

ELECTRONIC SUPPLEMENTARY INFORMATION

Exploring Anagostic Interactions in 5,15-Porphodimethene Metal Complexes

M. G. Derry Holaday,^a Gourav Tarafdar,^b Arun Kumar,^b M. L. P. Reddy,^c and A. Srinivasan^{*b}

^aPhotosciences and Photonics Section, ^cInorganic Chemistry Section, Chemical Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology (NIIST), Trivandrum 695 019, Kerala, India.

^bSchool of Chemical Sciences, National Institute of Science Education and Research, IOP Campus, Sainik School – P. O. Bhubaneswar – 751 005, Odisha, India. E-mail: srini@niser.ac.in

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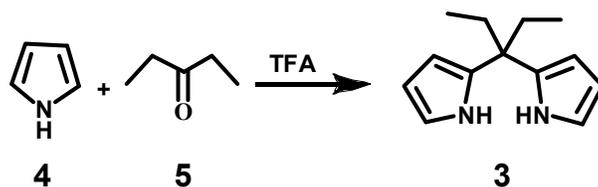
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1. Materials and methods

The reagents and materials for synthesis were used as obtained from Sigma - Aldrich chemical suppliers. All solvents were purified and dried by standard methods prior to use. NMR solvents were used as received. The NMR spectra were recorded with Bruker 400 MHz spectrometer with TMS as internal standard. ESI mass spectra were recorded on Bruker, microTOF-QII mass spectrometer. FAB mass spectra were obtained on a JEOL SX-120/DA6000 spectrometer using argon (6 KV, 10 mA) as the FAB gas. Electronic absorption spectra were recorded with Perkin Elmer – Lambda 750 UV-Visible spectrophotometer and data analyses were done using the UV-winlab software package. X-ray quality crystals for the compounds were grown by the slow diffusion of hexane over CH₂Cl₂ solution of the metal complexes. Single-crystal X-ray diffraction data of **1a**, **1c** and **1c'** were collected on a Bruker KAPPA APEX-II, four angle rotation system, MoK α radiation (0.71073 Å). The single crystal X-ray diffraction data of **1b** was collected on a Bruker AXS Kappa Apex 2 CCD diffractometer at 293(2) K. All experiments were carried out at room temperature (25 \pm 1°C), unless otherwise mentioned.

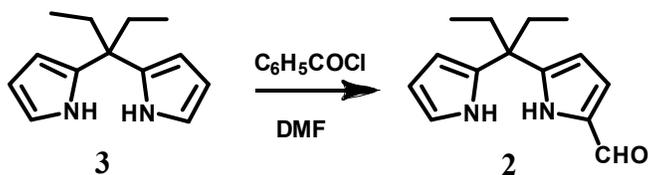
2. Synthesis

Synthesis of 5,5-di(ethyl)dipyrromethane (**3**)



Pyrrole **4** (15.5 g, 0.23 mol) and 3-pentanone **5** (1g, 0.01mol) were stirred under nitrogen atmosphere for 10 min at room temperature. Trifluoroacetic acid **TFA** (0.177 ml, 2.3 mmol) was added to the above mixture and the solution was stirred at room temperature for 45 min. After removal of the solvent, the crude product was purified by silica gel column chromatography (100–200 mesh). Column eluted with ethyl acetate : petroleum ether (1:99) gave colourless crystalline solid identified as **3**. Yield: 55%. ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.6 (brs, 2H, pyrrolyl NH), 6.57 (s, 2H, α -pyrrolyl CH), 6.11 (s, 4H, β -pyrrolyl CH), 1.95-1.91 (q, 4H, CH₂ H), 0.7-0.67 (t, 6H, methyl H). FAB mass (m/z): Calcd for C₁₃H₁₈N₂: 202.15; Found : 202.77.

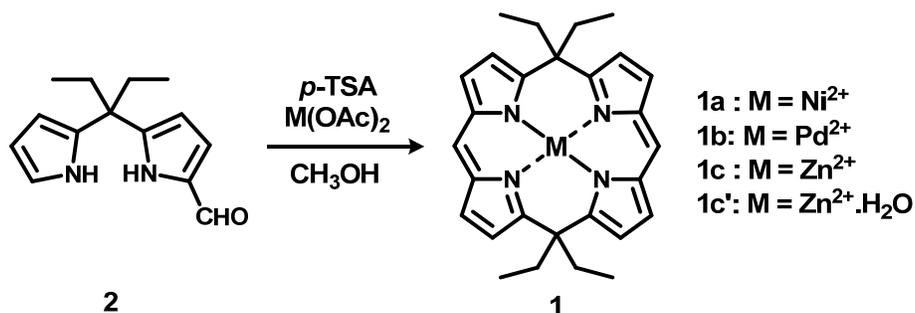
Synthesis of 1-formyl-5,5-di(ethyl)dipyrromethane (**2**)



To a stirred solution of dipyrromethane **3** (1.15 g, 5 mmol) in 10 mL of dry DMF cooled with ice-water bath was added dropwise a solution of benzoyl chloride (0.75 g, 5.4 mmol) in 2 mL of DMF under Ar. The mixture was stirred for 30 min at 0°C, and then allowed to warm to room temperature for 1.5 h. The solution was then diluted with Et₂O (50 mL) and extracted with water (3 x 15 mL), washed with Et₂O (1 x 10 mL), adjusted

to pH 8 with Na₂CO₃ solution, left overnight, cooled and the yellow precipitate was filtered off. The crude product was purified by column chromatography eluted with ethyl acetate : petroleum ether after an evaporation of most of the solvent gave 0.75 g (58%) of compound **2** as cream-white crystals. Spectral data for **2**: ¹H NMR (400 MHz, CDCl₃, 298 K): δ =9.3 (s, 1H, aldehyde CH), 8.9 (brs, 1H, pyrrolyl NH), 7.8 (brs, 1H, pyrrolyl NH), 6.91-6.90 (q, 1H, α-pyrrolyl CH), 6.69-6.68 (m, 1H, β-pyrrolyl CH), 6.24-6.22 (q, 1H, β-pyrrolyl CH), 6.15-6.11 (m, 2H, β-pyrrolyl CH), 2.06 -1.94 (q, 4H, CH₂ H), 0.75-0.71 (t, 6H, methyl H). FAB mass (m/z) : Calcd for C₁₄H₁₈N₂O : 230.30. Found : 231.70.

Synthesis of the **1a - 1c'** :



A solution of monoformyldipyrromethane **2** (100 mg, 1 mmol) in 15mL of methanol was degassed with nitrogen gas and stirred at room temperature for 30min., then a solution of *p*-toluenesulfonic acid (38 mg, 0.2 mmol) in 2mL of methanol was added in one portion and stirring continued for 5min. A solution of M(OAc)₂·4H₂O (1.0 mmol) in 10mL of methanol was added and the mixture was stirred for 8h, then 40 mL of water was added and the mixture was extracted with CH₂Cl₂ (40+20 mL), the combined organic layers were washed with NaHCO₃ solution, water, brine and dried with Na₂SO₄. The solvents were evaporated and the residue was purified by column chromatography (hexane–CH₂Cl₂) to afford corresponding metal complexes. The nickel **1a** and palladium **1b** calixphyrin gave 30% and 35% yield respectively. The yield of **1c** and **1c'** were 1% and 10% respectively.

