Supporting Information

Tuning the Porphyrin Building Block in Self-Assembled Cages for Branched-Selective Hydroformylation of Propene

Xiaowu Wang⁺, [a, c] Sandra S. Nurttila⁺ [a] Wojciech I. Dzik⁻ [a] René Becker⁻ [a] Jody Rodgers⁻ [b] and Joost N. H. Reek⁺[a]

chem_201702113_sm_miscellaneous_information.pdf
1 Materials and methods

All reactions were carried out under an atmosphere of N₂ using standard Schlenk techniques unless otherwise stated. CH₂Cl₂ was distilled from CaH₂ under N₂, and pentane and toluene were distilled from Na under N₂. NMR spectra were recorded on a Bruker AMX 300 (300.1 MHz, 75.5 MHz and 121.5 MHz for ¹H, ¹³C and ³¹P respectively), Bruker AMX 400 (400.1 MHz, 100.6 MHz and 162.0 MHz for ¹H, ¹³C and ³¹P respectively) and Bruker AMX 500 (500.1 MHz, 125.8 MHz and 202.5 MHz for ¹H, ¹³C and ³¹P respectively). CDCl₃ was used as a solvent unless otherwise noted and the ¹H NMR spectra were referenced to the solvent residual signal. ESI-MS measurements were recorded on a JEOL JMS SX/SX102A four sector mass spectrometer, UV-vis spectra were recorded on a Shimadzu UV-2000 spectrophotometer, using a 10 mm quartz cuvette. Gas chromatographic analyses of 1-octene hydroformylation were performed on a Shimadzu GC-17A apparatus. Gas chromatographic analyses of propene hydroformylation were performed both on a Trace GC-ultra apparatus (Thermo electron cooperation) and a Shimadzu GC-17A apparatus. Kinetic data were recorded by Brooks 0254. X-ray crystal diffraction data was collected on a Bruker D8 Quest Eco single crystal diffractometer equipped with a CMOS Photon 50 detector, using Mo Ka radiation. All reagents were purchased from commercial suppliers and used without further purification, unless otherwise noted. 1-octene was filtered over basic alumina before use. The following compounds were synthesized according to published procedures: P(m-py)₃[¹], Zn(II)TPP[²] and Zn(II)TPPL[³,⁴].
2 Synthesis of compounds

2.1 Preparation of tris-(3-pyridyl)phosphine

Modified literature procedure\(^1\): 1,2-Dibromoethane (2.0 mL, 23 mmol) was added dropwise to Mg turnings (7.0 g, 288 mmol) in 200 mL anhydrous THF, followed by the addition of 3-bromopyridine (10 mL, 103 mmol) at such a rate to maintain a steady reflux. The resulting mixture was heated at mild reflux at 56 °C for 30 minutes after the addition of 3-bromopyridine was complete, followed by the addition of 100 mL anhydrous THF. The reaction mixture was slowly added \textit{via} a cannula to a solution of PCl\(_3\) (2.2 mL, 25 mmol) in 50 mL anhydrous THF at -78 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with 5 mL N\(_2\) purged water and all volatiles were evaporated to yield a yellow sticky solid. Afterwards, 200 mL N\(_2\) purged diethylamine was added to the residue and the suspension was stirred for 30 minutes under N\(_2\). The yellow precipitate was filtered off quickly through a Büchner funnel in air and washed with diethylamine (3 x 70 mL). All organic fractions were combined and the solvent was quickly removed by rotary evaporation to give a bright yellow oil. The product was purified by flash column chromatography (silica, eluent: chloroform / hexane = 2 / 1, 1 % triethylamine) under a N\(_2\) atmosphere. Yield 1.6 g (light yellow oil, 24 % yield, afterwards low melting waxy compound). \(^1\)H NMR (300 MHz, CDCl\(_3\), 298 K): \(\delta = 8.64\) (m, 1H), \(8.54\) (m, 1H), \(7.58\) (m, 1H), \(7.32\) (m, 1H). \(^{31}\)P\({}^{1}\)H\(\) (121.5 MHz, CDCl\(_3\), 298 K): \(\delta = -24.4\) ppm.
Figure S 1. $^1$H NMR spectrum (300 MHz, 298 K) of P(m-py)$_3$ in CDCl$_3$.

Figure S 2. $^{31}$P$^1$H NMR spectrum (122 MHz, 298 K) of P(m-py)$_3$ in CDCl$_3$. 
2.2 Preparation of meso-tetraphenyl-2-oxa-3-oxoporphyrinato Zinc(ii)

Modified literature procedure\textsuperscript{[3,4]}:

**Step 1:** To a stirred mixture of 5,10,15,20-tetraphenylporphyrin (1.5 g, 2.4 mmol, 1 eq) and RuCl\(_3\) (248.9 mg, 1.2 mmol, 0.5 eq) in 1,2-dichloroethane (DCE) (750 mL) and water (750 mL), respectively, a DCE solution (20 mL) of 2,2’-bipyridine (187.4 mg, 1.2 mmol, 0.5 eq) was added. The solution was heated to 100 °C. A mixture of Oxone\textsuperscript{®} (7.377 g, 12 mmol, 5 eq) and NaOH (480 mg, 12 mmol, 5 eq) was added in 5 portions over a period of 5 h. The reaction was quenched with a saturated aqueous solution of Na\(_2\)S\(_2\)O\(_3\), where after the organic layer was separated and the aqueous layer was extracted twice with dichloromethane. The combined organic layers were dried with Na\(_2\)SO\(_4\), filtered, and concentrated under vacuum. The residue was purified by column chromatography (silica gel, eluent: CH\(_2\)Cl\(_2\) / hexane = 2 : 1) to give the product, 5,10,15,20-tetraphenylporpholactone, as a purple solid (yield 45 %, 683.3 mg, 1.08 mmol). \(^1\)H NMR (500 MHz, CDCl\(_3\), 293 K): δ = 8.80 (dd, \(J = 5.0, 1.7\) Hz, 1 H), 8.76 (dd, \(J = 5.0, 1.8\) Hz, 1 H), 8.70 (dd, \(J = 4.9, 1.7\) Hz, 1 H), 8.60 (d, \(J = 4.9\) Hz, 1 H), 8.58 (dd, \(J = 4.6, 1.4\) Hz, 1 H), 8.53 (d, \(J = 4.5\) Hz, 1H), 8.13 (m, 2 H), 7.98 (m, 2 H), 7.73 (m, 12 H), -1.66 (s, 1 H, NH), -2.03 (s, 1 H, NH).

**Step 2:** 5,10,15,20-Tetraphenylporpholactone (290 mg, 0.458 mmol, 1 eq) and Zn(OAc)\(_2\) were suspended in 120 mL solvent (CHCl\(_3\) / EtOH = 2 : 1). The reaction mixture was heated up to 70 °C for 2 h. Afterwards, the reaction mixture was cooled down and filtered through Celite. The filtrate was concentrated and purified by column chromatography (silica gel, eluent: CH\(_2\)Cl\(_2\), \(R_f = 0.44\)). The bright green band was collected and all the solvent was evaporated, which afforded a green purple solid in 80 % yield (255 mg, 0.366 mmol). \(^1\)H NMR (500 MHz, CDCl\(_3\), 298 K): δ = 8.72 (bs, 6 H), 8.13 (bs, 6 H), 7.8 (bs, 14 H). Due to strong self-aggregation, the peaks are broad and cannot be assigned. For better resolution of peaks, 2 eq. of pyridine was added. \(^1\)H NMR (500 MHz, CDCl\(_3\), 298 K): \(^1\)H NMR (500 MHz, CDCl\(_3\), 293 K): \(^1\)H NMR (500 MHz, CDCl\(_3\), 298 K): \(^1\)H NMR (500 MHz, CDCl\(_3\), 293 K): δ = 8.74 (d, \(J = 4.7\) Hz, 1 H, pyrrole-H), 8.66 (dd, \(J = 7.3\) Hz, 4.6 Hz, 2 H, pyrrole-H), 8.60 (d, \(J = 4.5\) Hz, 1 H, pyrrole-H), 8.54 (d, \(J = 4.5\) Hz, 1 H, pyrrole-H), 8.50 (d, \(J = 4.5\) Hz, 1 H, pyrrole-H), 8.10 (d, \(J = 7.7\) Hz, 4H), 8.05 (d, \(J = 6.7\) Hz, 2H, Ph-H), 7.93 (d, \(J = 6.2\) Hz, 2H, Ph-H), 7.70 (m, 12H, Ph-H), 7.17 (t, \(J = 7.5\) Hz, 2 H, p-Py), 6.58 (t, \(J = 7.5\) Hz, 4 H, m-Py), 5.93 (bs, 4 H, o-Py).
Figure S 3. $^1$H NMR spectrum (400 MHz, 298 K) of TPPL-2H in CDCl$_3$. 
Figure S 4. $^1$H NMR spectrum (300 MHz, 298 K) of Zn(II)TPPL and 2 eq. pyridine in CDCl$_3$.

