Perimeter Coordinated Diastereomeric Rh(I) Complex of Helically Twisted Weakly Aromatic Hybrid Singly N-Confused $\beta - \beta$ Fused Ferrocenoporphyrinoids

Nyancy Halder, Krushna Chandra Sahoo, Kumar Gourav, Dandamudi Usharani,* and Harapriya Rath*

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ABSTRACT: Expedient synthesis, spectroscopic, solid state structural proof, and theoretical study of helically twisted weakly aromatic hybrid singly N-confused ferrocenoporphyrinoids and the peripheral coordinated Rh(I) complex are reported. The X-ray crystal structure of the macrocycles reveals an ambiguously inverted pyrrole ring reinforcing regioselective β , β -linkage with the spatially adjacent N-confused N-methyl pyrrole ring leading to endocyclic extension of macrocyclic π -conjugation via tricyclic [5.5.5] moiety. The three-dimensional structure with built-in fused tricyclic [5.5.5] moiety has paved way to three-dimensional weak diatropicity with vis–NIR absorptions. The peripheral coordinated Rh(I) complex owing to helical chirality about the macrocyclic ring and planar chirality about the square planar Rh coordination



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site exists as a mixture of diastereomers (5:3) with well resolved ¹H NMR spectra anticipating weak aromaticity. The experimental spectroscopic measurements are in agreement with theoretically determined electronic structure and properties strongly elucidating sustained weak diatropic ring currents in twisted macrocycles both in neutral form and in the metalated complex. Further fragment molecular orbital approach and molecular orbital theory gave insights on the stability of N-confused $\beta-\beta$ fused oxo-ferrocenoporphyrinoids and formation of the selective peripheral coordinated Rh(I) complex.

INTRODUCTION

The chemistry of N-confused porphyrinoids has gained momentum over the years since the very first report by the Furuta and Latos-Grażyński groups¹ owing to their aromatic character, relatively long wavelength electronic absorption, and facile generation of organometallic derivatives with a large variety of metal ions (transition metals, main group metals, and lanthanides) along with the exceptional cases for stabilizing the unusual oxidation states of metals.² The asymmetric flexible skeleton of N-confused porphyrin favors more facile reinversion of N-confused pyrrole ring thereby sparking intramolecular bond formation (C-N bond formation between the inverted N-confused pyrrole ring and the neighboring pyrrole ring) or fusion in the inner core of the porphyrinoid via adequate chemical reactions leading to the novel N-fused porphyrins.³ The N-fused porphyrins are 18π aromatic compound with unexpected narrow HOMO-LUMO gap exhibiting absorption wavelength in the region of 800-1000 nm. It is worth mentioning that NIR absorptive/emissive chromophores have immense biomedical applications such as photodynamic therapy dyes and microscopic imaging agents.⁴ This has fostered fast growth of designing and synthesizing NIR absorbing/emissive porphyrinoids via altering the extent of π -conjugation and the degree of distortion from the planarity of the macrocycle. The N-confusion-fusion dichotomy conglomerated with the bathochromic effects brought about by fusion in tetrapyrrolic N-confused porphyrinoids has thus up-surged scientific demands for unraveling more and more such structural analogues. In our pursuit to foster global macrocyclic aromaticity (antiaromaticity) with NIR absorption in the smallest⁵ N-confused porphyrinoids, very recently we reported [16] planarantiaromatic trans-doubly N-confused porphyrinoids with NIR absorption^{6a} and NIR absorbing planar-aromatic [18] dithia and diselena trans doubly N-confused porphyrinoids.⁶ This antiaromaticity-aromaticity switching via reshuffling of core N(s) with S/Se_{1}^{6} and/or number of built-in carbo- or heterocycles, provided us clues for further development of novel N-confused porphyrinoids with fine-tuned properties. Additionally and most importantly, the chemistry of nonplanar aromaticity is an ever growing research field owing to the fact that deviation from planarity strongly perturbs the properties of π -systems.⁸ Twisted aromatics are one of the nonplanar π systems exhibiting chiroptical properties and dynamic behavior because of their helical molecular geometries.⁹ The creation of

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such nonplanar π systems has thus warranted much scientific interest to understand the limits and possibilities of such π systems. It is a well-known fact that the rotation of the two cyclopentadienyl rings about the Cp-Fe-Cp axis¹⁰ in the paradigmatic structural feature of ferrocenyl unit has been heralded as flexible "helicity-elements" in ansa-bridged systems¹¹ and ferrocene-containing peptides.¹² A noteworthy outcome of such helical structure is the high stereoselectivity¹³ of some of metallocene based polymerization catalysis. These amalgamated structural and scientific features of ferrocene in conjunction with the N-confused-fused dichotomy thus stimulated us to fundamentally explore the overwhelming π conjugation sustainability or the disruption of overall macrocyclic delocalization pathway leading to (or lack of) diamagnetic ring current upon incorporation of a ferrocenyl bridge in the conjugation pathway of N-confused porphyrinoids^{6a} by swapping one of the N-methyl pyrrole based precursor with a related ferrocene based precursor (Chart 1).

Chart 1. Swapping Planarity with Helicity



It is worth mentioning that under the fascinating attributes of N-confused-fused porphyrinoids,^{3b} incorporating a ferrocenyl moiety in the macrocyclic conjugation pathway of Nconfused porphyrinoids remains unprecedented so far,¹⁴ though there are previous reports of ansa-metallocene porphynoids (I-IV, Chart 2)¹⁵ of which ferrocenothiaporphyrin and dihydroferrocenothiaporphyrin (Chart 2, III) anticipated macrocyclic antiaromaticity and aromaticity providing evidence for direct transmission of π -electron conjugation across a d-electron metallocene.^{15a} Interestingly, ruthenocenoporphyrinoids^{15e} with an identical number of π electrons exhibited π -conjugated surface with topologically distinct states anticipating macrocyclic aromaticity and antiaromaticity owing to metallocene (ruthenocene) conformation. Thus, through this manuscript, we report the retrosynthesis and the structural isolation of hitherto unknown ferrocene bridged N-confused $\beta - \beta$ fused oxoporphyrinoids and the selective peripheral coordinated Rh(I) metal complex with ambiguity in pyrrole ring inversion. Most intriguingly, the ambiguous $C_{\beta} - C_{\beta}$ bond anticipated in the N-confused porphyrinoids leading to the formation of fused tripentacyclic ring [5.5.5] remained experimentally hitherto challenging as

Chart 2. Examples of Ferrocene Bridged Porphyrinoids



these happen to be the highly energetic isomers.¹⁶ Thus, it is scientifically warranted to understand the preferential formation of the $C_{\beta}-C_{\beta}$ bond via a pyrrole ring inversion¹⁷ via theoretical modeling of the related N-confused fused and Nconfused C–C fused porphyrinoids with (without) ferrocenyl bridge. The details of such studies are described in our manuscript in addition to spectroscopic and solid state structural analyses of newly reported macrocycles.

