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## **Design of Neutral Metallomesogens from 5,5-Dimethyldipyrromethane: Metal Ion Mediated Control of Folding and Hairpin Structures.**

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## Abstract

New ligands derived from 5,5-dimethyldipyrromethane and their corresponding neutral complexes with Zn(II) and Pd(II) are described. The ligands incorporate either hexacatenar [ $\mathbf{H}_2(\mathbf{1}^n)$ ,  $n = 1, 10, 12, 14$  and  $16$ ], tetracatenar [ $\mathbf{H}_2(\mathbf{2}^n)$ ,  $n = 1$  and  $16$ ] or an extended dicatenar structure [ $\mathbf{H}_2(\mathbf{3}^n)$ ,  $n = 1$  and  $16$ ]. Single crystal X-ray structure determinations on [ $\mathbf{Zn}_2(\mathbf{1}^1)_2$ ] and [ $\mathbf{Zn}_2(\mathbf{3}^1)_2$ ] confirm a distorted tetrahedral geometry at Zn(II) to afford double-stranded helical structures, while the Pd(II) species [ $\mathbf{Pd}(\mathbf{3}^1)$ ] shows a distorted square planar geometry with the ligand adopting an alternative hairpin conformation. The metal-free hexacatenar ligands  $\mathbf{H}_2(\mathbf{1}^n)$  ( $n = 10, 12, 14, 16$ ) and the corresponding complexes [ $\mathbf{Zn}_2(\mathbf{1}^{16})_2$ ] and [ $\mathbf{Pd}(\mathbf{1}^n)$ ] ( $n = 12, 14, 16$ ) are not mesomorphic. However, the tetracatenar complex [ $\mathbf{Zn}_2(\mathbf{2}^{16})_2$ ] generates a smectic mesophase, as confirmed by X-ray diffraction, while [ $\mathbf{Pd}(\mathbf{2}^{16})$ ] and the metal-free ligand  $\mathbf{H}_2(\mathbf{2}^{16})$  show no mesomorphic behaviour. Two of the extended dicatenar compounds,  $\mathbf{H}_2(\mathbf{3}^{16})$  and [ $\mathbf{Zn}_2(\mathbf{3}^{16})_2$ ] are non-mesomorphic, while [ $\mathbf{Pd}(\mathbf{3}^{16})$ ] displays a smectic A phase.

## Introduction

The area of metal-containing liquid crystals, so-called metallomesogens, has developed into an extensive field of research in recent years,<sup>[1]</sup> and covers a wide range of materials that have additional properties over and above their liquid crystal behaviour. These systems include thermotropic liquid crystals,<sup>[2]</sup> surfactants,<sup>[3]</sup> amphotropic materials,<sup>[4]</sup> polycatenar mesogens,<sup>[5]</sup> polymers,<sup>[6]</sup> dendrimers,<sup>[7]</sup> redox-active materials,<sup>[8]</sup> magnetic materials<sup>[9]</sup> and fullerene-containing liquid crystals.<sup>[10]</sup> A wide range of ligand architectures has been studied with complexation of the ligand to a metal ion often imparting liquid crystal behaviour or modifying this behaviour significantly.<sup>[1, 11]</sup> One particular molecular motif of growing interest in the literature and directly relevant to this report is the metallohelicate.<sup>[12]</sup> Recently, mesomorphic ionic metallohelicates have been described for tetrahedral Cu(I) salts of both 2,2'-bipyridine<sup>[13]</sup> and 2,2':6',2''-terpyridine.<sup>[14]</sup> These materials are derived from non-mesomorphic hexacatenar imine ligands with several complexes displaying columnar phases at or near room temperature. It was also observed that the

symmetry of the columnar phase changes with the elongation of the rigid central core from hexagonal, to lamello-columnar via a rectangular or oblique symmetry.<sup>[12e, 13b, 14]</sup>

Pyrrole-containing, thermotropic liquid crystalline compounds can be broadly categorised into two main groups. The first comprises the discotic macrocyclic compounds incorporating phthalocyanine or porphyrin rings,<sup>[15-25]</sup> although through ligand design Zn(II) porphyrins can display calamitic phases such as nematic and smectic A.<sup>[26]</sup> The second group are the calamitic, monomeric, *N*-substituted pyrroles that are subsequently polymerised to form poly(pyrrole) backbones.<sup>[27-30]</sup> There are naturally a few exceptions that fall outside these two categories, such as derivatives of diketopyrrolopyrroles<sup>[31]</sup> which display nematic and smectic A phases. Similarly, 2-substituted monomeric pyrroles<sup>[32, 33]</sup> can display nematic phases both as the free ligand and as the bis-complexes with Ni(II) and Cu(II) ions.

We report herein the incorporation of the 5,5-dimethyldipyrromethane unit as the core of a potential liquid-crystalline material capable of acting as a ligand to a variety of metal centres. Several features of the ligand design are noteworthy (Figure 1). Firstly, deprotonation of the pyrrolic N-centres followed by complexation with M(II) cations yields neutral molecules. Secondly, there is a loss of conjugation at the quaternary carbon between the pyrrolic rings, and thirdly, the sp<sup>3</sup> hybridised *meso*-carbon acts imparts a twist to the two pyrrole-imine binding sites. In this study, tetracatenar and hexacatenar ligands were studied in the metal-free state and also complexed to Pd(II) and Zn(II). The use of both square planar Pd(II) and tetrahedral Zn(II) nodes affords materials with different dispositions and relative conformations of the bound ligands leading potentially to modulation of their mesogenic behaviour. A further modification available to the dipyrrole system was the introduction of long chain imine substituents in the guise of additional phenyl rings with ester linkers (Figure 1b). The intention was to elongate the bound ligands to generate bent-core mesogens. Generally, such molecules require between five and seven aromatic rings,<sup>[34]</sup> and this achieved by **H<sub>2</sub>(3'')**, which incorporate six aromatic rings. Also, in keeping with the general design of such materials, the number of terminal aliphatic chains per molecule was

reduced to two. Thus, in this work we report the metal-induced mesomorphism of neutral M(II) complexes dependent upon the choice of ligand functionality. Additionally, we observe that the 5,5-dimethyldipyrromethane core can be directed in its co-ordination to a metal ion to yield binuclear helicates with tetrahedral Zn(II) and mononuclear hairpin complexes with square planar Pd(II). More significantly, the Zn(II) helicates reported herein represent the first examples of neutral metallohelicates which are mesomorphic.

Figure 1 here

## Results and Discussion

The ligand syntheses are illustrated in Scheme 1. 3,4-Di- and 3,4,5-trialkoxyanilines were synthesised according to literature procedures,<sup>[35,36]</sup> and were condensed with 5,5-dimethyl-1,9-diformyldipyrromethane in acidic conditions to form the desired Schiff-base pyrrole ligands.<sup>[37,38]</sup> The complexes were synthesised by deprotonation of the appropriate dipyrrolic ligand with NEt<sub>3</sub> and reaction with [Pd<sub>3</sub>(OAc)<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> or Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O in MeOH and CH<sub>2</sub>Cl<sub>2</sub>. The complexes [M<sub>x</sub>(1<sup>n</sup>)<sub>x</sub>] (M = Pd, x = 1, M = Zn x = 2; n = 1, 10, 12, 14, 16) and [M<sub>x</sub>(2<sup>n</sup>)<sub>x</sub>] (M = Pd, x = 1; M = Zn, x = 2; n = 1 and 16), and [M<sub>x</sub>(3<sup>n</sup>)<sub>x</sub>] (M = Pd, x = 1; M = Zn, x = 2; n = 1 and 16) were recrystallised by solvent diffusion of either Et<sub>2</sub>O or EtOH into a solution of the complex in CHCl<sub>3</sub>, affording the products in yields of 50-99%. MALDI-TOF mass spectrometry showed peaks that could be assigned to [Pd(1<sup>n</sup>)]<sup>+</sup> and [Zn<sub>2</sub>(1<sup>n</sup>)<sub>2</sub>]<sup>+</sup>, respectively, with the <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>) for these complexes at room temperature displaying resonances that are appropriate to either a symmetric ligand arrangement or rapid interchange between asymmetric structures.<sup>[37,39]</sup>

Scheme 1 here

Single crystals of [Zn<sub>2</sub>(1<sup>1</sup>)<sub>2</sub>].0.1CHCl<sub>3</sub>·3.35C<sub>4</sub>H<sub>10</sub>O were grown by diffusion of Et<sub>2</sub>O vapour into a solution of the complex in CHCl<sub>3</sub>, while single crystals of [Zn<sub>2</sub>(3<sup>1</sup>)<sub>2</sub>].CH<sub>2</sub>Cl<sub>2</sub> and [Pd(3<sup>1</sup>)] were grown by solvent diffusion of hexane into a solution of the complex in CH<sub>2</sub>Cl<sub>2</sub>. The single crystal X-ray structures of both [Zn<sub>2</sub>(1<sup>1</sup>)<sub>2</sub>].0.1CHCl<sub>3</sub>·3.35C<sub>4</sub>H<sub>10</sub>O (Figures 2 and 3) and [Zn<sub>2</sub>(3<sup>1</sup>)<sub>2</sub>].CH<sub>2</sub>Cl<sub>2</sub> (Figure 4) confirmed them to be binuclear species crystallising in space groups

$P2_1/n$  and  $P\bar{1}$ , respectively. The co-ordination geometry at Zn(II) in these complexes is strongly distorted tetrahedral (e.g., N-Zn-N angles range from 84.19(14) to 141.61(15)°; Table 1) with the four co-ordination sites occupied by one pyrrole nitrogen and one imine nitrogen from each ligand; the Zn-N(pyrrole) distances are shorter than the Zn-N(imine) ones. The bridging of tetrahedral Zn(II) centres by the ligands results in the formation of a double-stranded helicate with a Zn-Zn separation of 4.08 Å for  $[\text{Zn}_2(\mathbf{1}^1)_2]$  and 3.76 Å for  $[\text{Zn}_2(\mathbf{3}^1)_2]$ . These chiral compounds crystallise in centrosymmetric space groups, implying that there is a racemic mixture of molecules present within the crystals with the major and minor grooves of the M enantiomer being displayed in Figure 3. The ligands adopt an asymmetric arrangement in which  $\pi$ - $\pi$ -interactions<sup>[40]</sup> between opposing imino-pyrrole units of one half of each ligand promote the formation of a molecular cleft e.g. for  $[\text{Zn}_2(\mathbf{1}^1)_2]$  pyrrole N2'-pyrrole N3 = 3.542 Å, imino N4-pyrrole C2' = 3.417 Å and imino N1'-pyrrole C10 = 3.456 Å. This contrasts with the  $C_2$ -symmetric structure observed in solution by <sup>1</sup>H NMR spectroscopy at room temperature, which has been previously ascribed by one of us to a dynamic process that involves a rearrangement of the ligands without ligand dissociation to equilibrate the ligands within the binuclear molecular cleft structure without enantiomer exchange. It was further shown, that at 173K these analogous Zn(II) helicates show a doubling of all resonances which is consistent with the asymmetric structure seen in the solid state and results from the binuclear molecular cleft structure.<sup>39b</sup> Related diimino-5,5-dimethyldipyrromethane double-stranded helicates with Mn(II), Co(II), Fe(II) and Zn(II) cations have been prepared previously<sup>[39,41]</sup> and demonstrate a similar asymmetric arrangement of the bridging ligands, although the Zn-Zn separation at 4.69Å is longer than for the complexes described here. Due to the *meso*-carbon, the pyrrole rings from each ligand are twisted relative to each other. For example in  $[\text{Zn}_2(\mathbf{1}^1)_2]$ , the N2 and N3 pyrrole rings are twisted by 85.2(2)° relative to one another, with the same twist observed between the N2' and N3' rings. The phenyl rings are approximately co-planar with their respective pyrrole planes, confirmed by the dihedral angles between the C30 phenyl ring and the N3 pyrrole ring [6.869(4)°], the C20 phenyl ring and the N2 pyrrole ring [18.28(1)°], the C30' phenyl ring and

the N3' pyrrole ring [18.28(1)°] and between the C20' phenyl ring and the N2' pyrrole ring [16.430(9)°].

Figures 2 - 4 here

In the complex [Zn<sub>2</sub>(**3**<sup>1</sup>)<sub>2</sub>] the pyrrole rings in each ligand are substantially twisted relative to each other to accommodate the bridging of both metal cations (Table 1). Here the phenyl rings are also twisted relative to the pyrrole rings with three of the four terminal phenyl rings disordered. Consequently, their occupancy has been modelled over two sites and each ring experiences a different torsion angle.

Table 1 here

An alternative structure is observed for the complex [Pd(**3**<sup>1</sup>)], which crystallises in the triclinic space group *P*1̄, with a distorted square-planar co-ordination geometry about the central Pd(II) cation (Table 1) to form a hairpin structure (Figure 5). As for the Zn(II) complexes, the Pd-imine N bonds are slightly longer than those to the pyrrolic N-centres. Such a square-planar co-ordination geometry has previously been reported in a macrocyclic diimino-5,5-dimethyldipyrromethane Pd(II) complex.<sup>[42]</sup> The square-planar geometry at Pd(II) constrains the pyrrole rings to an almost planar arrangement with only a slight tetrahedral distortion of 0.055(2) Å. The rings experience a twist of only 5.9(4)° with respect to each other and the Pd(II) cation lies 0.014(2) Å out of the least squares mean plane defined by the four co-ordinating N atoms. Flexibility of the extended arms permits the two sets of phenyl rings to deviate from co-planarity, with the C20 and C30 rings twisted by 20.9(3)° and the C40 and C50 rings twisted by 16.3(2)° relative to one another. As is apparent from Figure 5 the phenyl rings are also twisted relative to the pyrrole rings. Due to steric restraints the C20 and C30 rings are twisted by only 34.2(2) and 40.8(2)° relative to the N2 and N3 pyrrole rings, respectively, while the C40 and C50 rings are twisted by 87.69 (14) and 76.40(14)° relative to the N2 and N3 rings, respectively.

Figure 5 here

### **Thermal behaviour of $H_2(1^n)$ , $[Pd(1^n)]$ and $[Zn(1^{16})]_2$**

The thermal behaviour of the ligands  $H_2(1^n)$  was investigated by polarised optical microscopy, and their transition temperatures are reported in Table 2. The metal-free ligands melted to isotropic liquids without formation of any mesophases but sometimes with a second crystal phase being observed. The three Pd(II) complexes,  $[Pd(1^{12})]$ ,  $[Pd(1^{14})]$  and  $[Pd(1^{16})]$ , exhibited similar behaviour as deduced by polarised optical microscopy with the absence of mesophase induction (Table 2). Between crossed-polarisers  $[Zn_2(1^{16})]_2$  begins to melt at 30°C and was fully cleared at 40°C. Unsurprisingly, the helical structure of binuclear  $[Zn_2(1^{16})]_2$  serves to lower both the melting and clearing temperatures relative to  $H_2(1^{16})$ .

