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Density functional studies on N-fused porphyrin. Electronic, magnetic and metal binding properties

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Paper dedicated to Professor Francois Mathey on the occasion of his 60th birthday

Abstract

Density functional calculations have been performed to understand the electronic and magnetic properties along with the metal complexation ability of N-fused porphyrin (NFP), and doubly-N-fused porphyrin (N_2FP). DFT computations predict that the planar N_2FP is a second order saddle point. The minimum energy structure, **5**, is nonplanar and 8.0 kcal mol^{-1} lower in energy than the planar structure. Despite the nonplanarity, N_2FP has only 3.0 kcal mol^{-1} additional strain energy compared to NFP. NFP can form stable metal complexes with Cu(I) metal ion. The most stable structure for Cu(I)NFP prefers dome conformation. Nucleus independent chemical shift (NICS) calculations reveal that NFP has much reduced global ring current (NICS −8.5). However, effective interaction between the two tri-pentacyclic rings in N_2FP enhances the global ring current (NICS −17.5). © 2002 Published by Elsevier Science B.V.

Keywords: Density functional studies; N-fused porphyrin; Metal binding properties

1. Introduction

Transition-metal porphyrin complexes have attracted considerable interest because of their relevance to biological systems as well as their catalytic activities in organic reactions. Conformational flexibility and the ability to complex with several metals at various oxidation levels make porphyrin systems an attractive template for various chemical transformations. Driven by the search for various practical applications [1], several novel pyrrole-based macrocycles such as contracted [2], expanded [3], confused [4] and carba-porphyrins [5] have been synthesized in recent times. Synthesis of each variant of porphyrin offers a unique opportunity to enhance our understanding of fundamental properties of these important systems. For example, expanded porphyrins, because of their large core size, stabilize several larger metal complexes that are difficult to prepare using porphyrins. An isomer of porphyrin and N-confused porphyrin (NCP), doubly N-confused porphyrin (N_2CP), was found to stabilize higher oxidation states of Ag and Cu [6].

A recent addition to the list of novel porphynoid systems is N-fused porphyrin (NFP). Furuta et al. reported an unusual reaction of NCP [7]. Substituted NCP *spontaneously* undergoes ring closure reaction to give, as the authors named, NFP. Under basic conditions, NCP is regenerated from NFP. NFP has unusual structural features; it is the first tri-pentacyclic planar porphyrin system, with a tri-coordinated nitrogen as a part of macrocycle. The fusion of two five-membered rings in the ring current pathway of NCP is expected to give dramatic changes in the electronic and magnetic properties. It was noted that NFP is slightly red shifted compared to NCP [7]. The popular description of porphyrin as a derivative of [18]annulene [8] is being modified by recent computations [9]. Magnetic studies have shown that the dominant ring current pathway in porphyrin and other related systems is a linear combination of [18], [24] and [26]annulene [8b].

Since there are no experimental reports on the metal complexation with NFP, we investigate computationally the possibility of stabilizing low oxidation state

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metal complexation. In addition, we also explore the structural and magnetic properties of unknown doubly-N-fused porphyrin (N_2FP), which can be envisaged by a double ring closure reaction of the appropriate N_2CP isomer [6]. In this report, besides, observing unusual magnetic properties of NFP, we propose that N_2FP is distinctly nonplanar with only 3 kcal mol^{-1} additional strain compared to NFP but probably as aromatic as NFP. In addition we also observe that NFP forms stable complex with Cu(I) metal ion preferentially forming dome conformation.

2. Computational methods

All the calculations were carried out using the Gaussian 98 program at B3LYP/6-31G* level of density functional theory [10]. Harmonic vibrational frequency calculations were performed on NFP and N_2FP to establish the nature of the stationary points. Metal systems are optimized at B3LYP/Lanl2DZ and B3LYP/SVP (all electron basis set) level of theory. Frequency calculations were done at B3LYP/Lanl2DZ level. To probe the nature of ring current in these systems we have used the Nucleus Independent Chemical Shift (NICS) [11] and ^1H chemical shifts. TMS has been used as reference in the ^1H chemical shift calculations. The magnetic calculations were done at HF/6-31+G*//B3LYP/6-31G* level to estimate the ring current.