3 Catalysis procedures and gas chromatographic analysis

3.1 1-Octene hydroformylation

Preparation of Schlenk solution of precatalyst: in a flame-dried Schlenk flask (15 mL) under N$_2$, the following substances were added and stirred for 5 min: metalloporphyrin (30 µmol), P(m-py)$_3$ stock solution in dry toluene ($26 \times 10^{-3}$ M, 10 µmol), dry toluene (5 mL), Rh(acac)(CO)$_2$ stock solution in dry toluene ($5 \times 10^{-3}$ M, 2 µmol), DIPEA (diisopropylethylamine, 0.01 mL), 1-octene (filtered over basic alumina, 1.6 mL, 10.214 mmol).

Catalytic reaction with incubation: A mini-autoclave (15 mL) was evacuated and flushed with N$_2$ three times. The Schlenk solution (without addition of 1-octene) was injected into the mini-autoclave with a 10 mL syringe and stainless steel needle (~25 cm) under N$_2$. 0.5 mL toluene was used to flush the Schlenk flask and transferred to the mini-autoclave. The system was carefully flushed three times with syngas (20 bar, CO / H$_2$ = 1 : 1). Then the autoclave was
pressurized to 20 bar (CO / H₂ = 1 : 1), immersed into a pre-heated oil bath at predefined temperature and stirred with constant speed (900 rpm). The solution in the autoclave was stirred for 1 h. Afterwards, the autoclave was depressurized and 1-octene (1.6 mL) was added with a 15 mL stainless steel needle. The autoclave was then carefully flushed three times with syngas (20 bar, CO / H₂ = 1 : 1) and the pressure subsequently adjusted to 20 bar. After 18 h, the reactor was cooled down in an ice bath, where after the autoclave was opened after the pressure was released. Three drops of n-tributylphosphite were added to the reaction mixture to quench the active rhodium catalyst. 10 µL of the reaction mixture was taken and diluted with 990 µL dichloromethane and injected into the GC directly without workup or product isolation.

1-Octene hydroformylation analyses were performed on a Shimadzu GC-17A apparatus (5 µL injection, split/splitless injector, J&W Scientific, DB-1J&W 30 m column, diameter 0.32 mm, film thickness 2.0 µm, carrier gas 600 kPa He, flow 7 mL/min, FID Detector). The oven was initially held at 70 ºC for 1 min, then increased to 120 ºC at a rate of 7 ºC per minute, the ramp was then increased to 13 ºC per minute until the temperature reached 250 ºC. The products could be identified with the following retention times: 1-octene (5.94 min), 3-octene (6.15 min), octane (6.20 min), 2-octene (6.40 min), decane (10.28 min), 2-methyloctanal (11.16 min), nonanal (11.83 min) (see Figure S 5). Only the linear product (nonanal) was calibrated against the internal standard (n-decane). It was assumed that the branched product would have the same response factor in the gas chromatograph. 1-octene was calibrated against the internal standard (n-decane) and it was assumed that all isomers of the substrate would also have a similar response factor in the gas chromatograph.
Figure S 5. A gas chromatogram after 1-octene hydroformylation.

3.2 Propene hydroformylation

Preparation of Schlenk solution of precatalyst: in a flame-dried Schlenk flask (15 mL) under N₂, the following substances were added and stirred for 5 min: metalloporphyrin (30 µmol), P(m-py)₃ stock solution in dry toluene (26x10⁻³ M, 10 µmol), dry toluene (5 mL), Rh(acac)(CO)₂ stock solution in dry toluene (5x10⁻³ M, 2 µmol), DIPEA (diisopropylethylamine, 0.01 mL) and 1-decane (0.5 mL, 2.565 mmol).

A mini-autoclave (15 mL) was evacuated and flushed with N₂ three times. The Schlenk solution was injected into the mini-autoclave with a 10 mL syringe and stainless steel needle (~25 cm) under N₂. 0.5 mL toluene was used to flush the Schlenk flask and transferred to the mini-autoclave. The system was carefully flushed with propene (8 bar) three times. Then the autoclave was charged with 8 bar propene (the volume was recorded by a flow meter). Afterwards, the gas in the charging line was released and the charging line was charged with the syngas mixed in the mixing unit (~ 400 mL) with the required CO / H₂ ratio (the volume was recorded by a flow meter). Afterwards, the autoclave was immersed into a pre-heated oil bath at predefined temperature and stirred with constant speed (900 rpm). The gas consumption during the reaction was recorded by a flow meter. After a set reaction time, the reactor was
cooled down in an ice bath and the autoclave was opened after the pressure had carefully been released. Three drops of n-tributylphosphite were added to the reaction mixture to quench the active rhodium catalyst.

Gas chromatographic analyses of propene hydroformylation were performed on two GC machines: 20 µL of the reaction mixture was taken and diluted with 980 µL toluene and injected into the GC directly without isolation of the products. Trace GC-ultra apparatus (Thermo electron corporation, Rtx®-1 (® crossbond® 100 % dimethyl polysiloxane), 30 meters, 0.25 mm ID, 0.25 µm, Max Prog. Temp. 350 ºC, Min Bleed at 330 ºC, split flow 50 mL/min, Split ratio 10, carrier gas 70 kPa He, FID Detector). The oven was initially held at 35 ºC for 0 min, then increased to 80 ºC at a rate of 3 ºC per minute and held for 5 min, the ramp was then increased to 10 ºC per minute until the temperature reached 150 ºC and held for 2 min. The products could be identified with the following retention times: isobutyraldehyde (2.64 min), n-butyraldehyde (2.86 min) and n-decane (15.37 min) (see Figure S 6). The GC was calibrated for propene hydroformylation using n-decane as an internal standard. Both the linear and branched products were calibrated against the internal standard and against each other.

20 µL of the reaction mixture was taken and diluted with 980 µL dichloromethane and injected into the GC directly without isolation/purification of the products. Shimadzu GC-17A apparatus (5µL injection, split/splitless injector, J&W Scientific, DB-1J&W 30 m column, diameter 0.32 mm, film thickness 2.0 µm, carrier gas 600 kPa He, flow 7 mL/min, FID Detector). The oven was initially held at 50 ºC for 3 min, then increased to 120 ºC at a rate of 7 ºC per minute, the ramp was then increased to 13 ºC per minute until the temperature reached 250 ºC. The products could be identified with the following retention times: dichloromethane (2.93 min), isobutyraldehyde (3.31 min), n-butyraldehyde (3.81 min) and n-decane (14.76 min) (see Figure S 7). The GC was calibrated for propene hydroformylation using n-decane as internal standard. Both the linear and branched products were calibrated against the internal standard and against each other.
Figure S 6. A gas chromatogram after propene hydroformylation.
**Channel A Results**

| Peak | Time (min) | Area | Area % |
|------|------------|------|--------|
| 1    | 2.93       | 29911302 | 63.036 |
| 2    | 3.31       | 996269   | 2.100  |
| 3    | 3.81       | 1057961  | 2.230  |

**Figure S 7.** A gas chromatogram after propene hydroformylation.

**4 Hydroformylation results**

**Table S 1.** Propene hydroformylation at different CO / H\(_2\) ratios using assembly L1 under 20 bar pressure at 80 °C.

| Entry | Reaction time (h) | Syngas ratio | aldehyde (mmol) | TOF (h\(^{-1}\)) | n-butyraldehyde (mmol) | iso-butyraldehyde (mmol) | TOF (h\(^{-1}\)) (n)\(^b\) | TOF (h\(^{-1}\)) (iso)\(^c\) | l/b |
|-------|-------------------|--------------|-----------------|------------------|------------------------|--------------------------|-------------------------|--------------------------|-----|
| 1     | 15.8              | CO/H\(_2\) = 1:1 | 15.5            | 2472             | 9.5                    | 6.0                      | 1514                    | 958                      | 1.58 |
| 2     | 16.1              | CO/H\(_2\) = 2:1 | 9.4             | 1081             | 5.1                    | 4.3                      | 583                     | 498                      | 1.17 |
| 3     | 18.4              | CO/H\(_2\) = 3:1 | 5.6             | 676              | 3.0                    | 2.6                      | 363                     | 313                      | 1.16 |
| 4     | 17.1              | CO/H\(_2\) = 1:2 | 6               | 3333             | 3.9                    | 2.0                      | 2203                    | 1130                     | 1.75 |
| 5     | 18.5              | CO/H\(_2\) = 1:3 | 10.3            | 3664             | 6.6                    | 3.7                      | 2332                    | 1332                     | 1.95 |

\(a\) 2 µmol Rh(acac)(CO)\(_2\), 10 µmol P(m-py), 30 µmol Zn(II)TPP, 0.01 mL DIPEA (N,N-Diisopropylethylamine), 5.5 mL toluene, if not noted, propene pressure is 8 bar, \(b\) n means n-butyraldehyde, \(c\) iso means isobutyraldehyde.
Table S 2. Propene hydroformylation at different temperatures using assembly L1 under 20 bar syngas (CO/H₂ = 1:1).

| Entry | Reaction time (h) | Temperature (°C) | aldehyde (mmol) | TOF (h⁻¹) | n-butyaldehyde (mmol) | iso-butyaldehyde (mmol) | TOF (h⁻¹) (n)ᵇ | TOF (h⁻¹) (n)ᵇ | l/b |
|-------|------------------|------------------|-----------------|-----------|----------------------|------------------------|----------------|----------------|-----|
| 1     | 19.7             | 40 ºC            | 11.00           | 347       | 6.06                 | 4.94                   | 185            | 162            | 1.23|
| 2     | 17.0             | 70 ºC            | 15.19           | 1456      | 8.87                 | 6.33                   | 850            | 606            | 1.40|
| 3     | 15.8             | 80 ºC            | 15.46           | 2472      | 9.46                 | 6.00                   | 1514           | 958            | 1.58|

a) 2 µmol Rh(acac)(CO)₂, 10 µmol P(m-Py)₃, 30 µmol Zn(II)TPP, 0.01 mL DIPEA (N,N-Diisopropylethylamine), 5.5 mL toluene, if not noted, propene pressure is 8 bar, b) n means n-butyaldehyde, c) iso means isobutyaldehyde.

