Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Dalton Transactions

An international journal of inorganic chemistry
www.rsc.org/dalton

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Exploring Anagostic Interactions in 5,15-Porphodimethene Metal Complexes

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By metal templating strategy, the 5,15-porphodimethene metal complexes were synthesized and confirmed by single crystal X-ray analysis. The anagostic interaction causes *distortion*, while hydrogen bonding interactions generate
10 *dimerisation* and *array formation* of these complexes.

Coordination compounds have been the focus of interest from many decades due to their ability to be used as active elements in fields like catalysis,[1a,2] medicinal chemistry,[1b] supramolecular chemistry[1c,1d] etc. The ability of these compounds is not just a
15 result of their chemical composition but also imparted to them through a deliberate consequence of noncovalent interactions between the constituent molecules.[2] Among these, hydrogen atom assisted interactions such as hydrogen bonding, agostic and anagostic interactions are highly significant. They play major role
20 in the structural stability, reactivity and applications like hydride extraction and elimination, which highlights the need for the study of these delicate interactions.[3] However, compared to agostic interactions, anagostic interactions are not well explored in the literature.[4]
25   Calixphyrins, which are the structural hybrids of porphyrins and calixpyrroles, provide an excellent base for exploring the anion and cation recognition properties.[5] Among the different categories of calixphyrins, 5,15-porphodimethene is an important class with partially conjugated and non-conjugated characters in
30 its framework. To date, many fruitful efforts have been made to design and synthesis of free-base and their metal complexes.[5-11]

  In general, porphodimethenes and its complexes are prepared through; (i) reductive alkylation at *meso* position of porphyrins;[6] (ii) dealkylation of octaalkylcalix[4]pyrrole;[7] and (iii) acid-
35 catalyzed condensation of oligopyrroles and acetone[8] or condensation of sterically hindered aldehyde and pyrrole.[9] In the methodologies (i) and (ii), the metal complexes of porphyrins / calixpyrroles are converted into respective 5,15-porphodimethene metal complex. In the methodology (iii), the metal complexes are
40 synthesized through stepwise strategies, where the first step involves the synthesis of free-ligand followed by metal ion insertion. In 2000, Sessler and co-workers demonstrated the synthesis of series of calix[4]phyrins with one, two and three sp³ hybridized *meso* carbons and introduced the cation complexation
45 by using ZnCl₂ in presence of Et₃N.[8b] Later in 2005, Lindsey and co-workers reported the Pd complex of porphodimethene, where the 1-acyldipyrromethane afforded less than 1% of respective metal complex by metal templating strategy. However, through

stepwise synthesis, the Pd complex was obtained in 22% yield.[10]
50 Same year, Wim Dehaen and co-workers adopted a similar strategy, where the acid-catalyzed condensation of 1-formyldipyrromethane afforded the free-base 5,15-porphodimethene with the maximum yield of 5.5% and utilized the metal templating strategy by Ni(II) as template and obtained
55 the respective complex in 28% yield.[11] Recently, series of core-modified porphodimethenes such as phosphole[12a] and benzene ring incorporated derivatives[12b-d] were reported, which were also synthesized as free-base followed by metal complexation or used as metal ion receptors.[12] Herein, we wish to report the synthesis
60 of 5,15-porphodimethene metal complexes, by single step metal templating strategy. In addition to the regular spectral analyses, all the complexes were confirmed by X-ray single crystal analysis. The present contribution is focused on the study of noncovalent interactions such as hydrogen bonding and anagostic
65 interactions using 5,15-porphodimethene metal complexes as platform. Apart from series of noncovalent interactions, the anagostic interaction explored here is hitherto unknown in porphyrin chemistry in general and calixphyrin chemistry in particular. Further, Zn(II) and its axial water coordinated complex
70 of 5,15-porphodimethene are not known in the literature.
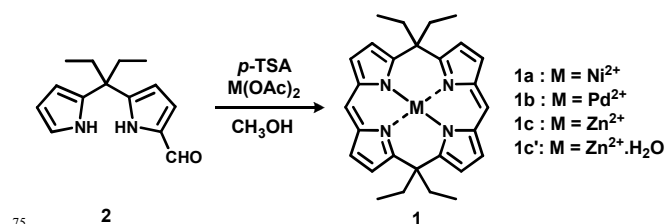
75 **Scheme 1** Synthesis of metal complexes **1a – 1c′**