RESULTS AND DISCUSSION

Scheme 1 reveals potentially interesting [3 + 1] acid catalyzed conventional oxidative condensation reaction of ferrocene tripyrrane $3/5^{15a}$ [synthesized from the dicarbinols $2/4^{18}$] and N-confused N-methyl dicarbinol 8^{6a} using p-toluenesulfonic acid (p-TSA) followed by subsequent chloranil oxidation^{6a} toward rational synthesis of singly N-confused $C_{\beta}-C_{\beta}$ fused oxoporphyrinoids 9/10. Repeated column chromatographic separation by silica gel (200–400 mesh) and preparative thin layer chromatography (PTLC) has led to the exclusive formation of 9/10 in 50% and 40% yield as the only product. Using 0.185 equiv of p-toluenesulfonic acid catalyst and high boiling solvent 1, 2-dichloro ethane solvent has led to the optimum yield of the desired products.

The new macrocycles have been thoroughly characterized via various spectroscopic and single-crystal X-ray diffraction analyses. The elemental composition of 9 and 10 were confirmed by positive-mode ESI-TOF mass spectrometry, which showed the parent ion peak at m/z 834.1825 and 906.1451 corresponding to macrocycles 9 and 10, respectively, with one oxo group (Figures S7-S8). The presence of CO group has been confirmed by a band at 1719 cm⁻¹ for 9 and 1722 cm^{-1} for 10 in the IR spectrum (Figures S10-S11). The electronic absorption spectrum of 9 displays a sharp Soret type band at 356 nm with a shoulder at 412 nm followed by an intense Q-band at 551 nm and a broad Q-band at 740 nm tailing up to 900 nm typifying porphyrinic nature with aromaticity^{19a} conjoined with a fused tripentacyclic [5.5.5] ring within macrocyclic cavity.^{3a,19b} The electronic absorption spectrum of 10 is extremely similar in shape and structure to the spectrum of 9 with an intense Soret like band at 346 nm, shoulder at 407 nm, and broad Q-type absorptions at 541 and 720 nm tailing up to 900 nm (Figure 1A).

The final confirmation for the formation of the macrocycle **9** has been achieved from solid state single crystal X-ray diffraction analysis. X-ray quality single crystals were obtained from slow evaporation of hexane/CH₂Cl₂ solutions of **9**. The ambiguity in the crystal structure is the C–C bond formation between pyrrole β positions (N-confused N-methyl pyrrole ring and the inverted imino type pyrrole ring)²⁰ in sharp contrast to the expected singly N-confused ferroceno



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Scheme 1. Synthesis of Macrocycles 9, 10, and 11



Figure 1. (A) UV-vis absorption spectra of 9/10 in CH₂Cl₂. (B,C) X-ray crystal structure of 9. B: Top view; C: Side view. Solvent molecules and hydrogen atoms except for β -CHS and N-CH₃ are omitted for clarity.

porphyrinoids 13/14.^{6a} This could be due to steric repulsions among many core hydrogens in case of 13/14. The unit cell anticipated the existence of four enantiomers with *P* and *M* helical configurations (only one enantiomer is shown in Figure 1B). The cyclopentadienyl rings happened to be in an anticlinal staggered conformation (the Cp-Ct-Ct'-Cp' torsional angle Φ equals 105.16°, Ct and Ct' denote centroids of the respective Cp rings, Cp = C8_1, Cp' = C13_1). Altered bond length distances with $C_{\alpha}-C_{\beta} > C_{\beta}-C_{\beta}$ (Table S1) in the pyrrole rings and the altered inner carbon–carbon bond length distances in the fused tripentacyclic ring [C(25)–C(26), C(35)–C(25), C(34)–C(35), and C(26)–C(23)] explicitly indicate the π -conjugation pathway through the amine pyrrole and fused tricyclic [5.5.5] moiety in the macrocycle 9.²¹

Macrocycle **10** lacks solid state structural proof at this moment.

The structural rigidity of the macrocycles 9/10 is well evident from temperature independent ¹H NMR spectral patterns (Figure S28). For the macrocycle 9 at ambient temperature, the broad peak at 5.62 ppm corresponding to NH of amino-type pyrrole ring has been confirmed based on the HSQC spectra (Figure S32) with lack of correlation with any carbon signal. In the 2D ROESY spectra (Figure S30), observation of the correlation between the peak at 5.62 and 2.69 ppm reveals the later signal as –CH proton (a) of ferrocene moiety. Such substantial shielding of ferrocene proton²² can be attributed to an appreciable degree of π -delocalization in the macrocycle where the electronic structure of ferrocene is affected by macrocyclic conjugation (though the

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Figure 2. (A) Completely assigned ¹H NMR spectra of 9. (B) Completely assigned ¹H NMR spectra of 11 in CD₂Cl₂ at 298 K.



Figure 3. (A) Cyclic voltammogram of 9 ($\sim 10^{-4}$ M). (B) Cyclic voltammogram of 10 ($\sim 10^{-4}$ M) in CH₂Cl₂ containing tetrabutylammonium perchlorate (0.01M) recorded at 100 mV s⁻¹ at 298 K.

ferrocene ring retains most of its peak positions which could be due to anticlinal staggered conformation). Complete assignment of all the individual signals (Figure 2A) has been achieved through a combination of homonuclear correlation techniques (COSY, Figure S29; ROESY, Figure S30) and heteronuclear correlation techniques (HSQC, Figure S32; HMBC, Figure S33). A similar NMR spectral pattern has been anticipated for macrocycle 10 (Figures S35-S42). The asymmetric nature of both the macrocycles 9 and 10 has been well anticipated with the distinct observation of four and eight signals in ¹⁹F NMR spectra (Figure S51). The helically twisted N-confused $\beta - \beta$ fused porphyrinoids 9 and 10 being unsymmetrical^{3a,c} in nature with an anticlinal staggered conformation of ferrocene (as anticipated from solid state Xray diffraction analysis of 9), observation of strong diamagnetic ring current is not expected for 9 and 10.^{15a} Most importantly, reduced aromaticity has been anticipated in most of the Nsubstituted N-confused porphyrinoids reported to date.23a,b

Thus, based on the observed chemical shift premises, macrocycles 9/10 could be qualitatively envisioned as weakly aromatic.²³

The macrocycles 9 and 10 have been found to be robust against electrochemical oxidation and reduction. Electrochemical properties of the new macrocycles were probed with cyclic voltammetry in dichloromethane using 0.1 M tetrabutylammoniumhexafluorophosphate as a supporting electrolyte. The macrocycle 9 exhibits two reversible waves for oxidation process at 0.51 V, 0.73 V and an irreversible oxidation wave at 1.25 V, while one irreversible reduction peak has been detected at ca. -1.05 V followed by a quasireversible reduction peak at ca. -1.52 V yielding an estimate of the electrochemical HOMO–LUMO gap (HLG) of 1.56 V (Figure 3A). Compared to bare ferrocene (Figure S54), the more positive (~90 mV) shift of oxidation potential can be accounted for the electronic interaction between macrocyclic π -system and the electroactive ferrocenyl moiety, which