Table S 3. Propene hydroformylation at different temperatures using assembly L2 under 50 bar syngas (CO/H₂ = 3:1).

| Entry | Reaction time (h) | Temperature (°C) | aldehyde (mmol) | TOF (h⁻¹) | l/b |
|-------|------------------|------------------|-----------------|-----------|-----|
| 1     | 19.7             | 40 ºC            | 0.5             | 80        | 1.03|
| 2     | 17.0             | 50 ºC            | 2.8             | 140       | 1.09|
| 3     | 15.8             | 60 ºC            | 5.6             | 330       | 1.13|

a) 2 µmol Rh(acac)(CO)₂, 10 µmol P(m-Py)₃, 30 µmol Zn(II)TPP, 0.01 mL DIPEA (N,N-Diisopropylethylamine), 5.5 mL toluene, if not noted, propene pressure is 8 bar.

5 UV-vis binding studies
5.1 UV-vis binding studies of Zn(II)TPP and Zn(II)TPPL with P(m-py)₃

The binding affinities of P(m-py)₃ towards Zn(II)TPP and Zn(II)TPPL were obtained by two separate UV-vis titrations in toluene; however, the data could not be used to assign possible cooperativity in the system. The difficulty in trying to find cooperativity lies in the fact that the system is saturated towards a 1:1 host-guest complex during the UV-vis titration as phosphine is added to the porphyrin and not the other way around. In fact, only in the very beginning of the titration is some 3:1 host-guest complex, where the cooperativity effect will be most pronounced, present. This can be more easily understood by inspecting the calculated species concentration for the titration of Zn(II)TPP with P(m-py)₃ (see Figure S8). The concentration of the 3:1 host-guest complex is essentially non-existent throughout the supramolecular
titration. Therefore, UV-vis titrations for the 3:1 host-guest complexes were performed only to determine binding constants but not to assign cooperativity.

**Figure S 8.** The calculated species concentration during the titration of Zn(II)TPP with P(m-py)_3 in toluene at 298 K. The concentration of the HHHG species is low throughout the titration.

A solution of host, Zn(II)TPP or Zn(II)TPPL, in degassed toluene, and a stock solution of guest, P(m-py)_3, containing the same concentration of host were prepared respectively. Aliquots of P(m-py)_3 from the guest stock solution were added directly to a quartz cuvette containing the host solution. Each titration was performed by around 50 measurements at 298 K. Up to ca. 80 guest equivalents were added. The progress of the titration was monitored by the shifts in the Q-bands of the porphyrin (Zn(II)TPP) or porpholactone (Zn(II)TPPL). The microscopic (K) and macroscopic (K_1/K_2/K_3) association constants were defined as follows, with α_1 and α_2 the respective cooperativity factors^{[5]} and (3; 1; 1/3) the respective statistical factors^{[6]}:

\[
K_1 = 3 \cdot K = \frac{[HG]}{[G][H]}, \quad K_2 = K \cdot \alpha_1 = \frac{[HGG]}{[HG][G]} \quad \text{and} \quad K_3 = \frac{1}{3} \cdot K \cdot \alpha_2 = \frac{[HGGG]}{[HGG][G]},
\]

The UV-vis absorption at wavelength λ of the host species Zn(II)TPP or Zn(II)TPPL over the course of the titration is described by (the guest species has negligible absorptivity at the wavelengths used):

\[
A_\lambda = \epsilon_H \cdot [H] + \epsilon_{HG} \cdot [HG] + \epsilon_{HHG} \cdot [HHG] + \epsilon_{HHHG} \cdot [HHHG]
\]

The general fitting procedure is described in section 7 of this Supporting Information.
5.1.1 UV-vis binding study of Zn(II)TPP with P(m-py)$_3$

![Chemical structures of Zn(II)TPP and P(m-py)$_3$](image)

**Table S 4.** Conditions used for the 3:1 host-guest UV-vis binding study at 298 K.

| Host          | Zn(II)TPP          |
|---------------|--------------------|
| Guest         | P(m-py)$_3$        |
| Conc host / M | 44.2 µM            |
| [G]/[H] range | 0 - 89             |
| Solvent       | Toluene            |
| T / K         | 298                |
Figure S 9. Fitted UV-vis titration curves of Zn(II)TPP with P(m-py)₃ in toluene. Top: observed (circles) and calculated (dotted line) UV-vis absorption vs the logarithm of equivalents P(m-py)₃ added; Middle: percentage error in the fit vs the logarithm of equivalents P(m-py)₃ added; Bottom: calculated species concentration vs the logarithm of equivalents P(m-py)₃ added.
Table S 5. Fitting results for the 3:1 host-guest system between Zn(II)TPP and P(m-py)$_3$ in toluene for $K = 2.51 \times 10^3$ M$^{-1}$ at 298 K, where $\alpha_1 = 1.0$ and $\alpha_2 = 1.0$.

| Wavelength (nm) | $\varepsilon_{HG} / 10^4$ | $\varepsilon_{HHG} / 10^4$ | $\varepsilon_{HHHG} / 10^4$ | $R^2$       |
|-----------------|--------------------------|---------------------------|----------------------------|------------|
| 550             | 1.02                     | 1.80                      | 3.14                       | 0.9998933 |
| 562             | 2.00                     | 2.73                      | 6.09                       | 0.9999335 |
| 589             | 0.38                     | 0.08                      | 2.64                       | 0.9998809 |
| 602             | 0.89                     | 0.80                      | 1.47                       | 0.9998390 |

5.1.2 UV-vis binding study of Zn(II)TPPL with P(m-py)$_3$

![Zn(II)TPPL and P(m-py)$_3$](image)

Table S 6. Conditions used for the 3:1 host-guest UV-vis binding study at 298 K.

| Host     | Zn(II)TPPL       |
|----------|------------------|
| Guest    | P(m-py)$_3$      |
| Conc host / M | 15.9 µM         |
| [G]/[H]$_0$ range | 0 - 84          |
| Solvent  | Toluene         |
| T / K    | 298             |
Figure S 10. Fitted UV-vis titration curves of Zn(II)TPPL with P(m-py)$_3$ in toluene. Top: observed (circles) and calculated (dotted line) UV-vis absorption vs the logarithm of equivalents P(m-py)$_3$ added; Middle: percentage error in the fit vs the logarithm of equivalents P(m-py)$_3$ added; Bottom: calculated species concentration vs the logarithm of equivalents P(m-py)$_3$ added.
Table S 7. Fitting results for the 3:1 host-guest system between Zn(II)TPPL and P(m-py)_3 in toluene for K = 1.02 x 10^4 M^-1 at 298 K, where \( \alpha_1 = 1.0 \) and \( \alpha_2 = 1.0 \).

| Wavelength (nm) | \( \epsilon_{HG} / 10^4 \) | \( \epsilon_{HHG} / 10^4 \) | \( \epsilon_{HHHG} / 10^4 \) | \( R^2 \) |
|----------------|-----------------|-----------------|-----------------|-------|
| 560            | 1.25            | 3.01            | 5.73            | 0.9999934 |
| 568            | 1.57            | 2.49            | 4.31            | 0.9999911 |
| 605            | 2.07            | 7.07            | 9.14            | 0.9999784 |
| 611            | 3.08            | 4.14            | 7.18            | 0.9999685 |

5.3 UV-vis binding studies of Zn(II)TPP and Zn(II)TPPL with pyridine

The binding affinities of pyridine towards Zn(II)TPP and Zn(II)TPPL in different solvents were obtained by separate UV-vis titrations in the solvents of interest. A solution of host, Zn(II)TPP or Zn(II)TPPL, in the solvent of choice, and a stock solution of guest, pyridine, containing the same concentration of host were prepared respectively. Aliquots of pyridine from the guest stock solution were added directly to a quartz cuvette containing the host solution. Each titration was performed at 298 K. Up to between ca. 10 and 8000 guest equivalents were added, depending on the solvent used. The progress of the titration was monitored by the shifts in the Q-bands of the porphyrin (Zn(II)TPP) or porpholactone (Zn(II)TPPL). The association constant was defined as follows:

\[
K = \frac{[HG]}{[G][H]}
\]

The UV-vis absorption at wavelength \( \lambda \) of the host species Zn(II)TPP or Zn(II)TPPL over the course of the titration is described by (the guest species has negligible absorptivity at the wavelengths used):

\[
A_\lambda = \epsilon_H \cdot [H] + \epsilon_{HG} \cdot [HG]
\]

The general fitting procedure is described in section 7 of this Supporting Information
5.3.1 UV-vis binding study of Zn(II)TPP with pyridine in toluene

Table S 8. Conditions used for the 1:1 host-guest UV-vis binding study at 298 K.