  The syntheses of the metal complexes were carried out according to the reaction sequence outlined in Scheme 1. The
80 synthetic methodology adopted here is basically a metal templating strategy, where stirring a methanol solution of 1-formyl-5,5-di(ethyl)dipyrromethane (**2**)[11] with acetates of nickel, palladium and zinc in the presence of *p*-toluenesulphonic acid as acid-catalyst afforded **1a** and **1b** in 30% and 35% yield,
85 respectively. On the other hand, the corresponding Zn complex (**1c**) was obtained in 1% yield along with axial-water coordinated polymorph **1c′** in 10% yield. The identity of the complexes were examined and confirmed by electronic, ¹H NMR spectral studies, ESI-MS and single crystal X-ray analyses (**ESI**†). The mass

spectral analysis of complexes **1a-1c′** shows the isotopically resolved signals at m/z 481.1964 (Calcd for $[(C_{28}H_{30}N_4Ni)]^+$ = 480.1824), 529.1683 (Calcd for $[(C_{28}H_{30}N_4Pd)]^+$ = 528.1505), 486.1914 (Calcd for $[(C_{28}H_{30}N_4Zn)]^+$ = 486.1762) and 487.5171 (Calcd for $[(C_{28}H_{32}N_4OZn)]^+$ = 504.1868) respectively. The single crystals of **1a-1c′** were grown at room temperature by vapour diffusion method in CH_2Cl_2/hexane solvent combination. Crystallographic data is listed in Table S2 (**ESI**†).

The ^{1}H NMR spectra of **1a**, **1b** and **1c′** were recorded in CDCl$_3$ at room temperature and shown in Fig. 1a. In general, the *meso*-CH protons are resonated as a sharp singlet in the range of 6.71 – 6.94 ppm. The doublets are centered at 6.44 to 6.78 ppm correspond to pyrrolic *β*-CH protons. The ethyl protons are observed as quartet / broad singlet around 2.05 – 2.50 ppm and triplet around 0.66 to 0.84 ppm, respectively. Furthermore, as compared to 1-formyl-5,5-di(ethyl)dipyrromethane **2**, the disappearance of the signals corresponding to pyrrolic *α*-CH and NH protons along with upfield shift of the 1-formyl-CH signals suggests the formation of the macrocycle with metal ion insertion. For example, the ^{1}H NMR spectrum of **1b** shows the *meso*-CH protons as singlet at 6.94 ppm, the pyrrolic *β*-CH protons resonate at 6.93 and 6.40 ppm, while the ethyl protons are at 2.05 and 0.82 ppm, respectively.

In addition to the regular pattern as that of **1b**, where the methylene protons in the *meso*-ethyl unit appears as a quartet, the respective protons in **1a** resonate as a broad peak at 2.46 ppm, which is 0.41 ppm downfield shifted as compared to **1b**. This was further investigated by the temperature dependent NMR measurements (Fig. 1b). Upon increasing the temperature from 298 to 323 K, the broad peak at 2.46 ppm (H$_a$ – H$_e$) converts into quartet. On the other side, upon lowering the temperature from 298 to 223 K, all the proton signals become broad, however, the methylene protons further split into three sets with the intensity ratio of 4:2:2 (Fig. 1b inset). Out of eight methylene protons, four are shifted to upfield and resonate at 2.07 ppm (H$_e$), which is exactly matching with the methylene proton signals of **1b** and **1c′**. The remaining four protons are shifted to downfield and resonate between 2.50 to 3.60 ppm (H$_d$ – H$_a$) suggests that these protons are in closer proximity to the metal center and have an interaction with it. The low yield of **1c** hampers the NMR characterization, however, **1c′** shows the regular pattern as that of **1b** and the axial water protons are resonated as a broad singlet at 2.01 ppm, which is further confirmed by D$_2$O exchange experiment.