Table 2 here

### **Thermal behaviour of $H_2(2^{16})$ , $[Pd(2^{16})]$ and $[Zn_2(2^{16})]_2$**

The tetracatenar metal-free ligand  $H_2(2^{16})$  and the complex  $[Pd(2^{16})]$  are non-mesomorphic, melting to isotropic fluid at 107°C and 90°C, respectively. In contrast, the complex  $[Zn_2(2^{16})]_2$  was found to be mesomorphic by polarised optical microscopy, differential scanning calorimetry (Table 2) and small-angle X-ray diffraction (Table 3). The DSC traces showed both melting and clearing temperatures in the first heating cycle in agreement with the observations from the microscopy.  $[Zn_2(2^{16})]_2$  melts into a mesophase at 57°C and clears at 77°C, however the later transition is accompanied by some decomposition. Unfortunately, the fluid texture observed by polarised optical microscopy is not a typical texture. XRD measurements allowed the characterisation of the mesophase formed by  $[Zn_2(2^{16})]_2$  as a lamellar phase from the one intense and three small diffraction peaks in the ratio 1:2:3:4, which were indexed as the (001), (002), (003) and (004) reflections of a layered structure (Figure 6) with a periodicity  $d = 30.5 \text{ \AA}$ .<sup>[43]</sup> Along these sharp reflections, one can observe the broad peak at 4.6 Å corresponding to the liquid-like ordering of the chains, and some residual broad peaks from the previous crystalline phase (at 17.66 and 13.6 Å). The presence of crystalline phase was due to the XRD measurements being carried out at 60 °C, above which the liquid crystalline phase was observed to decompose over the extended length of



the experiment. Using the periodicity of the smectic phase, and the molecular volume of the binuclear complex,  $V$  ( $V = 4790 \text{ \AA}^3$ ), we can estimate the overall molecular area, ( $A_M$ ) through the relationship  $A_M = V/d$ ; thus  $A_M = 155 \text{ \AA}^2$ , which when divided by four (2x4 chains), gives an acceptable value of the chain area ( $a_{ch} = 38.75 \text{ \AA}^2$ ). This shows that the chains are very disordered, likely to cover the large surface area of the metallic core, and are likely to be interdigitated.

Table 3 and Figure 6 here

From the single crystal structure of the closely related complex  $[\text{Zn}_2(\mathbf{1}^1)_2]$  the largest methoxycarbon to methoxycarbon separation is  $18.1 \text{ \AA}$  which, when combined with a length of approximately  $19 \text{ \AA}$  for each extended hexadecane chain,<sup>[44]</sup> suggests a potential fully-extended molecular length of  $56 \text{ \AA}$  for  $[\text{Zn}_2(\mathbf{2}^{16})_2]$ . From the XRD measurements of  $[\text{Zn}_2(\mathbf{2}^{16})_2]$  the periodicity  $d = 30.5 \text{ \AA}$ , which suggests significant interdigitation between the chains on adjacent layers within the smectic mesophase. Comparison of the phase transitions of the tetracatenar complexes  $[\text{M}_x(\mathbf{2}^{16})_x]$  with those of the hexacatenar complexes  $[\text{M}_x(\mathbf{1}^{16})_x]$ , confirm that reduction in the number of aliphatic chains from six to four has no significant effect on the thermal behaviour. The general absence of mesomorphism in the hexacatenar complexes and  $[\text{Pd}(\mathbf{2}^{16})]$  can be ascribed to the two bulky methyl groups at the *meso* position of the dipyrromethane ligand, which may reduce the tendency of the molecules to pack efficiently.

In  $[\text{Zn}_2(\mathbf{2}^{16})_2]$  the molecules do not stack, but due to the number of chains, they can be accommodated more easily within a smectic-like phase. Thus, by considering that in the Zn(II) complexes the ligands are disposed helically around the metal centre, the overall shape of the complex may be regarded as quasi-cylindrical. The molecular area ( $A_M$ ) of the complex in the smectic phase can then be estimated considering the parallel arrangement of all the complexes, so that:  $A_M = (\text{volume complex})/(\text{smectic periodicity})$ , *i.e.*  $ca 4,700 \text{ \AA}^3/30.4 \text{ \AA} = 155 \text{ \AA}^2$ . Since four chains irradiate from either sides of the cylinder, it leads to a chain-cross-section area of  $A_{CH} = A_M/4 = 38.75 \text{ \AA}^2$ . This is large compared to the average  $24 \text{ \AA}^2$  for a calamitic system in layers, but since the aromatic core is rather large, the chains may compensate the projection of the area. For the

three-chain system, the proportion of alkyl chains is likely too great, and it is anticipated that a single chain would be not sufficient. Thus, the tetracatenar ligand appears to correspond to the optimum arrangement. A few non-planar Zn(II) complexes have been reported to generate mesophases<sup>[45]</sup> with only a very few examples involving tetrahedral zinc(II) complexes.<sup>[46]</sup> Significantly,  $[\text{Zn}_2(\mathbf{2}^{16})_2]$  is of a neutral helicate showing mesomorphism.<sup>[12d, 12e]</sup>

### **Thermal behaviour of $\text{H}_2(\mathbf{3}^{16})$ , $[\text{Pd}(\mathbf{3}^{16})]$ and $[\text{Zn}_2(\mathbf{3}^{16})_2]$**

The ligand  $\text{H}_2(\mathbf{3}^{16})$  and the binuclear complex  $[\text{Zn}_2(\mathbf{3}^{16})_2]$  are non-mesomorphic, melting directly into the isotropic phase (Table 2). However,  $[\text{Pd}(\mathbf{3}^{16})]$  was found by polarised optical microscopy to melt into a smectic A phase at 140°C, finally clearing into an isotropic liquid at 230°C. The higher transition temperature of  $[\text{Pd}(\mathbf{3}^{16})]$  relative to  $[\text{Pd}(\mathbf{1}^{16})]$  and  $[\text{Pd}(\mathbf{2}^{16})]$  reflect the additional attractive interactions resulting from the extended polar core of supplementary phenyl rings and ester groups. That the compound  $\text{H}_2(\mathbf{3}^{16})$  is non-mesomorphic is probably a reflection of the reduction in the aliphatic chain density. Similarly, that the metallo-helicate complex  $[\text{Zn}_2(\mathbf{3}^{16})_2]$  is also non-mesomorphic is probably as a result of a combination of different factors. The tetrahedral geometry at the metal centres reduces the structural anisotropy of the compound and increases steric bulk relative to  $[\text{Pd}(\mathbf{3}^{16})]$ . In addition, the chain volume of  $[\text{Zn}_2(\mathbf{3}^{16})_2]$  varies greatly from both  $[\text{Zn}_2(\mathbf{1}^{16})_2]$  and  $[\text{Zn}_2(\mathbf{2}^{16})_2]$ . Hence, the change in balance of rigid and fluid moieties in  $[\text{Zn}_2(\mathbf{3}^{16})_2]$  precludes mesophase formation.

The complex  $[\text{Pd}(\mathbf{3}^{16})]$  generates a smectic A mesophase consistent with the crystal structure, which shows a hairpin structure that assembles into layers. Interestingly, a structurally-related ferrocenophane metallomesogen with an extended structure also shows a smectic phase.<sup>[47]</sup> We generally conclude that the 5,5-dimethyldipyrromethane core may not favour mesophase generation due to its narrower bite angle to the metal centre compared to typical bent-core mesogens.<sup>[35]</sup>

## **Conclusions**

The 1,9-diimino-5,5-dimethyl-dipyrromethane core has been shown to be flexible in its coordination which is mediated by the geometrical preferences of the metal ion to yield either binuclear helicates or mononuclear hairpin structures. New metallomesogens have been prepared and, indeed, the first example of a liquid crystal derived from a neutral metal helicate has been reported. The mesomorphism in one case has been unequivocally identified as a lamellar phase by X-ray diffraction methods. Extension of the imino-aromatic arms destabilises the mesomorphism within the Zn(II) helicates, but yields a Pd(II) complex which now displays a SmA mesophase.

## Experimental Section

NMR spectra were recorded on either a Bruker DPX300 FT-NMR spectrometer operating at 300.13 MHz for  $^1\text{H}$  and 75.48 MHz for broadband proton decoupled  $^{13}\text{C}$ , or a Jeol EX270 FT-NMR spectrometer operating at 270.17 MHz for  $^1\text{H}$  and 67.93 MHz for broadband proton decoupled  $^{13}\text{C}$ . Chemical shifts are referenced with respect to residual proton and carbon solvent (with  $\delta_{\text{H}} = 7.26$  ppm and  $\delta_{\text{C}} = 77.0$  ppm for  $\text{CDCl}_3$ ). IR spectra were obtained on a Nicolet AVATAR 360 FT-IR spectrometer as KBr pellets. FAB mass spectra were obtained on a Finnigan MAT TSQ-700 spectrometer at the University of Wales, Swansea, with 3-nitrobenzyl alcohol (NOBA) as matrix. MALDI-TOF mass spectra were obtained on a Voyager-DE-STR spectrometer at the University of Wales, Swansea, with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as matrix. EI and ES mass spectra were recorded by the Mass Spectrometry Service at the University of Nottingham. Elemental analyses (C, H, N) were carried out by the Analytical Department of the University of Nottingham.

Analysis by polarised optical microscopy was carried out using a Zeiss Labpol, or Olympus BH40 microscope equipped with a Link-Am HFS91 hot stage, TMS92 controller and LNP2 cooling unit. Analysis by DSC was carried out on either a Perkin-Elmer DSC7 instrument or a TA DSC 2920 instrument, using heating and cooling rates of either 5 or 10°C min<sup>-1</sup>. For analysis by XRD the powdered sample was filled in Lindemann capillaries of 1mm diameter. A linear

monochromatic Cu- $K_{\alpha}$  beam ( $\lambda = 1.5405\text{\AA}$ ) obtained with a sealed-tube generator (900W) and a bent quartz monochromator were used. The diffraction patterns were registered with a curved counter Inel CPS 120, for which the sample temperature was controlled within  $\pm 0.05^{\circ}\text{C}$ . Periodicities up to  $60\text{\AA}$  could be measured. An X-ray pattern was recorded every  $10^{\circ}\text{C}$  for each compound from the crystalline state up to the isotropic liquid.

### Synthesis of the ligands $\text{H}_2(\mathbf{1}^n)$

Figure 7 here

The target ligands were obtained by reaction of the appropriate aniline with the 1,9-diformyl-5,5-dimethyl-dipyrromethane under acidic conditions with the synthesis of  $\text{H}_2(\mathbf{1}^1)$  given as a typical example below.

### Synthesis of $\text{H}_2(\mathbf{1}^1)$

A solution of 3,4,5-trimethoxyaniline (0.801g, 4.4mmol) in  $\text{CHCl}_3$  ( $10\text{cm}^3$ ) was added to a stirred solution of 5,5-dimethyl-1,9-diformyldipyrromethane (0.504g, 2.2mmol) in warm MeOH ( $100\text{cm}^3$ ), after which a few drops of glacial AcOH were added and the solution stirred at room temperature for 1 h. The volume of the solvents were reduced *in vacuo*, resulting in the precipitation of a yellow solid, which was isolated by filtration, washed with  $\text{Et}_2\text{O}$  ( $20\text{cm}^3$ ) and dried *in vacuo*. The solids were recrystallised from  $\text{CHCl}_3$  and EtOH (0.81g, 88%). Elemental analysis: Calculated for  $\text{C}_{31}\text{H}_{36}\text{N}_4\text{O}_6$  (560.64) C 66.41, H 6.47, N 9.99; found C 66.30, H 6.42, N 10.17. IR (KBr pellet):  $\nu = 1619\text{s}$  (C=N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300.13MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}}$  8.16 (2H, s,  $\underline{\text{H}}_{\text{a}}$ C=N), 6.61 (2H, d,  $^3\text{J}_{\text{AX}} = 3.9\text{Hz}$ ,  $\underline{\text{H}}_{\text{b}}$ ), 6.39 (4H, s,  $\underline{\text{H}}_{\text{e}}$ ), 6.19 (2H, d,  $^3\text{J}_{\text{AX}} = 3.7\text{Hz}$ ,  $\underline{\text{H}}_{\text{c}}$ ), 3.86 (12H, s, lateral  $\text{OCH}_3$ ), 3.84 (6H, s, central  $\text{OCH}_3$ ), 1.74 (6H, s,  $\underline{\text{H}}_{\text{d}}$ ) ppm.  $^{13}\text{C}$  NMR (67.93MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{C}}$  153.5, 149.0, 147.6, 144.3, 136.0, 130.4, 117.4, 107.2, 98.0, 60.9, 56.0, 36.0, 28.6 ppm. ES MS:  $m/z = 561$  [ $\text{H}_2(\mathbf{1}^1)$ ] $^+$ .

### Characterisation of $\text{H}_2(\mathbf{1}^{10})$

A yellow solid (0.154g, 82%). Elemental analysis: Calculated for  $\text{C}_{85}\text{H}_{144}\text{N}_4\text{O}_6$  (1318.08) C 77.45, H 11.01, N 4.25; found C 77.01, H 11.59, N 4.22. IR (KBr pellet):  $\nu = 1591\text{s}$  (C=N)  $\text{cm}^{-1}$ .  $^1\text{H}$

NMR (300.13MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  8.12 (2H, s,  $\underline{\text{H}}_{\text{a}}\text{C}=\text{N}$ ), 6.59 (2H, br d,  $\underline{\text{H}}_{\text{b}}$ ), 6.37 (4H, s,  $\underline{\text{H}}_{\text{c}}$ ), 6.16 (2H, d,  $^3\text{J}_{\text{AX}} = 3.5\text{Hz}$ ,  $\underline{\text{H}}_{\text{c}}$ ), 3.94 (12H, m,  $\text{OCH}_2$ ), 1.81-1.26 (96H + 6H, m,  $\text{CH}_2 + \underline{\text{H}}_{\text{d}}$ ), 0.88 (18H, 2 overlapping triplets,  $\text{CH}_3$ ) ppm. MALDI-TOF MS:  $m/z = 1317 [\text{H}_2(\mathbf{1}^{10})]^+$ .