| Host       | Zn(II)TPP |
|------------|-----------|
| Guest      | Pyridine  |
| Conc host / M | 16 µM     |
| [G]₀/[H]₀ range | 0 - 600   |
| Solvent    | Toluene   |
| T / K      | 298       |
Figure S 11. Fitted UV-vis titration curves of Zn(II)TPP with pyridine in toluene. Top: observed (circles) and calculated (dotted line) UV-vis absorption vs the logarithm of equivalents pyridine added; Middle: percentage error in the fit vs the logarithm of equivalents pyridine added; Bottom: calculated species concentration vs the logarithm of equivalents pyridine added.
Table S 9. Fitting results for the 1:1 host-guest system between Zn(II)TPP and pyridine in toluene for \( K = 3.41 \times 10^3 \, \text{M}^{-1} \) at 298 K.

| Wavelength (nm) | \( \varepsilon_{HG} / 10^4 \) | \( R^2 \) |
|-----------------|-----------------|--------|
| 550             | 1.03            | 0.9997452 |
| 563             | 2.14            | 0.9998284 |
| 602             | 0.96            | 0.9996554 |

5.3.2 UV-vis binding study of Zn(II)TPPL with pyridine in toluene

Table S 10. Conditions used for the 1:1 host-guest UV-vis binding study at 298 K.

| Host          | Zn(II)TPPL |
|---------------|------------|
| Guest         | Pyridine   |
| Conc host / M | 8 \mu M    |
| \([G]_0/[H]_0\) range | 0 - 474    |
| Solvent       | Toluene    |
| T / K         | 298        |
Figure S 12. Fitted UV-vis titration curves of Zn(II)TPPL with pyridine in toluene. *Top:* observed (circles) and calculated (dotted line) UV-vis absorption vs the logarithm of equivalents pyridine added; *Middle:* percentage error in the fit vs the logarithm of equivalents pyridine added; *Bottom:* calculated species concentration vs the logarithm of equivalents pyridine added.
Table S 11. Fitting results for the 1:1 host-guest system between Zn(II)TPPL and pyridine in toluene for $K = 1.40 \times 10^4 \text{ M}^{-1}$ at 298 K.

| Wavelength (nm) | $\varepsilon_{HG} / 10^4$ | $R^2$     |
|-----------------|--------------------------|-----------|
| 568             | 1.46                     | 0.9996862 |
| 604             | 1.84                     | 0.9994996 |
| 611             | 3.05                     | 0.9997811 |

5.3.3 UV-vis binding study of Zn(II)TPP with pyridine in dichloromethane

Table S 12. Conditions used for the 1:1 host-guest UV-vis binding study at 298 K.

| Host   | Zn(II)TPP       |
|--------|-----------------|
| Guest  | Pyridine        |
| Conc host / M | 16 µM           |
| $[G_0] / [H_0]$ range | 0 - 314        |
| Solvent | Dichloromethane |
| $T / K$ | 298             |
Figure S 13. Fitted UV-vis titration curves of Zn(II)TPP with pyridine in dichloromethane. 
*Top:* observed (circles) and calculated (dotted line) UV-vis absorption vs the logarithm of equivalents pyridine added; *Middle:* percentage error in the fit vs the logarithm of equivalents pyridine added; *Bottom:* calculated species concentration vs the logarithm of equivalents pyridine added.
Table S 13. Fitting results for the 1:1 host-guest system between Zn(II)TPP and pyridine in dichloromethane for $K = 6.92 \times 10^3 \text{ M}^{-1}$ at 298 K.

| Wavelength (nm) | $\varepsilon_{HG} / 10^4$ | $R^2$     |
|-----------------|---------------------------|-----------|
| 548             | 0.80                      | 0.9998810 |
| 563             | 2.02                      | 0.9996708 |
| 603             | 1.00                      | 0.9984002 |

5.3.4 UV-vis binding study of Zn(II)TPPL with pyridine in dichloromethane

![Diagram of Zn(II)TPPL and Pyridine](image)

Table S 14. Conditions used for the 1:1 host-guest UV-vis binding study at 298 K.

| Host      | Zn(II)TPPL |
|-----------|------------|
| Guest     | Pyridine   |
| Conc host / M | 16 µM    |
| $[G]/[H]_0$ range | 0 - 10 |
| Solvent   | Dichloromethane |
| T / K     | 298        |
Figure S 14. Fitted UV-vis titration curves of Zn(II)/TPPL with pyridine in dichloromethane. *Top:* observed (circles) and calculated (dotted line) UV-vis absorption vs the logarithm of equivalents pyridine added; *Middle:* percentage error in the fit vs the logarithm of equivalents pyridine added; *Bottom:* calculated species concentration vs the logarithm of equivalents pyridine added.
Table S 15. Fitting results for the 1:1 host-guest system between Zn(II)TPPL and pyridine in dichloromethane for $K = 2.27 \times 10^4 \text{ M}^{-1}$ at 298 K.

| Wavelength (nm) | $e_{HG} / 10^4$ | $R^2$         |
|-----------------|-----------------|---------------|
| 557             | 0.76            | 0.9999254     |
| 566             | 1.10            | 0.9999276     |
| 601             | 0.89            | 0.9999005     |
| 609             | 1.82            | 0.9999281     |

5.3.5 UV-vis binding study of Zn(II)TPP with pyridine in acetone

![Zn(II)TPP and Pyridine](image)

Table S 16. Conditions used for the 1:1 host-guest UV-vis binding study at 298 K.

| Host      | Zn(II)TPP  |
|-----------|------------|
| Guest     | Pyridine   |
| Conc host / M | 8 µM      |
| [G]/[H]₀ range | 0 - 1100  |
| Solvent   | Acetone    |
| T / K     | 298        |
Figure S 15. Fitted UV-vis titration curves of Zn(II)TPP with pyridine in acetone. Top: observed (circles) and calculated (dotted line) UV-vis absorption vs the logarithm of equivalents pyridine added; Middle: percentage error in the fit vs the logarithm of equivalents pyridine added; Bottom: calculated species concentration vs the logarithm of equivalents pyridine added.
Table S 17. Fitting results for the 1:1 host-guest system between Zn(II)TPP and pyridine in acetone for $K = 7.05 \times 10^2 \text{ M}^{-1}$ at 298 K.

| Wavelength (nm) | $\varepsilon_{HG} / 10^4$ | $R^2$ |
|-----------------|--------------------------|-------|
| 555             | 1.56                     | 0.9999843 |
| 561             | 1.97                     | 0.9999763 |
| 601             | 1.05                     | 0.9995635 |

5.3.6 UV-vis binding study of Zn(II)TPPL with pyridine in acetone

Table S 18. Conditions used for the 1:1 host-guest UV-vis binding study at 298 K.

| Host          | Zn(II)TPPL |
|---------------|------------|
| Guest         | Pyridine   |
| Conc host / M | 8 µM       |
| [G]₀/[H]₀ range | 0 - 8000   |
| Solvent       | Acetone    |
| T / K         | 298        |
Figure S 16. Fitted UV-vis titration curves of Zn(II)TPPL with pyridine in acetone. Top: observed (circles) and calculated (dotted line) UV-vis absorption vs the logarithm of equivalents pyridine added; Middle: percentage error in the fit vs the logarithm of equivalents pyridine added; Bottom: calculated species concentration vs the logarithm of equivalents pyridine added.
Table S 19. Fitting results for the 1:1 host-guest system between Zn(II)TPPL and pyridine in acetone for $K = 8.57 \times 10^2 \text{M}^{-1}$ at 298 K.

| Wavelength (nm) | $\varepsilon_{HG}/10^4$ | $R^2$      |
|-----------------|-------------------------|------------|
| 562             | 1.42                    | 0.9999998  |
| 566             | 1.50                    | 0.9999994  |
| 606             | 2.57                    | 0.9999976  |
| 609             | 2.92                    | 0.9999935  |

5.3.7 UV-vis binding studies of Zn(II)TPP with pyridine in DOTP at three different temperatures

Table S 20. Conditions used for the 1:1 host-guest UV-vis binding study at 298 K.

| Host            | Zn(II)TPP                |
|-----------------|--------------------------|
| Guest           | Pyridine                 |
| Conc host / M   | 8 $\mu$M                 |
| $[G]/[H]_0$ range | 0 - 5000                |
| Solvent         | Dioctyl terephthalate    |
| T / K           | 298                      |
Figure S 17. Fitted UV-vis titration curves of Zn(II)TPP with pyridine in dioctyl terephthalate at 298 K. Top: observed (circles) and calculated (dotted line) UV-vis absorption vs the logarithm of equivalents pyridine added; Middle: percentage error in the fit vs the logarithm of equivalents pyridine added; Bottom: calculated species concentration vs the logarithm of equivalents pyridine added.
Table S 21. Fitting results for the 1:1 host-guest system between Zn(II)TPP and pyridine in dioctyl terephthalate for K = 2.98 x 10^2 M⁻¹ at 298 K.

| Wavelength (nm) | $\varepsilon_{HG} / 10^4$ | $R^2$  |
|-----------------|-----------------|-------|
| 554             | 1.34            | 0.9998919 |
| 563             | 2.09            | 0.9996650 |
| 603             | 1.04            | 0.9920728 |