3. Spectral Data for 1a - 1c'

Spectral data for **1a**: ^1H NMR (400 MHz, CDCl_3 , 298 K): δ = 6.71 (s, 2H, meso CH), 6.71 - 6.70 (d, J = 4 Hz, 4H, pyrrolic β CH), 6.18 - 6.16 (d, J = 4 Hz, 4H, pyrrolic β CH), 2.46 (brs, 8H, methylene H), 1.02 – 0.99 (t, 12H, methyl H). ^{13}C NMR (100 MHz, CDCl_3 , 25°C, TMS): δ = 164.13, 135.24, 130.64, 128.47, 116.20, 47.38, 29.71, 9.92. MS(ESI): m/z Calculated for $[(\text{C}_{28}\text{H}_{30}\text{N}_4\text{Ni})]^+$ = 480.1824; found = 481.1964

Spectral data for **1b**: ^1H NMR (400 MHz, CDCl_3 , 298K): δ = 6.94 (s, 2H, meso CH), 6.93-6.92 (d, J = 4 Hz, 4H, β pyrrolic H), 6.40-6.39 (d, J = 4 Hz, 4H, pyrrolic β CH), 2.09 – 2.04 (q, 8H, methylene H), 0.84 – 0.80 (t, 12H, methyl H). ^{13}C NMR (100 MHz, DMSO-d_6 , 25°C): δ = 160.31, 133.22, 131.90, 130.26, 116.75, 50.15, 35.38, 10.46. MS(ESI): m/z calculated for $[(\text{C}_{28}\text{H}_{30}\text{N}_4\text{Pd})]^+$ = 528.1505; found = 529.1683

Spectral data for **1c**: MS(ESI): m/z calculated for $[(\text{C}_{28}\text{H}_{30}\text{N}_4\text{Zn})]^+$ = 487.1762; found = 486.1914

Spectral data for **1c'**: ^1H NMR (400 MHz, CDCl_3 , 298 K): δ = 7.06 – 7.04 (d, J = 4 Hz, 4H, pyrrolic β CH), 6.92 (s, 2H, meso H), 6.48 - 6.47 (d, J = 4 Hz, 4H, pyrrolic β CH), 2.09 – 2.03 (q, 8H, methylene H), 2.01 (s, 2H, axial H_2O molecule), 0.70 – 0.66 (t, 12 H, methyl H). MS(ESI): m/z Calculated for $[(\text{C}_{28}\text{H}_{32}\text{N}_4\text{OZn})]^+$ = 504.1867 ; observed = 487.5171