#### Characterisation of $\text{H}_2(\mathbf{1}^{12})$

A beige/yellow solid (0.384g, 73%). Elemental analysis: Calculated for C<sub>97</sub>H<sub>168</sub>N<sub>4</sub>O<sub>6</sub> (1486.40) C 78.38, H 11.39, N 3.77; found C 78.19, H 11.65, N 3.58. IR (KBr pellet):  $\nu = 1616\text{m (C=N)}\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300.13MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  8.12 (2H, s,  $\underline{\text{H}}_{\text{a}}\text{C}=\text{N}$ ), 6.59(2H, br d,  $\underline{\text{H}}_{\text{b}}$ ), 6.37 (4H, s,  $\underline{\text{H}}_{\text{c}}$ ), 6.17 (2H, d,  $^3\text{J}_{\text{AX}} = 3.4\text{Hz}$ ,  $\underline{\text{H}}_{\text{c}}$ ), 3.94 (12H, 2 overlapping triplets,  $\text{OCH}_2$ ), 1.83-1.25 (120H + 6H, m,  $\text{CH}_2 + \underline{\text{H}}_{\text{d}}$ ), 0.87 (18H, 2 overlapping triplets,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (75.48MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{C}}$  153.7, 148.6, 142.4, 136.3, 130.1, 117.5, 107.2, 99.4, 94.5, 73.5, 69.1, 36.5, 32.0, 30.0, 29.9, 29.8, 29.8, 29.5, 29.5, 29.5, 28.9, 26.4, 22.8, 14.2 ppm. MALDI-TOF MS:  $m/z = 1486 [\text{H}_2(\mathbf{1}^{12})]^+$ .

#### Characterisation of $\text{H}_2(\mathbf{1}^{14})$

A yellow solid (0.868g, 76%). Elemental analysis: Calculated for C<sub>109</sub>H<sub>192</sub>N<sub>4</sub>O<sub>6</sub> (1654.71) C 79.12, H 11.70, N 3.39; found C 78.77, H 11.86, N 3.63. IR (KBr pellet):  $\nu = 1619\text{m (C=N)}\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300.13MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  8.13 (2H, s,  $\underline{\text{H}}_{\text{a}}\text{C}=\text{N}$ ), 6.57 (2H, d,  $^3\text{J}_{\text{AX}} = 3.6\text{Hz}$ ,  $\underline{\text{H}}_{\text{b}}$ ), 6.36 (4H, s,  $\underline{\text{H}}_{\text{c}}$ ), 6.16 (2H, d,  $^3\text{J}_{\text{AX}} = 3.7\text{Hz}$ ,  $\underline{\text{H}}_{\text{c}}$ ), 3.96 (12H, m,  $\text{OCH}_2$ ), 1.83-1.25 (144H, m,  $\text{CH}_2$ ), 174(6H, s,  $\underline{\text{H}}_{\text{d}}$ ), 0.88 (18H, 2 overlapping triplets,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (75.48MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{C}}$  153.5, 136.2, 115.4, 99.3, 73.5, 69.0, 31.9, 30.3, 29.7, 29.7, 29.4, 28.5, 26.1, 22.7, 14.1 ppm (four alkyl carbons obscured). MALDI-TOF MS:  $m/z = 1654 [\text{H}_2(\mathbf{1}^{12})]^+$ .

#### Characterisation of $\text{H}_2(\mathbf{1}^{16})$

A mustard yellow solid (0.40g, 67%). Elemental analysis: Calculated for C<sub>121</sub>H<sub>216</sub>N<sub>4</sub>O<sub>6</sub> (1823.03) C 79.72, H 11.94, N 3.07; found C 79.48, H 12.22, N 2.96. IR (KBr pellet):  $\nu = 1615\text{m (C=N)}\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300.13MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  8.13 (2H, s,  $\underline{\text{H}}_{\text{a}}\text{C}=\text{N}$ ), 6.57 (2H, d,  $^3\text{J}_{\text{AX}} = 3.5\text{Hz}$ ,  $\underline{\text{H}}_{\text{b}}$ ), 6.36 (4H, s,  $\underline{\text{H}}_{\text{c}}$ ), 6.16 (2H, d,  $^3\text{J}_{\text{AX}} = 3.6\text{Hz}$ ,  $\underline{\text{H}}_{\text{c}}$ ), 3.92 (12H, 2 overlapping triplets,  $\text{OCH}_2$ ), 1.80-1.25 (168H + 6H, m,  $\text{CH}_2 + \underline{\text{H}}_{\text{d}}$ ), 0.88 (18H, 2 overlapping triplets,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (75.48MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{C}}$  153.7, 153.4, 148.2, 142.3, 136.3, 132.4, 108.0, 99.3, 94.4, 73.5, 68.9, 31.9,

30.3, 29.7, 29.4, 26.1, 22.7, 14.1 ppm (nine alkyl carbons obscured). MALDI-TOF MS:  $m/z = 1823 [\text{H}_2(\mathbf{1}^{16})]^+$ .

The Zn(II) complexes were obtained by reaction of the appropriate ligand with Zn(II) acetate with the synthesis of the complex  $[\text{Zn}_2(\mathbf{1}^1)_2]$  given as an example below.

### Synthesis of $[\text{Zn}_2(\mathbf{1}^1)_2]$

A solution of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.035g, 0.16mmol) in methanol ( $5 \text{ cm}^3$ ) was added to a solution of  $\text{H}_2(\mathbf{1}^1)$  (0.085g, 0.15mmol) in  $\text{CH}_2\text{Cl}_2$  ( $20 \text{ cm}^3$ ). The orange solution was stirred for 30 min after which a few drops of  $\text{NEt}_3$  were added and the solution stirred for a further 24 h. The solution was reduced in volume under vacuum and MeOH was added to precipitate  $[\text{Zn}_2(\mathbf{1}^1)_2]$  as a yellow crystalline material that was isolated by filtration and recrystallised from  $\text{CHCl}_3$  and  $\text{Et}_2\text{O}$  (0.080g, 85%). Elemental analysis: Calculated for  $\text{C}_{62}\text{H}_{68}\text{N}_8\text{O}_{12}\text{Zn}_2 \cdot \text{CHCl}_3 \cdot 3\text{H}_2\text{O}$  (1421.45) C 53.02, H 5.23, N 7.73; found C 53.27, H 5.22, 7.80. IR (KBr pellet):  $\nu = 1588 \text{ s (C=N) cm}^{-1}$ .  $^1\text{H NMR}$  (300.13MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}}$  8.17 (2H, s,  $\underline{\text{H}}_{\text{aC=N}}$ ), 6.66 (2H, d,  $^3\text{J}_{\text{AX}} = 3.6\text{Hz}$ ,  $\underline{\text{H}}_{\text{b}}$ ), 6.17 (2H, d,  $^3\text{J}_{\text{AX}} = 3.6\text{Hz}$ ,  $\underline{\text{H}}_{\text{c}}$ ), 6.09 (4H, s,  $\underline{\text{H}}_{\text{e}}$ ), 3.74 (6H, s, central  $\text{OCH}_3$ ), 3.56 (12H, s, lateral  $\text{OCH}_3$ ) 1.62 (6H, s,  $\underline{\text{H}}_{\text{d}}$ ) ppm.  $^{13}\text{C NMR}$  (75.48MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{C}}$  158.3, 153.4, 149.0, 141.9, 135.8, 135.3, 122.0, 111.8, 97.0, 60.9, 55.7, 39.3, 29.7 ppm. FAB (LSI)MS:  $m/z = 1248 [\text{Zn}_2(\mathbf{1}^1)_2]^+$ .

### Characterisation of $[\text{Zn}_2(\mathbf{1}^{16})_2]$

A yellow/brown solid (0.093g, 83%). Elemental analysis: Calculated for  $\text{C}_{242}\text{H}_{428}\text{N}_8\text{O}_{12}\text{Zn}_2 \cdot \text{H}_2\text{O}$  (3790.83) C 76.67, H 11.43, N 2.96; found C 76.43, H 11.71, N 2.89. IR (KBr pellet):  $\nu = 1593 \text{ s (C=N) cm}^{-1}$ .  $^1\text{H NMR}$  (300.13MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}}$  8.09 (2H, s,  $\underline{\text{H}}_{\text{aC=N}}$ ), 6.58 (2H, br d,  $\underline{\text{H}}_{\text{b}}$ ), 6.09 (2H, br d,  $\underline{\text{H}}_{\text{c}}$ ), 6.03 (4H, s,  $\underline{\text{H}}_{\text{e}}$ ), 3.81 (4H, t,  $^3\text{J}_{\text{AX}} = 6.5\text{Hz}$ , central  $\text{OCH}_2$ ), 3.59 (8H, t,  $^3\text{J}_{\text{AX}} = 6.4\text{Hz}$ , lateral  $\text{OCH}_2$ ), 1.81-1.24 (168H + 6H, m,  $\underline{\text{CH}}_2 + \underline{\text{H}}_{\text{d}}$ ), 0.88 (18H, 2 overlapping triplets,  $\underline{\text{CH}}_3$ ) ppm.  $^{13}\text{C NMR}$  (67.93MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{C}}$  153.2, 148.8, 141.5, 135.8, 135.4, 121.6, 111.4, 109.3, 98.4, 73.4, 68.6, 39.2, 31.9, 30.3, 30.1, 29.8, 29.7, 29.6, 29.5, 29.4, 26.1, 22.7, 14.1 ppm (five alkyl carbons obscured). MALDI-TOF MS:  $m/z = 3771 [\text{Zn}_2(\mathbf{1}^{16})_2]^+$ .

The Pd(II) complexes were obtained by reaction of the appropriate ligand with Pd(II) acetate with the synthesis of the complex **[Pd(1<sup>1</sup>)]** given as an example below.

### Synthesis of **[Pd(1<sup>1</sup>)]**

To a solution of **H<sub>2</sub>(1<sup>1</sup>)** (0.104g, 0.19mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15cm<sup>3</sup>) was added Pd(OAc)<sub>2</sub> (0.042g, 0.19mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3cm<sup>3</sup>). The yellow/orange solution was stirred for 30 min, after which a few drops of NEt<sub>3</sub> were added and the solution became orange in colour. This mixture was stirred for 24 hours, reduced in volume under vacuum, and MeOH added to afford **[Pd(1<sup>1</sup>)]** as a yellow solid. The product was recrystallised from CHCl<sub>3</sub> and EtOH (0.082g, 67%). Elemental analysis: Calculated for C<sub>31</sub>H<sub>34</sub>N<sub>4</sub>O<sub>6</sub>Pd.H<sub>2</sub>O (683.06) C 54.51, H 5.31, N 8.20; found C 54.49, H 5.28, 8.48. IR (KBr pellet):  $\nu = 1585\text{s (C=N) cm}^{-1}$ . <sup>1</sup>H NMR (300.13MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  7.61 (2H, s, H<sub>a</sub>C=N), 6.93 (2H, d, <sup>3</sup>J<sub>AX</sub> = 4.0Hz, H<sub>b</sub>), 6.33 (2H, d, <sup>3</sup>J<sub>AX</sub> = 4.0Hz, H<sub>c</sub>), 6.15 (4H, s, H<sub>e</sub>), 3.80 (6H, s, central OCH<sub>3</sub>), 3.64 (12H, s, lateral OCH<sub>3</sub>) 1.69 (6H, s, H<sub>d</sub>) ppm. <sup>13</sup>C NMR (75.48MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{C}}$  158.5, 153.0, 152.4, 145.7, 136.3, 135.9, 119.5, 108.2, 99.7, 60.8, 55.6, 43.1, 32.1 ppm. FAB (LSI)MS: m/z = 664 **[Pd(1<sup>1</sup>)]<sup>+</sup>**.

### Characterisation of **[Pd(1<sup>10</sup>)]**

A yellow solid (0.311g, 93%). Elemental analysis: Calculated for C<sub>85</sub>H<sub>142</sub>N<sub>4</sub>O<sub>6</sub>Pd.H<sub>2</sub>O (1440.50) C 70.87, H 10.08, N 3.89; found C 70.36, H 9.60, N 3.72. IR (KBr pellet):  $\nu = 1589\text{s (C=N) cm}^{-1}$ . <sup>1</sup>H NMR (300.13MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  7.58 (2H, s, H<sub>a</sub>C=N), 6.89 (2H, d, <sup>3</sup>J<sub>AX</sub> = 3.9Hz, H<sub>b</sub>), 6.30 (2H, d, <sup>3</sup>J<sub>AX</sub> = 3.9Hz, H<sub>c</sub>), 6.08 (4H, s, H<sub>e</sub>), 3.83 (4H, t, <sup>3</sup>J<sub>AX</sub> = 6.5Hz, central OCH<sub>2</sub>), 3.63 (8H, t, <sup>3</sup>J<sub>AX</sub> = 6.5Hz, lateral OCH<sub>2</sub>) 1.74-1.28 (96H + 6H, m, CH<sub>2</sub> + H<sub>d</sub>), 0.88 (18H, overlapping triplets, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.48MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{C}}$  158.4, 152.9, 152.0, 145.0, 136.3, 136.1, 119.0, 107.8, 100.4, 73.4, 68.5, 43.0, 32.0, 30.6, 29.9, 29.7, 29.5, 29.4, 26.3, 26.2, 22.7, 14.1 ppm. MALDI-TOF MS: m/z = 1421 **[Pd(1<sup>10</sup>)]<sup>+</sup>**.

### Characterisation of **[Pd(1<sup>12</sup>)]**

A sticky brown solid (0.109g, 99%). Elemental analysis: Calculated for C<sub>97</sub>H<sub>166</sub>N<sub>4</sub>O<sub>6</sub>Pd.CHCl<sub>3</sub>.H<sub>2</sub>O (1728.19) C 68.11, H 9.86, N 3.24; found C 68.07, H 10.43, N 3.63. IR (KBr pellet):  $\nu = 1586\text{m}$

(C=N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300.13MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}}$  7.58 (2H, s,  $\underline{\text{H}}_{\text{a}}\text{C}=\text{N}$ ), 6.89 (2H, d,  $^3\text{J}_{\text{AX}} = 3.7\text{Hz}$ ,  $\underline{\text{H}}_{\text{b}}$ ), 6.30 (2H, d,  $^3\text{J}_{\text{AX}} = 3.9\text{Hz}$ ,  $\underline{\text{H}}_{\text{c}}$ ), 6.08 (4H, s,  $\underline{\text{H}}_{\text{e}}$ ), 3.85 (4H, t,  $^3\text{J}_{\text{AX}} = 6.4\text{Hz}$ , central  $\text{OCH}_2$ ), 3.63 (8H, t,  $^3\text{J}_{\text{AX}} = 6.6\text{Hz}$ , lateral  $\text{OCH}_2$ ) 1.71-1.27 (120H + 6H, m,  $\underline{\text{CH}}_2 + \underline{\text{H}}_{\text{d}}$ ), 0.88 (18H, overlapping triplets,  $\underline{\text{CH}}_3$ ) ppm.  $^{13}\text{C}$  NMR (75.48MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{C}}$  158.4, 152.8, 152.0, 144.9, 136.2, 136.0, 119.0, 107.8, 100.3, 73.3, 68.4, 42.8, 32.1, 32.0, 31.8, 30.5, 29.6, 29.3, 26.2, 26.1, 22.6, 22.5, 14.0 ppm. MALDI-TOF MS:  $m/z = 1589 [\text{Pd}(\mathbf{1}^{12})]^+$ .