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Figure 4. (A) NICS (0) value of 9a, 10, and 11a at B3LYP/LanL2DZ (Fe, Rh) and $6-31+G^{**}$ (for rest of the atoms) level of theory. (B) AICD plot of 9a, 10, and 11a at B3LYP/LanL2DZ (Fe, Rh) and $6-31+G^{**}$ (for rest of the atoms) level of theory.

becomes harder to oxidize. The low HLG gap reflects helically extended π -conjugation²⁴ in addition to a fused tripentacyclic [5.5.5] modality within the macrocyclic cavity.^{3a} On a similar note, **10** exhibits the two reversible waves for oxidation process at 0.54 and 0.75 V, while the first irreversible wave for the reduction process is at -1.03 V with an estimated HOMO–LUMO gap of 1.57 V (Figure 3B). The slightly higher HOMO–LUMO gap of **10** is in line with the observed electronic absorption spectra (Figure 1A), where relatively blue-shifted bands are anticipated in contrast to **9**.

Since, on the basis of our experimental characterization data, the type of electronic interaction between macrocyclic π system and ferrocenyl moiety in 9/10 is not clearly understood, DFT level geometry optimization has been carried out for fused and nonfused porphyrinoids with and without ferrocenyl bridge (9–20, Scheme 2) at B3LYP/LanL2DZ (Fe, Rh) and 6-31G** (for rest of atoms) level of theory²⁵ using the Gaussian 16 program.²⁶ Additionally the corroboration of the selective formation of 9/10 over 13/14 and the observed solution state weak aromaticity of 9/10 have been revealed. A comparative thermodynamic energy difference between 16 and 15 (11.0 kcal/mol) vs N_1 CP and TPP (23.63 kcal/mol)¹⁷ indicates N-confused porphyrinoids are stabilized with ferrocenyl unit incorporation. 13b, an intermediate structure of 9a and 13a, is 15.87 kcal/mol higher in energy than 13a due to induced additional ring strain as a result of inversion of normal pyrrole ring (Scheme 2, Figure S60). The thermodynamic stability of nonfused ferroceno porphyrinoids (13-16) is also reflected with the positive NICS $(0)^{27}$ and anticlockwise ring current of anisotropy induced current density (AICD)²⁸ plots indicating the antiaromatic nature of these macrocycles (Figures S63, S64). However, the π conjugation pathway of Scheme 3. (A) Mixing of Fragment Molecular Orbitals and Resulting Molecular Orbitals in Nonfused Ferrocenoporphyrinoid 13a; (B) Fused Ferrocenoporphyrinoid 9a; (C) Donor–Acceptor Orbitals Contribution for the Formation of N–M Bond in 11a



Figure 5. (A) UV-vis absorption spectra of 9/11 in CH₂Cl₂. (B,C) Molecular structure of 11a. B: Top view; C: Side view. Solvent molecules and hydrogen atoms except for β -CHs and N-CH₃ are omitted for clarity.

these macrocycles and degree of NICS (0) values depend on the twist induced due to the ferrocene unit. Therefore, we calculated the strain in the macrocyclic rings via defining the dihedral planes between the rings labeled as 1-5. Figure S67 depicts the strain/helicity of the macrocyclic rings through the dihedral angles (χ) between the ring planes. In 13a and 14, due to oxo N-confused pyrrole ring, there is an increase in the dihedral angle between ring planes [2-3:31.7° and 31.9°, 5-1:29.9° and 27.3° leading to distorted 2p orbitals at the meso center (Figure S67) and favoring the eclipsed conformation of FeCp₂. Further, in 13b due to the inversion of pyrrole ring, there could be a partial twist and out of phase orbitals at the meso center that could further lower the antiaromatic nature gradually. Also, the substitution of difluoro aryl at the meso center has reduced the electron density of 1-3 rings in the case of 14.

In stark contrast, fused ferrocenoporphyrinoids (9a and 10) have distinctly reduced localized aromaticity of the rings and

negative NICS (0) values $(-2.03 \text{ and } -4.96 \text{ ppm})^{23a}$ (Figure 4A) with clockwise ring current AICD plots (Figure 4B) signifying a weak aromatic nature. It is also reflected that the strain of the rings (Figure S67) is observed for 1-2 (31.8°, 36.0°, and 33.1°) and 2–3 ring planes (39.3°, 40.4°, and 37.8°). Near planar tripentacyclic ring (2' and 2'') induced strain to the adjacent pyrrole ring and FeCp₂ leading to staggered orientation of FeCp2 and a double twist in the porphyrinoids 9a and 10 with weak aromaticity. The earlier report on ferrocenothiaporphyrin and dihydroferrocenothiaporphyrin^{15a} indicated the $4n+2/4n \pi$ electron source of metallocene to macrocycle being crucial for paratropic/ diatropic macrocyclic ring current. We further analyzed the molecular orbitals of fused and nonfused porphynoids to understand the altered electronic structure of macrocycles and their nature.

The correlation diagram of the frontier molecular orbitals (Figure S68) of fused ferroceno porphyrinoid (9a) and

nonfused (13a) depicts the variation in nature and energy levels of π^{*}_{4} (HOMO) ferrocenyl bridge in the macrocycles (9/13) that has led to contribution of iron d orbitals to $a_{1\omega} a_{2\omega}$ and e_o thereby increasing the energy of the HOMO and lowering of LUMO orbital compared to TPP, whereas the additional stabilization of HOMO orbital in 9a compared to 13a is due to mixing of meso center 2p orbitals with pyrrole 2p orbitals in a fused tripentacyclic ring. In simple way, the lowering of the HOMO orbital can be explained by the mixing of fragment $FeCp_2$ (Ψ_{Fecp2}) orbitals and heterocyclic ring orbitals (Py₁, Py₂ and Py₃) (Scheme 3). The fragment orbitals of pyrrole (Ψ_{py1} and Ψ_{py2}) are closer to Ψ_{Fecp2} causing increased mixing of orbital and higher HOMO level in 13a (Scheme 3A). Contrarily, the fused ring (Ψ_{Py2}) and pyrrole (Ψ_{Pv1}) are far apart in **9a** having differential mixing with Ψ_{Fecp2} orbitals thereby reducing the energy of HOMO (Scheme 3B). This leads to an increased HOMO-LUMO gap supporting the stability of 9a over 13a (Scheme 3). The transition of $\pi_4^* - \pi_5^*$ (HOMO–LUMO) explains the absorption of visible region bands in the steady state absorption spectra of 9/10 and is in accord with the experimental spectroscopic observations (Figures S56 and S57, Table S8, S9).