While excavating the structural features of all the complexes, we found that **1a** is embedded with multiple type of noncovalent interactions involving the hydrogen atoms. The single crystal X-ray structure of **1a** is shown in Fig. 2a and 2b where one of the *meso*-ethyl units (C1-H1A) shows an unusual electrostatic interaction with the Ni centre. The distance and angle of C1-H1A…Ni is 2.72 Å and 130°, respectively. As evident from the literature,[3,4] these interactions in which a hydrogen atom is held close to a metal centre are termed as anagostic or pre-agostic interactions. Such interactions are characterized by **M···H** distance ranging from 2.3 to 2.9 Å and **M···H–C** bond angle of 110° to 170° with a NMR downfield shift for the **M···H–C** proton.[3,4] The observed results are well within the limit of anagostic interactions and the downfield shift of the methylene protons from the NMR spectral analysis further confirm such
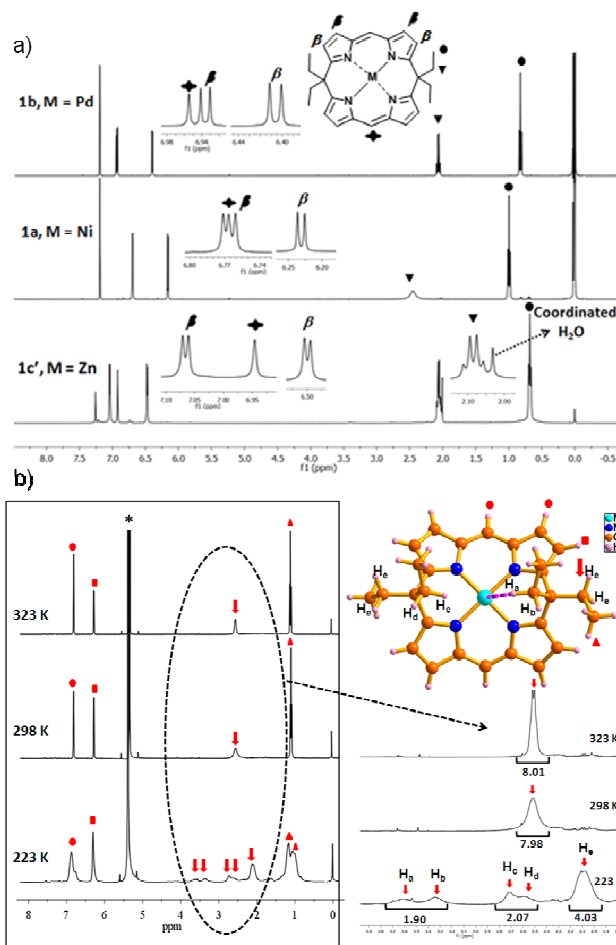

Fig. 1 NMR spectral analysis. a) ^{1}H NMR spectrum of **1a, 1b, 1c′** with expansions as inset. b) Temperature dependent ^{1}H NMR spectral changes of **1a**. The inset shows the expansion in the methylene protons signals.

interactions. It is pertinent to point out here that such an interaction is hitherto unknown in 5,15-porphodimethene metal complexes. In addition to such interaction, **1a** shows intermolecular hydrogen bonding interactions, where *meso*-CH of one unit (C10-H10) interacts with Ni of another unit to generate the self-assembled dimer and also generates the 1-D array, where one unit of pyrrolic *β*-CH (C18-H18) interacts with next unit pyrrolic *π* cloud. 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, 163°, respectively (Fig. S13†). Overall, the *β*-anagostic interaction between the ethyl group and the nickel centre leads to the lowering of symmetry and *distortion* of the molecule as evident from the NMR and crystal analysis of **1a**. The hydrogen bonding interaction leads to self-assembled *dimerisation* as well as 1-D *array formation*.

The crystal analysis of **1b** reveals that two units of metal complexes are present in the unit cell, where both the units are perpendicular to each other and are connected through strong intermolecular hydrogen bonding interactions. The *meso*-CH (C5-H5) and the pyrrolic *β*-CH (C7-H7) of one unit interact with