### Characterisation of $[\text{Pd}(\mathbf{1}^{14})]$

A brown solid (0.107g, 98%). Elemental analysis: Calculated for  $\text{C}_{109}\text{H}_{190}\text{N}_4\text{O}_6\text{Pd}\cdot\text{H}_2\text{O}$  (1777.13) C 73.67, H 10.89, N 3.15; found C 73.45, H 10.78, N 3.13. IR (KBr pellet):  $\nu = 1586\text{s}$  (C=N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300.13MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}}$  7.58 (2H, s,  $\underline{\text{H}}_{\text{a}}\text{C}=\text{N}$ ), 6.89 (2H, d,  $^3\text{J}_{\text{AX}} = 4.0\text{Hz}$ ,  $\underline{\text{H}}_{\text{b}}$ ), 6.30 (2H, d,  $^3\text{J}_{\text{AX}} = 4.0\text{Hz}$ ,  $\underline{\text{H}}_{\text{c}}$ ), 6.08 (4H, s,  $\underline{\text{H}}_{\text{e}}$ ), 3.83 (4H, t,  $^3\text{J}_{\text{AX}} = 6.4\text{Hz}$ , central  $\text{OCH}_2$ ), 3.63 (8H, t,  $^3\text{J}_{\text{AX}} = 6.5\text{Hz}$ , lateral  $\text{OCH}_2$ ) 1.68-1.26 (144H + 6H, m,  $\underline{\text{CH}}_2 + \underline{\text{H}}_{\text{d}}$ ), 0.88 (18H, overlapping triplets,  $\underline{\text{CH}}_3$ ) ppm.  $^{13}\text{C}$  NMR (67.93MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{C}}$  158.5, 153.0, 152.2, 145.1, 136.4, 136.2, 119.1, 107.9, 100.5, 73.5, 68.7, 43.0, 32.2, 31.9, 30.9, 30.6, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.2, 26.3, 22.8, 14.2 ppm. MALDI-TOF MS:  $m/z = 1758 [\text{Pd}(\mathbf{1}^{14})]^+$ .

### Characterisation of $[\text{Pd}(\mathbf{1}^{16})]$

A yellow solid (0.191g, 93%). Elemental analysis: Calculated for  $\text{C}_{121}\text{H}_{214}\text{N}_4\text{O}_6\text{Pd}\cdot\text{H}_2\text{O}$  (1945.45) C 74.70, H 11.19, N 2.88; found C 74.73, H 11.40, N 2.77. IR (KBr pellet):  $\nu = 1585\text{m}$  (C=N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300.13MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}}$  7.58 (2H, s,  $\underline{\text{H}}_{\text{a}}\text{C}=\text{N}$ ), 6.89 (2H, d,  $^3\text{J}_{\text{AX}} = 3.9\text{Hz}$ ,  $\underline{\text{H}}_{\text{b}}$ ), 6.30 (2H, d,  $^3\text{J}_{\text{AX}} = 3.9\text{Hz}$ ,  $\underline{\text{H}}_{\text{c}}$ ), 6.07 (4H, s,  $\underline{\text{H}}_{\text{e}}$ ), 3.83 (4H, t,  $^3\text{J}_{\text{AX}} = 6.5\text{Hz}$ , central  $\text{OCH}_2$ ), 3.62 (8H, t,  $^3\text{J}_{\text{AX}} = 6.3\text{Hz}$ , lateral  $\text{OCH}_2$ ) 1.71-1.26 (168H, m,  $\underline{\text{CH}}_2$ ), 1.57 (6H, s,  $\underline{\text{H}}_{\text{d}}$ ), 0.88 (18H, overlapping triplets,  $\underline{\text{CH}}_3$ ) ppm.  $^{13}\text{C}$  NMR (75.48MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{C}}$  158.9, 152.9, 152.1, 145.0, 136.3, 136.1, 119.0, 107.8, 100.5, 73.4, 68.6, 43.0, 32.2, 31.9, 30.9, 30.6, 29.8, 29.3, 26.3, 26.2, 22.7, 14.1 ppm (six alkyl carbons obscured). MALDI-TOF MS:  $m/z = 1926 [\text{Pd}(\mathbf{1}^{16})]^+$ .

### Synthesis of the tetracatenar ligands $\text{H}_2(\mathbf{2}^n)$



Figure 8 here

### Characterisation of $\text{H}_2(\mathbf{2}^1)$

A yellow solid (0.496g, 74%). Elemental analysis: Calculated for  $\text{C}_{29}\text{H}_{32}\text{N}_4\text{O}_4 \cdot \text{CHCl}_3 \cdot \text{H}_2\text{O}$  (637.98) C 56.48, H 5.53, N 8.78; found C 56.66, H 5.27, N 8.78. IR (KBr pellet):  $\nu = 1620\text{s}$  (C=N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300.13MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}}$  8.16 (2H, s,  $\underline{\text{H}}_{\text{a}}\text{C}=\text{N}$ ), 6.84 (2H, d,  $^3J_{\text{AB}} = 8.4\text{Hz}$ ,  $\underline{\text{H}}_{\text{g}}$ ), 6.76 (4H, m,  $\underline{\text{H}}_{\text{e}} + \underline{\text{H}}_{\text{f}}$ ), 6.57 (2H, d,  $^3J_{\text{AX}} = 3.7\text{Hz}$ ,  $\underline{\text{H}}_{\text{b}}$ ), 6.15 (2H, d,  $^3J_{\text{AX}} = 3.7\text{Hz}$ ,  $\underline{\text{H}}_{\text{c}}$ ), 4.77 (2H, br s,  $\underline{\text{NH}}$ ), 3.87 (12H, s,  $\text{OCH}_3$ ), 1.76 (6H, s,  $\underline{\text{H}}_{\text{d}}$ ) ppm.  $^{13}\text{C}$  NMR (75.48MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{C}}$  149.3, 148.3, 147.2, 144.9, 144.1, 130.2, 117.0, 112.0, 111.5, 106.8, 105.0, 56.0, 55.8, 35.9, 28.4 ppm. ES MS:  $m/z = 501 [\text{H}_2(\mathbf{2}^1)]^+$ .

### Characterisation of $[\text{H}_2(\mathbf{2}^{16})]$

A yellow solid (0.248g, 96%). Elemental analysis: Calculated for  $\text{C}_{89}\text{H}_{152}\text{N}_4\text{O}_4 \cdot \text{H}_2\text{O}$  (1360.20) C 78.59, H 11.41, N 4.12; found C 78.41, H 11.40, N 4.38. IR (KBr pellet):  $\nu = 1619\text{s}$  (C=N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300.13MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}}$  8.15 (2H, s,  $\underline{\text{H}}_{\text{a}}\text{C}=\text{N}$ ), 6.84 (2H, d,  $^3J_{\text{AB}} = 8.5\text{Hz}$ ,  $\underline{\text{H}}_{\text{g}}$ ), 6.72 (4H, m,  $\underline{\text{H}}_{\text{e}} + \underline{\text{H}}_{\text{f}}$ ), 6.55 (2H, d,  $^3J_{\text{AX}} = 3.6\text{Hz}$ ,  $\underline{\text{H}}_{\text{b}}$ ), 6.15 (2H, d,  $^3J_{\text{AX}} = 3.6\text{Hz}$ ,  $\underline{\text{H}}_{\text{c}}$ ), 3.99 (8H, m,  $\text{OCH}_2$ ), 1.83 – 1.25 (112H + 6H, m,  $\text{CH}_2 + \underline{\text{H}}_{\text{d}}$ ), 0.88 (12H, overlapping triplets,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (75.48MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{C}}$  149.7, 148.0, 147.3, 144.9, 144.2, 130.3, 117.0, 114.5, 112.5, 107.2, 102.7, 69.7, 69.1, 36.0, 31.9, 29.7, 29.6, 29.4, 29.3, 28.5, 26.0, 22.7, 14.1 ppm (seven alkyl carbons obscured). ES MS:  $m/z = 1343 [\text{H}_2(\mathbf{2}^{16})]^+$ .

### Characterisation of $[\text{Zn}_2(\mathbf{2}^1)_2]$

A yellow solid (0.081g, 60%). Elemental analysis: Calculated for  $\text{C}_{58}\text{H}_{60}\text{N}_8\text{O}_8\text{Zn}_2 \cdot \text{CH}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$  (1230.87) C 57.57, H 5.24, N 9.10; found C 57.58, H 5.18, N 9.06. IR (KBr pellet):  $\nu = 1609\text{s}$  (C=N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300.13MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}}$  8.16 (2H, s,  $\underline{\text{H}}_{\text{a}}\text{C}=\text{N}$ ), 6.67 (2H, d,  $^3J_{\text{AB}} = 8.7\text{Hz}$ ,  $\underline{\text{H}}_{\text{g}}$ ), 6.59 (4H, m,  $\underline{\text{H}}_{\text{e}} + \underline{\text{H}}_{\text{f}}$ ), 6.23 (2H, d,  $^3J_{\text{AB}} = 2.4\text{Hz}$ ,  $\underline{\text{H}}_{\text{b}}$ ), 6.13 (2H, d,  $^3J_{\text{AB}} = 2.4\text{Hz}$ ,  $\underline{\text{H}}_{\text{c}}$ ), 3.89 (6H, s,  $\text{OCH}_3$ ), 3.43 (6H, s,  $\text{OCH}_3$ ), 1.60 (6H, s,  $\underline{\text{H}}_{\text{d}}$ ) ppm.  $^{13}\text{C}$  NMR (75.48MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{C}}$  157.9, 149.1, 146.2, 140.1, 135.9, 121.3, 111.3, 108.7, 106.1, 56.0, 55.3, 39.2, 29.8 ppm. MALDI-TOF MS:  $m/z = 1128 [\text{Zn}_2(\mathbf{2}^1)_2]^+$ .

### Characterisation of [Zn<sub>2</sub>(2<sup>16</sup>)<sub>2</sub>]

A yellow solid (0.099g, 90%). Elemental analysis: Calculated for C<sub>178</sub>H<sub>300</sub>N<sub>8</sub>O<sub>8</sub>Zn<sub>2</sub>.1/2H<sub>2</sub>O (1423.57) C 75.57, H 10.76, N 3.96; found C 75.34, H 10.91, N 4.05. IR (KBr pellet):  $\nu = 1606\text{m}$  (C=N) cm<sup>-1</sup>. <sup>1</sup>H NMR (300.13MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  8.10 (2H, s, H<sub>a</sub>C=N), 6.66 (2H, d, <sup>3</sup>J<sub>AB</sub> = 8.7Hz, H<sub>g</sub>), 6.53 (4H, m, H<sub>e</sub> + H<sub>f</sub>), 6.20 (2H, d, <sup>3</sup>J<sub>AB</sub> = 2.4Hz, H<sub>b</sub>), 6.10 (2H, d, <sup>3</sup>J<sub>AB</sub> = 3.4, H<sub>c</sub>), 3.87 (4H, t, <sup>3</sup>J<sub>AX</sub> = 6.7Hz, OCH<sub>2</sub>), 3.42 (4H, t, <sup>3</sup>J<sub>AX</sub> = 6.6Hz, OCH<sub>2</sub>), 1.75 – 1.26 (112H + 6H, m, CH<sub>2</sub> + H<sub>d</sub>), 0.88 (12H, 2 overlapping triplets, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.48MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{C}}$  158.1, 152.2, 149.1, 146.0, 140.1, 135.9, 121.1, 114.3, 111.1, 108.6, 107.9, 69.8, 67.8, 39.3, 32.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.2, 26.1, 22.8, 14.2 ppm (six alkyl carbons obscured). MALDI-TOF MS: m/z = 2811 [Zn<sub>2</sub>(2<sup>16</sup>)<sub>2</sub>]<sup>+</sup>.

### Characterisation of [Pd(2<sup>1</sup>)]

An orange microcrystalline solid (0.065g, 53%). Elemental analysis: Calculated for C<sub>29</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub>Pd.CHCl<sub>3</sub> (724.37) C 49.74, H 4.31, N 7.73; found C 50.12, H 4.78, N 8.01. IR (KBr pellet):  $\nu = 1592\text{m}$  (C=N) cm<sup>-1</sup>. <sup>1</sup>H NMR (300.13MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  7.58 (2H, s, H<sub>a</sub>C=N), 6.90 (2H, d, <sup>3</sup>J<sub>AX</sub> = 3.9Hz, H<sub>b</sub>), 6.48 (2H, d, <sup>3</sup>J<sub>AB</sub> = 8.4Hz, H<sub>g</sub>), 6.41 (2H, dd, <sup>3</sup>J<sub>AB</sub> = 8.4Hz, <sup>4</sup>J<sub>AM</sub> = 2.4Hz, H<sub>f</sub>), 6.32 (4H, overlapping doublets, H<sub>e</sub> + H<sub>c</sub>), 3.81 (6H, s, OCH<sub>3</sub>), 3.60 (6H, s, OCH<sub>3</sub>), 1.70 (6H, s, H<sub>d</sub>) ppm. <sup>13</sup>C NMR (75.48MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{C}}$  158.1, 152.1, 148.8, 147.0, 143.1, 136.2, 118.9, 113.5, 110.9, 107.7, 106.4, 56.1, 55.4, 43.1, 32.2 ppm. MALDI-TOF MS: m/z = 604 [Pd(2<sup>1</sup>)]<sup>+</sup>.