Table S 22. Conditions used for the 1:1 host-guest UV-vis binding study at 323 K.

| Host     | Zn(II)TPP   |
|----------|-------------|
| Guest    | Pyridine    |
| Conc host / M | 8 µM       |
| $[G]_0/[H]_0$ range | 0 - 19500 |
| Solvent  | Dioctyl terephthalate |
| T / K    | 323         |
Figure S 18. Fitted UV-vis titration curves of Zn(II)TPP with pyridine in dioctyl terephthalate at 323 K. Top: observed (circles) and calculated (dotted line) UV-vis absorption vs the logarithm of equivalents pyridine added; Middle: percentage error in the fit vs the logarithm of equivalents pyridine added; Bottom: calculated species concentration vs the logarithm of equivalents pyridine added.
Table S 23. Fitting results for the 1:1 host-guest system between Zn(II)TPP and pyridine in dioctyl terephthalate for $K = 2.57 \times 10^2 \text{ M}^{-1}$ at 323 K.

| Wavelength (nm) | $\varepsilon_{HG} / 10^4$ | $R^2$ |
|-----------------|---------------------------|-------|
| 554             | 1.35                      | 0.9999091 |
| 563             | 1.94                      | 0.9999033 |
| 603             | 0.91                      | 0.9990042 |

Table S 24. Conditions used for the 1:1 host-guest UV-vis binding study at 348 K.

| Host | Zn(II)TPP        |
|------|------------------|
| Guest| Pyridine         |
| Conc host / M | 8 µM           |
| [G]₀/[H]₀ range | 0 - 31200       |
| Solvent | Dioctyl terephthalate |
| T / K     | 348              |
Figure S 19. Fitted UV-vis titration curves of Zn(II)TPP with pyridine in dioctyl terephthalate at 348 K. Top: observed (circles) and calculated (dotted line) UV-vis absorption vs the logarithm of equivalents pyridine added; Middle: percentage error in the fit vs the logarithm of equivalents pyridine added; Bottom: calculated species concentration vs the logarithm of equivalents pyridine added.
Table S 25. Fitting results for the 1:1 host-guest system between Zn(II)TPP and pyridine in dioctyl terephthalate for \( K = 0.89 \times 10^2 \) M\(^{-1}\) at 348 K.

| Wavelength (nm) | \( \varepsilon_{HG} / 10^4 \) | \( R^2 \) |
|----------------|------------------|---------|
| 554            | 1.25             | 0.99991994 |
| 563            | 1.86             | 0.99992723 |
| 603            | 0.91             | 0.99959877 |

5.3.8 UV-vis binding studies of Zn(II)TPPL with pyridine in DOTP at three different temperatures

![Zn(II)TPPL and Pyridine structure](structure.png)

Table S 26. Conditions used for the 1:1 host-guest UV-vis binding study at 298 K.

| Host   | Zn(II)TPPL |
|--------|------------|
| Guest  | Pyridine   |
| Conc host / M | 8 µM |
| \([G]/[H]_0\) range | 0 - 3000 |
| Solvent         | Dioctyl terephthalate |
| \(T / K\)      | 298        |
Figure S 20. Fitted UV-vis titration curves of Zn(II)TPPL with pyridine in dioctyl terephthalate at 298 K. Top: observed (circles) and calculated (dotted line) UV-vis absorption vs the logarithm of equivalents pyridine added; Middle: percentage error in the fit vs the logarithm of equivalents pyridine added; Bottom: calculated species concentration vs the logarithm of equivalents pyridine added.
Table S 27. Fitting results for the 1:1 host-guest system between Zn(II)TPPL and pyridine in dioctyl terephthalate for $K = 1.02 \times 10^3 \text{ M}^{-1}$ at 298 K.

| Wavelength (nm) | $\varepsilon_{HG} / 10^4$ | $R^2$ |
|-----------------|-------------------------|------|
| 562             | 1.32                    | 0.9999904 |
| 568             | 1.51                    | 0.9999909 |

Table S 28. Conditions used for the 1:1 host-guest UV-vis binding study at 323 K.

| Host          | Zn(II)TPPL |
|---------------|------------|
| Guest         | Pyridine   |
| Conc host / M | 8 µM       |
| [G]$_0$/[H]$_0$ range | 0 - 23800 |
| Solvent       | Dioctyl terephthalate |
| T / K         | 323        |
Figure S 21. Fitted UV-vis titration curves of Zn(II)TPPL with pyridine in dioctyl terephthalate at 323 K. Top: observed (circles) and calculated (dotted line) UV-vis absorption vs the logarithm of equivalents pyridine added; Middle: percentage error in the fit vs the logarithm of equivalents pyridine added; Bottom: calculated species concentration vs the logarithm of equivalents pyridine added.
**Table S 29.** Fitting results for the 1:1 host-guest system between Zn(II)TPPL and pyridine in dioctyl terephthalate for $K = 3.38 \times 10^2 \text{M}^{-1}$ at 323 K.

| Wavelength (nm) | $\varepsilon_{HG} / 10^4$ | $R^2$   |
|-----------------|---------------------------|---------|
| 563             | 1.30                      | 0.99999533 |
| 568             | 1.43                      | 0.99993876 |
| 607             | 2.48                      | 0.99950259 |
| 612             | 3.12                      | 0.99973978 |

**Table S 30.** Conditions used for the 1:1 host-guest UV-vis binding study at 348 K.

| Host      | Zn(II)TPPL |
|-----------|------------|
| Guest     | Pyridine   |
| Conc host / M | 8 µM     |
| $[G]/[H]_0$ range | 0 - 63200 |
| Solvent   | Dioctyl terephthalate |
| T / K     | 348        |
Figure S 22. Fitted UV-vis titration curves of Zn(II)TPPL with pyridine in dioctyl terephthalate at 348 K. Top: observed (circles) and calculated (dotted line) UV-vis absorption vs the logarithm of equivalents pyridine added; Middle: percentage error in the fit vs the logarithm of equivalents pyridine added; Bottom: calculated species concentration vs the logarithm of equivalents pyridine added.
**Table S 31.** Fitting results for the 1:1 host-guest system between Zn(II)TPPL and pyridine in dioctyl terephthalate for $K = 1.88 \times 10^2 \text{ M}^{-1}$ at 348 K.

| Wavelength (nm) | $\varepsilon_{HG} / 10^4$ | $R^2$         |
|-----------------|---------------------------|---------------|
| 563             | 1.14                      | 0.99999882    |
| 568             | 1.25                      | 0.99999331    |
| 607             | 1.95                      | 0.99995590    |
| 612             | 2.47                      | 0.99993955    |

6 NMR binding studies

6.1 Job plot analysis of Zn(II)TPPL with pyridine

In order to determine the binding stoichiometry of the complex, a Job plot analysis was performed by tracking the changes in the $^1$H NMR spectrum of Zn(II)TPPL with varying amounts of pyridine in CDCl₃\(^7,8\). Stock solutions (5 mM) of Zn(II)TPPL and pyridine were prepared separately in CDCl₃. Nine NMR samples were prepared with different ratios of Zn(II)TPPL and pyridine so that the total concentration of Zn(II)TPPL + pyridine for each sample was 5 mM (see Table S 32). The total volume of each sample was kept at 1 mL. Each NMR sample was measured at 25 °C. As shown in Figure S 23, the resonance of the proton on the pyridine was shifted downfield as the mole fraction of Zn(II)TPPL was increased. The relative shift of one of the $^1$H NMR signals of pyridine with the mole fraction of pyridine is listed in Table S 30. The Job plot, indicating a 1:1 host guest complex (see Figure S 24), was obtained by plotting $([\delta \Delta G]_{\text{observed}}-[G]_{\text{initial}})/([G]_{\text{final}}-[G]_{\text{initial}})$ vs $([G]/([H]+[G]))$. For more details, see references: \(^7,8\).
**Table S 32.** Data for the Job plot collected by $^1$H NMR titration in CDCl$_3$ at 298 K.

| Entry | Guest/ μL | Host/ μL | [G]/[G]+[H] | $\delta$ observed (Pyridine) | $\frac{(\delta_{\text{observed}}-\delta_{\text{initial}})}{(\delta_{\text{final}}-\delta_{\text{initial}})} \times$ molar fraction of host |
|-------|-----------|----------|--------------|-----------------------------|------------------------------------------------------------------|
| 1     | 100       | 500      | 0.1667       | 7.1700                     | 0.1106                                                           |
| 2     | 150       | 450      | 0.2500       | 7.0680                     | 0.1572                                                           |
| 3     | 200       | 400      | 0.3333       | 6.8850                     | 0.2318                                                           |
| 4     | 250       | 350      | 0.4167       | 6.6360                     | 0.3123                                                           |
| 5     | 300       | 300      | 0.5000       | 6.4060                     | 0.3544                                                           |
| 6     | 350       | 250      | 0.5833       | 6.2150                     | 0.3554                                                           |
| 7     | 370       | 230      | 0.6167       | 6.1460                     | 0.3469                                                           |
| 8     | 410       | 190      | 0.6833       | 6.0540                     | 0.3085                                                           |
| 9     | 480       | 120      | 0.8000       | 6.0250                     | 0.1992                                                           |