The ambiguously formed $C_{\beta}-C_{\beta}$ fused tripentacyclic ring in ferrocenoporphyrinoids (9/10) has led to a relatively small and congested inner cavity of both the macrocycles. This has been anticipated with the selective peripheral coordination of 9 with Rh(I) metal (in contrast to other transition metals such as Ni, Pd, Cu) under inert condition at ambient temperature leading to complex 11 as brown solids in 93% yield, while isolation of Rh(I) complex 12 was not possible at our end. The elemental composition of 11 was confirmed by positive-mode ESI-TOF mass spectrometry, which showed the parent ion peak at m/z992.0708 (Figure S9). The bands for C=O group in the IR spectrum of 11 (Figure S12) are observed at 1735.5, 1997.12, and 2071.09 cm⁻¹.

The steady state electronic absorption spectral pattern of **11** remained almost invariant with respect to **9**, convincing for the possibility of peripheral coordination of $Rh(I)^{29}$ with the observation of a Soret band at 352 nm, shoulder at 422 nm, intense Q-type band at 583 nm (32 nm red-shifted compared to **9**), and broad band at 758 nm tailing up to 1000 nm (Figure 5A) (~100 nm red-shifted compared to **9**).

The ¹H NMR spectral pattern of Rh(I) complex 11 also strongly supported peripheral coordination of rhodium to the inverted imine type pyrrole nitrogen atom of the macrocycle 9 (Figure 2B). The spectrum displayed two sets of signals in the entire region. On the basis of the relative peak intensities, the acquisition of two isomers 11a and 11b (Figure 2B) could be visualized. The induced chemical shift nonequivalence in the ¹H NMR spectra (with meagerly distinguishable anisochronous NMR resonances) may be due to helical chirality about the macrocyclic ring and plane chirality about the square planar Rh coordination site leading to the existence of diastereomers 11a and 11b (via orientation of chlorine atom with respect to the N-Rh bond) (Figure 2B). To differentiate the isomers, labeling has been done in red and blue alphabets (Figure 2B). On the basis of the correlations observed in the 2D spectra (Figures S44–S49), signals for the existence of two diastereoisomers of Rh(I) complexes 11a and 11b could be assigned. Temperature dependent NMR studies were carried out for exploring the possible isomeric selectivity (Figure S43). Though the sparingly soluble nature of 11 in the high boiling deuterated solvent made it difficult to record variable high

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temperature ¹H NMR spectra, at lower temperatures, however, no drastic change was visible, nor was any shift in the ppm values for the signals. This clearly indicates the existence of the nonequilibrating isomers **11a**, **11b**. The ratio of the two isomers was found to be 5:3 based on the integration ratio of the proton signals in ¹H NMR spectroscopy and was further strongly concluded from the integration of the observed eight signals in ¹⁹F NMR spectra of **11** (Figure S51) in sharp contrast to four signals for **9**. A comparative ¹H NMR spectra of the rhodium complex **11** with its free base **9** (Figures 2A, 2B) reveals meagre change in the chemical shift values of each proton signal in **11** compared to **9**, strongly supporting an outer coordinating fashion of rhodium metal.

The peripheral coordination of Rh(I) in 11 has been finally confirmed by solid state single crystal X-ray diffraction analysis where structural proof of only one of the isomers (11a) has been possible at our end (Figure 5B, 5C). The molecular structure of 11a is torsionally distorted, with the internal torsional angles of the helix varying in the range from -10.8 to 28.1° (Table S7). The two Cp rings in 11a adopt an anticlinal staggered conformation (the Cp-Ct-Ct'-Cp' torsional angle Φ equals 100.39° for 11a, Ct and Ct' denote centroids of the respective Cp rings, CCp = C14, CCp' = C22). The rhodium metal is coordinated to the inverted imine pyrrole nitrogen, and the other coordination sites of the metal are occupied by two carbonyl groups and one chloride. The geometry around the metal center is square planar, and the rhodium metal is oriented with an angle of \sim 72.85° to the plane of the fused tripentacyclic ring of the complex. The selected bond length parameters, dihedral angles, and torsional angles of 11a have been shown in tabulated form (Table S2, Table S4, Table S5, Table S7).

The aromaticity of 11a is also confirmed from NICS (0) value of -4.26 ppm (Figure 4A) and clockwise ring current as anticipated from ACID plot (Figure 4B). The peripheral coordination of Rh has reduced the mixing of outer ring and inner ring π -conjugation pathways of the fused tricyclic [5.5.5] moiety in the macrocycle leading to an enhanced inner ring π conjugation. The steady state absorption spectra of 11a are in accord with experiments exhibiting similar orbital transitions as anticipated in 9a (Figure S58). It is noted that, thermodynamically, diastereomer 11b is 1.52 kcal/mol higher than 11a (Figure S55), supporting the existence of these isomers in a 5:3 ratio in ¹H NMR spectra (Figure 2B). Further understanding of the frontier molecular orbitals of 9, metal salts, and 11a (Figures S72, S73) indicated that lone pair orbital of inverted imino pyrrole ring nitrogen $\left(N_{lp}\right)$ acts as the donor and the metal d orbital of Rh, Cu, Ni, and Pd salts act as acceptors. The lower energy of the metal acceptor $(\sigma^*_{x^2-y^2})$ orbital in Rh leads to a better interaction of the $N_{lp}\xspace$ donor that results in stabilizing N-Rh bond and ease of forming a peripheral coordination complex over other metal salts (Cu, Ni and Pd) (Scheme 3C and Figure S73). The perimeter coordinated Rh metal is also supported from electrochemical studies of 11. 11 exhibits the first quasireversible wave for oxidation process at 0.59 V followed by two irreversible oxidation processes at 1.09 and 1.53 V, while there are two irreversible waves for reduction process at -0.90 V and -1.39 V with an estimated HOMO-LUMO gap of 1.49 V (Figure S52). This lowering of HLG compared to 9 is in line with the ~ 100 nm redshift in the NIR region anticipated in the electronic absorption spectra of 11 compared to 9 (Figure 5A).

CONCLUSION

In summary, we have experimentally achieved the first ever ferroceno N-confused $\beta - \beta$ fused oxoporphyrinoids with an inverted pyrrole ring debating the frequently asked open question for pyrrole ring flipping in more compact N-confused tetrapyrrolic porphyrinoids and/or porphyrinoids. The consequence of such pyrrole ring inversion is the configurationally enforced $\beta - \beta$ linkage with the N-confused pyrrole ring leading to the formation of fused tripentacyclic rings and thus exhibiting the signatorial electronic absorption spectral pattern tailing up to the vis-NIR region. Comparison of electronic structure, bonding of fused and nonfused porphyrinoids with ferrocenyl bridge through fragment molecular orbital approach elucidated the stability of N-confused $C_{\beta}-C_{\beta}$ fused hybrid ferrocenoporphyrinods and the selective peripheral mode of coordination of Rh(I) metal. We would explore electronically intriguing analogues of such types of retrosynthetically designed axial chiral macrocycles in order to anticipate their practical use as chiral auxiliaries or chiral ligands for catalytic asymmetric synthesis. Synthesis of such dynamic porphyrinoids is currently under progress from the author's laboratory.