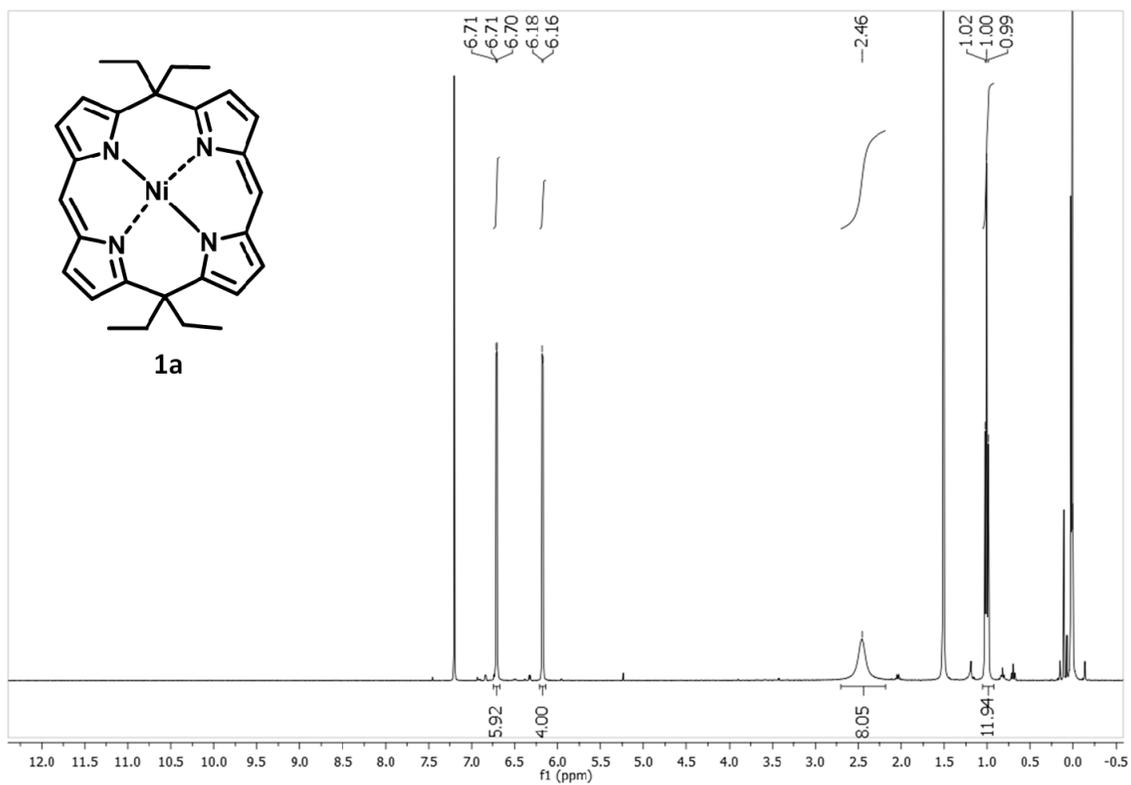


Fig. S1 ^1H NMR spectrum of **1a** in CDCl_3

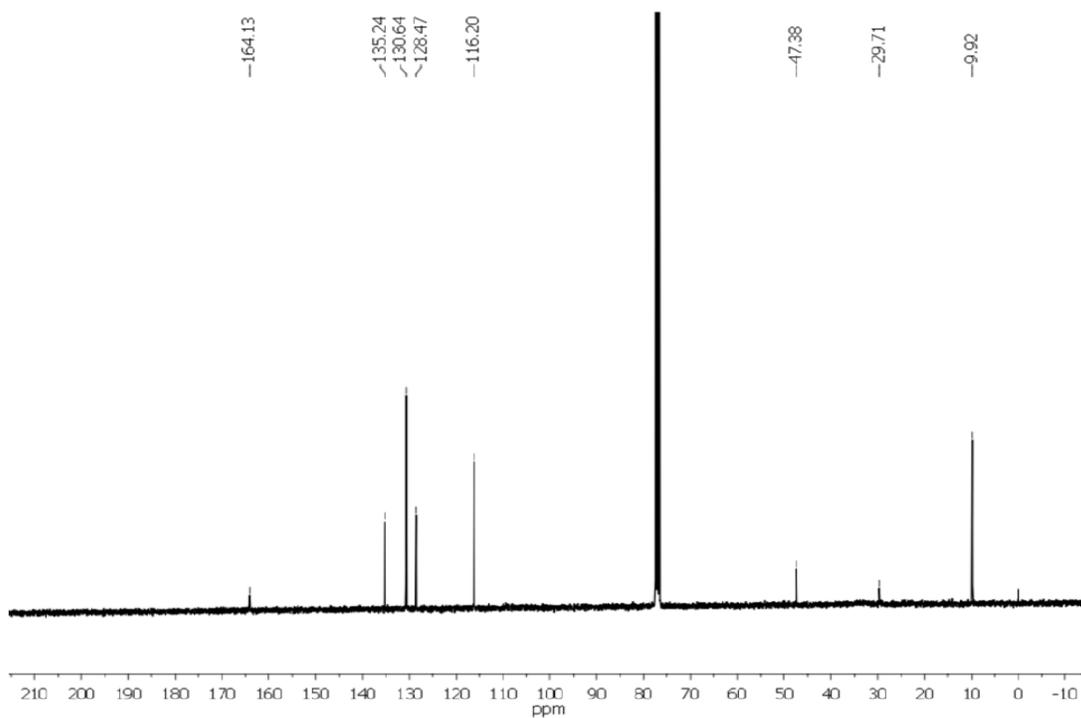


Fig. S2 ^{13}C NMR Spectrum of **1a** in CDCl_3

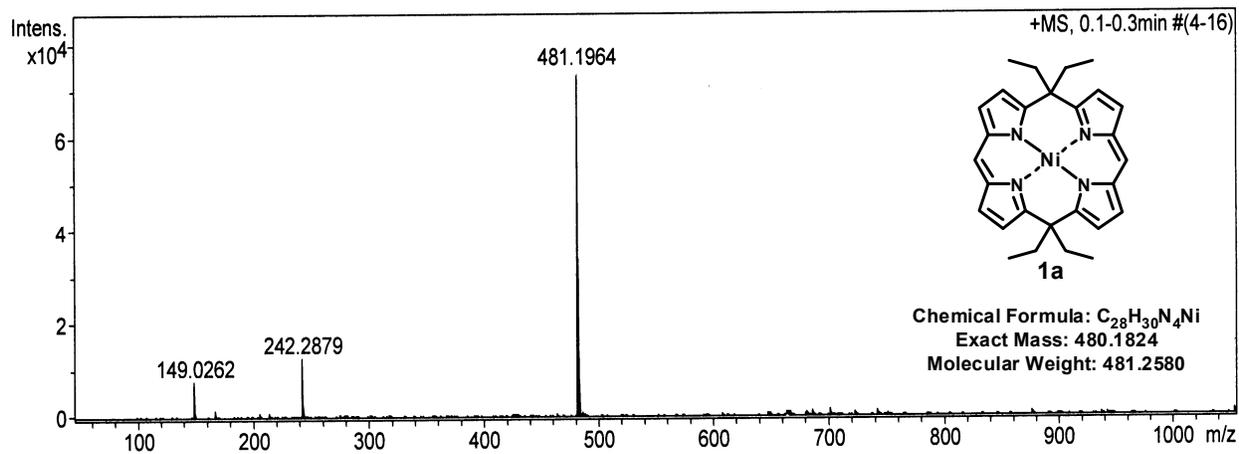


Fig. S3 ESI-Mass spectrum of **1a**

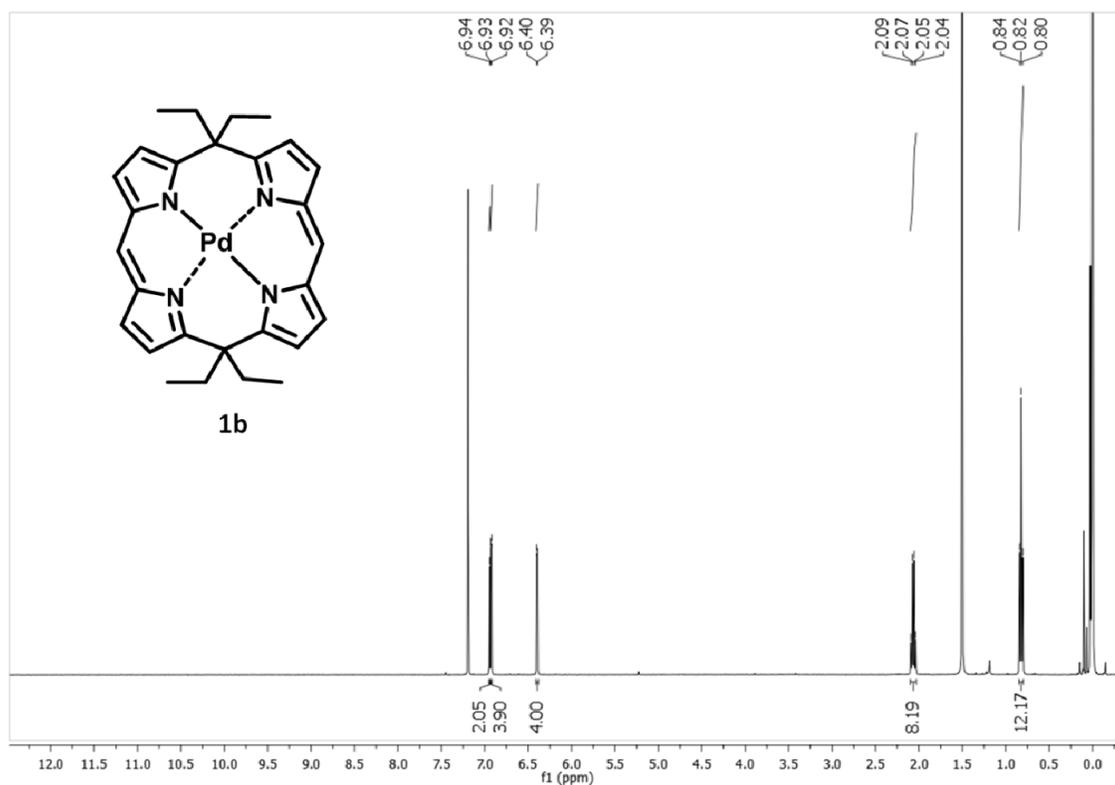


Fig. S4 ¹H NMR spectrum of **1b** in $CDCl_3$