### Characterisation of [Pd(2<sup>16</sup>)]

A yellow solid (0.296g, 90%). Elemental analysis: Calculated for C<sub>89</sub>H<sub>150</sub>N<sub>4</sub>O<sub>4</sub>Pd (1446.59) C 73.89, H 10.45, N 3.87; found C 73.52, H 10.52, N 3.86. IR (KBr pellet):  $\nu = 1589\text{w}$  (C=N) cm<sup>-1</sup>. <sup>1</sup>H NMR (300.13MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  7.56 (2H, s, H<sub>a</sub>C=N), 6.88 (2H, d, <sup>3</sup>J<sub>AX</sub> = 3.9Hz, H<sub>b</sub>), 6.46 (2H, d, <sup>3</sup>J<sub>AB</sub> = 8.3Hz, H<sub>g</sub>), 6.36 (2H, dd, <sup>3</sup>J<sub>AB</sub> = 8.4Hz, <sup>4</sup>J<sub>AM</sub> = 2.13Hz, H<sub>f</sub>), 6.31 (4H, overlapping doublets, H<sub>e</sub> + H<sub>c</sub>), 3.87 (4H, t, <sup>3</sup>J<sub>AX</sub> = 6.6Hz, OCH<sub>2</sub>), 3.58 (4H, t, <sup>3</sup>J<sub>AX</sub> = 6.7Hz, OCH<sub>2</sub>), 1.76 (6H, s, H<sub>d</sub>), 1.56 – 1.26 (112H, m, CH<sub>2</sub>), 0.88 (12H, 2 overlapping triplets, CH<sub>3</sub>) ppm. <sup>13</sup>C

NMR (75.48MHz, CDCl<sub>3</sub>, 298 K):  $\delta_C$  158.3, 152.0, 149.4, 147.1, 143.5, 136.4, 118.8, 113.1, 113.7, 108.2, 107.7, 70.0, 68.5, 43.1, 32.2, 31.9, 29.8, 29.7, 29.5, 29.4, 29.3, 26.2, 26.1, 22.6, 14.1 ppm (five alkyl carbons obscured). MALDI-TOF MS:  $m/z = 1447$  [Pd(2<sup>16</sup>)]<sup>+</sup>.

### Synthesis of the extended dipyrrole ligands H<sub>2</sub>(3<sup>n</sup>)

The extended [(4-alkoxy)benzoyloxy]-4-aniline (n = 1 or 16) was prepared by the modification of literature methods.<sup>[35,36]</sup>

### Characterisation of methyl-4-hexadecyloxybenzoate

A white solid (11.2g, 90%). Elemental analysis: Calculated for C<sub>24</sub>H<sub>40</sub>O<sub>3</sub> (376.57) C 76.55, H 10.71, N 0.00; found C 76.13, H 10.48, N 0.00. IR (KBr pellet):  $\nu = 1719$ s (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (300.13MHz, CDCl<sub>3</sub>, 298 K):  $\delta_H$  7.98 (2H, d, J<sub>AA'XX'</sub> = 8.9Hz, *o*-HArCO<sub>2</sub>Me), 6.90 (2H, d, J<sub>AA'XX'</sub> = 8.9Hz, *m*-HArCO<sub>2</sub>Me), 4.00 (2H, t, <sup>3</sup>J<sub>AX</sub> = 6.6Hz, OCH<sub>2</sub>), 3.88 (3H, s, OCH<sub>3</sub>), 1.80 (2H, m, OCH<sub>2</sub>CH<sub>2</sub>-), 1.56-1.25 (28H, m, CH<sub>2</sub>), 0.88 (3H, t, <sup>3</sup>J<sub>AX2</sub> = 6.7Hz, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.48MHz, CDCl<sub>3</sub>, 298 K):  $\delta_C$  166.8, 162.9, 131.5, 122.2, 113.9, 68.1, 51.7, 31.9, 29.6, 29.5, 29.3, 29.1, 25.9, 22.6, 14.1 ppm (seven alkyl carbons obscured). CI MS:  $m/z = 376$  [L]<sup>+</sup>.

### Characterisation of 4-hexadecyloxybenzoic acid

A white solid (9.83g, 99%). Elemental analysis: Calculated for C<sub>23</sub>H<sub>38</sub>O<sub>3</sub>.CH<sub>2</sub>Cl<sub>2</sub>.H<sub>2</sub>O (465.49) C 61.93, H 9.09, N 0.00; found C 62.06, H 8.54, N 0.00. IR (KBr pellet):  $\nu = 2999$ br,s (O-H), 1693vs (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (300.13MHz, CDCl<sub>3</sub>, 298 K):  $\delta_H$  8.04 (2H, d, J<sub>AA'XX'</sub> = 8.8Hz, *o*-HArCO<sub>2</sub>Me), 6.93 (2H, d, J<sub>AA'XX'</sub> = 8.9Hz, *m*-HArCO<sub>2</sub>Me), 4.02 (2H, t, <sup>3</sup>J<sub>AX</sub> = 6.6Hz, OCH<sub>2</sub>), 1.80 (2H, m, OCH<sub>2</sub>CH<sub>2</sub>-), 1.46-1.25 (28H, m, CH<sub>2</sub>), 0.88 (3H, t, <sup>3</sup>J<sub>AX</sub> = 6.7Hz, CH<sub>3</sub>) ppm. EI MS  $m/z = 362$  [L]<sup>+</sup>.

### Characterisation of 4-(4'-methoxybenzoyloxy)nitrobenzene

An off-white solid (4.02g, 81%). Elemental analysis: Calculated for C<sub>14</sub>H<sub>11</sub>N<sub>1</sub>O<sub>5</sub> (273.24) C 61.54, H 4.06, N 5.13; found C 61.55, H 4.07, N 4.89. IR (KBr pellet):  $\nu = 1730$ s (C=O), 1510m (C-NO<sub>2</sub>), 1351s (C-NO<sub>2</sub>) cm<sup>-1</sup>. <sup>1</sup>H NMR (300.13MHz, CDCl<sub>3</sub>, 298 K):  $\delta_H$  8.32 (2H, d, J<sub>AA'XX'</sub> = 9.1Hz, *o*-

$\underline{\text{HArNO}}_2$ ), 8.15 (2H, d,  $J_{\text{AA}'\text{XX}'}$  = 9.0Hz,  $o\text{-}\underline{\text{HArCO}}_2^-$ ), 7.41 (2H, d,  $J_{\text{AA}'\text{XX}'}$  = 9.0Hz,  $m\text{-}\underline{\text{HArNO}}_2$ ), 7.01 (2H, d,  $J_{\text{AA}'\text{XX}'}$  = 9.0Hz,  $m\text{-}\underline{\text{HArCO}}_2^-$ ), 3.91 (3H, s,  $\text{OCH}_3$ ) ppm.  $^{13}\text{C}$  NMR (75.48MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{C}}$  164.4, 163.9, 155.9, 145.2, 132.5, 125.2, 122.6, 120.6, 114.0, 55.6 ppm. CI MS:  $m/z$  = 274  $[\text{L}]^+$ .

#### **Characterisation of 4-(4'-hexadecyloxybenzoyloxy)nitrobenzene**

A light yellow solid (3.05g, 75%). Elemental analysis: Calculated for  $\text{C}_{29}\text{H}_{41}\text{NO}_5 \cdot 0.5\text{H}_2\text{O}$  (492.65) C 70.70, H 8.59, N 2.84; found C 71.13, H 8.42, N 3.00. IR (KBr pellet):  $\nu$  = 1720s (C=O), 1515m (C-NO<sub>2</sub>), 1347s (C-NO<sub>2</sub>)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300.13MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}}$  8.31 (2H, d,  $J_{\text{AA}'\text{XX}'}$  = 9.0Hz,  $o\text{-}\underline{\text{HArNO}}_2$ ), 8.13 (2H, d,  $J_{\text{AA}'\text{XX}'}$  = 8.9Hz,  $o\text{-}\underline{\text{HArCO}}_2^-$ ), 7.40 (2H, d,  $J_{\text{AA}'\text{XX}'}$  = 9.0Hz,  $m\text{-}\underline{\text{HArNO}}_2$ ), 6.98 (2H, d,  $J_{\text{AA}'\text{XX}'}$  = 8.9Hz,  $m\text{-}\underline{\text{HArCO}}_2^-$ ), 4.05 (2H, t,  $^3J_{\text{AX}}$  = 6.6Hz,  $\text{OCH}_2$ ), 1.85-1.25 (28H, m,  $\text{CH}_2$ ), 0.87 (3H, t,  $^3J_{\text{AX}}$  = 6.7Hz,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (75.48MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{C}}$  163.8, 155.9, 145.1, 132.4, 126.0, 125.1, 122.6, 120.2, 114.4, 68.3, 33.8, 31.9, 29.6, 29.5, 29.3, 29.0, 25.9, 24.8, 22.6, 14.0 ppm (five alkyl carbons obscured).

#### **Characterisation of 4-(4'-methoxybenzoyloxy)aniline**

A white solid (1.75g, 58%). Elemental analysis: Calculated for  $\text{C}_{14}\text{H}_{13}\text{N}_1\text{O}_3$  (243.26) C 69.12, H 5.39, N 5.76; found C 69.02, H 5.44, N 5.41. IR (KBr pellet):  $\nu$  = 3468m (NH<sub>2</sub>), 3385m (NH<sub>2</sub>), 1710s (C=O)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300.13MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}}$  8.14 (2H, d,  $J_{\text{AA}'\text{XX}'}$  = 8.9Hz,  $o\text{-}\underline{\text{HArCO}}_2^-$ ), 6.98 (4H, overlapping doublets,  $m\text{-}\underline{\text{HArCO}}_2^-$  +  $m\text{-}\underline{\text{HArNH}}_2$ ), 6.70 (2H, d,  $J_{\text{AA}'\text{XX}'}$  = 6.5Hz,  $o\text{-}\underline{\text{HArNH}}_2$ ), 3.89 (3H, s,  $\text{OCH}_3$ ), 3.65 (2H, br s, NH<sub>2</sub>) ppm.  $^{13}\text{C}$  NMR (75.48MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{C}}$  165.4, 163.6, 144.1, 142.9, 132.1, 122.2, 122.0, 115.5, 113.6, 55.4 ppm. CI MS:  $m/z$  = 243  $[\text{L}]^+$ .

#### **Characterisation of 4-(4'-hexadecyloxybenzoyloxy)aniline**

A white solid (0.872g, 47%). Elemental analysis: Calculated for  $\text{C}_{29}\text{H}_{43}\text{N}_1\text{O}_3$  (453.66) C 76.78, H 9.55, N 3.09; found C 76.64, H 9.33, N 2.80. IR (KBr pellet):  $\nu$  = 3425m (NH<sub>2</sub>), 3340m (NH<sub>2</sub>), 1719vs (C=O)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (270.17MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}}$  8.11 (2H, d,  $J_{\text{AA}'\text{XX}'}$  = 8.6Hz,  $o\text{-}\underline{\text{HArCO}}_2^-$ ), 6.95 (4H, overlapping doublets,  $m\text{-}\underline{\text{HArCO}}_2^-$  +  $m\text{-}\underline{\text{HArNH}}_2$ ), 6.69 (2H, d,  $J_{\text{AA}'\text{XX}'}$  =

6.5Hz, *o*-HArNH<sub>2</sub>), 4.02 (2H, t, <sup>3</sup>J<sub>AX</sub> = 6.6Hz, OCH<sub>2</sub>), 3.70 (2H, br s, NH<sub>2</sub>) 1.80 –1.25 (28H, m, CH<sub>2</sub>), 0.87 (3H, t, <sup>3</sup>J<sub>AX</sub> = 6.6Hz, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.48MHz, CDCl<sub>3</sub>, 298 K): δ<sub>C</sub> 165.5, 163.3, 144.0, 143.2, 132.1, 122.4, 121.8, 115.7, 114.2, 68.3, 31.9, 29.7, 29.4, 29.1, 26.0, 22.7, 14.1 ppm (eight alkyl carbons obscured). CI MS: m/z = 453 [L]<sup>+</sup>.

Figure 9 here

### Characterisation of H<sub>2</sub>(3<sup>1</sup>)

A yellow solid (0.523g, 73%). Elemental analysis: Calculated for C<sub>41</sub>H<sub>36</sub>N<sub>4</sub>O<sub>6</sub>·H<sub>2</sub>O (698.76) C 70.47, H 5.48, N 8.02; found C 70.84, H 5.20, N 7.97. IR (KBr pellet): ν = 1724vs (C=O), 1616s (C=N) cm<sup>-1</sup>. <sup>1</sup>H NMR (270.17MHz, CDCl<sub>3</sub>, 298 K): δ<sub>H</sub> 8.15 (4H, d, J<sub>AA'XX'</sub> = 6.7Hz, *o*-HArCO<sub>2</sub>-), 8.14 (2H, s, H<sub>a</sub>C=N), 7.17 (8H, overlapping doublets, *o*-HArN=C- + *m*-HArN=C-), 6.98 (4H, d, J<sub>AA'XX'</sub> = 9.0Hz, *m*-HArCO<sub>2</sub>), 6.62 (2H, d, <sup>3</sup>J<sub>AX</sub> = 3.7Hz, H<sub>b</sub>), 6.17 (2H, d, <sup>3</sup>J<sub>AX</sub> = 3.7Hz, H<sub>c</sub>), 3.89 (6H, s, OCH<sub>3</sub>), 1.67 (6H, s, H<sub>d</sub>) ppm. <sup>13</sup>C NMR (75.48MHz, d-DMSO, 298 K): δ<sub>C</sub> 164.4, 163.7, 151.0, 150.2, 147.8, 145.2, 132.0, 130.4, 122.6, 121.5, 121.0, 117.2, 114.3, 106.6, 55.7, 35.4, 27.6 ppm. ES MS: m/z = 681 [H<sub>2</sub>(3<sup>1</sup>)]<sup>+</sup>.

### Characterisation of H<sub>2</sub>(3<sup>16</sup>)

A yellow solid (0.396g, 79%). Elemental analysis: Calculated for C<sub>71</sub>H<sub>96</sub>N<sub>4</sub>O<sub>6</sub>·H<sub>2</sub>O C 76.17, H 8.82, N 5.00; found C 75.92, H 8.62, N 5.51. IR (KBr pellet): ν = 1734s (C=O), 1614s (C=N) cm<sup>-1</sup>. <sup>1</sup>H NMR (300.13MHz, CDCl<sub>3</sub>, 298 K): δ<sub>H</sub> 8.15 (2H, s, H<sub>a</sub>C=N), 8.13 (4H, d, J<sub>AA'XX'</sub> = 8.9Hz, *o*-HArCO<sub>2</sub>-), 7.16 (8H, overlapping doublets, *o*-HArN=C- + *m*-HArN=C-), 6.97 (4H, d, J<sub>AA'XX'</sub> = 8.9Hz, *m*-HArCO<sub>2</sub>), 6.72 (2H, br d, H<sub>b</sub>), 6.23 (2H, d, <sup>3</sup>J<sub>AX</sub> = 3.5 Hz, H<sub>c</sub>), 4.04 (4H, t, <sup>3</sup>J<sub>AX</sub> = 6.6Hz, OCH<sub>2</sub>), 1.86 – 1.26 (22H, m, CH<sub>2</sub>), 0.88 (6H, t, <sup>3</sup>J<sub>AX</sub> = 6.6Hz, H<sub>d</sub>) ppm. <sup>13</sup>C NMR (75.48MHz, CDCl<sub>3</sub>, 298 K): δ<sub>C</sub> 165.0, 163.5, 148.7, 132.2, 122.3, 121.8, 121.7, 121.5, 115.7, 114.3, 68.3, 31.9, 29.7, 29.3, 29.1, 28.6, 26.0, 22.7, 14.1 ppm (eight alkyl plus four aromatic carbons obscured).

