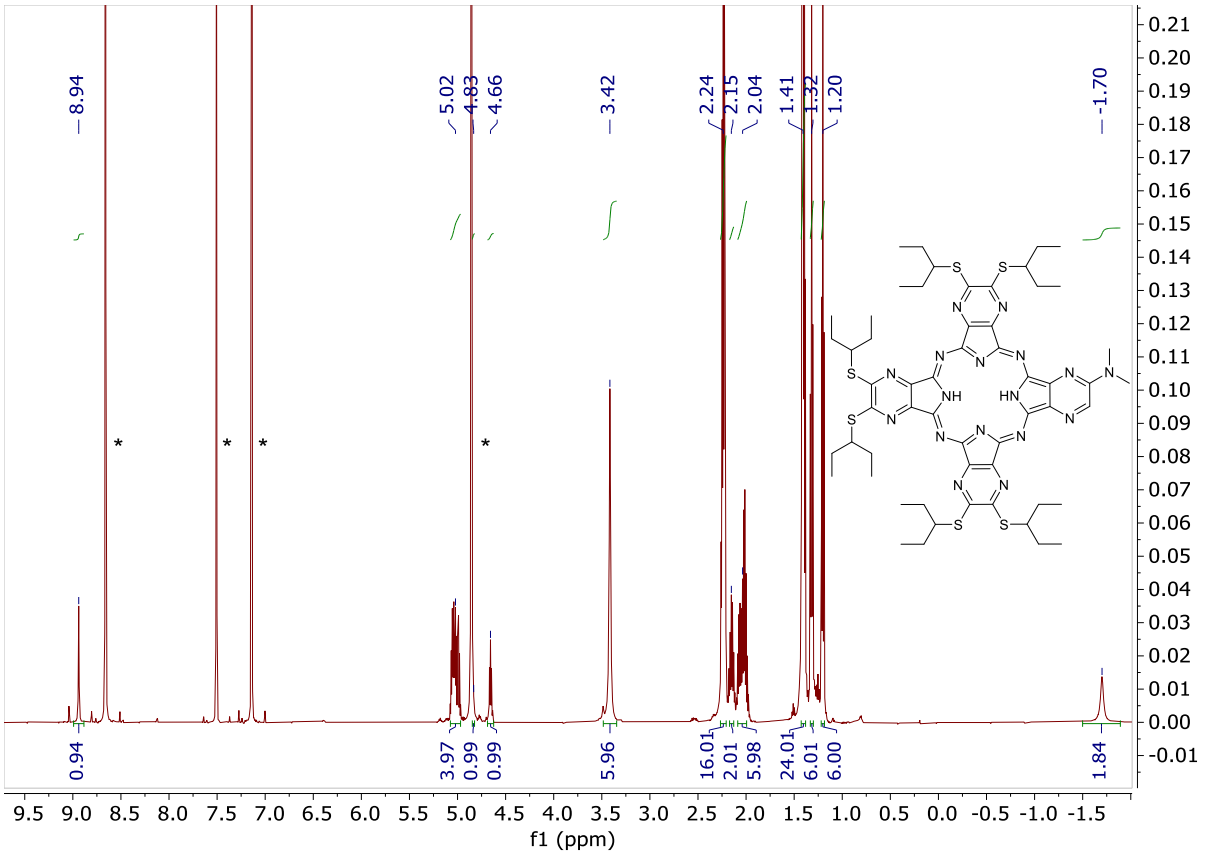

Fig S59. ^{1}H NMR (600 MHz, pyridin-d_5) of **20H2**. Asterisk marks residual of solvents.