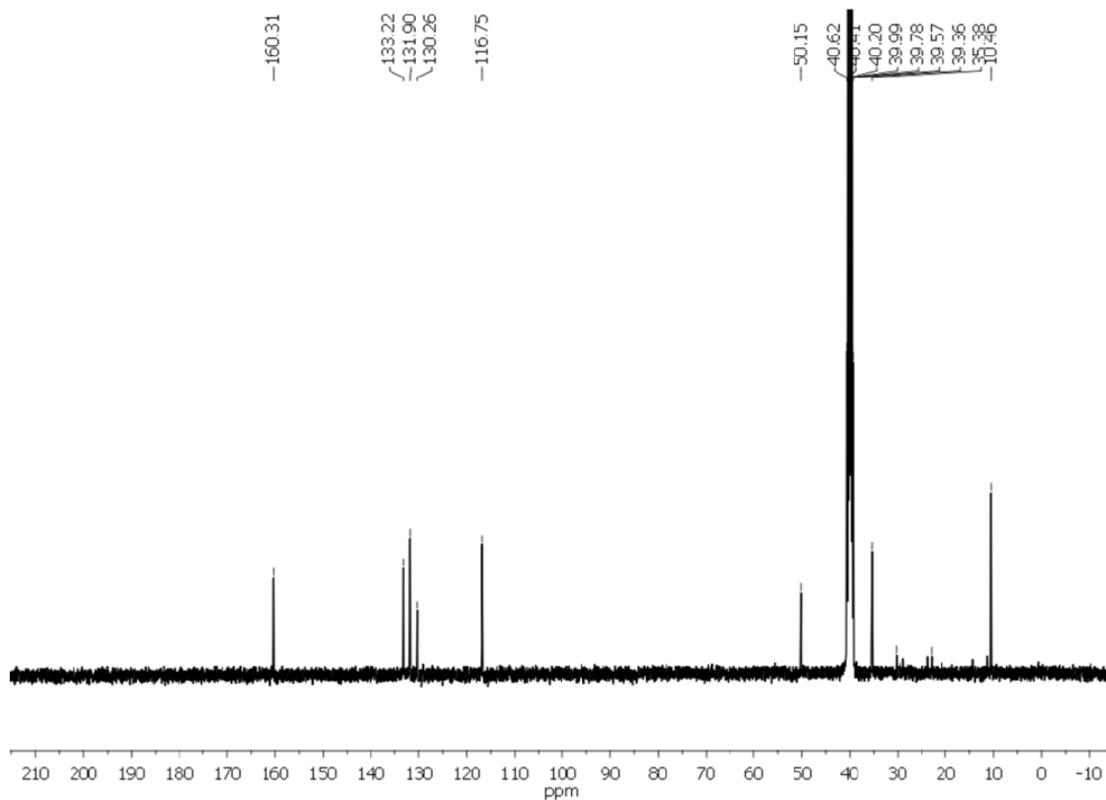


Fig. S5 ^{13}C NMR spectrum of **1b** in DMSO- d_6

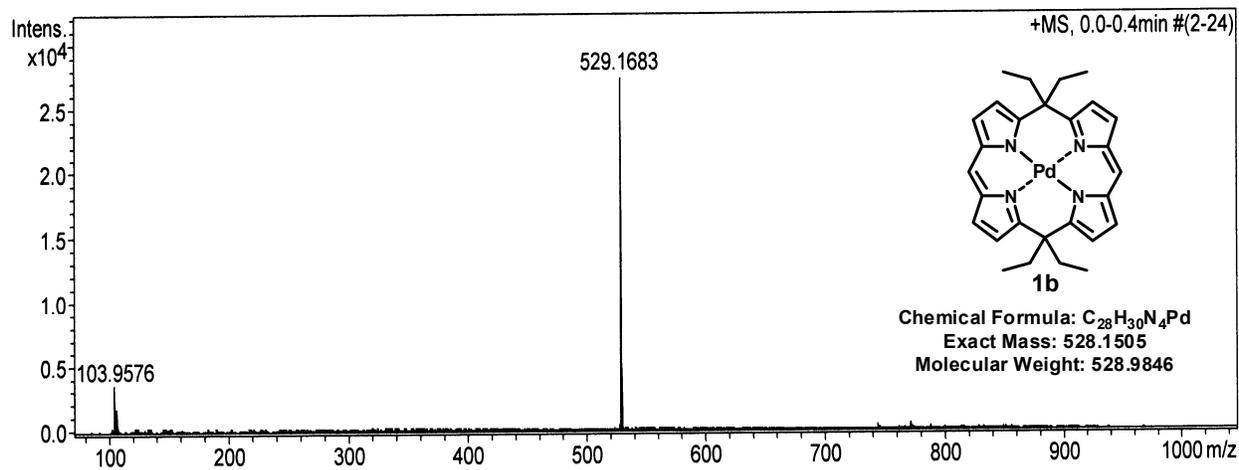


Fig. S6 ESI-Mass spectrum of **1b**

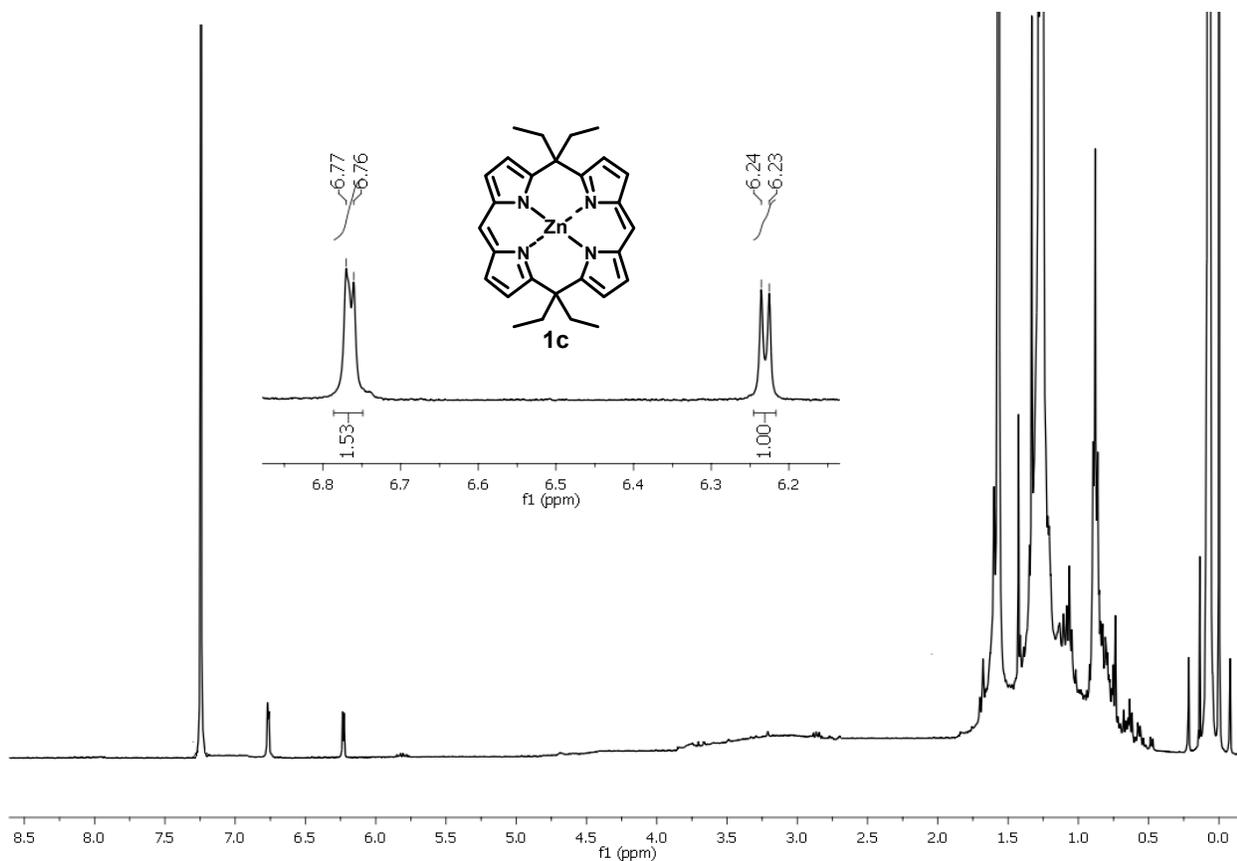


Fig. S7 ^1H NMR spectrum of **1c** in CDCl_3 .
The aliphatic protons are obscured by the solvent impurities.

