ESI for:

Merging Catalysis and Supramolecular Aggregation Features of Triptycene based Zn(salphen)s

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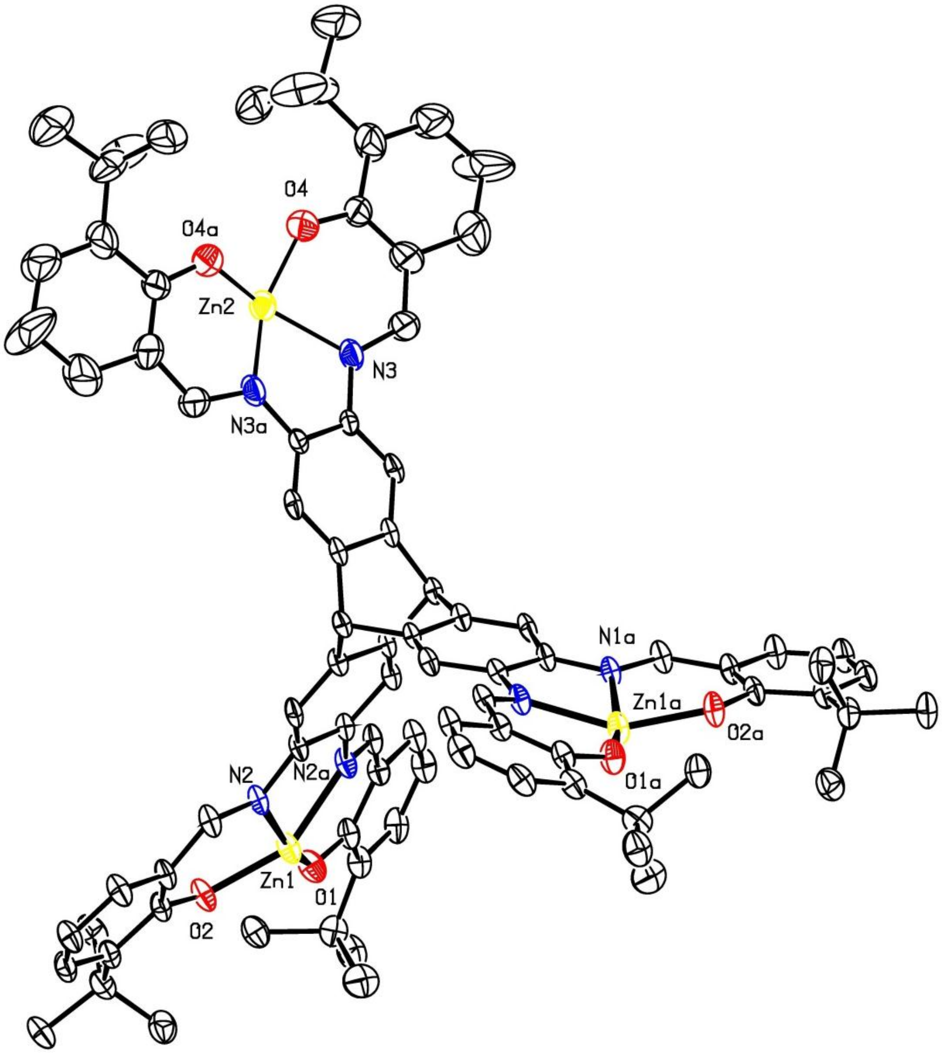
Content:

X-ray molecular structure for Zn$_3$ complex **1**:



Note: co-crystallized solvent molecules, H-atoms and coordinating solvent molecules are not shown for clarity reasons. The disorder is also not shown in the graphical representation. Details can be found in the related paper text and/or in the cif file.

UV-Vis titration studies with complex **8**:

The dimerization constant was determined for **8** by monitoring the disruption of the dimeric complex upon the addition of competitive pyridine using UV-Vis. Upon addition of pyridine, the absorption maximum at λ = 409 nm increased and a typical red-shift to λ = 424 nm occurred (see Figure S1 below). The isosbestic point at λ = 401 nm suggested the presence of multiple species in solution.

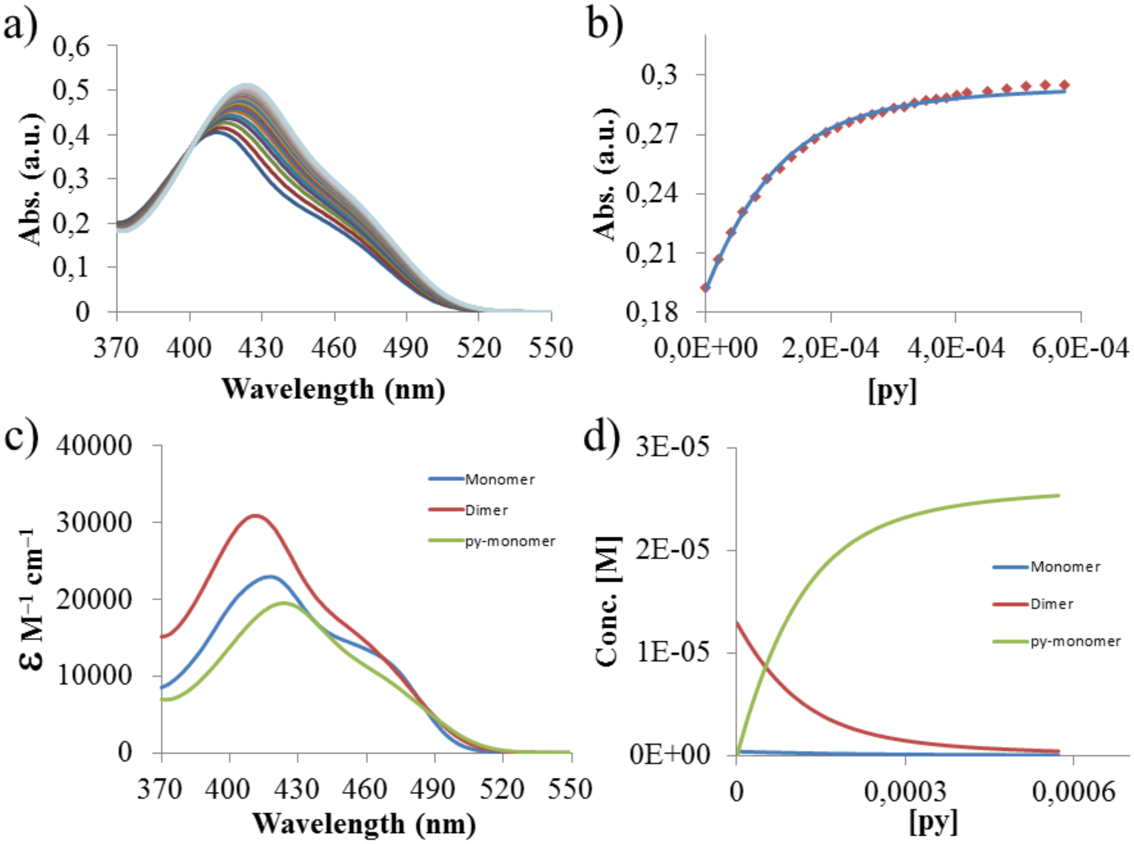
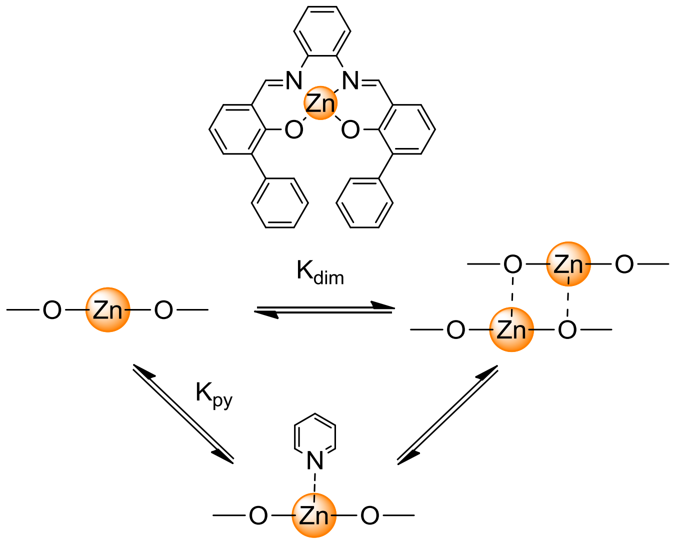