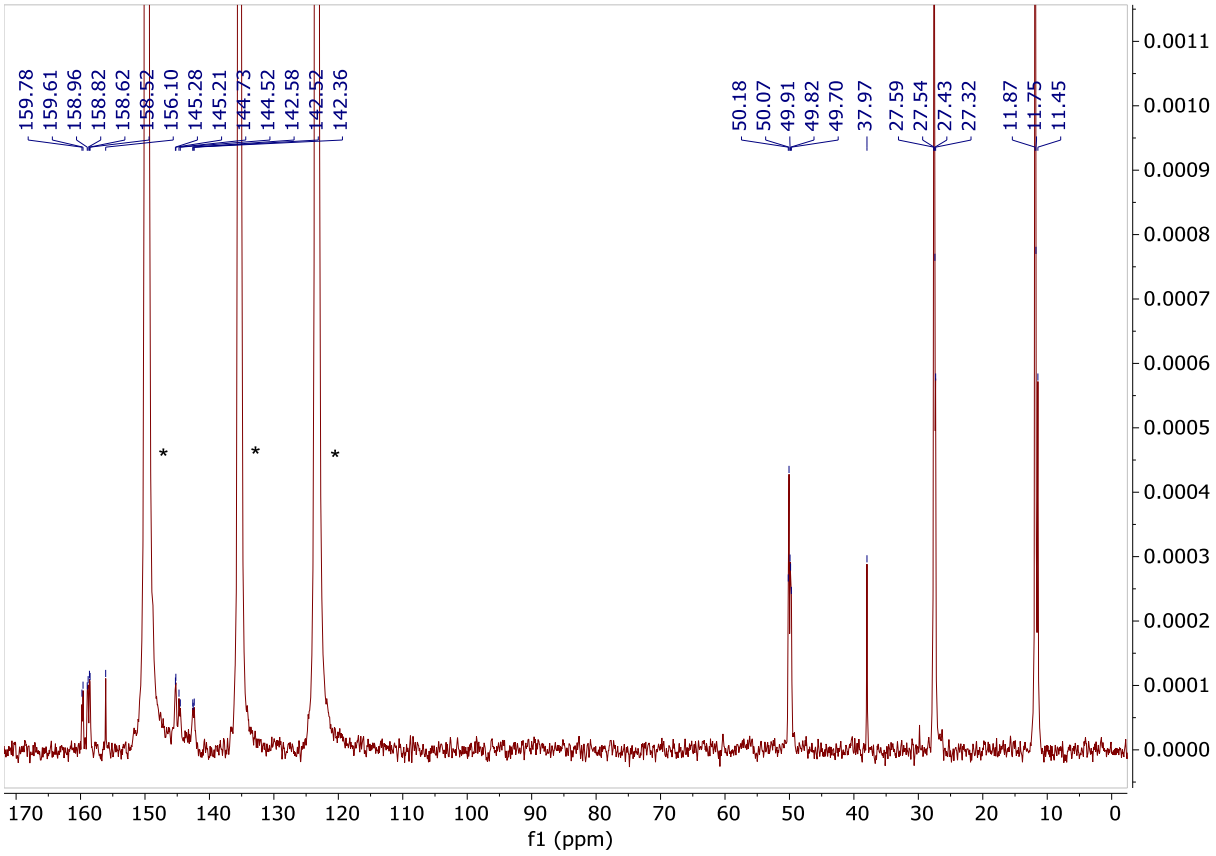

Fig S60. ^{13}C NMR (150 MHz, pyridin-d_5) of **20H2**. Asterisk marks residual of solvents.