3. Results and discussion

Formally, all the systems considered here (Fig. 1) have 26 π electrons. Inverted pyrrole rings of NCP (**2**), and N_2CP (**4**), deviate from the porphyrin mean plane by 23.5 and 27.0°, respectively, conforming the experimental [12] and theoretical [13] observations. Note that the CH vector in NCP and N_2CP, is not in the plane of the five-membered ring but makes angles 14.2 and 16.4°, respectively. As a consequence the π orbitals on the two sides of the inverted pyrrole ring are not equivalent.

NFP (**3**) is a planar minimum at the B3LYP/6-31G* level. The geometrical parameters of the optimized structure agree well with the reported X-ray structure [6]. The important bond distances, especially around tri-coordinated nitrogen, 1.401, 1,404 and 1.391 Å, have been reproduced quite satisfactorily, 1.406, 1.408 and 1.385 Å, by current level of calculations. The N–H hydrogen in NFP is within the hydrogen bonding range to the nearest nitrogen atoms. The N···H (1.753 Å) and N···H (1.813 Å) (Fig. 1) distances suggest a hydrogen bond with the nitrogen atoms. The variations in C–C and C–N bond lengths in the tri-pentacyclic ring of NFP can be best understood by comparing with model systems **6** and **7**. The average C–C and C–N distances of tri-pentacyclic ring in NFP are 1.421 and 1.380 Å, respectively. These bond lengths agree with the corresponding ones in **6** ($C–C_{av.} = 1.416$ Å and $C–N_{av.} = 1.384$ Å) and **7** ($C–C_{av.} = 1.425$ Å and $C–N_{av.} = 1.395$ Å). Notice that there is hardly any change in the average C–C and C–N bond lengths on going from model systems (**6** and **7**) to NFP, indicating that being a part of macrocycle with additional π electrons has little effect on the structural parameters of the tri-pentacyclic ring.

Introducing another five-membered ring to NFP drastically alters the structure. In the present report we have considered a *trans*-isomer of N_2CP reported in the above reference. Both the isomers have nearly equal energy [14]. The planar doubly-N-fused porphyrin (C_s), is a second order saddle point and 8.2 kcal mol^{-1} higher in energy as compared to the nonplanar N_2FP (C_i) minimum. Usually nonplanar distortions of porphyrin ring result in slight stabilization of energy around 1 or 2 kcal mol^{-1}; substantial energy stabilization observed in the present systems should reflect in the properties. The major structural change on going from planar N_2FP to nonplanar N_2FP is the increase in N···N distances. The $N_1 \cdots N_3$ and $N_1 \cdots N_2$ nonbonded distances 2.220, and 2.639 Å became 2.429 and 2.838 Å, respectively. Nearly 0.2 Å increase in the nonbonding distance reduces much of the repulsive interaction between the nitrogen atoms. This results in a deviation of N_2FP from planarity. The preferential deviation is from dicoordinated nitrogen atoms. They are above and below the plane by 21.6°. As a consequence the whole tri-pentacyclic unit deflects in the opposite direction to the molecular mean plane passing through the *meso* carbon atoms. Despite the nonplanarity, the average bond lengths ($C–C_{av.}$ (1.420 Å) and $C–N_{av.}$ (1.383 Å)) are similar to those in NFP (**3**).

Nonplanarity of porphyrin and other related systems occurs for both electronic and steric reasons [15]. Nature of the metal atom, electron-withdrawing axial ligands, and small core size are some of the major reasons for nonplanarity [16]. In addition, intrinsic distortions can be achieved by placing sterically bulky substituents at the periphery of the macrocycle [17]. The major consequence of the nonplanar distortions is a significant rise in the HOMO energy level resulting in the red shifts in the electronic absorption spectra [17].

In agreement with experimental observations [16] and theoretical calculations [17], the main effect of the nonplanarity in terms of electronic structure is the raise in HOMO energy level. The HOMO and LUMO of NFP (**3**), and N_2FP (**5**), are based on the tri-pentacyclic rings. This results in substantial raise in the HOMO energy of NFP and N_2FP (Fig. 2) compared to NCP and N_2CP, whereas LUMO energies vary to a lesser extent. The destabilized HOMO of N_2FP is expected to