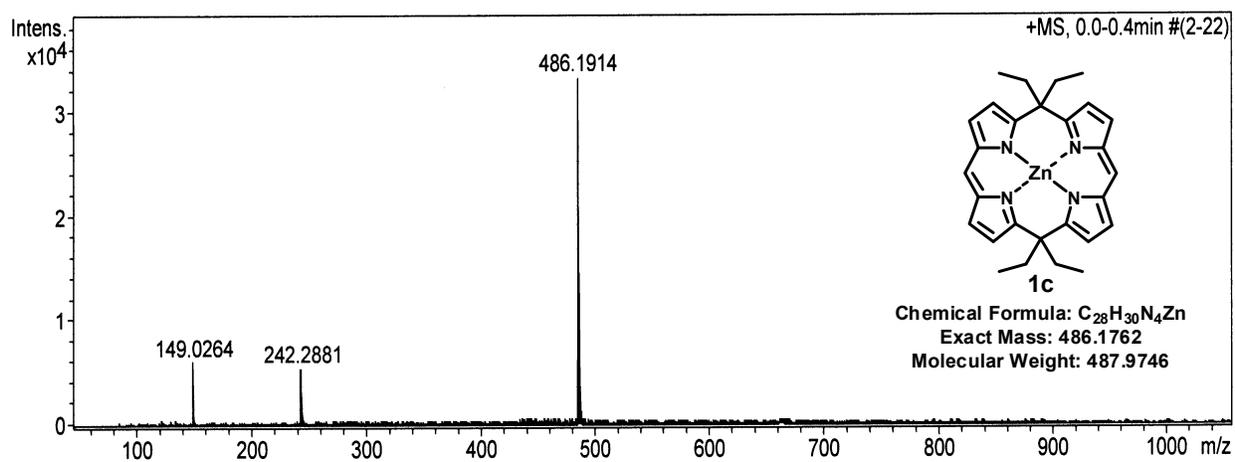


Fig. S8 ESI-Mass spectrum of **1c**

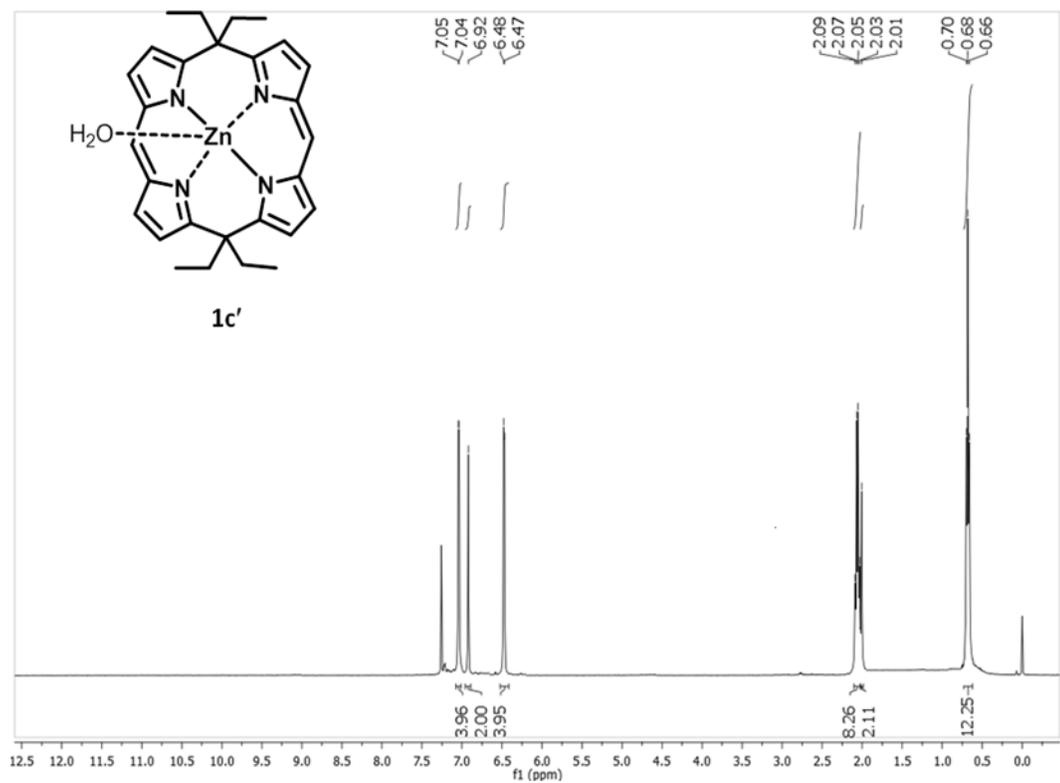


Fig. S9 ¹H NMR spectrum of **1c'** in CDCl₃

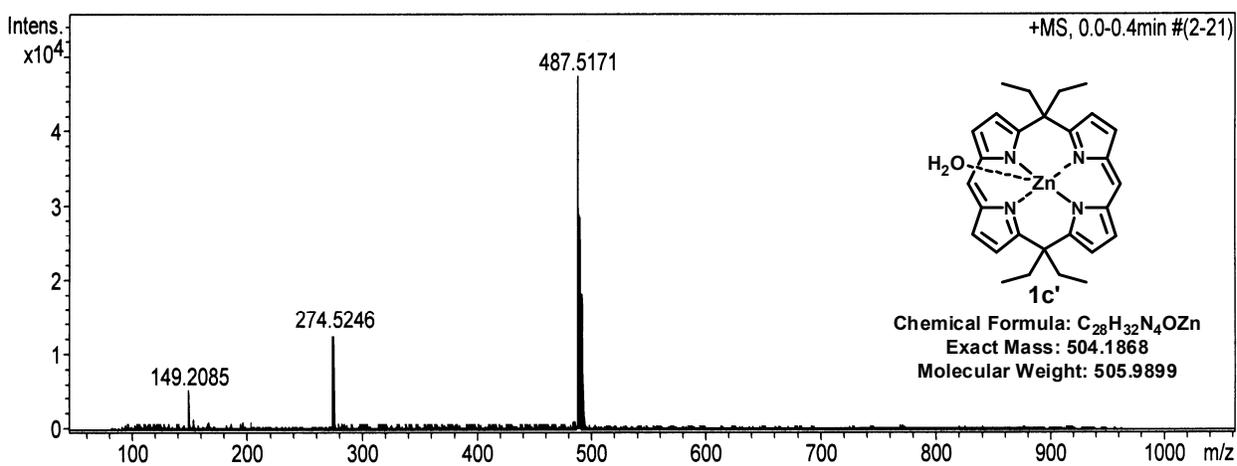


Fig. S10 ESI-Mass spectrum of **1c'**

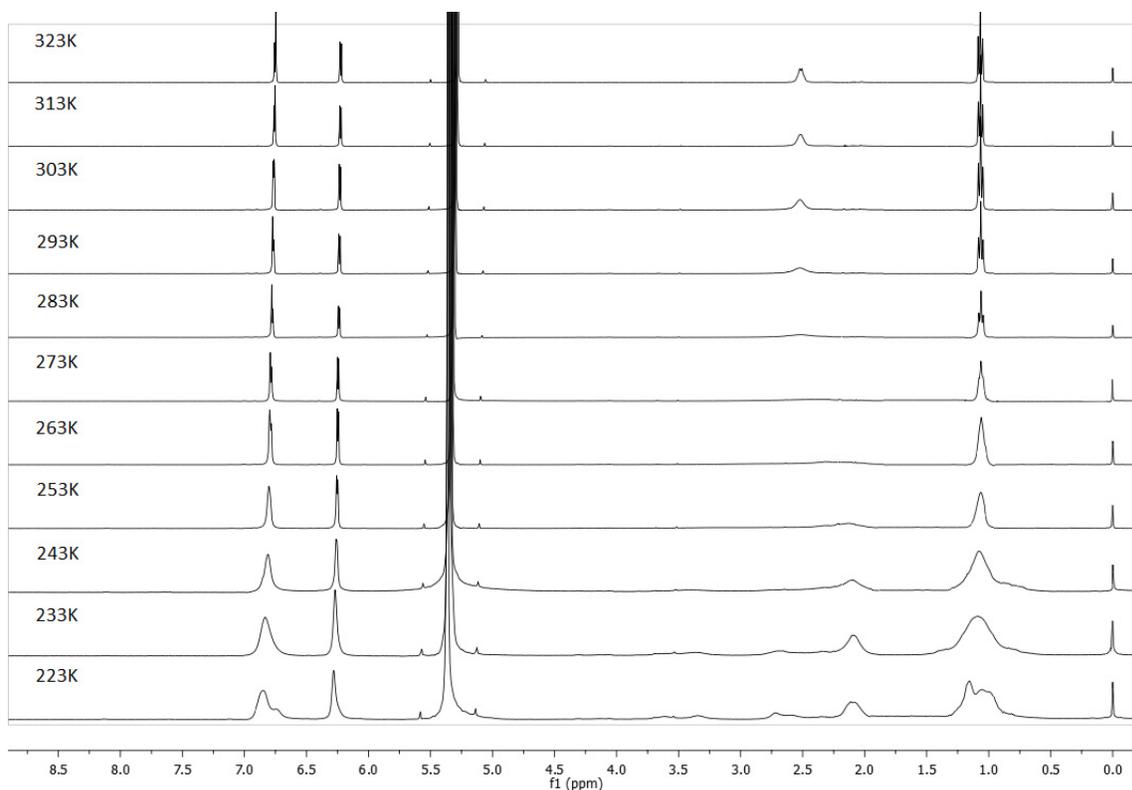
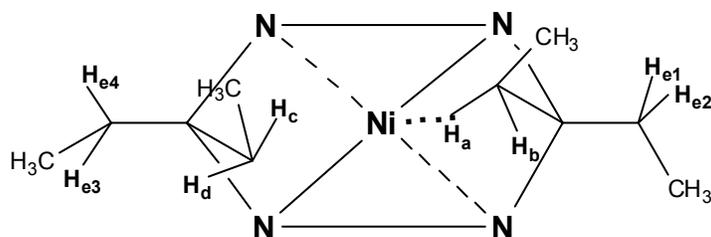


Fig. S11 Variable temperature ^1H NMR spectrum of **1a** in CD_2Cl_2

Possible Isomers:



1a has a total of 8 methylene protons (**a**, **b**, **c**, **d**, **e1-e4**) and all are equally probable to have anagostic interaction with the metal center. As a result, 8 conformational isomers are possible which will be in dynamic equilibrium in solution state at high temperature. At low temperature, this rotational motion is arrested and one of the conformers is present as observed in the crystalline state.

Experimentally, **1a** was separated by column chromatography as single isomer and further confirmed by single crystal X-ray analysis.