### Characterisation of [Zn<sub>2</sub>(3<sup>1</sup>)<sub>2</sub>]

A yellow solid (0.087g, 77%). Elemental analysis: Calculated for C<sub>82</sub>H<sub>68</sub>N<sub>8</sub>O<sub>12</sub>Zn<sub>2</sub> (1488.24) C 66.18, H 4.61, N 7.53; found C 65.59, H 4.66, N 7.22. IR (KBr pellet): ν = 1741vs (C=O), 1605s

(C=N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300.13MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}}$  8.17 (2H, s,  $\underline{\text{H}}_{\text{a}}\text{C}=\text{N}$ ), 8.10 (4H, d,  $J_{\text{AA}'\text{XX}'} = 7.0\text{Hz}$ ,  $o\text{-}\underline{\text{H}}\text{ArCO}_2^-$ ), 6.98 (8H, overlapping doublets,  $o\text{-}\underline{\text{H}}\text{ArN}=\text{C}-$  +  $m\text{-}\underline{\text{H}}\text{ArN}=\text{C}-$ ), 6.87 (4H, d,  $J_{\text{AA}'\text{XX}'} = 8.8\text{Hz}$ ,  $m\text{-}\underline{\text{H}}\text{ArCO}_2$ ), 6.72 (2H, d,  $^3J_{\text{AX}} = 3.6\text{Hz}$ ,  $\underline{\text{H}}_{\text{b}}$ ), 6.21 (2H, d,  $^3J_{\text{AX}} = 3.6\text{Hz}$ ,  $\underline{\text{H}}_{\text{c}}$ ), 3.88 (6H, s,  $\text{OCH}_3$ ), 1.56 (6H, s br,  $\underline{\text{H}}_{\text{d}}$ ) ppm.  $^{13}\text{C}$  NMR (75.48MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{C}}$  164.9, 163.8, 158.8, 150.9, 147.8, 144.2, 135.9, 132.2, 122.6, 122.4, 121.8, 120.6, 113.8, 111.9, 55.5, 39.4, 29.8 ppm. MALDI-TOF MS:  $m/z = 1488 [\text{Zn}_2(\mathbf{3}^1)]^+$ .

### Characterisation of $[\text{Zn}_2(\mathbf{3}^{16})_2]$

A yellow solid (0.087g, 65%). Elemental analysis: Calculated for  $\text{C}_{142}\text{H}_{188}\text{N}_8\text{O}_{12}\text{Zn}_2 \cdot \text{H}_2\text{O}$  (2347.85) C 72.09, H 8.18, N 4.74; found C 72.12, H 8.20, N 4.72. IR (KBr pellet):  $\nu = 1734\text{s}$  (C=O),  $1605\text{s}$  (C=N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300.13MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}}$  8.17 (2H, s,  $\underline{\text{H}}_{\text{a}}\text{C}=\text{N}$ ), 8.11 (4H, d,  $J_{\text{AA}'\text{XX}'} = 9.4\text{Hz}$ ,  $o\text{-}\underline{\text{H}}\text{ArCO}_2^-$ ), 7.00 (4H, d,  $J_{\text{AA}'\text{XX}'} = 8.9\text{Hz}$ ,  $o\text{-}\underline{\text{H}}\text{ArN}=\text{C}-$ ), 6.94 (4H, d,  $J_{\text{AA}'\text{XX}'} = 9.0\text{Hz}$ ,  $m\text{-}\underline{\text{H}}\text{ArN}=\text{C}-$ ), 6.86 (4H, d,  $J_{\text{AA}'\text{XX}'} = 8.9\text{Hz}$ ,  $m\text{-}\underline{\text{H}}\text{ArCO}_2$ ), 6.72 (2H, d,  $^3J_{\text{AX}} = 3.6\text{Hz}$ ,  $\underline{\text{H}}_{\text{b}}$ ), 6.21 (2H, d,  $^3J_{\text{AX}} = 3.7\text{Hz}$ ,  $\underline{\text{H}}_{\text{c}}$ ), 4.04 (4H, t,  $^3J_{\text{AX}} = 6.6\text{Hz}$ ,  $\text{OCH}_2$ ), 1.83-1.26 (23H, m,  $\text{CH}_2$ ), 1.55 (6H, s,  $\underline{\text{H}}_{\text{d}}$ ), 0.88 (6H, t,  $^3J_{\text{AX}} = 6.7\text{Hz}$ ,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (75.48MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{C}}$  164.9, 163.4, 158.8, 150.9, 147.8, 144.2, 135.9, 132.2, 122.4, 121.5, 120.6, 114.2, 68.3, 39.4, 31.9, 29.7, 29.3, 29.1, 26.0, 22.7, 14.1 ppm (nine alkyl carbons plus two aromatic carbons obscured). MALDI-TOF MS:  $m/z = 2329 [\text{Zn}_2(\mathbf{3}^{16})_2]^+$ .

### Characterisation of $[\text{Pd}(\mathbf{3}^1)]$

A bright yellow solid (0.061g, 52%). Elemental analysis: Calculated for  $\text{C}_{41}\text{H}_{34}\text{N}_4\text{O}_6\text{Pd}_1$  (785.15) C 62.72, H 4.36, N 7.14; found C 62.18, H 4.26, N 7.17. IR (KBr pellet):  $\nu = 1723\text{vs}$  (C=O),  $1616\text{s}$  (C=N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300.13MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}}$  7.89 (4H, d,  $J_{\text{AA}'\text{XX}'} = 7.0\text{Hz}$ ,  $o\text{-}\underline{\text{H}}\text{ArCO}_2^-$ ), 7.60 (2H, s,  $\underline{\text{H}}_{\text{a}}\text{C}=\text{N}$ ), 6.94 (2H, d,  $^3J_{\text{AX}} = 3.9\text{Hz}$ ,  $\underline{\text{H}}_{\text{b}}$ ), 6.84 (8H, overlapping doublets,  $o\text{-}\underline{\text{H}}\text{ArN}=\text{C}-$  +  $m\text{-}\underline{\text{H}}\text{ArN}=\text{C}$ ), 6.77 (4H, d,  $J_{\text{AA}'\text{XX}'} = 8.9\text{Hz}$ ,  $m\text{-}\underline{\text{H}}\text{ArCO}_2$ ), 6.34 (2H, d,  $^3J_{\text{AX}} = 4.0\text{Hz}$ ,  $\underline{\text{H}}_{\text{c}}$ ), 3.87 (6H, s,  $\text{OCH}_3$ ), 1.71 (6H, s,  $\underline{\text{H}}_{\text{d}}$ ) ppm. MALDI-TOF MS:  $m/z = 784 [\text{Pd}(\mathbf{3}^1)]^+$ .

### Characterisation of $[\text{Pd}(\mathbf{3}^{16})]$

A yellow solid (0.084g, 68%). Elemental analysis: Calculated for  $C_{71}H_{94}N_4O_6Pd_1 \cdot 2H_2O$  (1241.98) C 68.66, H 7.95, N 4.51; found C 69.00, H 7.72, N 4.46. IR (KBr pellet):  $\nu = 1728s$  (C=O),  $1606s$  (C=N)  $cm^{-1}$ .  $^1H$  NMR (300.13MHz,  $CDCl_3$ , 298 K):  $\delta_H$  7.88 (4H, d,  $J_{AA'XX'} = 8.7Hz$ , *o*-HArCO<sub>2</sub>-), 7.60 (2H, s, H<sub>a</sub>C=N), 6.94 (2H, d,  $^3J_{AX} = 3.9Hz$ , H<sub>b</sub>), 6.84 (8H, overlapping doublets, *m*-HArN=C- + *m*-HArN=C-), 6.75 (4H, d,  $J_{AA'XX'} = 8.7Hz$ , *m*-HArCO<sub>2</sub>), 6.34 (2H, d,  $^3J_{AX} = 3.9Hz$ , H<sub>c</sub>), 3.99 (4H, t,  $^3J_{AX} = 6.5Hz$ , OCH<sub>2</sub>), 1.92-1.27 (56H, m, CH<sub>2</sub>), 1.71 (6H, s, H<sub>d</sub>), 0.88 (6H, t,  $^3J_{AX} = 6.6Hz$ , CH<sub>3</sub>) ppm.  $^{13}C$  NMR (75.48MHz,  $CDCl_3$ , 298 K):  $\delta_C$  164.5, 163.2, 158.5, 152.2, 148.6, 146.5, 136.4, 132.1, 123.1, 122.1, 121.5, 119.4, 114.0, 108.1, 68.2, 43.2, 32.1, 31.9, 29.7, 29.5, 29.4, 29.2, 26.0, 22.7, 14.1 ppm (five alkyl carbons obscured). MALDI-TOF MS:  $m/z = 1206 [Pd(3^{16})]^+$ .

CCDC 671535-671537 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](http://www.ccdc.cam.ac.uk/data_request/cif)

**Supporting Information:** Crystal structure determinations for  $[Zn_2(1^1)_2] \cdot 0.15CHCl_3 \cdot 3.35C_4H_{10}O$ ,  $[Zn_2(3^1)_2] \cdot CH_2Cl_2$  and  $[Pd(3^1)]$  including crystal data and refinement details.

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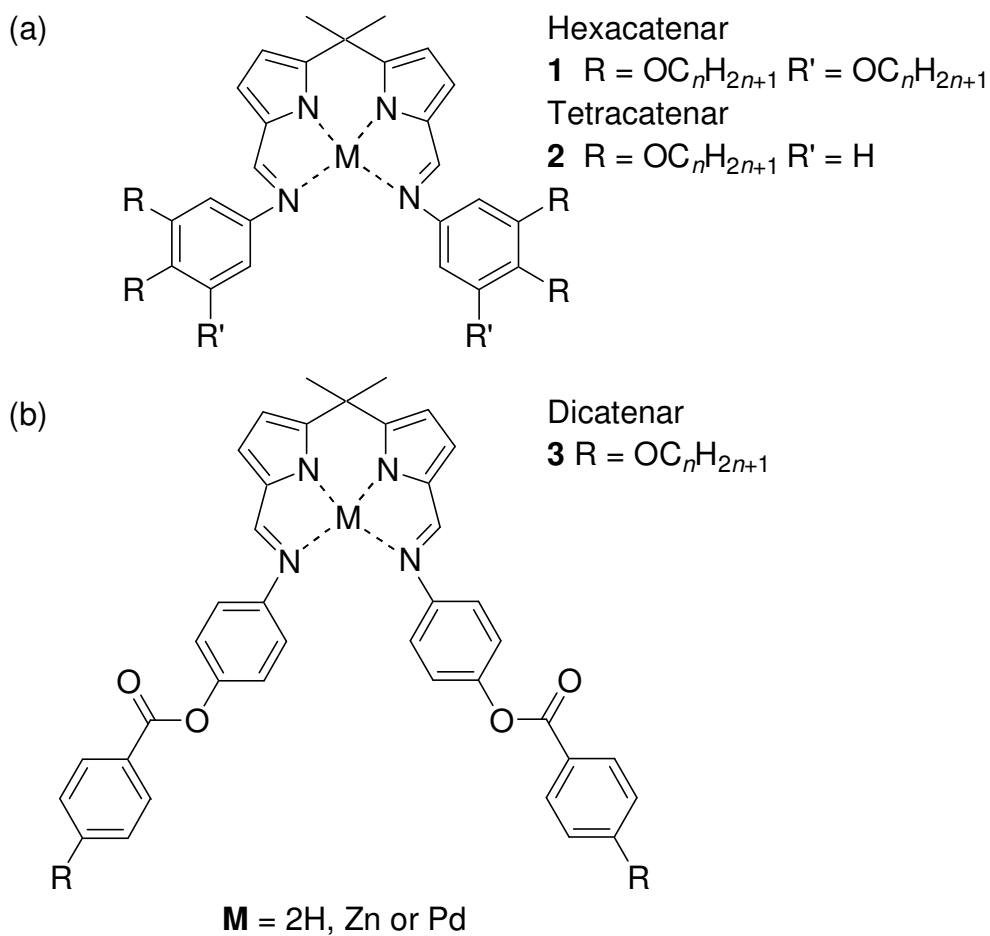
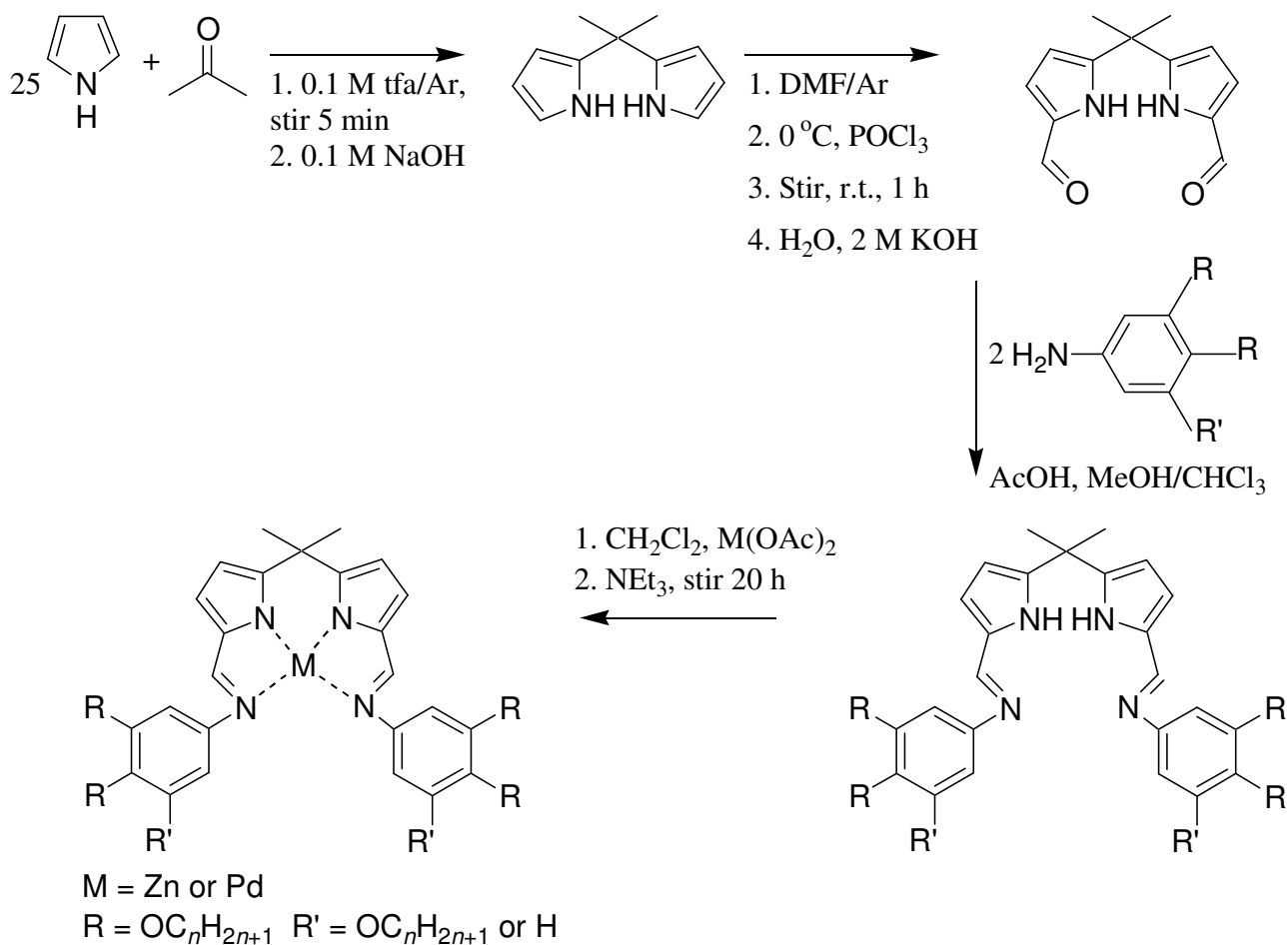