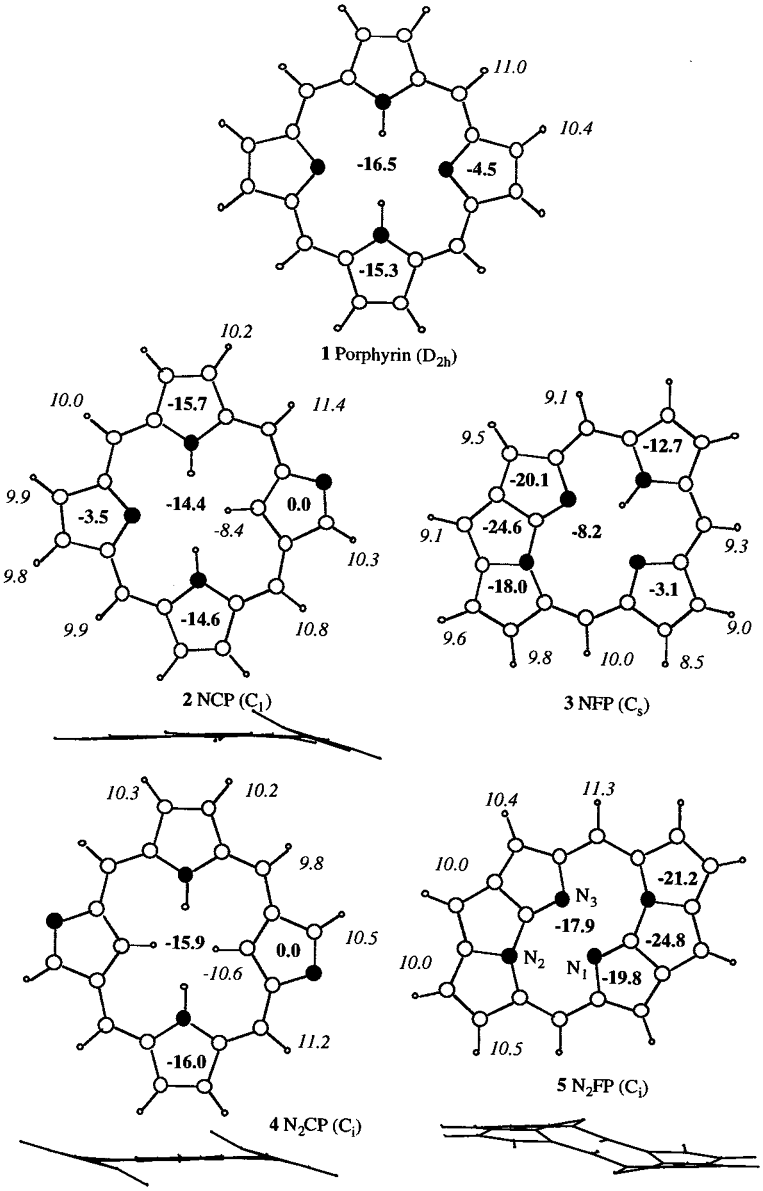


Fig. 1. NICS values (in bold) in ppm and ^{1}H chemical shifts (in italics) compared to TMS for the structures **1**–**5**.

influence electronic absorption spectra, with the corresponding large red shift.

The best way to calculate strain energies (SEs) is the use of homodesomotic equations, which preserve similar bond types on both sides of the equation. However, judicious choice of the reference systems is imperative in calculations of SEs. The energy required to form NFP and N_2FP are compared (Eqs. (1)–(4), Fig. 3) from open chain reference systems and NCP and N_2CP. The reference systems used in energy equations represent the dominant resonance structure present in both NFP and N_2FP.

$$\mathbf{8}+\mathbf{3}=\mathbf{2}+\mathbf{7} \quad -21.6 \text{ kcal mol}^{-1} \tag{1}$$

$$\mathbf{9}+\mathbf{5}=\mathbf{4}+\mathbf{6} \quad -34.1 \text{ kcal mol}^{-1} \tag{2}$$

$$\mathbf{10}+\mathbf{3}=\mathbf{2}+\mathbf{7} \quad -15.2 \text{ kcal mol}^{-1} \tag{3}$$

$$\mathbf{11}+\mathbf{5}=\mathbf{4}+\mathbf{6} \quad -27.4 \text{ kcal mol}^{-1} \tag{4}$$

$$2\text{NCP}+\text{N}_2\text{FP}=2\text{NFP}+\text{N}_2\text{CP} \quad -3.3 \text{ kcal mol}^{-1} \tag{5}$$