**Figure S 23.** $^1$H NMR (500 MHz, 298 K) binding study between Zn(II)TPPL and pyridine in CDCl$_3$. 
6.2 NMR binding studies of Zn(II)TPP and Zn(II)TPPL with P(m-py)₃

The binding affinities of P(m-py)₃ towards Zn(II)TPP and Zn(II)TPPL were obtained by two separate ¹H and ³¹P NMR titrations in toluene-d₈. A solution of host P(m-py)₃ in degassed toluene-d₈, and stock solutions of guests, Zn(II)TPP and Zn(II)TPPL, containing the same concentration of P(m-py)₃ were prepared respectively. Aliquots of each guest from the stock solution were added directly to an NMR tube containing the P(m-py)₃ solution under N₂. Each titration was performed by around 30 measurements at 298 K. Up to ca. 6 guest equivalents were added. All proton signals were referenced to the solvent residual peak. The progress of the titration was monitored by the relative shifts of the peaks of P(m-py)₃ in both ¹H and ³¹P NMR upon binding to Zn(II)TPP or Zn(II)TPPL. The microscopic (K) and macroscopic (K₁/K₂/K₃) association constants were defined as follows, with α₁ and α₂ the respective cooperativity factors⁵ and (3; 1; 1/3) the respective statistical factors⁶:

\[
K_1 = 3 \cdot K = \frac{[H_G]}{[G][H]}, \quad K_2 = K \cdot \alpha_1 = \frac{[H_G G]}{[H_G][G]}, \quad \text{and} \quad K_3 = \frac{1}{3} \cdot K \cdot \alpha_2 = \frac{[H_G G G]}{[H_G G][G]}
\]

The NMR chemical shift for each trackable atom of the host species P(m-py)₃ over the course of the titration is described by:
\[
\delta_{\text{atom}} = \delta_H \cdot \frac{[H]}{[H]_0} + \delta_{HG} \cdot \frac{[HG]}{[H]_0} + \delta_{HGG} \cdot \frac{[HGG]}{[H]_0} + \delta_{HGGG} \cdot \frac{[HGGG]}{[H]_0}
\]

The general fitting procedure is described in section 7 of this Supporting Information.

6.2.1 NMR binding study of Zn(II)TPP with P(m-py)₃

![Diagram](image)

**Table S 33.** Conditions used for the 1:3 host-guest NMR binding study at 298 K.

| Host         | P(m-py)₃            |
|--------------|---------------------|
| Guest        | Zn(II)TPP           |
| Conc host / M| 1.5 mM              |
| [G]/[H]₀ range | 0 - 6               |
| Solvent      | Toluene-d8          |
| T / K        | 298                 |
Figure S 25. Fitted $^1$H and $^{31}$P NMR titration curves of Zn(II)TPP with P(m-py)$_3$ in toluene-d$_8$. Top: observed (circles) and calculated (dotted line) NMR chemical shift vs the logarithm of equivalents Zn(II)TPP added; Middle: percentage error in the fit vs the logarithm of equivalents Zn(II)TPP added; Bottom: calculated species concentration vs the logarithm of equivalents Zn(II)TPP added.
Table S 34. Fitting results for the cooperative 1:3 host-guest system between P(m-py)$_3$ and Zn(II)TPP in toluene-d8 for $K = 2.50 \times 10^3$ M$^{-1}$ at 298 K, where $\alpha_1 = 2.8$ and $\alpha_2 = 4.8$.

| Observable (ppm) | HG coefficient | HGG coefficient | HGGG coefficient | $R^2$       |
|------------------|----------------|-----------------|------------------|-------------|
| 6.55 (1H)        | 6.19           | 5.09            | 4.50             | 0.9999962   |
| 7.06 (1H)        | 6.51           | 4.82            | 2.72             | 0.9999752   |
| -24.48 (31P)     | -24.32         | -24.49          | -25.48           | 0.9999993   |

6.2.2 NMR binding study of Zn(II)TPPL with P(m-py)$_3$

Table S 35. Conditions used for the 1:3 host-guest NMR binding study at 298 K.

| Host       | P(m-py)$_3$            |
|------------|------------------------|
| Guest      | Zn(II)TPPL             |
| Conc host / M | 1.2 mM                |
| [G]$_0$/[H]$_0$ range | 0 - 5                 |
| Solvent    | Toluene-d8             |
| T / K      | 298                    |

Figure S 26. Fitted $^1$H and $^{31}$P NMR titration curves of Zn(II)TPPL with P(m-py)$_3$ in toluene-d$_8$. Top: observed (circles) and calculated (dotted line) NMR chemical shift vs the logarithm of equivalents Zn(II)TPPL added; Middle: percentage error in the fit vs the logarithm of equivalents Zn(II)TPPL added; Bottom: calculated species concentration vs the logarithm of equivalents Zn(II)TPPL added.
Table S 36. Fitting results for the mildly cooperative 1:3 host-guest system between P(m-py)$_3$ and Zn(II)TPPL in toluene-d$_8$ for $K = 1.51 \times 10^4$ M$^{-1}$ at 298 K, where $\alpha_1 = 1.2$ and $\alpha_2 = 1.2$.

| Observable (ppm) | HG coefficient | HGG coefficient | HGGG coefficient | $R^2$     |
|------------------|----------------|-----------------|------------------|-----------|
| 6.55 ($^1$H)    | 6.25           | 6.08            | 5.08             | 0.9999718 |
| -24.48 ($^{31}$P) | -24.37         | -24.50          | -23.96           | 0.9999996 |

7 General titration fitting procedure

Regardless of the supramolecular model and spectroscopic method, the fitting procedure for the determination of the association constants is as follows: At each titration point $n$ in $N$ (the total number of titration points) the initial concentrations for the host and guess species [$H$]$_{0,n}$ and [$G$]$_{0,n}$ are known, as are the observed values for either chemical shift $\delta_{\text{atom,obs,n}}$ or absorption $A_{\lambda,\text{obs,n}}$, which we will collectively call $O_{\text{obs,n}}$. The fitting procedure is based around the COBYLA numerical optimization routine$^{[9]}$ which tries to minimize the difference between the observed values and calculated values, given the constraint that association constants and concentrations are greater than zero:

$$\text{minimize } F_n = |O_{\text{obs,n}} - O_{\text{calc,n}}|, \quad n \in N$$

subject to $\{[S]_n; K; \alpha \} \geq 0$ for all species $S = \{H, G, HG, HGG, \ldots\}$

The objective function $F_n$ for the optimization procedure calculates $O_{\text{calc,n}}$ through the formulae for $A_{\lambda}$ or $\delta_{\text{atom}}$ (vide supra). E.g. in the case of a 1:1 HG titration followed by UV-vis, the objective function becomes:

$$F_n = |O_{\text{obs,n}} - O_{\text{calc,n}}| = |A_{\text{obs,n}} - A_{\text{calc,n}}| = |A_{\text{obs,n}} - \varepsilon_H[H] + \varepsilon_{HG}[HG]|$$

Given initial guesses for the association constants $\{K; \alpha\}$, [$H$] and [HG] can be calculated from the initial concentrations [$H$]$_0$ and [G]$_0$. Since the fitting procedure calls this routine very often (in our cases roughly between $10^2$ and $10^6$ times per fitting procedure, depending on the size of the problem (e.g. HG versus HGGG)), we use a ‘rapid numerical integration algorithm for finding the equilibrium state of a system of coupled binding reactions’.$^{[10]}$ The objective function is then evaluated using initial guesses for the species coefficients ($\delta$ or $\varepsilon$), and the
optimization routine determines whether a minimum has been found or that the initial guesses have to be adjusted to provide a better fit to the data.

When a minimum has been found, the error distributions (difference between calculated and observed values) are visually checked for trends. If trends are observed that point towards a different model (e.g. cooperativity versus no cooperativity, or HHG versus HHHG), these models are fitted to the data as well and the different error distributions are compared between models.

**Initial guesses and quality of fit**

Since multi-parameter optimizations are difficult problems to accurately solve (many parameters, little observables), the quality of the fit should be scrutinized: The microscopic association constant in larger (e.g. 1:3) systems should be in the range for the same constant in the 1:1 system in the same solvent. The species coefficients (δ or ε) have to make sense, such that e.g. in the case of a HHHG system where the host H is tracked by UV-vis, the relation $\epsilon_{HG} \approx \frac{1}{2} \epsilon_{HHG} \approx \frac{1}{3} \epsilon_{HHHG}$ should hold, since the absorptivity per ‘bound host’ molecule shouldn’t change appreciably in the system. Initial guesses for the optimization procedure are made using similar, simplified relations and ideas, where e.g. in a HHHG UV-vis titration, almost all host molecules are bound in the HG form at the end of the titration curve, allowing for an estimate of $\epsilon_{HG}$ and thereby estimates of all other coefficients. Starting from these ‘proper’ guesses, the optimization routine is generally both fastest and most accurate.

The accuracy of these optimizations turns out to be an ill-defined problem in supramolecular chemistry.[11] Our current understanding of this problem (after fitting a broad range of ‘bad’ and ‘good’ titrations), is that non-accurate additions during titrations translate directly into a noisy energy landscape with a noisy minimum. Combined with the fact that optimization routines can never guarantee to find a global minimum, the found minimum is heavily dependent on the quality of the titration data and on the direction through which the minimum is approached (i.e. the initial guesses). Thus, when a minimum is found by the optimization routine, we approach this minimum from multiple sides to assure this is in fact a global minimum, or to get an estimate on the size of the minimum. E.g. if we approach a one-dimensional problem from two extreme initial guesses and find minima at 900 and 1100, respectively, we conclude that the actual minimum is somewhere between these values and
thereby immediately get a rough estimate of the accuracy with which we can determine the association constant.