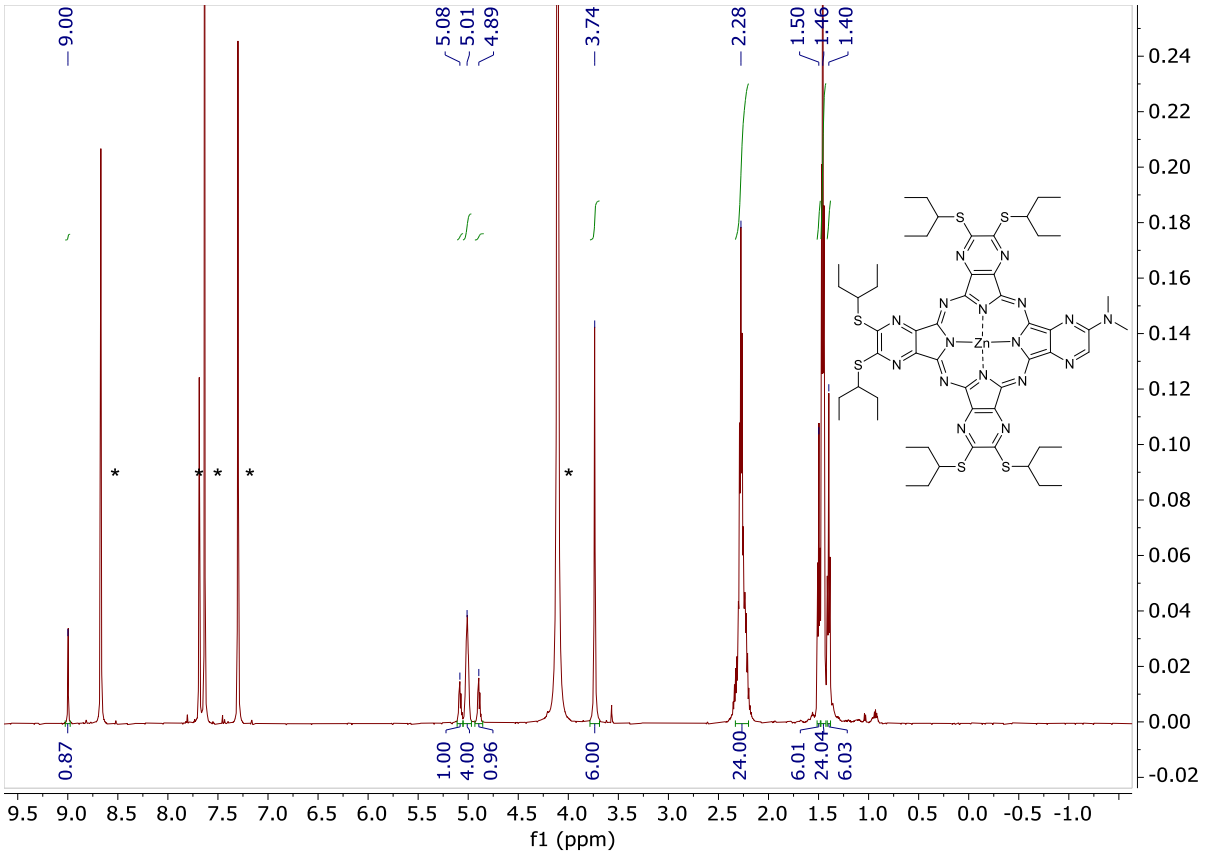

Fig S61. ^{1}H NMR (600 MHz, $CDCl_3$/pyridine-d_5 – 3 : 1) of **20Zn**. Asterisk marks residual of solvents.