Two sets of reference molecules were considered for the evolution of strain energies in Eqs. (1)–(4). While in the first set (Eqs. (1) and (2)) the reference molecules represent tri-pentacyclic parts of NCP and N_2CP; in the Eqs. (3) and (4) isomers of reference molecules have been used to mimic the later stage of the formation of NFP and N_2FP. In either case the strain energy of N_2FP (34.1 (27.4) kcal mol^{-1} from Eqs. 2 (4)) is less than twice that of the NFP (21.6 (15.2) kcal mol^{-1} Eqs. 1 (3)). Considering the spontaneous formation of NFP,

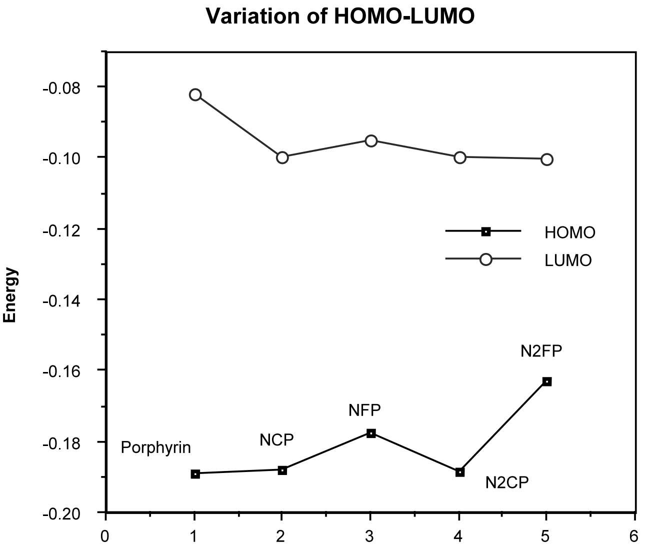
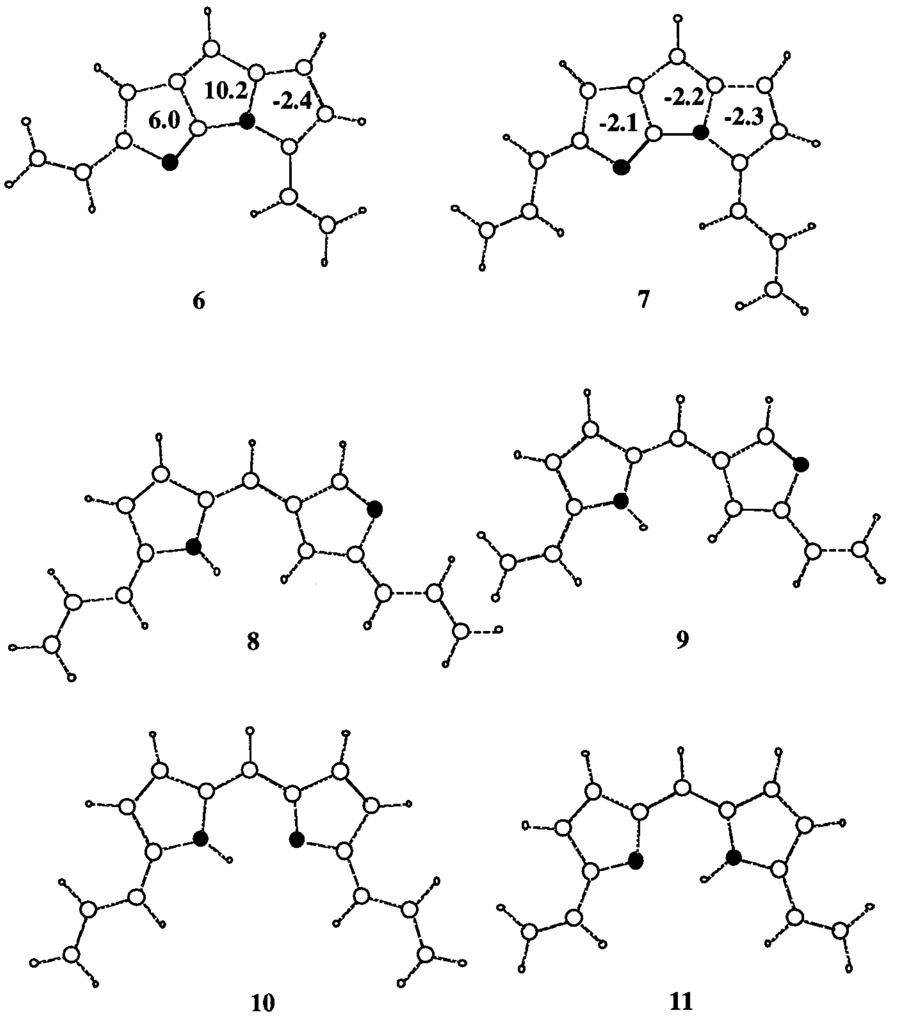