Figure 1: (a) Hexacatenar 5,5'-dimethyldipyrrole complexes,  $[M_x(\mathbf{1}^n)_x]$ , ( $M = 2H, Pd, x = 1; M = Zn, x = 2; n = 1, 10, 12, 14, 16$ ) and the tetracatenar 5,5'-dimethyldipyrrole complexes,  $[M_x(\mathbf{2}^n)_x]$ , ( $M = 2H, Pd, x = 1; M = Zn, x = 2; n = 1$  or  $16$ ). (b) Extended 5,5'-dimethyldipyrrole complexes,  $[M_x(\mathbf{3}^n)_x]$  ( $M = 2H, Pd, x = 1; M = Zn, x = 2; n = 1$  or  $16$ ).



Scheme 1: Synthetic route to **H<sub>2</sub>(1'')**, **H<sub>2</sub>(2'')** and the complexes **[M<sub>x</sub>(1'')<sub>x</sub>]** (M = Pd, *x* = 1; M = Zn, *x* = 2; *n* = 1, 10, 12, 14, 16) and **[M<sub>x</sub>(2'')<sub>x</sub>]** (M = Pd, *x* = 1; M = Zn<sup>2+</sup>, *x* = 2; *n* = 1, 16).

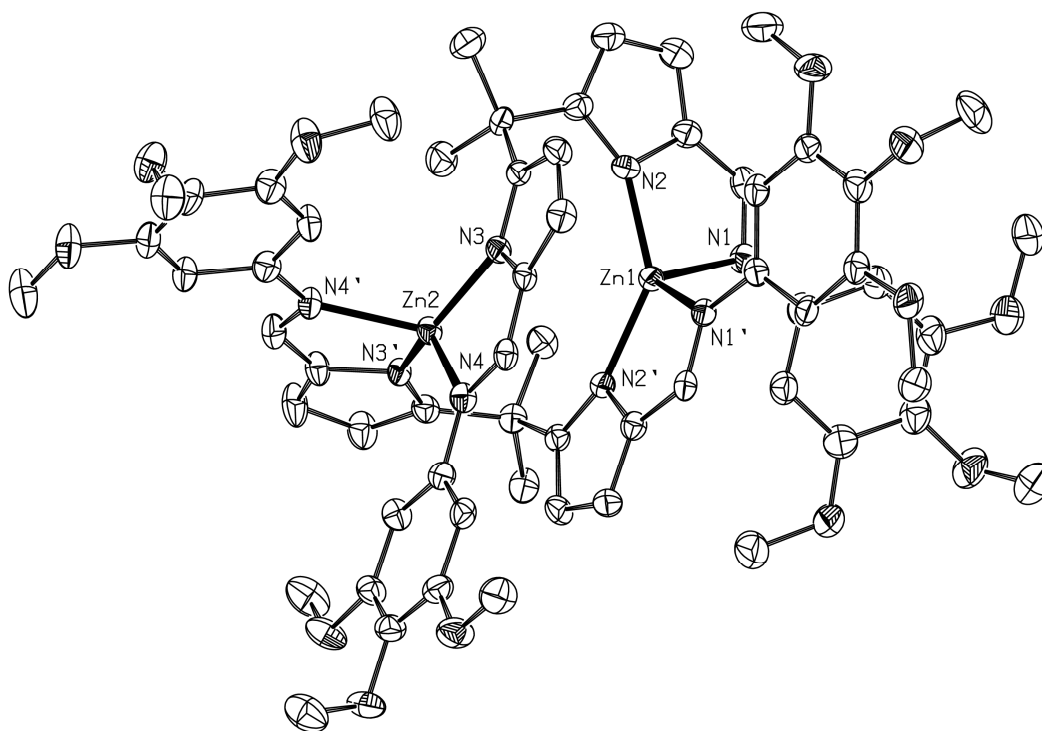


Figure 2: A view of the structure of  $[\text{Zn}_2(\mathbf{1}^1)] \cdot 0.1\text{CHCl}_3 \cdot 3.35\text{C}_4\text{H}_{10}\text{O}$  with displacement ellipsoids drawn at the 50% probability level. For clarity, hydrogen atoms and solvents of crystallisation have been omitted, and only the atoms involved in co-ordination have been labelled.

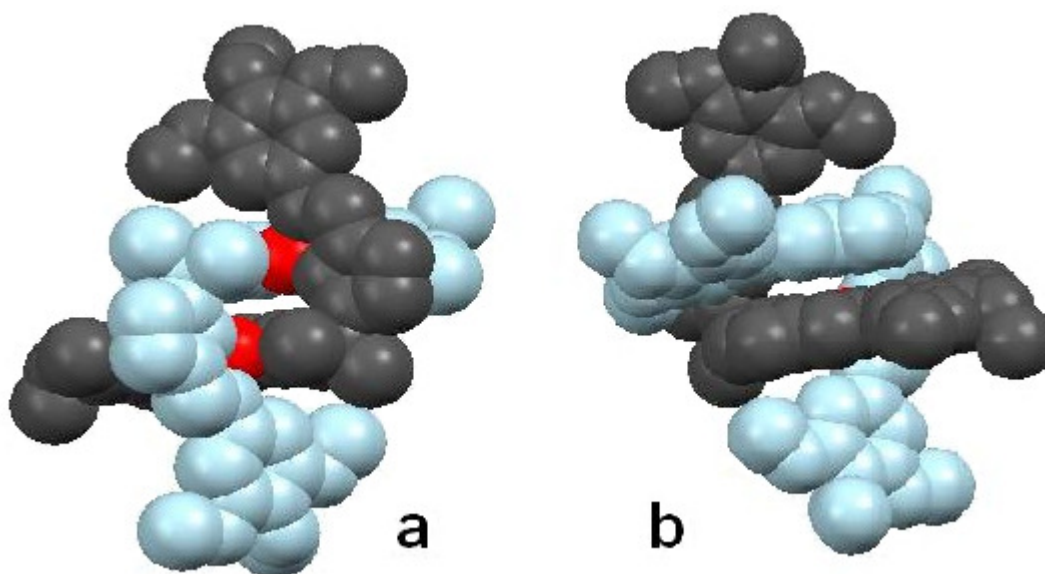


Figure 3: Representations showing the major groove (a) and minor groove (b) in the helical complex  $[\text{Zn}_2(\mathbf{1}^1)]$ .

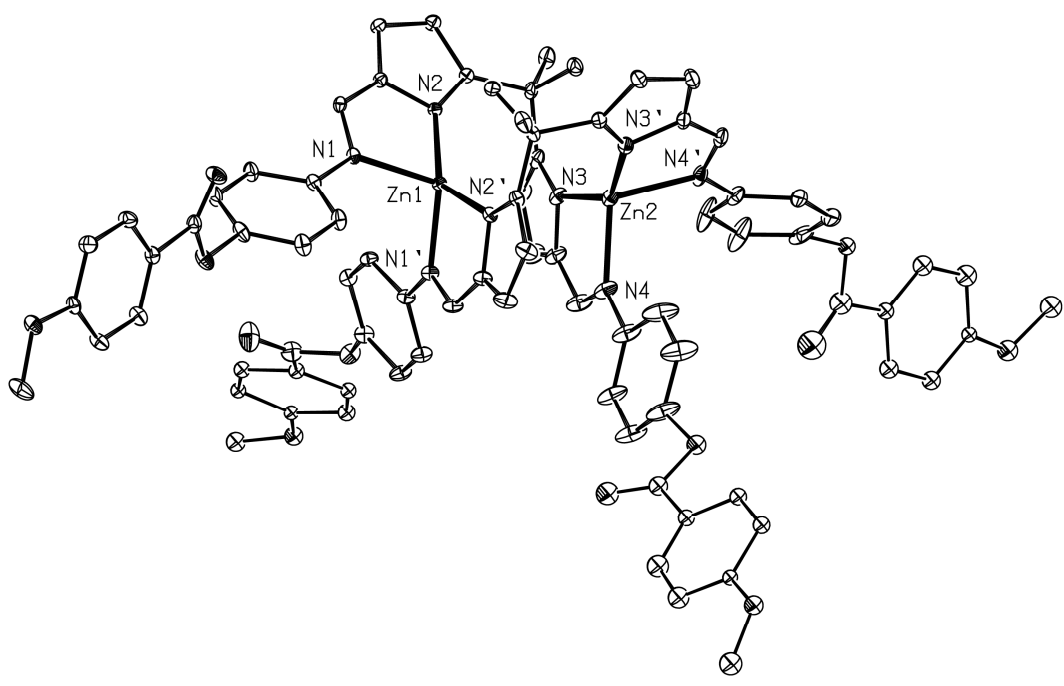


Figure 4: View of the structure of  $[\text{Zn}_2(\mathbf{3}^1)_2] \cdot \text{CH}_2\text{Cl}_2$  with displacement ellipsoids drawn at the 20% probability level. For clarity, hydrogen atoms and solvent molecules have been omitted, and only the atoms involved in co-ordination have been labelled.

Table 1. Selected bond lengths (Å) and angles (°) for  $[\text{Zn}_2(\mathbf{1}^1)_2] \cdot 0.1\text{CHCl}_3 \cdot 3.35\text{C}_4\text{H}_{10}\text{O}$ ,  $[\text{Zn}_2(\mathbf{3}^1)_2] \cdot \text{CH}_2\text{Cl}_2$  and  $[\text{Pd}(\mathbf{3}^1)]$ .

	$[\text{Zn}_2(\mathbf{1}^1)_2]$	$[\text{Zn}_2(\mathbf{3}^1)_2]$		$[\text{Pd}(\mathbf{3}^1)]$
Zn1-N1	2.100(4)	2.096(3)	Pd1-N1	2.089(3)
Zn1-N2	1.979(3)	1.958(3)	Pd1-N2	1.940(3)
Zn1-N1'	2.059(3)	2.036(3)	Pd1-N3	1.938(3)
Zn1-N2'	1.997(3)	1.988(3)	Pd1-N4	2.092(3)
Zn2-N4	2.047(4)	2.033(3)		
Zn2-N3	1.977(3)	1.985(3)		
Zn2-N4'	2.094(3)	2.098(3)		
Zn2-N3'	1.974(3)	1.959(3)		
N1-Zn1-N2	84.19(14)	84.42(11)	N1-Pd1-N2	80.11(14)
N1-Zn1-N2'	117.82(14)	110.82(11)	N2-Pd1-N3	87.65(14)
N1-Zn1-N1'	106.20(14)	105.82(11)	N3-Pd1-N4	80.02(13)
N1'-Zn1-N2	120.44(14)	130.53(11)	N1-Pd1-N4	112.40(13)
N1'-Zn1-N2'	85.18(14)	84.75(12)	N2-Pd1-N4	167.34(13)
N2-Zn1-N2'	141.61(15)	137.49(12)	N1-Pd1-N3	167.05(13)
N4-Zn2-N3	85.17(14)	84.94(14)		
N4-Zn2-N3'	124.85(14)	131.65(13)		
N4-Zn2-N4'	109.09(14)	104.80(14)		
N4'-Zn2-N3	112.78(14)	109.32(13)		
N4'-Zn2-N3'	84.65(14)	84.20(14)		
N3-Zn2-N3'	139.51(15)	137.56(12)		
Dihedral angle between N2 and N3 pyrrole rings	85.2(2)	80.0(2)	Dihedral angle between N2 and N3 pyrrole rings	5.9(4)
Dihedral angle between N2' and N3' pyrrole rings	85.2(2)	79.6(2)		



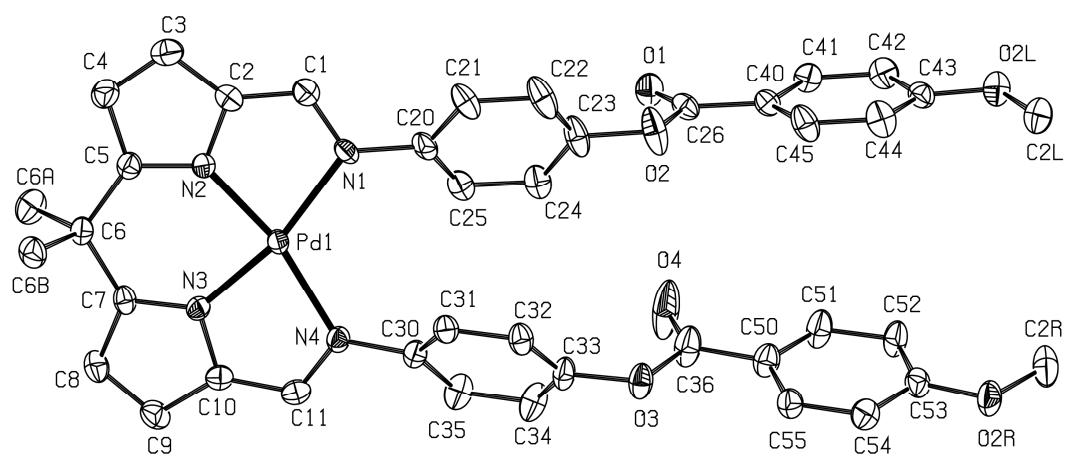


Figure 5. A view of the structure of **[Pd(3<sup>1</sup>)]** showing the relative orientations of the pyrrole and phenyl rings. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms have been omitted for clarity.