8 Van`t Hoff analysis of binding in DOTP

A variable temperature UV-vis titration study of an 8 μM host (H₁; Zn(II)TPP, H₂; Zn(II)TPPL) solution in dioctyl terephthalate (DOTP) with increasing guest (G; Pyridine) was performed. The experimental data, fitted curves and the determined 1:1 host-guest association constants have been shown in previous sections of this Supporting Information. During the titrations the temperature of the cuvette was allowed to stabilize for 10 min after which it was kept at the measured temperature during data acquisition. A van `t Hoff analysis of the association constants at different temperatures allowed us to determine the enthalpy (ΔH⁰) and entropy (ΔS⁰) of complexation for both Zn(II)TPP and Zn(II)TPPL with pyridine.

8.1 Van `t Hoff plot for binding between Zn(II)TPP and pyridine

Table S 37. Association constants for 1:1 binding between Zn(II)TPP and pyridine in DOTP at different temperatures.

| T / K  | $T^{-1} / K^{-1}$ | K / M⁻¹ | lnK   |
|--------|------------------|---------|-------|
| 298.15 | 0.003354         | 298     | 5.6970935 |
| 323.15 | 0.003095         | 257     | 5.5490761 |
| 348.15 | 0.002872         | 89.3    | 4.4920015  |

T: absolute temperature in Kelvin (K). K: association constant of Zn(II)TPP with pyridine in DOTP at different temperatures. lnK: the Y axis parameters in the van `t Hoff plot. $T^{-1}$: the X axis parameters in the van `t Hoff plot.

\[
\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (I)
\]

\[
\Delta S/R = -3.6263 \quad \Delta S = -30.15 \text{ J·mol}^{-1} \cdot \text{K}^{-1} \quad \Delta S^0 = -7.21 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}
\]

\[
-\Delta H/R = 2875 \quad \Delta H = -23.91 \text{ kJ} \cdot \text{mol}^{-1} \quad \Delta H^0 = -5.71 \text{ kcal} \cdot \text{mol}^{-1}
\]

S-54
Figure S 27. Van ’t Hoff analysis of the binding of Zn(II)TPP with pyridine in DOTP at different temperatures.

8.2 Van ’t Hoff plot for binding between Zn(II)TPPL and pyridine

Table S 38. Association constants for 1:1 binding between Zn(II)TPPL and pyridine in DOTP at different temperatures.

| T / K  | T⁻¹ / K⁻¹ | K / M⁻¹ | lnK  |
|-------|-----------|---------|------|
| 298.15| 0.003354  | 1020    | 6.9275579 |
| 323.15| 0.003095  | 338     | 5.8230459 |
| 348.15| 0.002872  | 188     | 5.2364420 |

T: absolute temperature in Kelvin (K). K: association constant of Zn(II)TPP with pyridine in DOTP at different temperatures. lnK: the Y axis parameters in the van ’t Hoff plot. T⁻¹: the X axis parameters in the van ’t Hoff plot.

\[
\ln K = \frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (1)
\]

\[\Delta S/R = -4.6548 \quad \Delta S = -38.70 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \quad \Delta S^o = -9.25 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\]

\[\Delta H/R = 3424 \quad \Delta H = -28.47 \text{ kJ} \cdot \text{mol}^{-1} \quad \Delta H^o = -6.80 \text{ kcal} \cdot \text{mol}^{-1}\]
9 Gas-uptake curve and turnover frequency (TOF) calculation

9.1 One example of turnover frequency (TOF) calculation

Gas consumption was recorded by Brooks 0254 (Brooks Instruments, read out and control electronics) each second. The gas consumption is also calibrated by independent GC analysis at the end of the reaction. For this reason, n-decane was added as an internal standard to establish a reliable calibration for the GC results. After several attempts, a GC calibration was established for both butyraldehyde and isobutyraldehyde. The equations: \( y = 0.302x - 0.074 \) and \( y = 0.303x - 0.023 \) are established and used for calibrated value for butyraldehyde and isobutyraldehyde, respectively. These two equations are used for the calculation of the yield of the aldehydes, \( l/b \) ratio and TOF calculation. The maximal slope of aldehyde formation was used for the \( \text{TOF}_{\text{max}} \) (see Figure S 29).

Since the catalysis was started without prior gas-liquid equilibration and catalyst incubation period, the initial gas uptake data is not caused solely by substrate conversion (in the first 0.5-1 h). These effects are larger at smaller pressure/higher CO concentration and low temperature \( (\leq 25 ^\circ \text{C}) \). In general, a shorter incubation time \( (\leq 1 \text{ h}) \) was observed at higher \( \text{H}_2 \) pressure and

Figure S 28. Van 't Hoff analysis of the binding of Zn(II)TPP with pyridine in DOTP at different temperatures.
higher temperature while higher CO pressure and low temperature cause a longer incubation time (~ 2 h). Typically, the rates at the beginning of the reaction deviate from the trend displayed during most of the reaction period. Therefore, the gas up-take values in the initial period were not taken into account when this effect was significant. Selected gas up-take curve data corresponding to the text experiments are displayed in this section.

Let´s take an example to see how we establish the relationship between the gas consumption (mL), aldehyde formation (mmol), the amount of internal reference (1-octene, mmol), aldehyde GC calibration equations and TOF (h⁻¹) (see Figure S 29). The experiment is related to Table S 2, entry 3.

![Figure S 29. Gas-uptake curve (mL) vs reaction time (s).](image)

Figure S 29 shows a general trend of the gas-uptake along the reaction time. Based on the data obtained from GC, we can calculate the amount of the aldehydes obtained (see Table S 39).

### Table S 39. Aldehyde formation by calculation from GC data.

| A (butyraldehyde) (mmol) | A (isobutyraldehyde) (mmol) | A (decane) (mmol) | n (butyraldehyde) (mmol) | n (isobutyraldehyde) (mmol) | n (total aldehyde) (mmol) | n (decane) (mmol) | gas-uptake (mL) | l/b |
|------------------------|-----------------------------|------------------|--------------------------|-----------------------------|---------------------------|-----------------|--------------|-----|
| 2127504                | 1402102                     | 2045464          | 9.463                    | 5.997                       | 15.460                    | 2.565           | 323.132      | 1.58|

A means the integral area of aldehydes from GC, the molar amount of decane is constant (0.5 mL, 2.565 mmol, the molar amount of butyraldehyde and isobutyraldehyde were calculated from the following two equation which were obtained by GC calibration: y = 0.302x - 0.074 (butyraldehyde) and y = 0.303x - 0.023 (isobutyraldehyde), l/b = (linear aldehyde)/(branched aldehyde).
The first 970 s reaction time was not taken into account due to equilibration and catalyst incubation period. The maximum slope of the gas-uptake curve was chosen and used for the calculation of TOF\(_{\text{max}}\). As for gas-uptake curve of Figure S 29, the maximum slope is from 970 s to 4592 s, which shows excellent linearity (see Figure S 30). The molar amount of aldehydes during this period can be calculated. Based on \(l/b\) ratio both the total amount of n-butyraldehyde (linear) and isobutyraldehyde (branched) can be calculated (see Table S 40).

**Figure S 30.** Zoom in on the Figure S 29. The gas up-take shows excellent linearity in the first minutes of catalysis.

**Table S 40.** Calculation of the formation of aldehydes within a certain time period.

| time (s) | gas consumption (mL) | time gap (s) | gas gap (mL) | gas-uptake total (mL) | aldehyde total (mmol) | aldehydes (1h) (mmol) |
|---------|----------------------|--------------|--------------|-----------------------|-----------------------|-----------------------|
| 970     | 61.363               | 3622         | 82.915       | 323.132               | 15.46                 | 3.967                 |
| 4592    | 144.278              |              |              |                       |                       |                       |

(\text{aldehydes (1h) = (gas gap/gas-uptake total*aldehyde total)})

The \(\text{TOF}_{\text{max}}\) can also be obtained from the total amount of aldehydes divided by the catalyst loading and the reaction time of interest. Likewise, the \(\text{TOF}_{\text{max}}\) of n-butyraldehyde (linear) and isobutyraldehyde (branched) can be calculated, respectively (see Table S 39).

**Table S 41.** \(\text{TOF}_{\text{max}}\) calculation.

| linear aldehyde total (mmol) | branched aldehyde total (mmol) | linear aldehyde (1 h) (mmol) | branched aldehyde (1 h) (mmol) | \(\text{TOF}_{\text{max}}\) (linear) (mol/(mol(Rh).h\(^{-1}\))) | \(\text{TOF}_{\text{max}}\) (branched) |
|-------------------------------|--------------------------------|-----------------------------|-------------------------------|-------------------------------------------------|-------------------------------|
| 9.463                         | 5.997                          | 2.428                       | 1.539                         | 1207                                            | 765                           |

linear aldehyde (1h) = (gas gap/gas-uptake total*linear aldehyde total)), (branched aldehyde (1h) = (gas gap/gas-uptake total*branched aldehyde total)). \(\text{TOF}_{\text{max}} = n(\text{aldehyde})/n(\text{Rh}).h^{-1}\), \(n(\text{Rh}) = 2 \mu\text{mol.}\)
Likewise, all other experimental data were processed in the same way.