EXPERIMENTAL SECTION

Materials and Methods. Electronic absorption spectra were measured with a PerkinElmer Lambda 950 UV-visible-NIR spectrophotometer. ¹H NMR spectra were recorded on a Bruker AVIII 500 MHz spectrometer, Bruker AVIII 400 MHz, Bruker DPX-300 MHz spectrometer and chemical shifts were reported as the delta scale in ppm relative to CHCl₃ (δ = 7.26 ppm) and CH₂Cl₂ (δ = 5.32 ppm) as internal reference for ¹H and ¹³C NMR CHCl₃ (δ = 77.00 ppm) and CH₂Cl₂ (δ = 55.00 ppm). Structural assignments were made with additional information from gCOSY, gROESY, gHSQC, and gHMBC experiments. ESI HR-MS data were recorded using a Waters QTOF Micro YA263 spectrometer. All solvents and chemicals were of reagent grade quality, obtained commercially, and used without further purification except as noted. For spectral measurements, anhydrous dichloromethane was obtained by refluxing and distillation over CaH2. Dry THF was obtained by refluxing and distillation over pressed sodium metal. Thin layer chromatography (TLC) was carried out on alumina sheets coated with silica gel 60 F₂₅₄ (Merck 5554), and gravity column chromatography were performed using Merck Silica Gel 230-400 mesh. Aluminum Oxide (Basic) grade II was purchased from Sigma-Aldrich.

X-ray Structure Determination. A suitable shining green crystal of size $0.1 \times 0.1 \times 0.1$ mm³ of free base 9 was mounted on a Bruker APEX-III CCD diffractometer with a fine-focus sealed tube Mo K α radiation ($\lambda = 0.71073$ Å) X-ray source. The total exposure time was 9.60 h. The frames were integrated with the Bruker SAINT Software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 36 892 reflections to a maximum θ angle of 27.27° (0.78 Å resolution), of which 8381 were independent (average redundancy 4.402, completeness = 98.4%, R_{int} = 8.67%, R_{sig} = 7.39%) and 6142 (73.28%) were greater than 2σ (F^2). The final cell constants of a = 6.7646(13) Å, b = 11.332(2) Å, c =49.598(10) Å, $\beta = 93.769(6)^{\circ}$, volume = 3793.8(13) Å³, are based upon the refinement of the XYZ-centroids of 9908 reflections above $20 \sigma(I)$ with 4.874° < 2θ < 53.97°. Data were corrected for absorption effects using the multiscan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.595. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9550 and 0.9550. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P121/c1, with Z = 4 for the formula unit, $C_{51}H_{31}F_4FeN_3O$. The final anisotropic full-matrix least-squares refinement on F^2 with 619 variables converged at R1 = 8.68%, for the observed data and wR_2 = 24.94% for all data. The goodness-of-fit was 1.055. The largest peak in the final difference electron density synthesis was 0.906 $e^{-}/Å^{3}$ and

the largest hole was $-0.909 \text{ e}^-/\text{Å}^3$ with an RMS deviation of 0.109 e⁻/Å³. On the basis of the final model, the calculated density was 1.460 g/cm³ and F(000), 1712 e⁻.

A suitable shining green crystal of size $0.1 \times 0.1 \times 0.1 \text{ mm}^3$ of Rhcomplex 11 was mounted on a Bruker APEX-III CCD diffractometer with a fine-focus sealed tube Mo K α radiation ($\lambda = 0.71073$ Å) X-ray source. The total exposure time was 4.30 h. The frames were integrated with the Bruker SAINT Software package using a narrowframe algorithm. The integration of the data using a triclinic unit cell yielded a total of 28 964 reflections to a maximum θ angle of 27.51° (0.77 Å resolution), of which 11 877 were independent (average redundancy 2.439, completeness = 99.1%, R_{int} = 3.90%, R_{sig} = 4.72%) and 10362 (87.24%) were greater than 2σ (F^2). The final cell constants of a = 13.130(4) Å, b = 13.707(4) Å, c = 16.508(5) Å, $\alpha =$ $86.227(9)^{\circ}, \beta = 87.130(10)^{\circ}, \gamma = 61.680(9)^{\circ}, \text{ volume} = 2609.1(14)$ Å³, are based upon the refinement of the XYZ-centroids of 9658 reflections above 20 σ (I) with 5.857° < 2 θ < 54.97°. Data were corrected for absorption effects using the multiscan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.746. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9330 and 0.9330. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P1, with Z = 2 for the formula unit, C53H31ClF4FeN3O3Rh. The final anisotropic fullmatrix least-squares refinement on F^2 with 597 variables converged at R1 = 4.61%, for the observed data and wR2 = 11.06% for all data. The goodness-of-fit was 1.066. The largest peak in the final difference electron density synthesis was $0.706 \text{ e}^{-}/\text{Å}^{3}$ and the largest hole was $-0.769 \text{ e}^-/\text{Å}^3$ with an RMS deviation of 0.083 e $^-/\text{Å}^3$. On the basis of the final model, the calculated density was 1.308 g/cm^3 and F(000), 1036 e⁻. SQUEEZE program was used for final refinement of 11.

Computational Chemistry. X-ray crystal structures of 9, 11a, and 11b along with the observed ¹H NMR spectra were optimized using hybrid density functional B3LYP^{25a,b,c} and LanL2DZ^{25d,e,f} (for metal atoms) and 6-31G** basis set.²⁵ On the basis of 9 and 11a, 9b, 11c, and 10 were built and optimized. Electronic structure modeled structures of ferrocenoporphyrin (15), ferroceno N-confused porphyrin (16) and ferroceno N-confused oxoporphyrin (13a, 14), and pyrrole inverted ferroceno N-confused oxo porphyrin (13b) were optimized at the same level of theory. The electronic structure of Xray crystal structure of N-fused porphyrin (17), modeled N-confused C-fused porphyrin (18, 19), and N-confused C-fused oxo porphyrin (20) were also optimized at the same level of theory. Harmonic vibration frequency analysis of optimized structures (9-20) at same level of theory confirms them as stationary points. The stimulated steady state absorption spectra was obtained for 9, 10, 11a, and 11b from time dependent density functional (TD-DFT)³¹ method in the presence of dichloromethane solvent with implicit polarizable continuum model (PCM) using the integral equation formalism variant (IEFPCM)³² at B3LYP/LanL2DZ (for metal atoms) and 6-31G** (for all other atoms) level of theory. The nature of aromaticity of these molecules (9-20) were assessed from the nuclear chemical independent shift²⁷ NICS (0) value and anisotropy of the current-induced density $(ACID)^{28}$ that employs gauge independent atomic orbital (GIAO) method³³ and the continuous set of gauge transformations (CSGT)³⁴ methods, respectively. AICD plot was plotted using POVRAY 3.7 for Windows. Fragment molecular orbital diagram was constructed based on frontier Kohn-Sham molecular orbital analysis of optimized geometries of 9 and 11, $Rh(Cl)(CO)_{2}$, (Rh(Cl)(CO)₂)₂, Ni(CH₃COO)₂, Pd(CH₃COO)₂, and Cu- $(CH_3COO)_2$ complexes. All the above-mentioned calculations were done using Gaussian 16 A.03.²