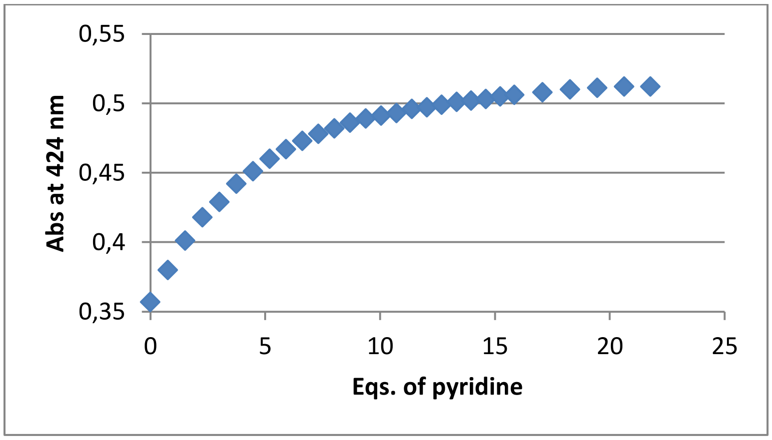
*Figure S1: (A) Spectral changes of complex **8** upon the addition of pyridine carried out in toluene at [**8**] = 2.63×10^{-5} M, and (B) the corresponding titration curves and data fits at λ = 424 nm. (C) Simulated spectra and (D) Simulated concentration profiles for this titration at the specified equilibrium constants.*

The pyridine titration data for complex **8** was analysed with Specfit/32[1] considering the binding model shown in Scheme S1, which includes three coloured species (monomer, dimer and the pyridine-coordinated complex). If we assume the value of pyridine association is similar to a Zn(salphen) complex having two *tert*-butyl substituents in the 3-position ($K_{py} = 5.89 \times 10^5$ M^{-1})[2] then the dimerization constant K_{dim} is determined at 7.31 (± 0.01) × 10^8 M^{-1}.



Scheme 1: the involved equilibria; K_{dim} is the stability constant of the dimeric complex and K_{py} denotes the association constant for pyridine binding.

[**8**] = 2.63 x 10^{-5} M:



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[1] Specfit/32^{TM}, version 3.0; Spectra Software Associates. Specfit/32 is a multivariate data analysis program for modeling and fitting multi-wavelength titration data sets giving more reliable parameters than single-wavelength fits. For software details and the related nonlinear algorithms see: a) H. Gampp, M. Maeder, C. J. Meyer, D. A. Zuberbühler, *Talanta* **1985**, *32*, 95; b) H. Gampp, M. Maeder, C. J. Meyer, D. A. Zuberbühler, *Talanta* **1986**, *33*, 943.

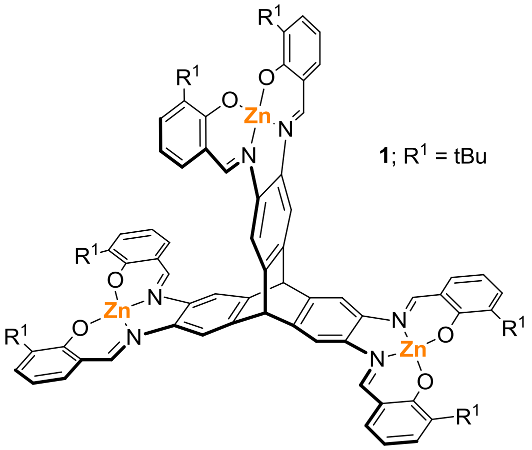
[2] J. A. A. W. Elemans, S. J. Wezenberg, M. J. J. Coenen, E. C. Escudero-Adán, J. Benet-Buchholz, D. den Boer, S. Speller, A. W. Kleij, S. De Feyter, *Chem. Commun.* **2010**, *46*, 2548.

UV-Vis titration carried out for **1** and **6**, **7**, **9**, and **10**:

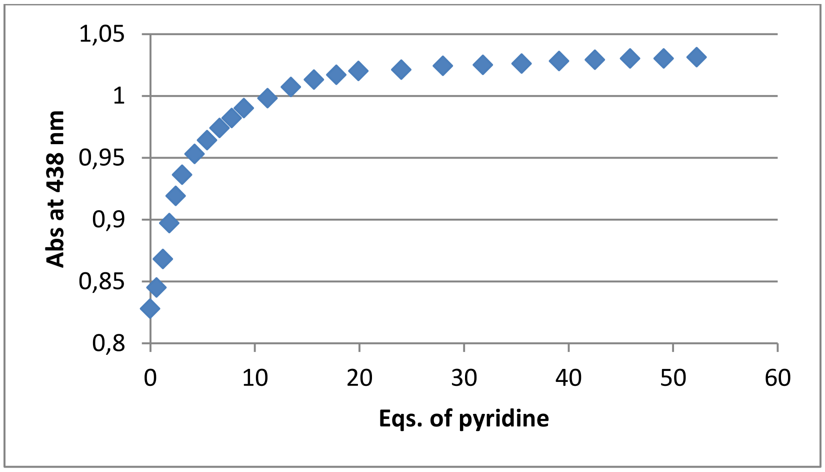
General information: A solution of the host was prepared in dry toluene at an approximate 1×10^{-5} M concentration. A solution of guest (or better: titrant = pyridine or 1,2-epoxyhexane) was prepared using the host solution as solvent medium in order to keep the concentration of the host constant after each addition of guest. Aliquots of the guest solution were added stepwise to 2.00 mL of the host solution in a 1.00 cm quartz cuvette. After each addition, a UV-Vis spectrum was acquired. The absorbance at the λ_{max} of the characteristic band of Zn(salphen)s (region 400-450 nm) was plotted against the equivalents of guest added.