Fig. 2. A comparison of HOMO and LUMO energies for **1**–**5** calculated at B3LYP/6-31G* level.

energetically N_2FP seems to be a feasible synthetic target. A direct comparison of NFP and N_2FP, as in Eq. (5), gives an idea of extra strain energy required for N_2FP (**5**). From Eq. (5) it is clear that only 3.3 kcal mol^{-1} extra strain energy accumulates in N_2FP. It should be noted that all the above equations have not been corrected for their aromatic stabilization, which are different to each other.

4. Metal complexation of NFP

Porphyrin and its isomers, like NCP and N_2CP, are primarily tetradentate ligands, involved in stabilizing +2 and higher oxidation states. To achieve lower oxidation state, a common method is to reduce either chemically or electrochemically. One-electron reduction occurs either at the ligand to from the porphyrin π-radical cation ($M^{n+}P^{\bullet -}$) or to give lower oxidation metal-



6 **7**

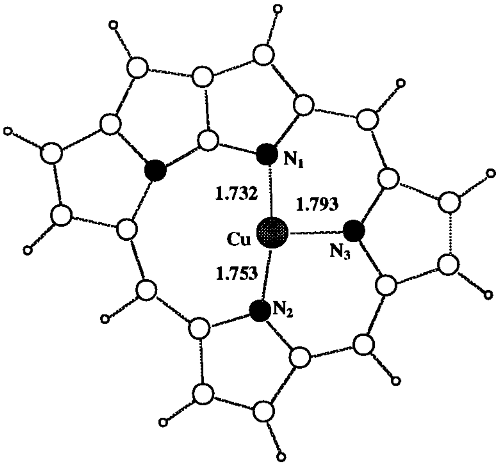
8 **9**

10 **11**

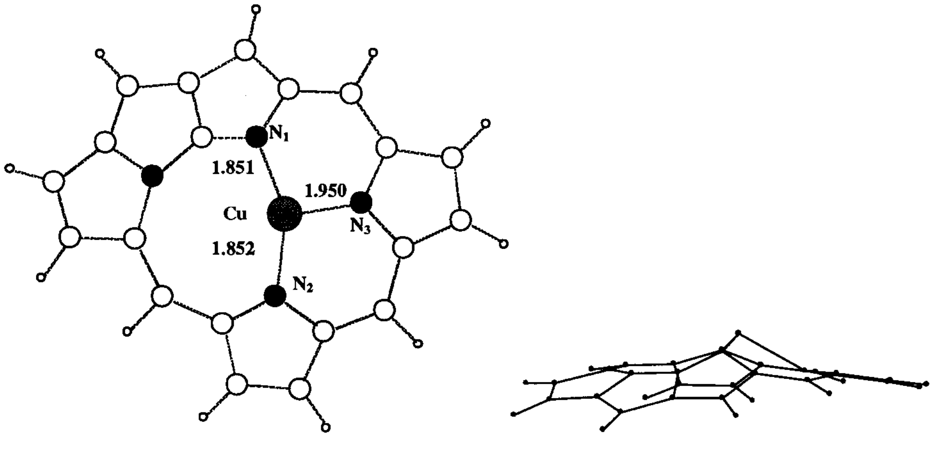
Fig. 3. Structures of reference molecules considered for strain energy calculations. NICS values (ppm) for **6** and **7** (in bold) are also given.

loporphyrin ($M^{(n-1)+}P$). When the energy levels of metal d orbitals and ligand π* orbitals are sufficiently close as in the case of Ni^{II} and Cr^{III}, it becomes difficult to assign unequivocally the oxidation state of the metal [18,19].