Synthesis. Synthesis of 2. To a 250 mL round-bottomed flask equipped with a magnetic bar, ferrocene (1.32 g, 7.13 mmol) was placed followed by dry THF (40 mL). The reaction mixture was stirred under inert atmosphere. $N_iN_iN'_iN'$ -Tetramethyl ethylenediamine (3.2 mL, 0.021 mol) was added followed by stirring for half an hour at room temperature. Afterward *n*-BuLi in hexane (1.6 M) (13.04 mL, 0.021 mol) was added through rubber septa dropwise, and yellow turbidity started forming. The reaction mixture was stirred at

room temperature for 2 h and then heated in an oil bath to 66 °C for 1 h. The reaction mixture was brought to room temperature after which it was brought to ice cold temperature. At ice cold temperature, benzaldehyde (1.72 mL, 0.017 mol) in dry THF (40 mL) was then added dropwise to the reaction mixture, and the reaction mixture was stirred for 2 h. The reaction mixture was quenched by saturated NH₄Cl (aq) solution, product was extracted by diethyl ether, and dried over Na₂SO₄. The crude product was precipitated out by hexane and purified by silica gel column chromatography using ethyl acetate—hexane (1:4) solution. The solvent was removed under reduced pressure to yield 2. Yield 2.00 g (70%). Mp 124–126 °C.

Anal. Calcd for $C_{24}H_{22}FeO_2$: C, 72.38, H, 5.57. Found: C, 71.74, H, 5.80. ¹H NMR (CDCl₃, 300 MHz) δ 7.23–7.47 (m, 10H), 5.51 (s, 1H), 5.42 (s, 1H), 4.15–4.45 (m, 10H), ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 144.3, 143.7, 128.5, 128.4, 127.1, 126.4, 126.3, 72.9, 72.1, 68.4, 67.1. HRMS (ESI-TOF) m/z [M]⁺ Calcd for $C_{24}H_{22}FeO_2$ 398.0970, found 398.0971.

Synthesis of 3. 2 (2.0 g, 5.05 mmol) was reacted with excess pyrrole (69 mL, 1.05 mol) in the presence of catalytic amount of TFA. After 45 min, reaction was quenched with DCM and neutralized with 0.1 N NaOH solution. The organic phase was extracted with DCM, water-washed for two times, and dried over anhydrous Na_2SO_4 . The excess solvent was removed in a rotary evaporator under reduced pressure. The crude mixture was purified by silica gel column using hexane–ethyl acetate (11:1) solution. Yield 2.3 g (92%).

Anal. Calcd for $C_{32}H_{28}FeN_2$: C, 77.42; H, 5.69; N, 5.64. Found: C, 77.53; H, 5.49; N, 5.34. ¹H NMR (CDCl₃, 300 MHz) δ 7.74 (br, 2H), 7.15–7.32 (m, 10H), 6.59 (s, 2H), 6.09 (s, 2H), 5.78–5.81 (m, 2H), 4.87 (s, 2H), 3.86–4.11 (m, 8H). ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 143.7, 134.8, 128.7, 128.6, 128.4, 126.7, 116.4, 108.2, 106.6, 69.7, 69.4, 69.2, 68.9, 44.9. HRMS (ESI-TOF) *m*/*z* [M + H]⁺ Calcd for $C_{32}H_{28}FeN_2$ 496.1602, found 496.1603.

Synthesis of 4. To a 250 mL round-bottomed flask equipped with a magnetic bar, ferrocene (1.32 g, 7.13 mmol) was placed followed by dry THF (40 mL). The reaction mixture was stirred under inert atmosphere. N,N,N',N'-Tetramethyl ethylenediamine (3.2 mL, 0.021 mol) was added followed by stirring for half an hour at room temperature. Afterward n-BuLi in hexane (1.6 M) (13.04 mL, 0.021 mol) was added through rubber septa dropwise, and yellow turbidity started forming. The reaction mixture was stirred at room temperature for 2 h and then heated in an oil bath to 66 °C for 1 h. The reaction mixture was brought to room temperature after which it was brought to ice cold temperature. At ice cold temperature, 2,6-difluorobenzaldehyde (1.8 mL, 0.017 mol) in dry THF (40 mL) was then added dropwise to the reaction mixture, and the reaction mixture was stirred for 2 h. The reaction mixture was quenched by saturated NH₄Cl (aq) solution, product was extracted by diethyl ether, and dried over Na2SO4. The crude product was precipitated out by hexane and purified by silica gel column chromatography using ethyl acetatehexane (1:4) solution. The solvent was removed under reduced pressure to yield 4. Yield 2.1 g (63%). Mp 130-132 °C.

Anal. Calcd for $C_{24}H_{18}F_4O_2Fe: C, 61.30; H, 3.86.$ Found: C, 61.91; H, 4.12. ¹H NMR (CDCl₃, 300 MHz) δ 7.16–7.25 (m, 2H), 6.82– 6.92 (m, 4H), 5.86 (m, 1H), 5.77 (s, 1H), 4.21–4.62 (m, 8H), 3.35 (br, 1H), 3.05 (br, 1H). ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 162.5, 159.2, 129.6, 112.4, 112.1, 68.7, 65.9, 64.9. HRMS (ESI-TOF) m/z[M + Na]⁺ Calcd for $C_{24}H_{18}F_4O_2FeNa$ 493.0490, found 493.0492.

Synthesis of 5. 4 (2.1 g, 4.46 mmol) was reacted with excess pyrrole (69 mL, 1.05 mol) in the presence of catalytic amount of TFA. After 45 min, reaction was quenched with DCM and neutralized with 0.1 N NaOH solution. The organic phase was extracted with DCM, water-washed for two times, and dried over anhydrous Na_2SO_4 . The excess solvent was removed in rotary evaporator under reduced pressure. The crude mixture was purified by silica gel column using hexane–ethyl acetate (11:1) solution. Yield 2.07g (82%).