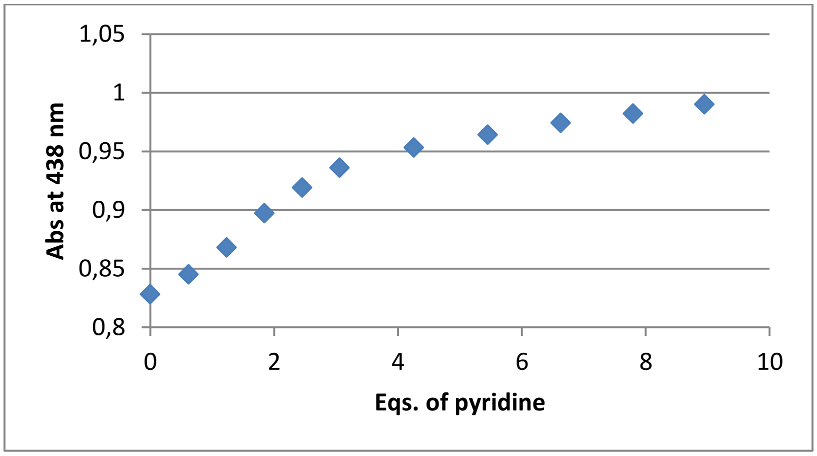
UV-Vis titration carried out with **PYRIDINE** as titrant:

Complex **1**:

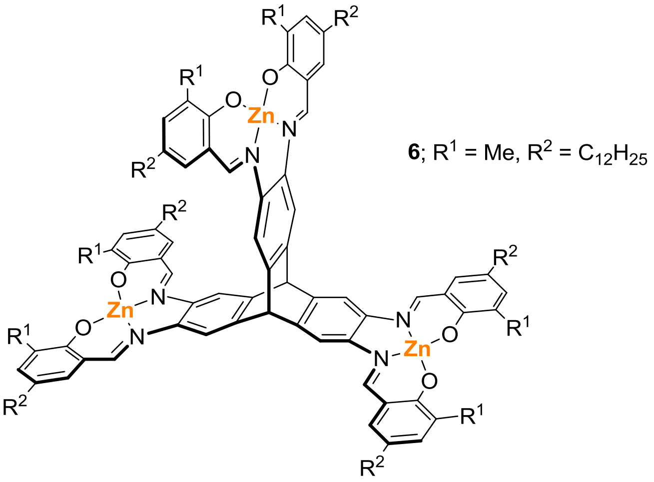


[**1**] = 1.00 × 10^{-5} M

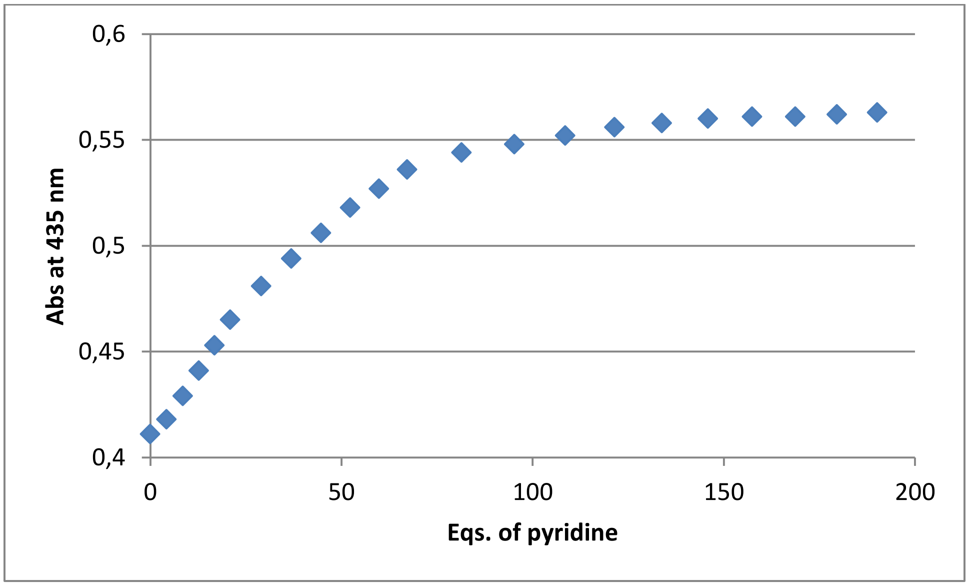




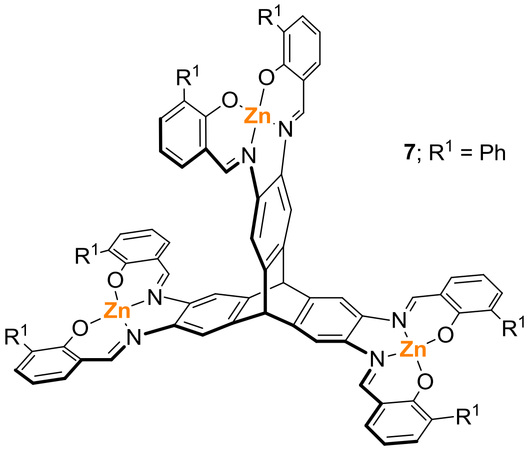
Complex **6**:



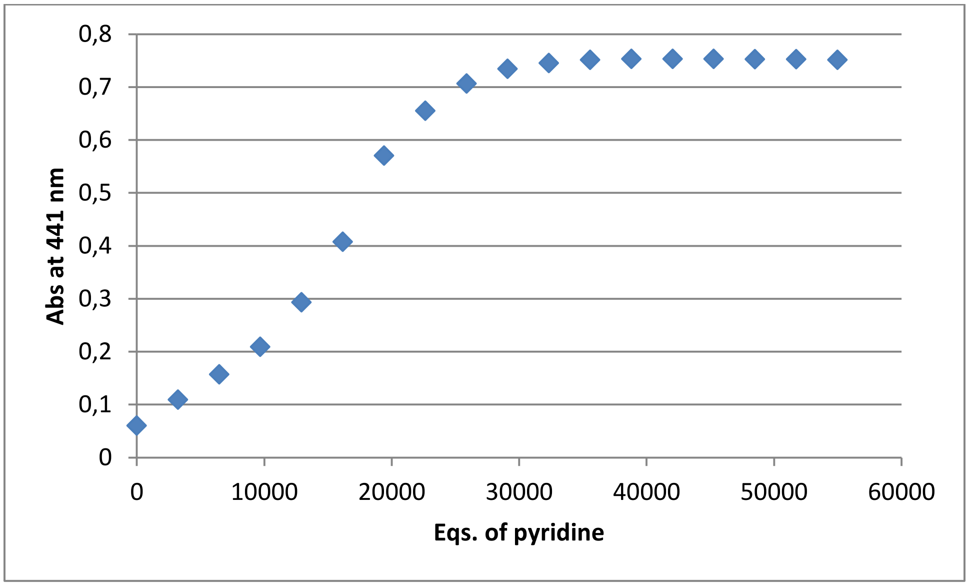
[**6**] = 0.93 × 10^{-5} M



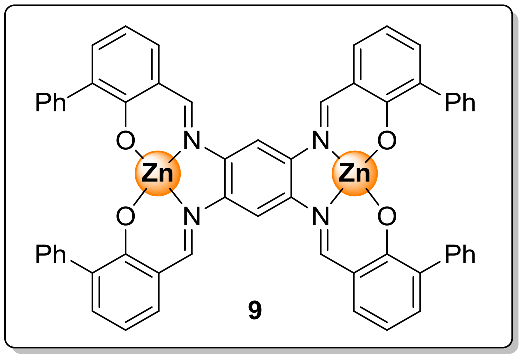
Complex **7**:



[**7**] = 0.96×10^{-5} M



Complex **9**:



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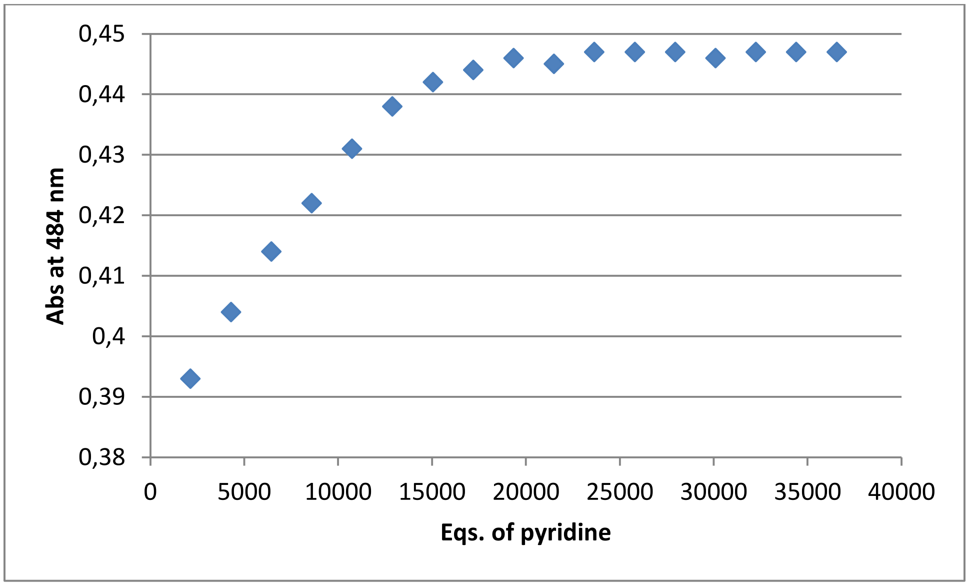
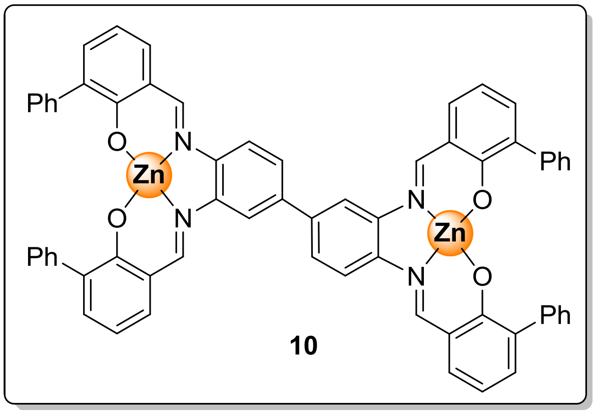
[**9**] = 1.01×10^{-5} M



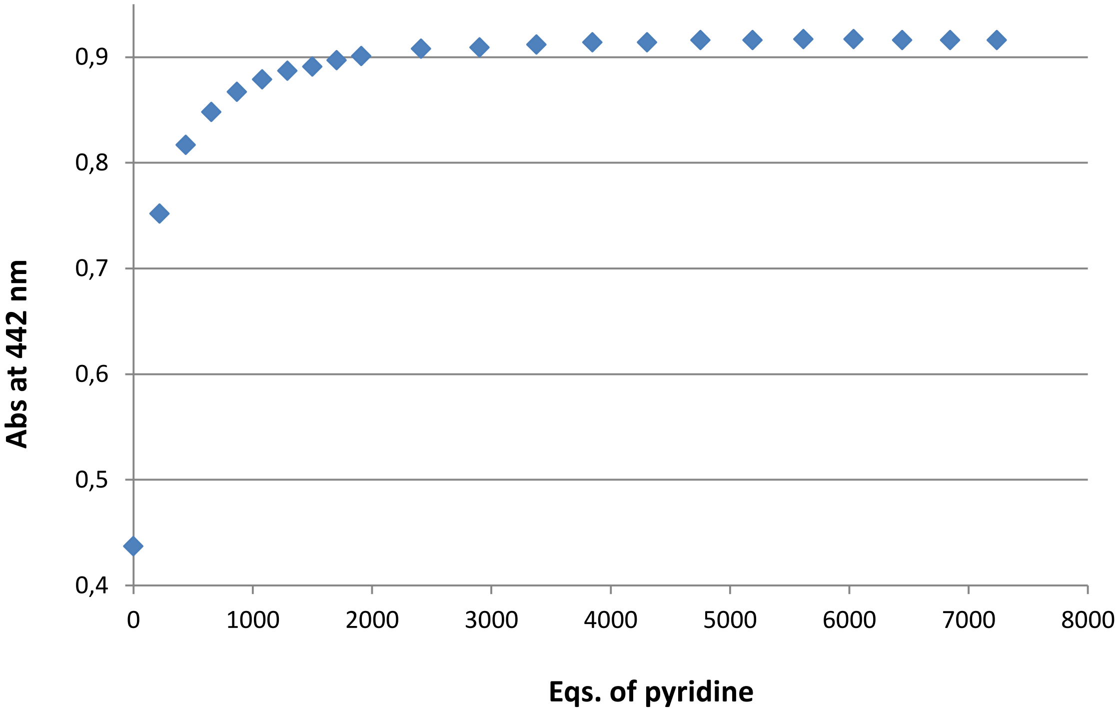
Please note that due to the rather insoluble nature of complex* ***9* *in toluene the titration was started with an initial amount of pyridine already present.*