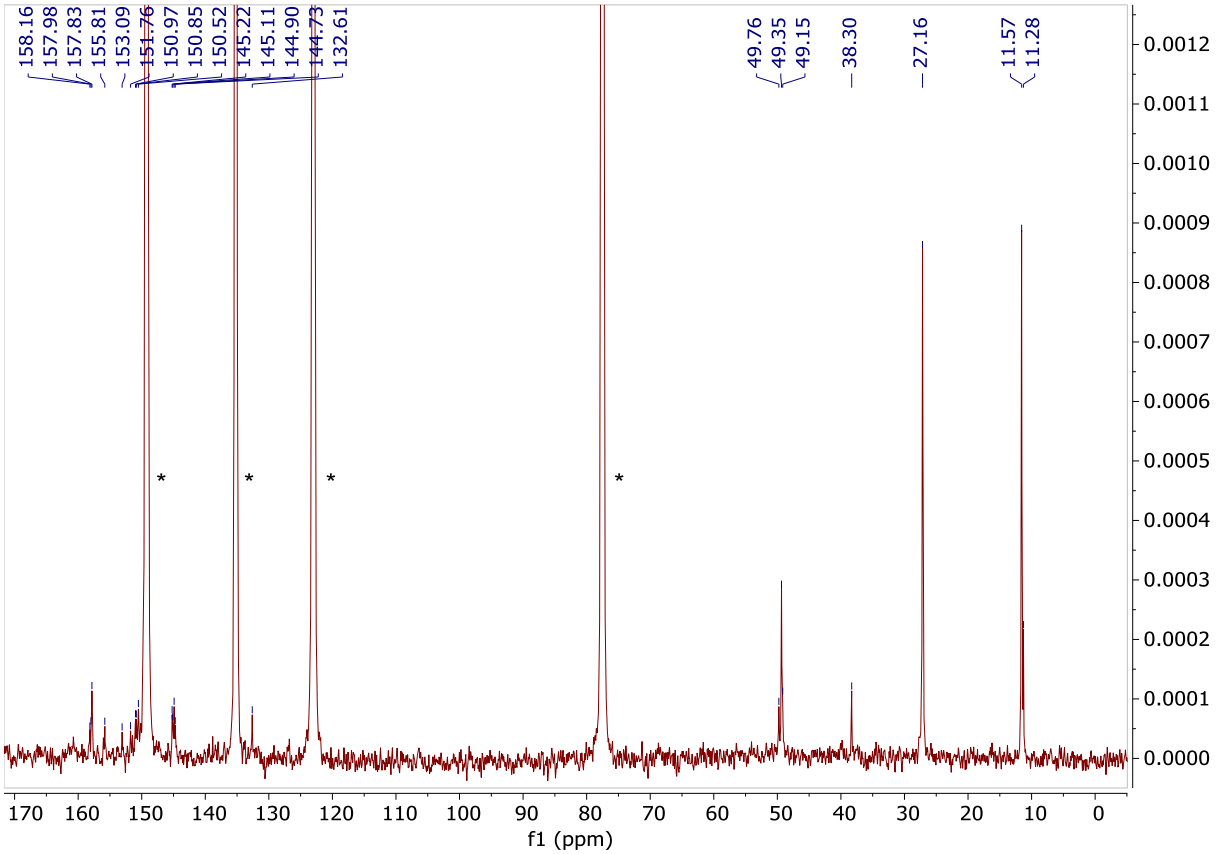

Fig S62. ^{13}C NMR (150 MHz, $CDCl_3$/pyridine-d_5 – 3 : 1) of **20Zn**. Asterisk marks residual of solvents.

References

1. K. Kameyama, M. Morisue, A. Satake and Y. Kobuke, *Angew. Chem., Int. Ed.*, 2005, **44**, 4763-4766.
2. M. García-Iglesias, K. Peuntinger, A. Kahnt, J. Krausmann, P. Vázquez, D. González-Rodríguez, D. M. Guldi and T. Torres, *J. Am. Chem. Soc.*, 2013, **135**, 19311-19318.
3. V. Bandi, M. E. El-Khouly, V. N. Nesterov, P. A. Karr, S. Fukuzumi and F. D'Souza, *J. Phys. Chem., C*, 2013, **117**, 5638-5649.
4. H. Xu and D. K. P. Ng, *Inorg. Chem.*, 2008, **47**, 7921-7927.
5. D. M. Guldi, J. Ramey, M. V. Martinez-Diaz, A. d. l. Escosura, T. Torres, T. Da Ros and M. Prato, *Chem. Commun.*, 2002, 2774 - 2775.
6. M. E. El-Khouly and S. Fukuzumi, *Photochem. Photobiol. Sci.*, 2016, **15**, 1340-1346.
7. B. Platzer, B. Berionni Berna, M. Bischetti, D. O. Cicero, R. Paolesse, S. Nardis, T. Torres and D. M. Guldi, *Chem. Eur. J.*, 2022, **28**, e202103891