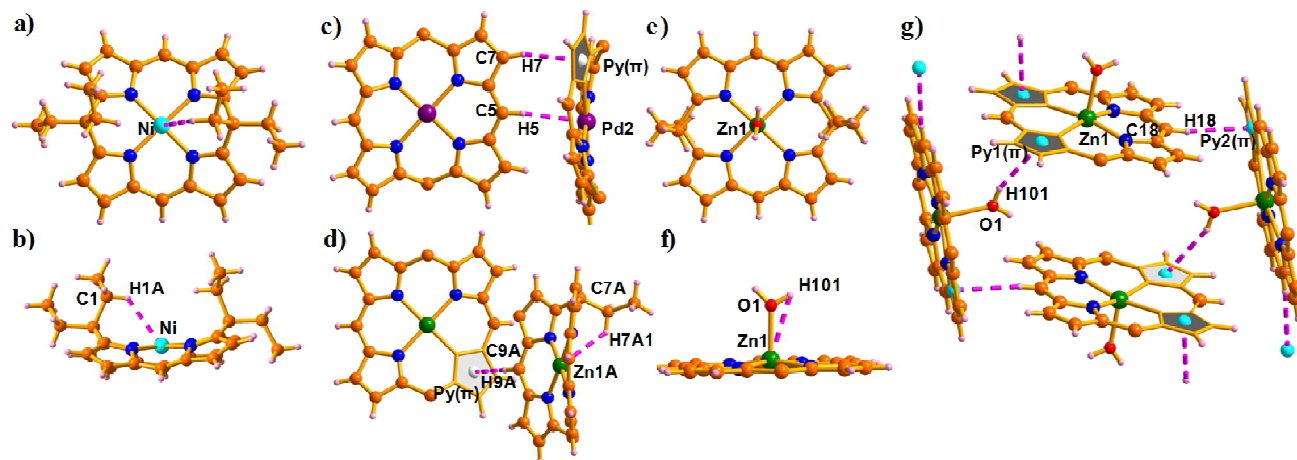# Dalton Transactions

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Fig. 2 Single crystal X-ray structure of **1a-1c′**. (a) **1a** top view; (b) **1a** side view with anagostic interaction; (c and d) self-assembled dimer of **1b** and **1c**; (e) and (f) top and side view with axial water molecule of **1c′** and (g) 2-D supramolecular assembly of **1c′**. The *meso* di-ethyl units which are not involved in any interactions are omitted for clarity in **1b**, **1c** and **1c′**.

the Pd metal (Pd2) and pyrrolic π-cloud Py(π) of second unit and generate the dimeric complex with the distances and angles of C5-H5…Pd2 and C7-H7…Py(π) are 2.89 Å, 157° and 1.70 Å, 162° respectively, as shown in Fig. 2c. The distance between two Pd in **1b** is 7.07 Å. Unlike **1a**, **1b** lacks the formation of 1-D array interaction. Due to the absence of anagostic interaction, **1b** generates a more symmetric structure as evident from the crystal structure and the NMR spectral analyses.

The single crystal X-ray structure of **1c** is shown in Fig. 2d. As observed in **1b**, the unit cell of **1c** also contains two units of respective metal complexes, which are perpendicular to each other. The distance between two Zn in **1c** is 8.30 Å. These two units are connected through intermolecular hydrogen bonding interaction, where *meso*-hydrogen (H9A) of the second unit interacts with pyrrolic π cloud of the first unit and generates the dimeric complex. In addition, there is an intramolecular hydrogen bonding interaction in the second unit between one of the *meso*-ethyl unit (C7A-H7A1) with Zn1A. The distances and angles of C9A-H9A…Py (π) and C7A-H7A1…Zn1A are 2.84 Å, 165° and 2.84 Å, 130°, respectively. The latter interactions are well within the anagostic or pre-agostic interaction as observed in **1a**. The single crystal analysis of **1c** also generates the self-assembled dimer as well as 1-D array. The self-assembled dimer is formed from one of the two metal complexes from the unit cell, where *meso*-CH (C11A-H11A) are in intermolecular hydrogen bonding interaction with the pyrrolic π cloud, the distance and angle of C11A-H11A…Py(π) is 2.78 Å, 141° (Fig. S15C†). On the other hand, both the metal complexes present in the unit cell combinedly generate the 1-D array through intermolecular hydrogen bonding interaction, where *meso*-CH (C9B-H9B) of the first unit interacts with the pyrrolic π-cloud of the second unit. The distance and angle of C9B-H9B…Py (π) is 2.82 Å and 165°, respectively (Fig. S15D†). Thus in short, the hydrogen bond interactions in **1c** play a key role in *dimerisation* and 1-D *array*

formations as in the case of **1a**.

The single crystal X-ray structure and analysis of **1c′** is shown in Fig. 2e, 2f and 2g. As predicted from the NMR spectral analysis, Zn1 in **1c** is further coordinated to the H_2O molecule to generate **1c′**. One of the hydrogens (H101) in the H_2O molecule is in intramolecular hydrogen bonding with Zn1 with a distance of 2.71Å (Fig. 2f). Unlike **1c**, the coordinated H_2O molecule pushes the Zn1 to the center of the cavity and generates a planar structure which is unprecedented in the calixphyrin coordination chemistry. The Zn1 is 0.23Å above the plane of the four pyrrolic nitrogens and 0.26Å above the mean plane of the macrocyclic ring. The crystal analysis of **1c′** generates two 1-D intermolecular hydrogen bonding interactions, which are between; (i) one of the hydrogen atoms (H101) in the coordinated H_2O molecule with one of the pyrrolic-π [Py1(π)] clouds, and (ii) one of the *meso*-CHs (C18-H18) with another pyrrolic-π (Py2(π)) cloud. The distances and angles of O1-H101…Py1(π) and C18-H18…Py2(π)] are 2.81, 2.88 Å and 161°, 171° respectively (Fig. S17†). Combining these two 1-D arrays, **1c′** generates 2-D supramolecular assembly in the solid state (Fig. 2g). As evident from the NMR and crystal structure, **1c′** lacks anagostic interactions due to the stronger interaction of the apical water molecule with Zinc metal center.