9.2 Selected gas up-take curves related to the experiments

The curves were related to the results presented in the text and Supporting Information. For each calculation, see attached excel file.

Figure S 31. Gas up-take (mL) vs reaction time (s) (Table 8, entry 1).

Figure S 32. Gas up-take (mL) vs reaction time (s) (Table 8, entry 2).
Figure S 33. Gas up-take (mL) vs reaction time (s) (Table S 2, entry 1).

Figure S 34. Gas up-take (mL) vs reaction time (s) (Table S 1, entry 1).
**Figure S 35.** Gas up-take (mL) vs reaction time (s) (Table S 1, entry 2).

**Figure S 36.** Gas up-take (mL) vs reaction time (s) (Table S 1, entry 3).
**Figure S 37.** Gas up-take (mL) vs reaction time (s) (Table S 1, entry 4).

**Figure S 38.** Gas up-take (mL) vs reaction time (s) (Table S 1, entry 5).
**Figure S 39.** Gas up-take (mL) vs reaction time (s) (Table 6, entry 1).

**Figure S 40.** Gas up-take (mL) vs reaction time (s) (Table 6, entry 2).
Figure S 41. Gas up-take (mL) vs reaction time (s) (Table 6, entry 3).

Figure S 42. Gas up-take (mL) vs reaction time (s) (Table 6, entry 4).
**Figure S 43.** Gas up-take (mL) vs reaction time (s) (Table 7, entry 2).

**Figure S 44.** Gas up-take (mL) vs reaction time (s) (Table 7, entry 3).
**Figure S 45.** Gas up-take (mL) vs reaction time (s) (Table 7, entry 4).

**Figure S 46.** Gas up-take (mL) vs reaction time (s) (Table S 3, entry 1).
**Figure S 47.** Gas up-take (mL) vs reaction time (s) (Table S 3, entry 2).

**Figure S 48.** Gas up-take (mL) vs reaction time (s) (Table S 3, entry 3).
Figure S 49. Gas up-take (mL) vs reaction time (s) (Table 8, entry 4).

10 Cage and cavity volume determination

To see what influence the replacement of a porphyrin, Zn(II)TPP, with a porpholactone, Zn(II)TPPL, has on the size of the cage and its interior cavity, simple volume calculations based on the crystal structures were undertaken. The crystal structure of the parent cage based on Zn(II)TPP is published\textsuperscript{12}, and in this contribution the crystal structure of the second generation cage was resolved. In Figure S 50 the X-ray crystal structure of assembly L3 from two perspectives is shown.
Figure S 50. X-ray crystal structures of assembly L3 (CCDC number: 1541162). Thermal ellipsoids are drawn with 50% probability. Left, view from top of the structure showing the cage formed by the three porpholactone moieties, two of which are engaged in a CH-π interaction. Right, view from the side showing the tilting of the porpholactone units towards the phosphorus atom. Solvent molecules and hydrogen atoms have been omitted for clarity. Colour code: C, white; N, blue; O, red; P, purple; Zn, green.

X-ray single crystal determination

C_{144}H_{90}N_{15}O_{7}PZn_{3} + 2(C_{7}H_{8}) + disordered solvent Fw = 2553.73 (Derived values do not contain the contribution of the disordered solvent.), violet-red rough fragment, 0.32 x 0.20 x 0.11 mm, triclinic, P-1 (no. 2), a = 18.0306(10), b = 20.7321(12), c = 21.3054(12) Å, α = 95.628(3), β = 99.410(3), γ = 106.576(3), V = 7441.8(7) Å³, Z = 2, D_x = 1.140 g cm⁻³ (Derived values do not contain the contribution of the disordered solvent.), µ = 0.548 mm⁻¹ (Derived values do not contain the contribution of the disordered solvent.). In total, 203052 reflections were measured on a Bruker D8 Quest Eco diffractometer, equipped with a TRIUMPH monochromator and a CMOS PHOTON 50 detector (λ = 0.71073 Å) up to a resolution of (sin
$\theta/\lambda_{\text{max}} = 0.83 \, \text{Å}^{-1}$ at a temperature of 150(2) K. The intensity data were integrated with the Bruker APEX2 software.$^{[13]}$ Absorption correction and scaling was performed with SADABS.$^{[14]}$ (0.64–0.75 correction range). In total, 26675 reflections were unique ($R_{\text{int}} = 0.085$), of which 19584 were observed [$I > 2\sigma(I)$]. The structure was solved with direct methods using the program SHELXS-97$^{[15]}$ and refined with SHELXL-2013 against $F^2$ of all reflections. One of the porpholactone moieties is positionally disordered (rotation over a 90 degree axis) and the lactone moiety was refined as occupying two sites with the occupancy factors of 0.64 and 0.36. The structure contains voids (1695 Å$^3$ per unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the PLATON package$^{[16]}$, resulting in 226 electrons per unit cell. 1657 parameters were included in the least-squares refinement. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. R1/wR2 [$I > 2\sigma(I)$]: 0.0606/0.1751. $S = 1.020$. Residual electron density between -0.78 and 1.18 e Å$^{-3}$. Geometry calculations and checking for higher symmetry was performed with the PLATON program.

**Volume calculation**

The online utility of the Voss Volume Voxelator$^{[17]}$ was used to calculate the volume of the cages (with 2 Å probe radius) and of the cavity (with 12 Å large and 1.2 Å small probe radius) where the catalyst is situated. A comparison of the surface areas, cage volumes and interior cavity volumes for both assemblies is shown in Table S 40. All parameters indicate that the second generation cage $L_2$ is overall smaller and has a smaller cavity than $L_1$.

**Table S 40.** Surface areas, cage volumes and interior cavity volumes for assemblies $L_1$ and $L_2$.

| Calculated parameter          | Assembly $L_1$ | Assembly $L_2$ |
|------------------------------|----------------|----------------|
| Cage volume (Å$^3$)          | 3381           | 3173           |
| Surface area (Å$^2$)         | 1642           | 1562           |
| Cavity volume (Å$^3$)        | 230            | 135            |
In Figure S 51 the outer surfaces of cages $\textbf{L1}$ and $\textbf{L2}$ are shown, and below that in Figure S 52 the inner cavity of the cages has been presented without including the phosphine, to better illustrate the differences in the shape of the cavity.

**Figure S 51.** The calculated outer surfaces of cage $\textbf{L1}$ (left) and $\textbf{L2}$ (right).

**Figure S 8.** The inner cavity volumes of cage $\textbf{L1}$ (left) and $\textbf{L2}$ (right). Here the phosphine has been omitted for illustration purposes only, aiming at describing the differences in cavity shapes between assemblies $\textbf{L1}$ and $\textbf{L2}$.
11 References

[1] A. M. Kluwer, I. Ahmad, J. N. H. Reek, *Tetrahedron Lett.* **2007**, *48*, 2999-3001.

[2] A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, L. Korsakoff, *J. Org. Chem.* **1967**, *32*, 476-476.

[3] Y. Yu, H. Lv, X. Ke, B. Yang, J.-L. Zhang, *Adv. Synth. Catal.* **2012**, *354*, 3509-3516.

[4] T. C. Eisenschmid, G. A. Miller, R. R. Peterson, A. G. Abatjoglou, *Hydroformylation process with improved control over product isomers*, US20100069680, Dow Technology Investments, **2010**.

[5] C. A. Hunter, H. L. Anderson, *Angew. Chem. Int. Ed. Engl.* **2009**, *48*, 7488-7499.

[6] G. Ercolani, C. Piguet, M. Borkovec, J. Hamacek, *J. Phys. Chem. B* **2007**, *111*, 12195-12203.

[7] K. Choi, A. D. Hamilton, *J. Am. Chem. Soc.* **2001**, *123*, 2456-2457.

[8] M. A. Hossain, J. M. Llinares, S. Mason, P. Morehouse, D. Powell, K. Bowman-James, *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 2335-2338.

[9] M. J. D. Powell in *Advances in Optimization and Numerical Analysis*; S. Gomez, J.-P. Hennart, Ed., Springer Netherlands, Cambridge, **1994**, 9, 51-67.

[10] D. Bray, S. Lay, *Comput. Appl. Biosci.* **1994**, *10*, 471-476.

[11] D. Brynn Hibbert, P. Thorardson, *Chem. Commun.* **2016**, *52*, 12792-12805.

[12] V. Bocokić, A. Kalkan, M. Lutz, A. L. Spek, D. T. Gryko, J. N. H. Reek, *Nat. Commun.* **2013**, *4*, 2670.

[13] Bruker, APEX2 software, Madison, WI, USA, **2014**.

[14] SAINT, version 6.02, and SADABS, version 2.03; Bruker AXS, Inc., Madison, WI, **2002**.

[15] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.

[16] A. L. Spek, *Acta Cryst.* **2009**, *D65*, 148-155.

[17] N. R. Voss, M. Gerstein, *Nucleic Acids Res.* **2010**, *38*, W555-562.