Kumar et al. examined the reduction of Cu^{II} porphyrin and found that one electron reduction results in π-radical anion and two electron reduction produces whether Cu^{II} phlorins or Cu^{II} chlorines [20]. NFP has a unique ligand environment; only three of the four N atoms are available for coordination and with one proton NFP can stabilize metals in the +1 oxidation state. We have investigated Cu^{I} complexation with NFP. The B3LYP/SVP optimized structures are shown in Fig. 4. Considering the ionic radius of Cu^{I} (0.96 Å) is considerably larger than Cu^{II} (0.72 Å), the planar (C_s) form is not expected to be a minimum. Frequency calculations at B3LYP/Lanl2DZ level show that structure **12** has three imaginary frequencies (820.0i, 77.8i and 35.2i cm^{-1}). Following the largest imaginary frequency leads to the structure **13**, which is 32.5 kcal mol^{-1} more stable in energy than the planar **12**. The overall structure of **13** reflects the dome conformation. The major structural changes are Cu–N distances. These are substantially elongated on going from planar form, **12** to the dome conformation, **13**. Both Cu–N_1 and Cu–N_2 distances are stretched from 1.732 to 1.851 Å and 1.753 to 1.852 Å. Similarly, Cu–N_3 distance is also elongated from 1.793 to 1.950 Å. These changes in the Cu–N distances reflect that the planar conformation is highly strained and the strain is considerably relieved in dome conformation. The HOMO and HOMO-1 of **13** are basically metal-based orbitals, while the LUMO is porphyrin based.



12 C_s **0.0 kcal/mol**



13 C_1 **-32.5 kcal/mol**

side view of **13**

Fig. 4. B3LYP/SVP optimized structures of Cu(I)NFP along with relative energies in kcal mol^{-1}.

5. Magnetic properties of porphyrins 1–5

The difficulties in evaluating stabilization energies and the strong dependence of ASE on the choice of reference systems make the energetic criteria a rather poor choice to understand aromaticity. To circumvent this problem, and for better understanding of the presence of ring current perhaps the best way is to use magnetic criteria. NICS calculations are readily done and reliable indicators of aromaticity. The main advantage of NICS is that it does not depend on the choice of the reference molecules. This eliminates subjectivity in the understanding of the aromatic character of related molecules. Since all the systems considered here are 26 π electron species, NICS values can be used for comparative purposes. Large negative values of NICS indicate aromatic character (e.g. -13.7 for benzene) and positive values indicate antiaromatic character ($+40.0$ for cyclobutadiene) and nearly zero for nonaromatic molecules (2.0 for cyclohexane).

The computed NICS values of all the systems along with ^{1}H chemical shifts are given in Fig. 1. Porphyrin and its isomers, NCP (**3**), and N_2CP (**4**), possess very similar NICS values (-16.5, -14.4 and -15.9, respectively), implying that pyrrole inversion has little effect on the global ring current. In addition, the pattern of local ring currents, which defines the ring current path, at individual five-membered rings, is also very similar (Fig. 1).

Both NFP (**3**), and N_2FP (**5**), show dramatic magnetic behavior. Formation of one fused five-membered ring, as in NFP, attenuates the global ring current to nearly half of the NCP value (NICS of NFP -8.2 and for NCP -14.4). However, fusing another five-membered ring as in N_2FP (**5**), does not further reduce the ring current as anticipated. Instead the NICS value of N_2FP is as large as that of N_2CP. Thus, N_2FP is more aromatic than NFP. This anomalous behavior of N_2FP can be rationalized by considering the local aromaticity at individual rings. In fact, the ring current in the reference systems **6** and **7** makes a point. While **6** is an antiaromatic 12 π electron tri-pentacyclic ring with large positive NICS values (see Fig. 1), **7** is nonaromatic with very small positive NICS values. However, when the tripentacyclic ring is a part of the aromatic system, there is a dramatic change in the NICS values. Huge negative NICS values of the five-membered rings in tripentacyclic part of NFP (-18.0, -24.6 and -20.1, see Fig. 1), not only indicate complete turnover in magnetic behavior compared to the isolated fragments (form nonaromatic/antiaromatic to highly aromatic) but also show that ring current is largely localized at the fused rings. Concentration of ring current at the fused five-membered rings explains the decrease in the global aromaticity of NFP. However, in N_2FP, effective interaction between the two tripentacyclic rings enhances the global aromaticity. Thus, N_2FP has more global ring current than NFP. The increased aromaticity in N_2FP over NFP is also manifested in a more downfield shift of *meso*-CH protons. The ^{1}H chemical shifts of *meso*-CH hydrogens in N_2FP (-11.3 ppm) compared to the average *meso*-CH chemical shifts in NFP (-9.5 ppm).

In conclusion, we have shown that in contrast to the NFP, N_2FP is nonplanar, more red shifted and more aromatic without much additional strain. NFP can form stable metal complexes with low-valent metal ions. Due to the larger core size of Cu(I) compared to Cu(II), complexation of Cu(I) with NFP results in dome conformation.

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