Complex **10**:



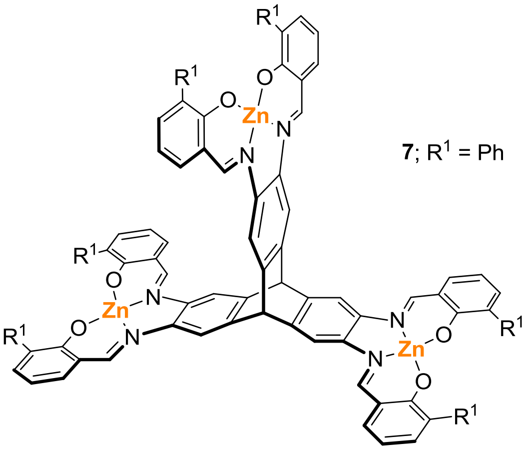
10

[**10**] = 0.84×10^{-5} M

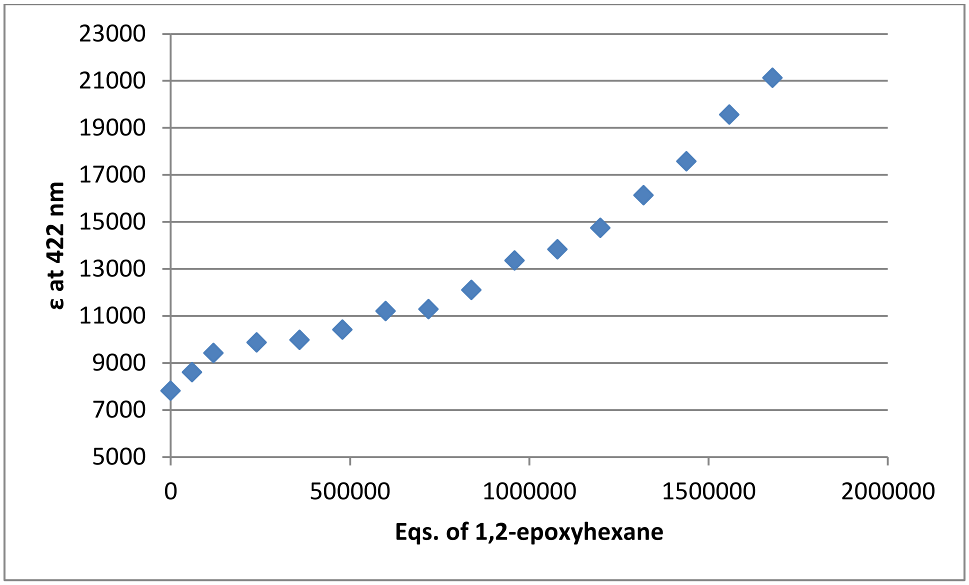


UV-Vis titration carried out with **1,2-EPOXYHEXANE** as titrant:

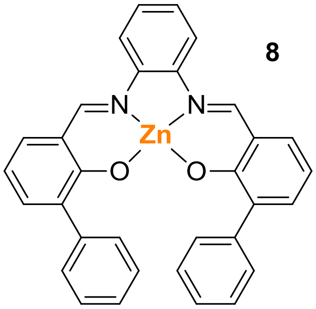
Complex **7**:



[**7**] = 0.35 × 10^{-5} M

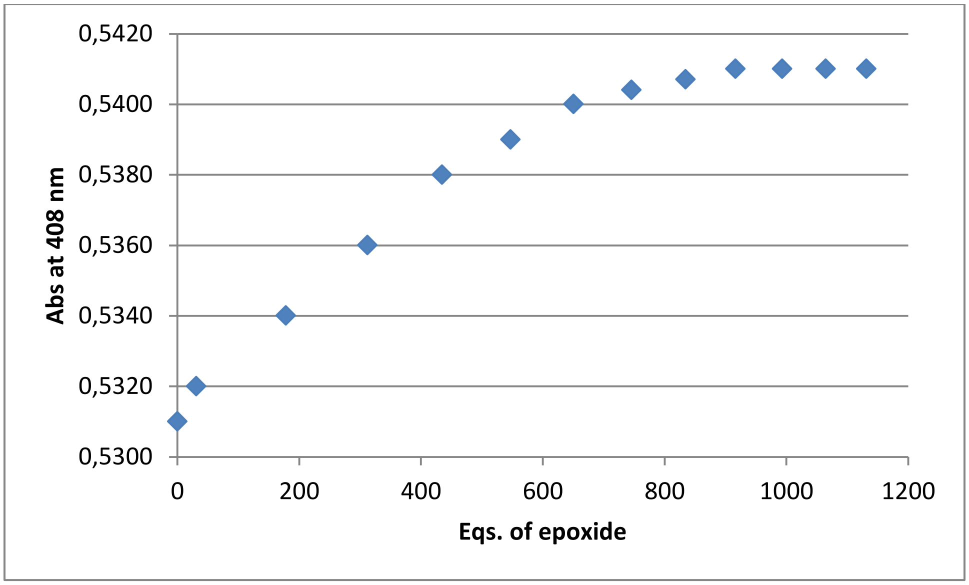


Complex **8**:

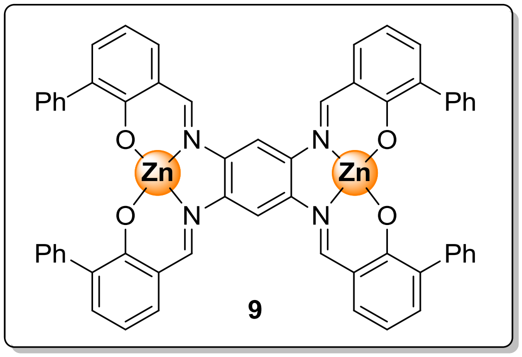


8

[**8**] = 2.63 × 10^{-5} M

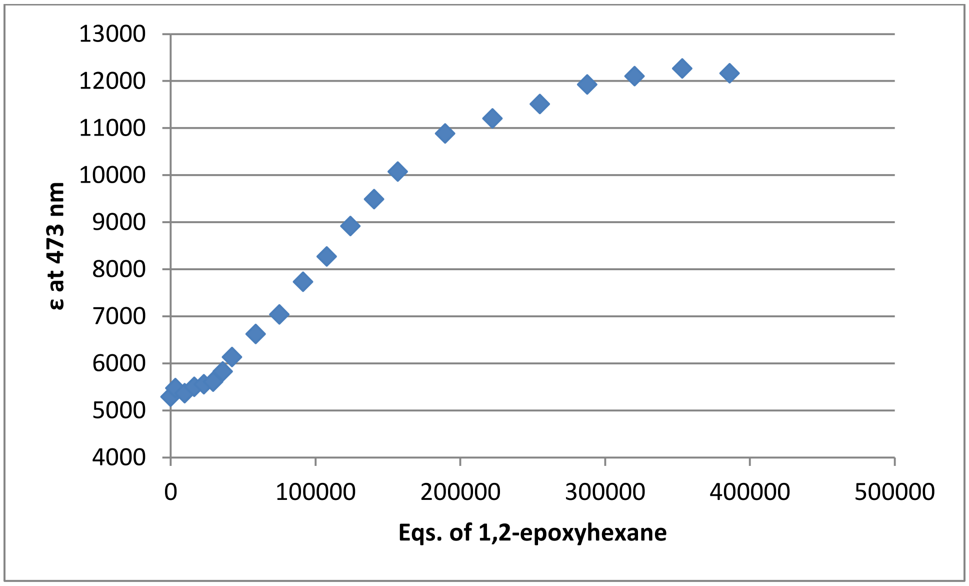


Complex **9**:

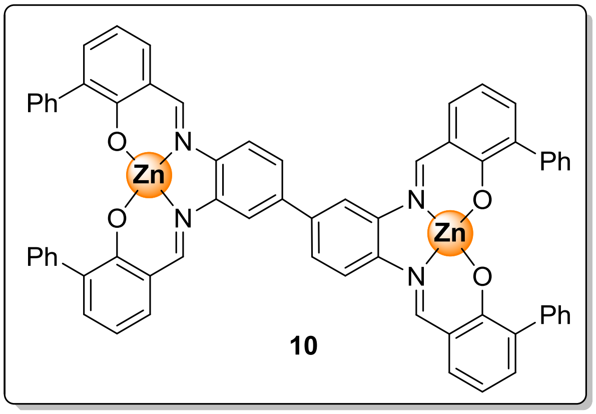


9

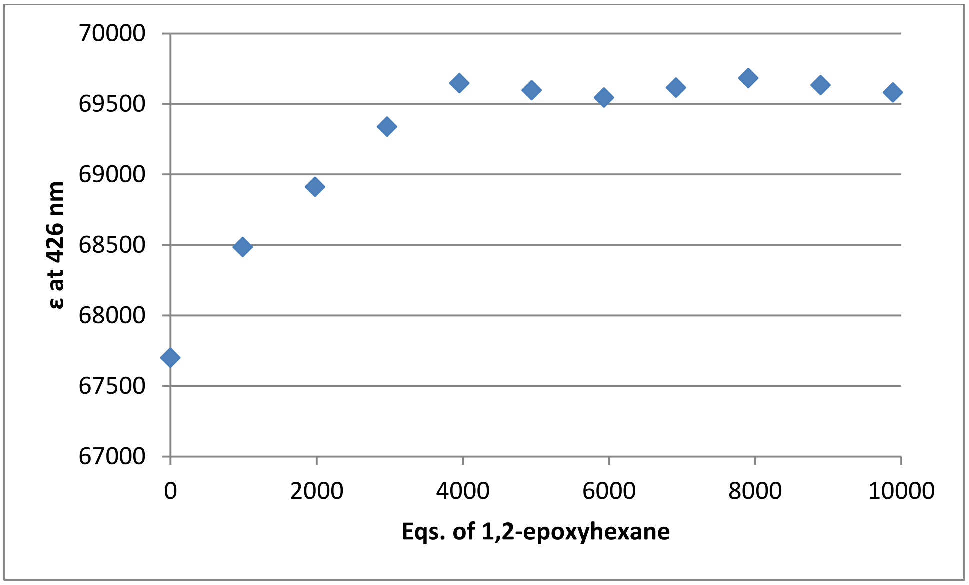
[**9**] = 1.27×10^{-5} M



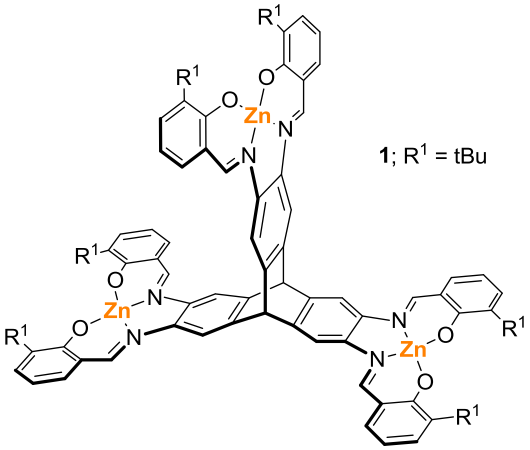
Complex **10**:



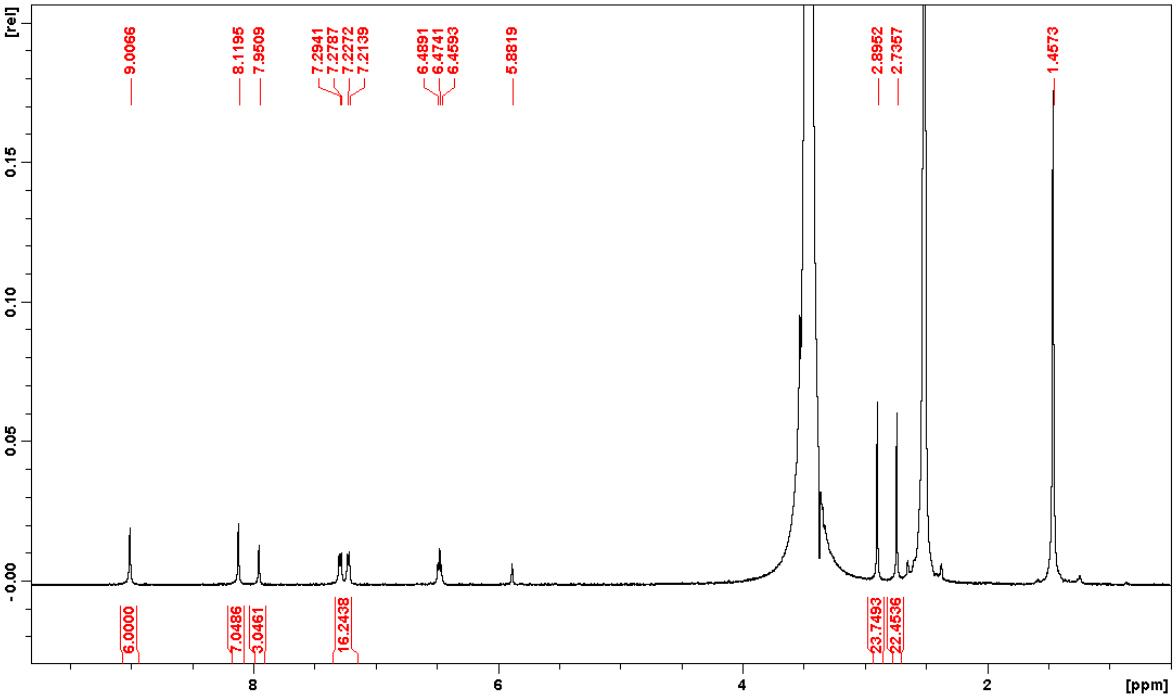
[**10**] = 0.84×10^{-5} M



^{1}H NMR spectrum of isolated complex **1**:

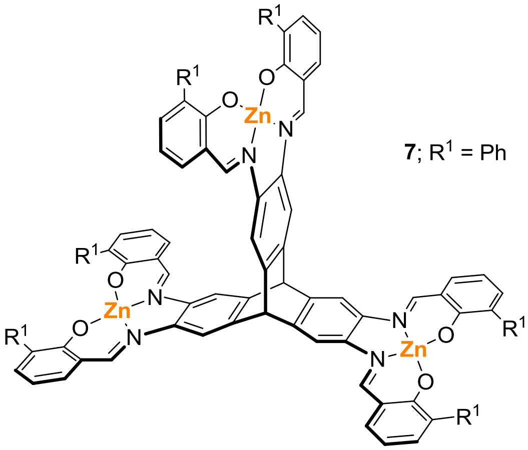


1; R^1 = tBu

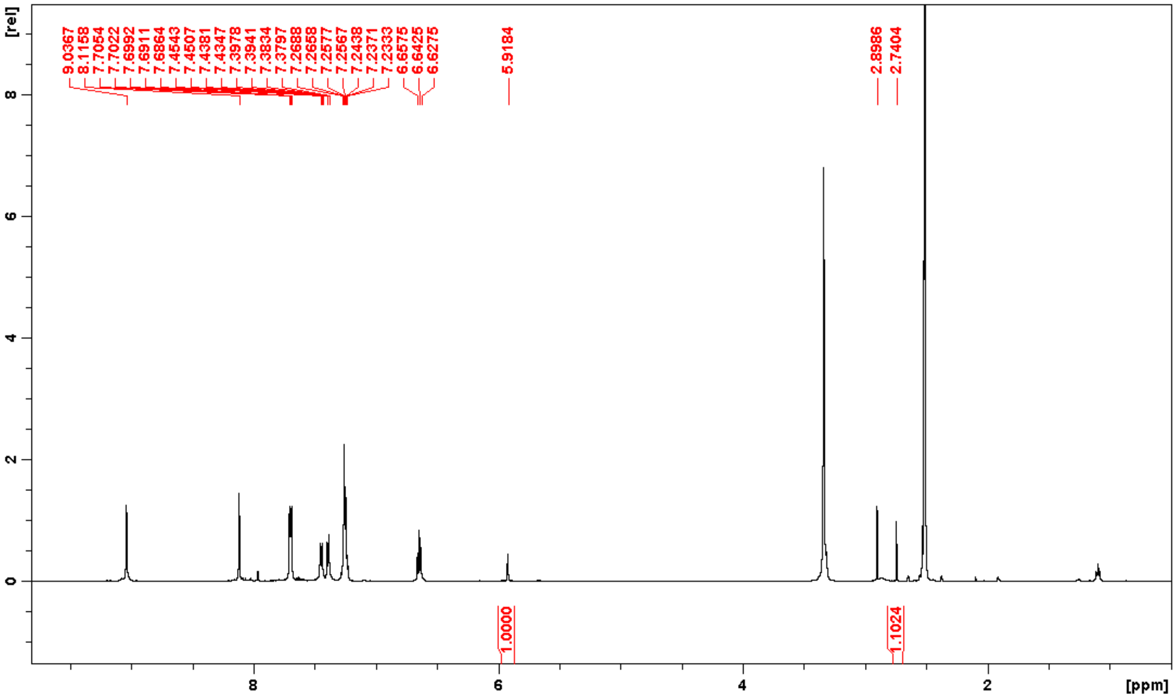


The ^{1}H NMR analysis ([D$_6$]DMSO) of isolated **1** confirms the presence of around 3 molecules of DMF; note the peaks at 2.73/2.89 ppm and around 7.95 ppm (CH of DMF).

^{1}H NMR spectrum of isolated complex **7**:

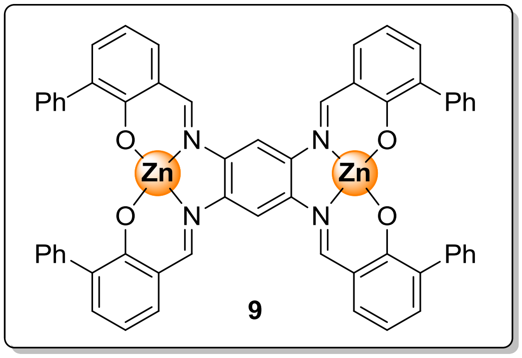


7; R^1 = Ph

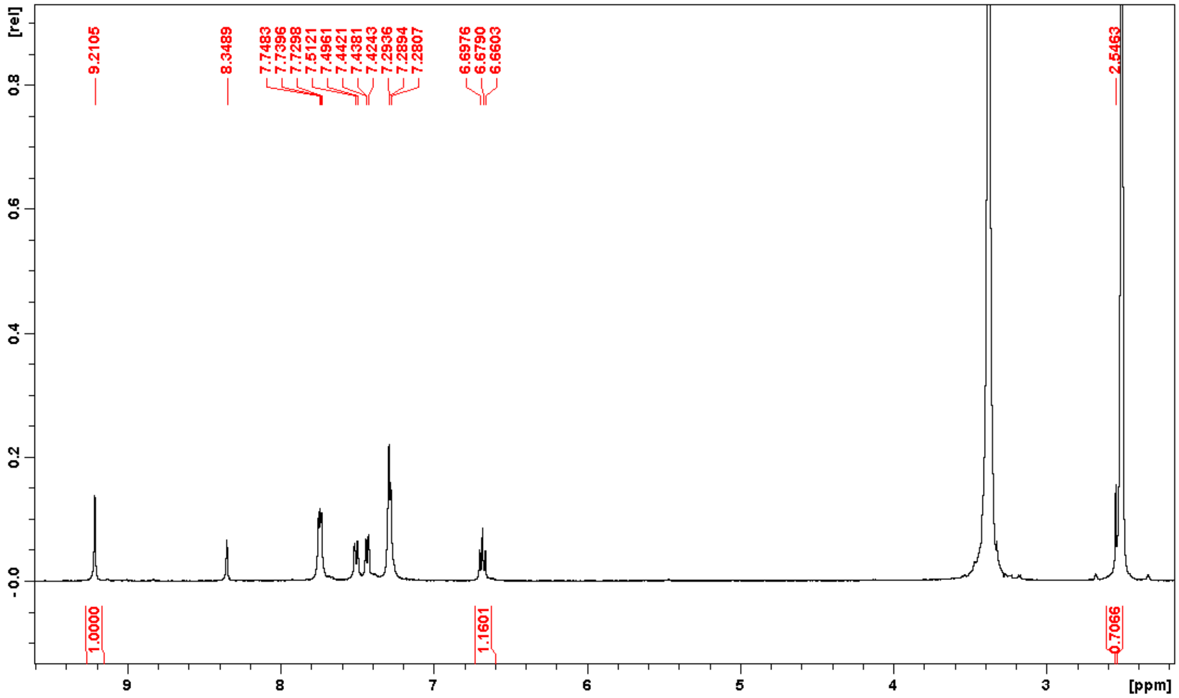


The ^{1}H NMR analysis ([D$_6$]DMSO) of isolated **7** confirms the presence of around 1 molecule of DMF; note the peaks at 2.74/2.90 ppm and around 5.92 ppm (CH of **7**).

^{1}H NMR spectrum of isolated complex **9**:

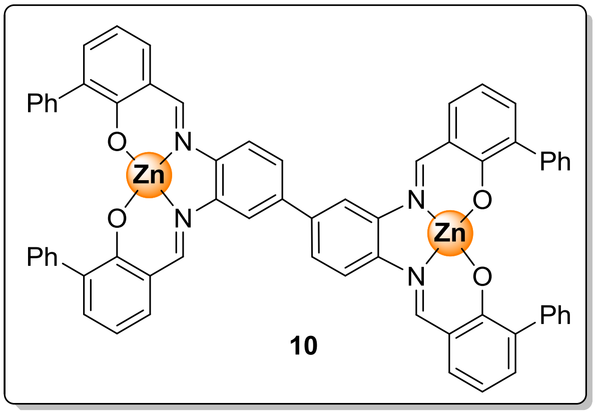


9



The ^{1}H NMR analysis ([D$_6$]DMSO) of isolated **9** confirms the presence of around 0.5 molecule of DMSO; note the peaks at 2.54 ppm (DMSO) versus the one around 9.21 ppm (CH=N of **9**).

^{1}H NMR spectrum of isolated complex **10**:



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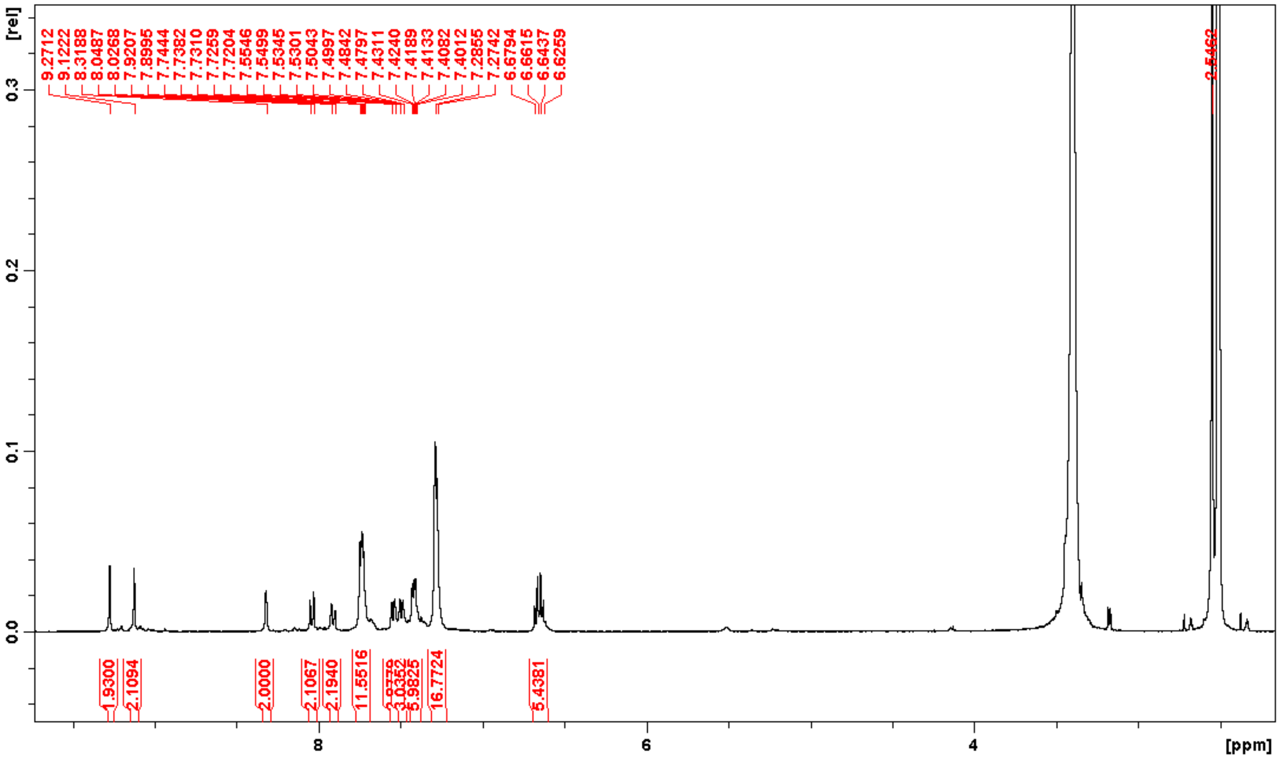
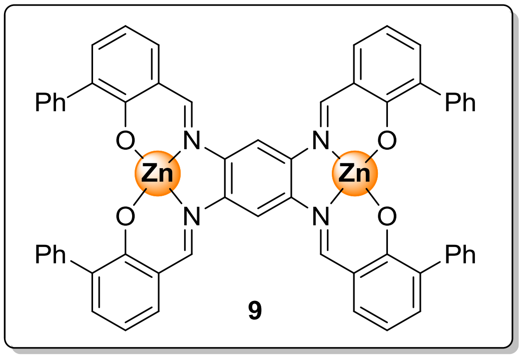


The ^{1}H NMR analysis ([D$_6$]DMSO) of isolated **10** confirms the presence of DMSO though the exact amount could not be determined due to strong overlap with the deuterated solvent; note the peaks at 2.54 ppm (DMSO-H$_6$).

The product was recrystallized from DMSO/MeOH but not all DMSO could be removed by this procedure as is clearly visible.

Catalyst recycling attempt using complex **9**:



9

During the Et_2O extraction procedure an inseparable mixture of two liquid phases (see above) was obtained, which proved to be impractical for catalyst recycling. The same feature was noted upon recycling **10**/NBu_4I under similar conditions.