The electronic spectral analysis of the complexes **1a-1c′** in $CHCl_3$ consists of two broad bands around 386 to 518 nm with considerable difference in intensity. The bands centered around 500 nm are assigned to π–π* transition.[13] **1a** shows absorption maxima at 423 nm with shoulder around 518 nm; on the other hand, **1b** shows a broad band at 386 nm with an intense band at 472 nm (Fig. 3). The molar extinction coefficient values of the complexes are summarized in Table S1 suggests that the intense bands are around 2.5 fold higher than the broad ones. All the metal complexes have practically no emission.
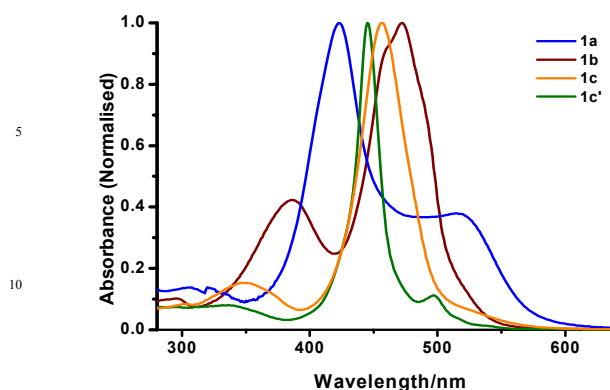
Fig. 3 Normalised absorption spectra of **1a** - **1c′** in CHCl₃.

Conclusion

In summary, noncovalent interactions like hydrogen bonding and anagostic interactions play a decisive role in structure, geometry and properties of the metal complexes. We have successfully explored the role of noncovalent interactions governing the structure and stability of the metal incorporated 5,15-porphodimethene synthesized via metal templated methodology. Investigation of the crystal structure revealed that **1a** and **1c** were found to show a rare case of **M···H–C** anagostic interactions in addition to the normal hydrogen bond interactions. The anagostic interaction explored here demonstrated the structural features in 5,15-porphodimethene metal complexes for the first time. The extra coordinated water molecule in **1c′** converts the roof like conformer to planar form which is hitherto unknown in the calixphyrin metal complexes. Overall, the anagostic type interaction leads to structural *distortions* while the hydrogen bond interaction leads to *dimerisations* and *array formations*. The role of these interactions in H-activation, catalytic application and receptor properties of these complexes are currently going on in our group.

Acknowledgments

Notes and references

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†Electronic Supplementary Information (ESI) available: [Experimental sections, supplementary results, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org. The X-ray data were also deposited with the CCDC-930500 for **1a**, CCDC-930501 for **1b**, CCDC-930502 for **1c** and CCDC-930503 for **1c′**]. See DOI: 10.1039/b000000x/

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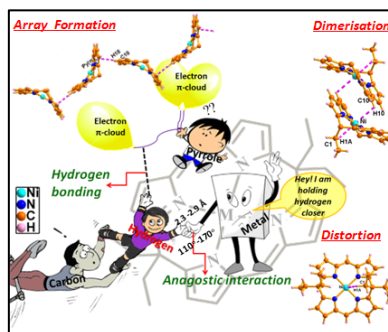
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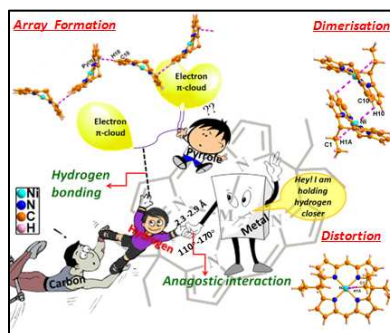
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By using 5,15-porphodimethene metal complexes, the weak noncovalent anagaostic interaction is explored by variable temperature NMR studies and further confirmed by single crystal X-ray analysis.