4. Electronic absorption spectra of 1a – 1c'

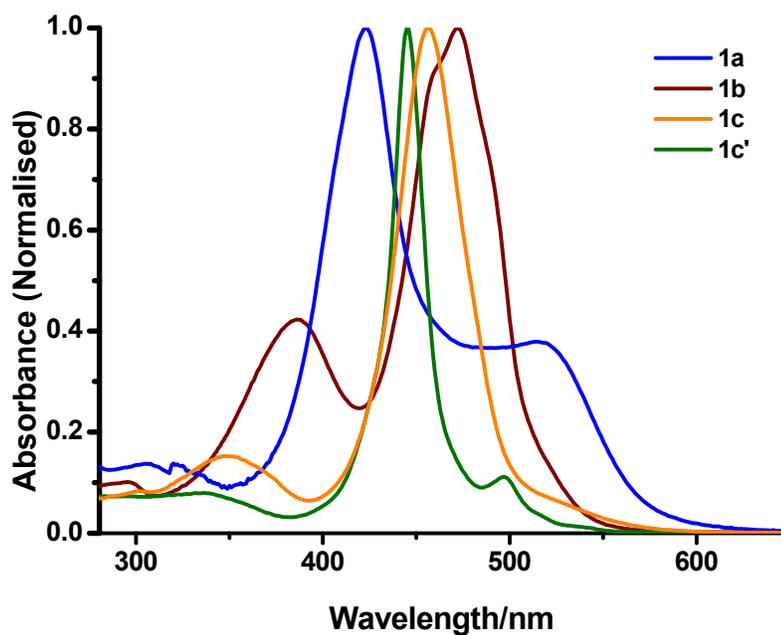


Fig. S12 Normalised electronic absorption spectra of 1a - 1c'

5. The molar extinction coefficient values of 1a – 1c'

| Metal complex | λ/nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) |
|---------------|--|
| 1a | 423 (1.92×10^4); 518 (7.65×10^3) |
| 1b | 386 (2.3×10^4); 472 (5.39×10^4) |
| 1c | 349 (2.75×10^3); 456 (1.83×10^4) |
| 1c' | 445 (7.15×10^4); 496 (2.88×10^4) |

Table S1 Electronic spectral data and molar absorption coefficient values of 1a-1c'

6. Single Crystal X-ray Structure and Analysis of 1a

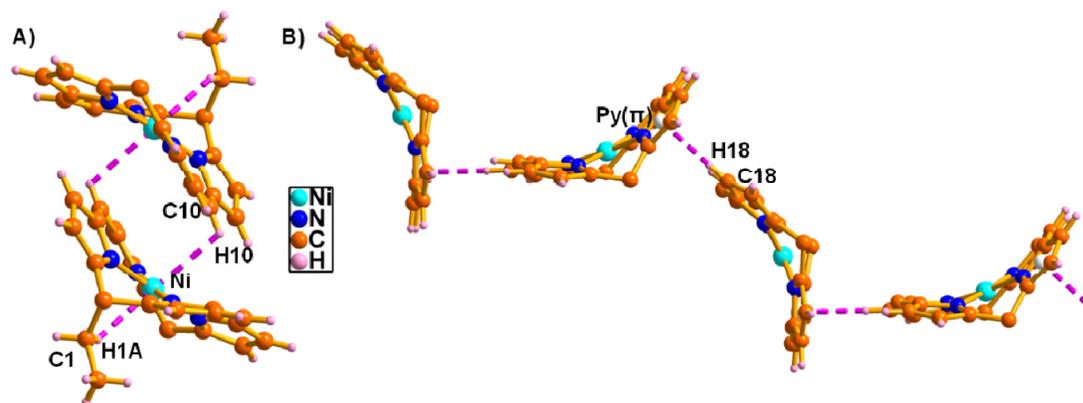


Fig. S13 Single crystal X-ray analysis of **1a**. A) Self-assembled dimer and B) 1-D array. The distances and angles of self-assembled dimer (C10-H10..Ni) and 1-D array (C18-H18...Py(π)) are 2.84 Å, 105° and 2.67 Å and 163°, respectively. The *meso*-di-ethyl units are omitted for clarity.