Table 2. Transition temperatures with the corresponding enthalpy changes for  $\text{H}_2(\text{L}^n)$ ,  $[\text{Pd}(\text{L}^n)]$  and  $[\text{Zn}_2(\text{L}^n)_2]$  <sup>[a]</sup>

$L^n$	Transitions ( $^{\circ}\text{C}$ ) and enthalpy changes ( $\Delta\text{H}$ in $\text{kJmol}^{-1}$ )		
	$\text{H}_2(\text{L}^n)$	$[\text{Pd}(\text{L}^n)]$	$[\text{Zn}_2(\text{L}^n)_2]$
$1^{10}$	Cr 49.0 [98.2] I	-	-
$1^{12}$	Cr1 2.6[4.0] Cr2 43.6 [44.0] I	Cr 48[13.3] I	-
$1^{14}$	Cr1 25.3 [3.8] Cr2 36.5 [104.2] I	Cr1 18.3 [1.9] Cr2 38.1 [67.5] I	-
$1^{16}$	Cr 41.3 [149.2] I	Cr 42.0 [79.3] I	Cr 35.8 [80.7] I
$2^{16}$	Cr 107.1 [148.4] I	Cr 57 [18.6] Sm 77 <sup>X</sup> I	Cr1 79.2 [52.1] Cr2 89.8 [78.5] I
$3^{16}$	Cr1 48[19.9] Cr2 93[25.0] Cr3 119[3.17] Cr4 142[ 4.88] Cr5 153[1.56] I	Cr 48 <sup>X</sup> I	Cr 140 [24.2] Sm <sub>A</sub> 230 <sup>X</sup> I

[a] Cr, Cr1- Cr5 are crystalline phases; Sm is a smectic mesophase; I is the isotropic liquid and X signifies that clearing is accompanied by some decomposition and therefore no enthalpy is reported.

Table 3. For  $[\text{Zn}_2(2^{16})_2]$  indexation information obtained by XRD studies <sup>[a]</sup>

$T/^{\circ}\text{C}$	$d_{\text{meas}}/\text{\AA}$	hk	$d_{\text{calc}}/\text{\AA}$	Mesophase	Transitions ( $^{\circ}\text{C}$ ) and enthalpy changes ( $\Delta\text{H}$ in $\text{kJmol}^{-1}$ )
60	30.52	001	30.4	Sm at $T = 60^{\circ}\text{C}$	Cr 57 [18.6] Sm 77 <sup>X</sup> I
	15.23	002	15.2	$d = 30.4 \text{\AA}$	
	10.16	003	10.1	$A_M = 155 \text{\AA}^2$	
	7.54	004	37.6		
	4.6	Br			

[a] T = temperature at which data was measured;  $d_{\text{meas}}$ , and  $d_{\text{calc}}$  are the measured and calculated diffraction spacings, respectively;  $00l$  is the indexation of the lamellar phase; Sm is a smectic mesophase;  $d$  is the periodicity and  $A_M$  is the molecular area; Cr is a crystalline phase; I is the isotropic liquid; and X signifies that clearing is accompanied by some decomposition therefore no enthalpy is reported.

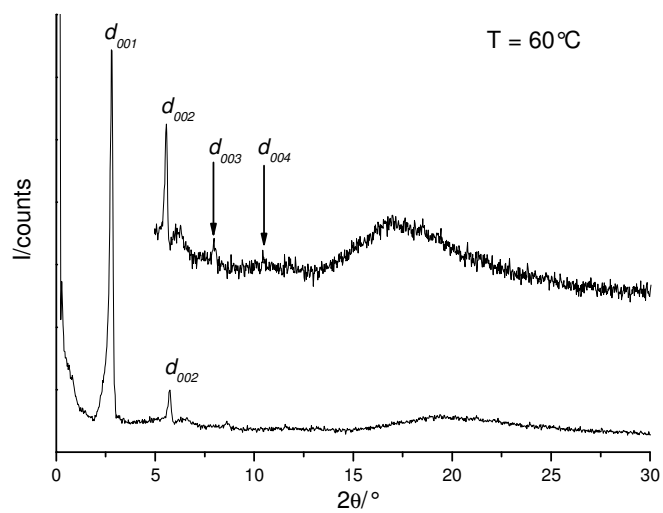


Figure 6: Diffractogram of  $[\text{Zn}_2(\mathbf{2}^{16})_2]$  at  $60^\circ\text{C}$ .

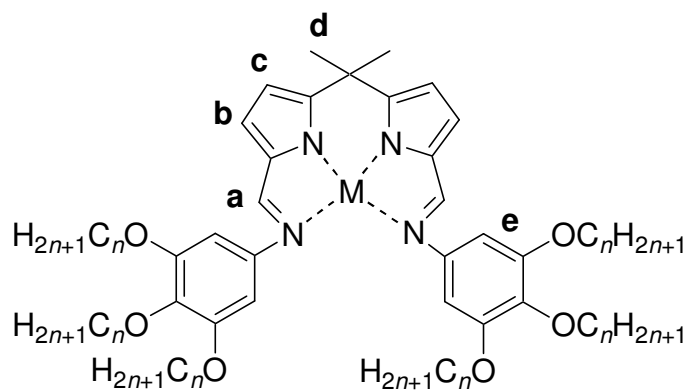


Figure 7: View of the ligands  $\text{H}_2(\mathbf{1}^n)$ , with selected hydrogen atoms labelled a-e in reference to the NMR spectral assignments.

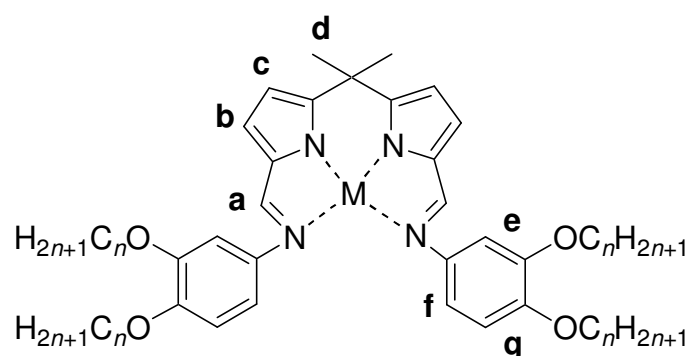


Figure 8: View of the ligands  $\mathbf{H}_2(\mathbf{2}'')$ , with selected hydrogen atoms labelled a-g in reference to the NMR spectral assignments.

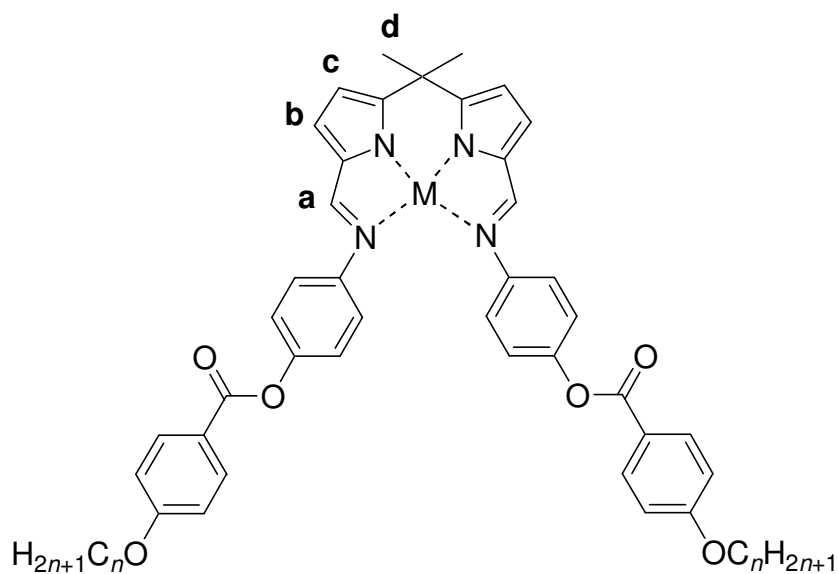


Figure 9: View of the extended dipyrrole ligands,  $\mathbf{H}_2(\mathbf{3}'')$ , with selected hydrogen atoms labelled a-d in reference to the NMR spectral assignments.



## SUPPORTING INFORMATION

### Crystal structure determinations

#### [Zn<sub>2</sub>(1<sup>1</sup>)<sub>2</sub>].0.15CHCl<sub>3</sub>·3.35C<sub>4</sub>H<sub>10</sub>O

Several molecules of solvent were found to be included in the lattice. These comprise one fully-occupied, ordered molecule of diethyl ether, while another molecule of diethyl ether (occupancy 0.85) is overlaid with a molecule of chloroform (occupancy 0.15) in which one chlorine atom is disordered over two equally occupied (0.075) sites. A third molecule of diethyl ether lies with the central oxygen atom lying on a crystallographic inversion centre and the adjacent carbon atom disordered over two half-occupied sites (half molecule in asymmetric unit). The final diethyl ether molecule exhibits two overlapping orientations with occupancies of 0.60 and 0.40. The last two diethyl ether molecules were modelled with isotropic displacement parameters and appropriate geometric restraints were applied.

#### [Zn<sub>2</sub>(3<sup>1</sup>)<sub>2</sub>].CH<sub>2</sub>Cl<sub>2</sub>

Disorder was identified in several terminal groups of the metal complex and was modelled by two half-occupied sites for each atom. Isotropic displacement parameters and appropriate geometric restraints were applied.

#### [Pd(3<sup>1</sup>)]

Twinning was identified in this structure and took the form of a 180° rotation about the [011] direction. The relevant twin law was (-1 0 0, -0.24 0.2 0.8, -0.24 1.2 -0.2) and the twin fraction refined to 0.16.

**Table S1 Crystal data and refinement details**

	[Zn <sub>2</sub> (1 <sup>1</sup> ) <sub>2</sub> ].0.1CHCl <sub>3</sub> ·3.35C <sub>4</sub> H <sub>10</sub> O	[Zn <sub>2</sub> (3 <sup>1</sup> ) <sub>2</sub> ].CH <sub>2</sub> Cl <sub>2</sub>	[Pd(3 <sup>1</sup> )]
<b>Crystal data</b>			
Chemical formula	C <sub>75.55</sub> H <sub>91.60</sub> Cl <sub>0.30</sub> N <sub>8</sub> O <sub>15.35</sub> Zn <sub>2</sub>	C <sub>83</sub> H <sub>70</sub> Cl <sub>2</sub> N <sub>8</sub> O <sub>12</sub> Zn <sub>2</sub>	C <sub>41</sub> H <sub>34</sub> N <sub>4</sub> O <sub>6</sub> Pd
<i>M<sub>r</sub></i>	1498.74	1573.11	785.12
Cell setting, space group	Monoclinic, <i>P2<sub>1</sub>/n</i>	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	150 (2)	150 (2)	150 (2)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.1924 (9), 15.0537 (10), 38.352 (3)	10.8280 (14), 13.868 (2), 24.757 (3)	10.723 (2), 12.353 (2), 13.847 (3)
$\alpha$ , $\beta$ , $\gamma$ (°)	90, 94.166 (2), 90	86.729 (2), 83.778 (2), 79.859 (2)	68.143 (3), 89.402 (3), 80.348 (3)
<i>V</i> (Å <sup>3</sup> )	7596.4 (9)	3635.2 (8)	1675.5 (9)
<i>Z</i>	4	2	2
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	1.310	1.437	1.556
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.71	0.80	0.61
Crystal form, colour	Lath, yellow	Block, orange	Lath, yellow
Crystal size (mm)	0.54 × 0.20 × 0.07	0.20 × 0.16 × 0.11	0.25 × 0.12 × 0.06

<b>Data collection</b>			
Diffractometer	Bruker SMART APEX CCD area detector	Bruker SMART1000 CCD area detector	Bruker SMART1000 CCD area detector
Data collection method	$\omega$	$\omega$	$\omega$
Absorption correction	Multi-scan	Multi-scan	Multi-scan
$T_{\min}$	0.830	0.880	0.773
$T_{\max}$	1.000	1.000	1.00
No. of measured, independent and observed reflections	57078, 13308, 10794	32028, 16161, 10094	14506, 7424, 6205
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\text{int}}$	0.049	0.046	0.034
$\theta_{\text{max}}$ (°)	25.0	27.5	27.6
<b>Refinement</b>			
Refinement on	$F^2$	$F^2$	$F^2$
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.068, 0.157, 1.14	0.058, 0.152, 1.01	0.046, 0.123, 1.07
No. of reflections	13308 reflections	16161 reflections	7424 reflections
No. of parameters	904	926	470
H atom treatment	Constrained to parent site	Constrained to parent site	Constrained to parent site
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 24.33P]$ where $P = (F_o^2 + 2F_c^2)/3$	Calculated $w = 1/[\sigma^2(F_o^2) + (0.059P)^2 + 4.419P]$ where $P = (F_o^2 + 2F_c^2)/3$	Calculated $w = 1/[\sigma^2(F_o^2) + (0.056P)^2 + 2.642P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}}$	0.001	0.001	0.005
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.82, -0.75	0.67, -0.92	1.19, -1.46

Computer programs: *Bruker SMART version 5.625* (Bruker, 2001); *Bruker SMART version 5.624* (Bruker, 2001); *Bruker SAINT version 6.36a* (Bruker, 2000); *Bruker SAINT version 6.36a* (Bruker, 2002); *Bruker SAINT*; *Bruker SHELXTL* (Bruker, 2001); *Bruker SAINT*; *Bruker SHELXTL* (Bruker, 2001); *ROTAX/WINGX*; *SHELXS-97* (Sheldrick, 1990); *SIR92* (Altomare et al., 1994); *SHELXL-97* (Sheldrick, 1997); *SHELXL97* (Sheldrick, 1997); *enCIFer* (CCDC, 2003); *PLATON* (Spek, 2003); *enCIFer* (Allen et al., 2004); *PLATON* (Spek, 2003).