Anal. Calcd for $C_{32}H_{24}F_4FeN_2$: C, 67.62; H, 4.26; N, 4.93. Found: C, 67.39; H, 4.28; N, 4.80. ¹H NMR (CDCl₃, 300 MHz) δ 8.12 (br, 2H). 7.16–7.25 (m, 2H), 6.89–6.62 (m, 4H), 6.62 (s, 2H), 6.09 (s, 2H), 5.95 (m, 2H), 5.55 (s, 2H), 3.95–4.08 (m, 8H). ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 162.5, 162.4, 159.1, 131.9, 128.3, 116.5, 112.1, 111.7, 108.1, 106.4, 70.1, 67.8, 68.7, 58.5. HRMS (ESI-TOF) m/z [M]⁺ Calcd for C₃₂H₂₄F₄FeN₂ 568.1225, found 568.1223.

Synthesis of 7. To a stirred solution of 2,6-difluorobenzoyl chloride (7.07 mL, 56.32 mmol) and anhydrous AlCl₃ (7.5 g, 56.32 mmol) in 41 mL dry DCM, *N*-methyl pyrrole (2 mL, 22.52 mmol) was added dropwise at room temperature. The reaction mixture was refluxed in an oil bath for 22 h in inert atmosphere. The completion of the reaction mixture was monitored by TLC. It was then quenched with aqueous NaHCO₃ in ice cold condition. The organic phase was extracted three times with DCM, water-washed, and dried over anhydrous Na₂SO₄. Solvent was removed under reduced pressure. The crude mixture was chromatographed on a silica gel column using hexane–ethyl acetate (4:1) solution. The solvent was evaporated and light yellow solid was obtained. Yield 3.2 g (40%). Mp 135–137 °C.

Anal. Calcd for $C_{19}H_{11}F_4NO_2$: C 63.16, H 3.07, N, 3.88. Found: C 63.19, H 3.09, N 3.83. ¹H NMR (CDCl₃, 300 MHz): 7.35–7.46 (m, 2H), 7.31 (s, 1H), 7.07 (s, 1H), 6.94–7.00 (m, 4H), 4.08(s, 3H). ¹³C{¹H} NMR (CDCl₃, 75 MHz): 181.6, 178.6, 160.8, 160.8, 160.7, 158.8, 158.8, 158.7, 136.8, 132.9, 132.0, 131.9, 131.9, 131.8, 131.7, 125.3, 123.2, 117.9, 117.7, 117.5, 112.2, 112.1, 112.0, 112.0, 111.9, 38.5. HRMS (ESI-TOF) m/z [M + H]⁺ Calcd for $C_{19}H_{11}F_4NO_2$ 362.0799, found 362.0796.

Synthesis of **8**. 7 (1.5 g, 4.1 mmol) was reduced with LiAlH₄ (1.26 g, 33.2 mmol) in dry THF under N₂ atmosphere for 4 h at 0 °C. The reduced product was extracted with EtOAc and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure to yield **8**. Yield 1.45 g (97%). Mp 164–166 °C.

Anal. Calcd for $C_{19}H_{15}F_4NO_2$: C, 62.47; H, 4.14; N, 3.83. Found: C, 62.45; H, 4.16; N, 3.82. ¹H NMR (CDCl₃, 300 MHz) δ 7.17–7.30 (m, 2H), 6.83–6.96 (m, 4H), 6.45 (br, 1H), 6.08 (br, 1H), 6.00 (s, 1H), 5.89 (s, 1H), 3.69 (s, 3H), 2.76 (br, 1H), 2.57 (br, 1H). ¹³C{¹H} NMR (CDCl₃,75 MHz) δ 132.3, 129.5, 128.8, 123.8, 128.8, 123.8, 121.7, 112.0, 111.8, 111.7, 111.5, 107.3, 62.9, 61.3, 34.1. HRMS (ESI-TOF) m/z [M + 3H]⁺ Calcd for $C_{19}H_{17}F_4NO_2$ 368.1268, found 368.1267.

Synthesis of **9**. Tripyrrane **3** (0.496 g, 1 mmol) and diol **8** (0.365 g, 1 mmol) were taken in a round-bottom flask, to which 740 mL of dry DCE was added and stirred for 15 min under nitrogen atmosphere to get a clear solution. *p*-Toluenesulfonic acid (0.035 g, 0.185 mmol) was added to the reaction mixture and stirred for 90 min under dark condition. After that, *p*-chloranil (0.735 g, 3 mmol) was added and the resulting mixture was refluxed in an oil bath for 90 min in open air. After complete removal of solvent from crude mixture by rotary evaporator, the compound was purified using basic alumina followed by repeated silica gel column chromatography using dichloromethane–hexane (3:2) solution to obtain compounds **9** as dark violet solid. Yield 418 mg (50%). Mp > 350 °C.

[9]: UV-vis (CH₂Cl₂, λ [nm], (ϵ [M⁻¹ cm⁻¹ × 10⁴]), 298 K) 356 (3.47), 412 (1.22), 551 (0.69), 740 (0.31). Anal. Calcd for C₅₁H₃₁F₄FeN₃O: C, 73.48; H, 3.75; N, 5.04. Found: C, 73.18; H, 3.25; N, 5.18. ¹H NMR (CD₂Cl₂, 500 MHz) δ 7.32–7.53 (m, 12H, Ph–CH), 6.91–7.09 (m, 4H, Ph–CH), 6.53 (s, 1H, Pyrrole-β-CH), 6.36–6.41 (m, 2H, Pyrrole-β-CH), 5.62 (br, 1H, NH), 4.65 (m, 1H, Fc-b), 4.47-4.48 (m, 2H, Fc-c,j), 4.25 (m, 1H, Fc-i), 4.23 (m, 1H, Fc-k), 3.85 (m, 1H, Fc-l), 3.79 (m, 1H, Fc-d), 2.95 (s, 3H, Methyl-CH), 2.69 (m, 1H, Fc-a). ${}^{13}C{}^{1}H{}$ NMR (CD₂Cl₂, 125 MHz) δ 178.7, 171.9, 171.4, 166.7, 162.5, 160.6, 156.7, 153.9, 144.4, 143.7, 139.7, 136.9, 135.6, 134.9, 133.5, 121.5, 130.9, 130.8, 130.2, 130.0, 130.0, 129.4, 129.1, 128.7, 128.4, 127.7, 127.7, 126.8, 126.3, 112.5, 112.3, 111.9, 108.4, 108.1, 94.3, 81.3, 79.1, 76.4, 75.3, 73.4, 73.7, 70.8, 70.6, 68.1, 31.7. ¹⁹F NMR (CD₂Cl₂, 376.5 MHz) δ -107.19, -108.07, -111.04, -112.19. HR-ESI-TOF (m/z) 834.1825 [M + H]⁺ (834.1827 calc. for $[C_{51}H_{31}F_4FeN_3O]^+$).