7. Single Crystal X-ray Structure and Analysis of **1b**

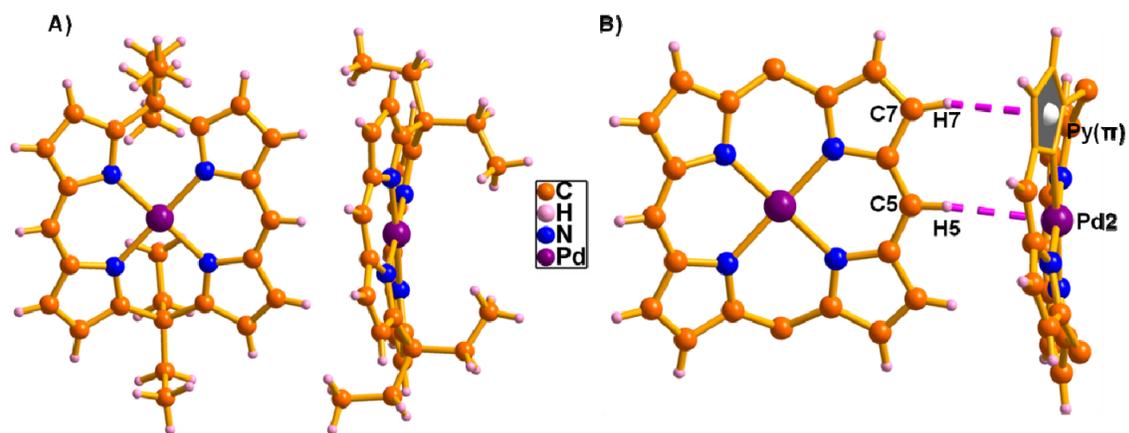


Fig. S14 Single crystal X-ray structure of **1b**. A) Top view and B) side view with intermolecular hydrogen bonding interactions. The distances and angles of C5-H5...Pd2 and C7-H7...Py(π) are 2.89 Å, 157° and 1.70 Å, 162° respectively. The units which are not involved in the hydrogen bonding interactions are omitted for clarity in the side view.

8. Single Crystal X-ray Structure and Analysis of 1c

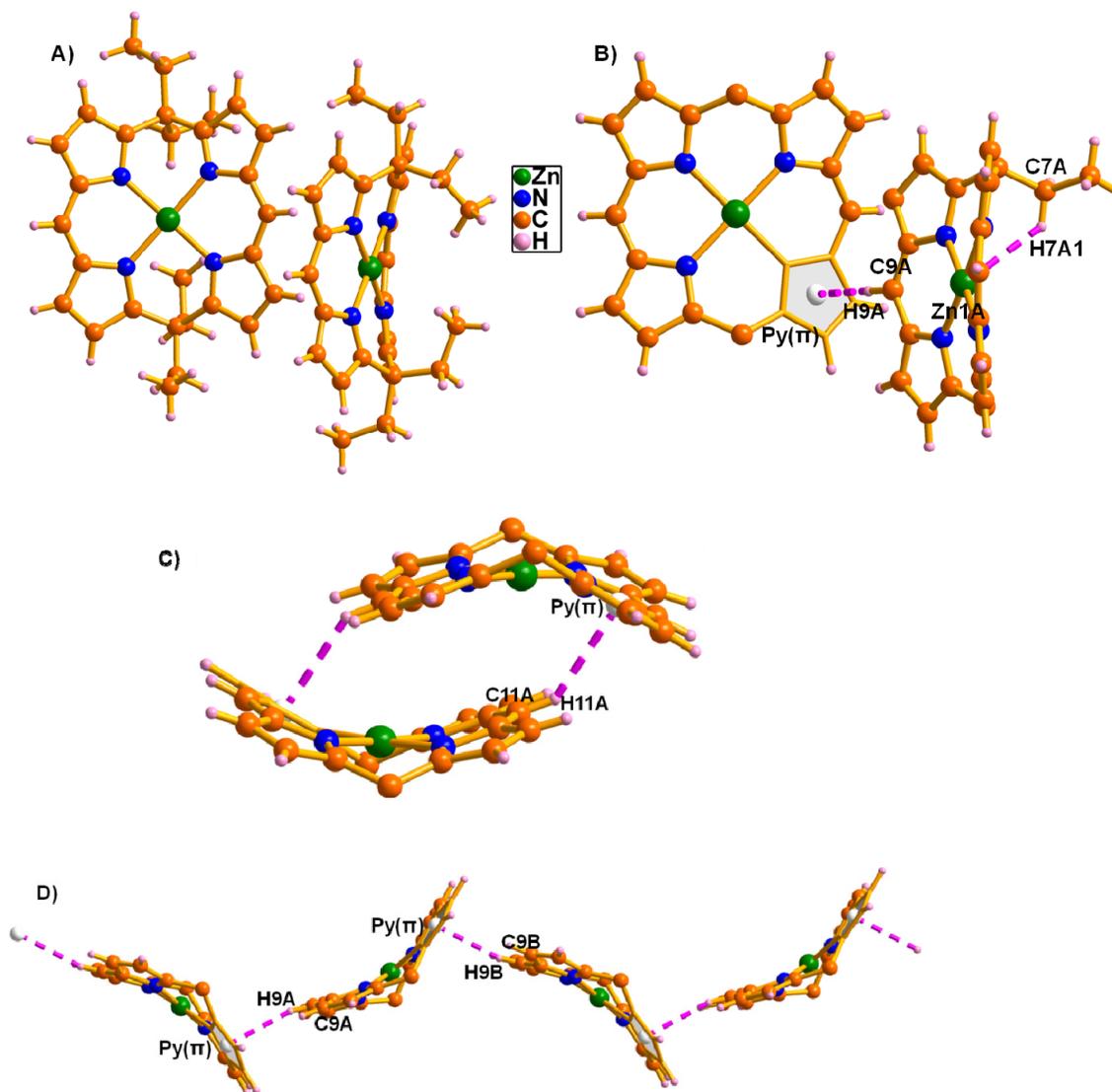


Fig. S15 Single crystal X-ray structure of 1c. A) Top view; B) side view with intra- and intermolecular hydrogen bonding interactions; The distances and angles of C9A-H9A...Py (π) and C7A-H7A1...Zn1A are 2.84 Å, 165° and 2.84 Å and 130°, respectively. C) self-assembled dimer formed by hydrogen bonding interaction with C11A-H11A...Py (π) distance 2.78 Å and angle 141° and D) 1-D array with C9B-H9B...Py (π) distance and angle is 2.82 Å and 165° respectively. The units which are not involved in the hydrogen bonding interactions are omitted for clarity.

9. Single Crystal X-ray Structure and Analysis of 1c'

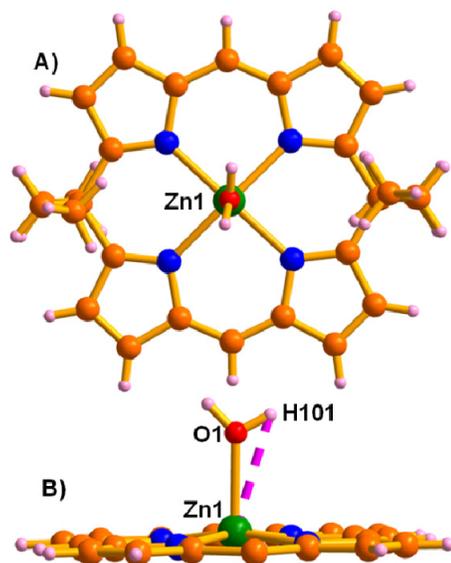


Fig. S16 Single crystal X-ray structure of **1c'**. A) Top view; B) side view, where the *meso* di-ethyl groups are omitted for clarity. Zn1 is coordinated to the H₂O molecule, where one of the hydrogens in the H₂O molecule is in intramolecular hydrogen bonding with Zn1 with a distance of 2.71Å.

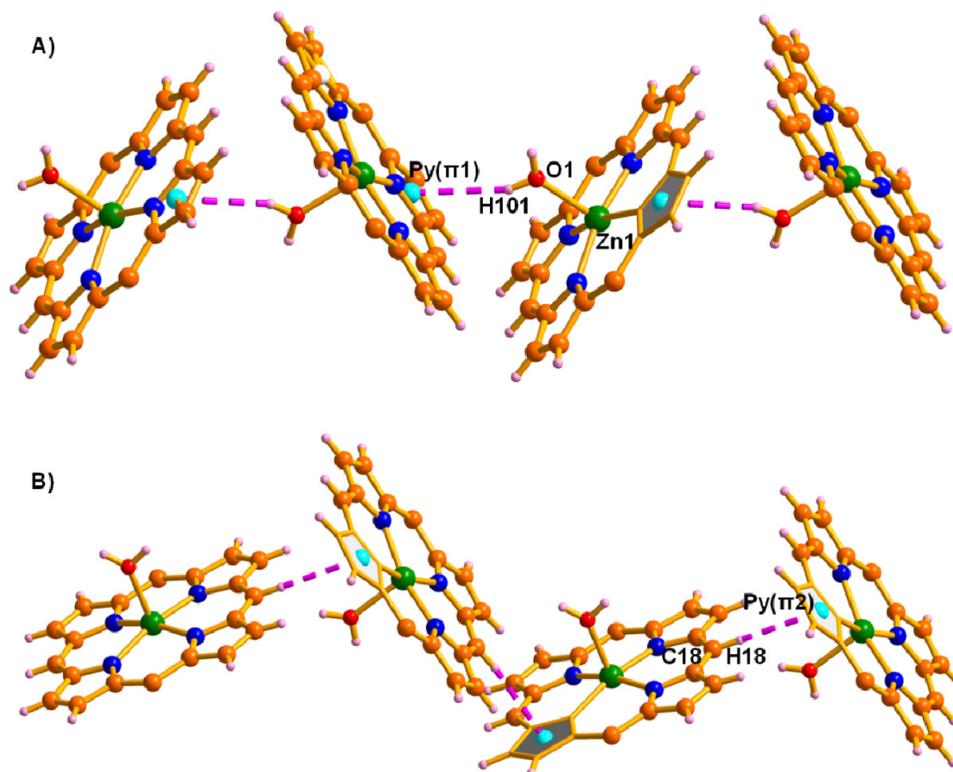


Fig. S17 1-D arrays of **1c'**. The distances and angles of A) O1-H101...Py(π 1) and B) C18-H18...Py(π 2) are 2.81, 2.88 Å and 161°, 171° respectively. The units which are not involved in the hydrogen bonding interactions are omitted for clarity.

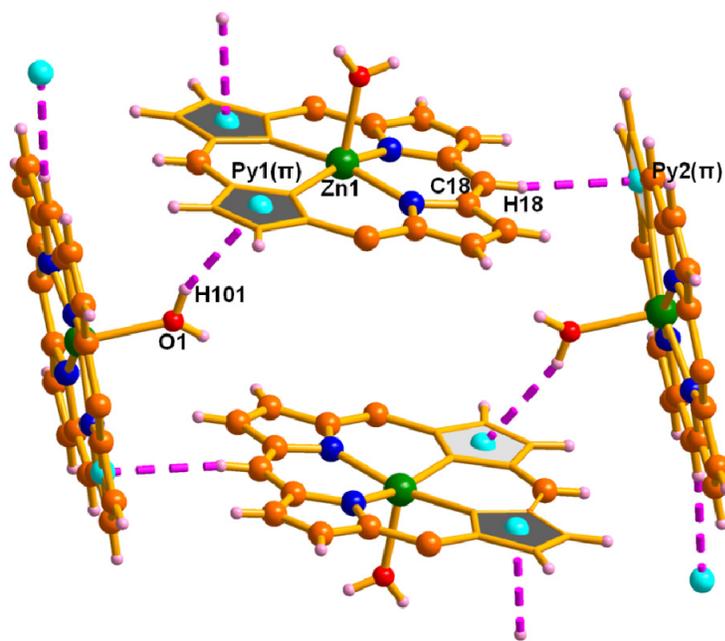


Fig. S18 2-D supramolecular assembly of **1c'**. The *meso* di-ethyl groups are omitted for clarity.

10. Crystal data for **1a** - **1c'**

| | 1a | 1b | 1c | 1c' |
|---|---|--|---|--|
| Formula | C ₂₈ H ₃₀ N ₄ Ni | C ₅₆ H ₆₀ N ₈ Pd ₂ | C ₂₈ H ₃₀ N ₄ Zn | C ₂₈ H ₃₂ N ₄ OZn |
| <i>M</i> /g mol ⁻¹ | 481.27 | 1057.92 | 487.93 | 505.95 |
| <i>T</i> /K | 296(2) | 293(2) | 296(2) | 296(2) |
| Crystal dimensions/mm ³ | 0.12 x 0.09 x 0.07 | 0.20 x 0.05 x 0.05 | 0.11 x 0.09 x 0.07 | 0.13 x 0.11 x 0.09 |
| Crystal system | monoclinic | monoclinic | triclinic | monoclinic |
| Space group | P21/c | P21/n | P-1 | P21/c |
| <i>a</i> /Å | 12.010(5) | 16.5817(15) | 12.1113(5) | 11.925(5) |
| <i>b</i> /Å | 14.987(5) | 14.4709(12) | 12.3679(6) | 13.851(5) |
| <i>c</i> /Å | 13.483(5) | 20.188(2) | 16.5343(7) | 15.547(5) |
| α /° | 90.000(5) | 90.00 | 90.498(3) | 90.000(5) |
| β /° | 103.165(5) | 99.123(5) | 103.219(3) | 103.945(5) |
| γ /° | 90.000(5) | 90.00 | 103.893(3) | 90.000(5) |
| <i>V</i> /Å ³ | 2363.1(15) | 4783.0(8) | 2335.23(18) | 2492.3(16) |
| <i>Z</i> | 4 | 4 | 4 | 4 |
| ρ_{calcd} /mg m ⁻³ | 1.353 | 1.469 | 1.388 | 1.348 |
| μ /mm ⁻¹ | 0.845 | 0.799 | 1.076 | 1.013 |
| <i>F</i> (000) | 1016 | 2176 | 1024 | 1064 |
| Reflns. collected | 9161 | 7299 | 8506 | 7591 |
| Indep.reflns.[<i>R</i> (int)] | 7236 [0.0447] | 8420[0.0517] | 8506 [0.0475] | 7591 [0.0651] |
| Max/min transmission | 0.9432 and 0.9054 | 0.922 and 0.801 | 0.9285 and 0.8909 | 0.9143 and 0.8796 |
| Data/restraints/parameters | 7236/0/298 | 8420/0/604 | 8506/1/595 | 7591/2/319 |
| GOF on <i>F</i> ² | 1.042 | 1.090 | 1.120 | 1.028 |
| Final <i>R</i> indices[<i>I</i> > 2 σ (<i>I</i>)] | <i>R</i> 1 = 0.0462, w <i>R</i> 2 = 0.1348 | <i>R</i> 1 = 0.0399, w <i>R</i> 2 = 0.1004 | <i>R</i> 1 = 0.0758, w <i>R</i> 2 = 0.2315 | <i>R</i> 1 = 0.0384, w <i>R</i> 2 = 0.0861 |
| <i>R</i> indices (all data) | <i>R</i> ₁ =0.0705 | <i>R</i> ₁ =0.0707 | <i>R</i> ₁ =0.0994 | <i>R</i> ₁ =0.0703 |
| Largest diff peak and hole [e Å ⁻³] | 1.628 and -0.414 | 0.787 and -0.707 | 1.742 and -0.741 | 0.533 and -0.255 |

Table S2 Crystal data for **1a** - **1c'**

CCDC-930500 for **1a**, CCDC-930501 for **1b**, CCDC-930502 for **1c** and CCDC-930503 for **1c'** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.