Synthesis of **10**. Tripyrrane **5** (0.568 g, 1 mmol) and diol **8** (0.365 g, 1 mmol) were taken in a round-bottom flask, to which 740 mL of dry DCE was added and stirred for 15 min under nitrogen atmosphere to get a clear solution. *p*-Toluenesulfonic acid (0.035 g, 0.185 mmol) was added to the reaction mixture and stirred for 90 min under dark condition. After that, *p*-chloranil (0.735 g, 3 mmol) was added and the resulting mixture was refluxed in an oil bath for 90 min

in open air. After complete removal of solvent from crude mixture by rotary evaporator, the compound was purified using basic alumina followed by repeated silica gel column chromatography using dichloromethane—hexane (2:3) solution to obtain compounds **10** as dark violet solid. Yield 364 mg (40%). Mp > 350 $^{\circ}$ C

[10]: UV-vis (CH₂Cl₂, λ [nm], (ϵ [\dot{M}^{-1} cm⁻¹ × 10⁴]), 298 K) 346 (3.29), 407 (1.21), 541 (0.69), 720 (0.26). Anal. Calcd for C₅₁H₂₇F₈FeN₃O: C, 67.64; H, 3.01; N, 4.64. Found: C, 67.24; H, 2.81; N, 4.62. ¹H NMR (CD_2Cl_2 , 500 MHz) δ 7.34–7.46 (m, 4H, Php-CH), 6.90-7.09 (m, 8H, Ph-m-CH), 6.50 (d, 1H, J = 4.5 Hz, Pyrrole- β -CH), 6.43 (s, 1H, Pyrrole- β -CH), 6.41 (d, 1H, J = 4.5 Hz, Pyrrole-β-CH), 5.62 (br, 1H, NH), 4.80 (s, 1H, Fc-b), 4.53 (m, 1H, Fc-c), 4.44 (m, 1H, Fc-j), 4.25 (m, 2H, Fc-i,k), 3.84 (m, 2H, Fc-l,d), 2.96 (s, 3H, Methyl-CH), 2.72 (m, 1H, Fc-a). ¹³C{¹H} NMR (CD₂Cl₂, 125 MHz) δ 178.6, 171.3, 162.6, 161.4, 161.1, 160.7, 159.5, 148.9, 140.7, 135.1, 130.9, 130.7, 130.5, 130.3, 129.8, 129.5, 126.4, 126.4, 125.4, 119.6, 117.4, 117.1, 116.4, 111.9, 111.8, 111.6, 111.5, 111.2, 111.0, 110.8, 108.4, 107.2, 99.6, 92.5, 85.3, 84.9, 81.1, 78.0, 74.2, 74.2, 73.5, 73.4, 71.3, 71.2, 69.9, 68.7, 27.0. ¹⁹F NMR (CD₂Cl₂, 376.5 MHz) δ -106.12, -108.12, -109.55, -109.69, -110.86, -111.90, -112.36. HR-ESI-TOF (m/z) 906.1451 $[M + H]^+$ (906.1449 calc. for $([C_{51}H_{27}F_8FeN_3O]^+)$.

Synthesis of 11 [P-RhCl (CO)₂]. A mixture of 9 (10 mg, 12.0 μ mol) and [RhCl(CO)₂]₂ (2.4 mg, 6.0 μ mol) in CH₂Cl₂ (20 mL) was stirred at room temperature for 1 h. The resulting solution was concentrated to dryness under reduced pressure, and the residue was recrystallized from CH₂Cl₂/hexane to afford the rhodium(I) complex 11 as a dark green powder. Yield 11.5 mg (95%). Mp > 350 °C.

11 as a dark green powder. Yield 11.5 mg (95%). Mp > 350 °C. [11]: UV-vis (CH₂Cl₂, λ [nm], (ϵ [M⁻¹ cm⁻¹ × 10⁴]), 298 K) 352 (3.61), 422 (1.39), 583 (0.84), 758 (0.29). Anal. Calcd for C₅₃H₃₁F₄FeClN₃O₃Rh: C, 61.92; H, 3.04; N, 4.09. Found: C, 61.82; H, 2.98; N, 4.14. ¹H NMR (CD₂Cl₂, 500 MHz) δ [A] 7.32-7.47 (m, 12H, Ph–CH), 6.92–7.02 (m, 4H, Ph–CH), 6.75 (s, 1H, Pyrrole-β-CH (h), 6.37-6.42 (m, 2H, Pyrrole-β-CH (e, f)), 5.79 (br, 1H, NH (g)), 4.95 (s, 1H, Fc-b), 4.60 (br, 2H, Fc-c,j), 4.29 (s, 1H, Fc-i), 4.27 (s, 1H, Fc-k), 3.74 (br, 1H, Fc-l), 3.70 (s, 1H, Fc-d), 2.88 (s, 3H, Methyl-CH, m), 2.78 (s, 1H, Fc-a); $[\mathbf{B}]$ 6.78 (s, 1H, Pyrrole- β -CH(h'), 6.40–6.43 (m, 2H, Pyrrole-β-CH(e',f')), 5.81 (br, 1H, NH (g')), 4.91 (s, 1H, Fc-b'), 4.57 (m, 2H, Fc-c',j'), 4.34 (s, 1H, Fc-i'), 4.27 (s, 1H, Fc-k'), 3.75 (m, 2H, Fc-d'), 3.64 (s, 2H, Fc-l'), 2.82 (s, 3H, Methyl-CH, m'), 2.84 (m, 1H, Fc-a'). ¹³C{¹H} NMR (CD₂Cl₂, 125 MHz) δ 196.6, 181.7, 171.5, 165.0, 156.9, 150.94, 150.95, 151.0, 147.6, 140.3, 140.2, 139.0, 135.0, 134.1, 133.4, 133.2, 131.7, 131.3, 129.9, 129.3, 128.7, 128.5, 128.4, 128.2, 128.1, 127.0, 125.8, 125.7, 125.5, 125.2, 122.3, 121.8, 121.2, 116.7, 112.6, 112.0, 111.9, 111.5, 111.4, 111.3, 111.1, 98.3, 92.1, 87.0, 86.0, 82.8, 81.2, 80.5, 80.4, 74.8, 74.6, 74.1,73.0, 72.8, 72.6,72.1, 71.4, 71.8, 70.9, 27.1. ¹⁹F NMR $(CD_2Cl_2, 376.5 \text{ MHz}) \delta [A] -108.12, -110.00, -114.86, -116.70;$ [B] -106.73, -112.76, -115.42, -115.75. HR-ESI-TOF (m/z) 992.0708 $[M - Cl]^+$ (992.0707 calc. for $([C_{53}H_{31}F_4FeN_3O_3Rh]^+)$.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00407.

Scheme S1, HR-ESI-TOF mass spectra, IR spectra, NMR spectra (¹H NMR, ¹³C{¹H} NMR, variable temperature ¹H NMR, ¹H–¹H COSY, ¹H–¹H ROESY, HMBC, HSQC, ¹⁹F), conformational dynamics of **9**, **10**, and **11**, and results of DFT calculations (PDF)

FAIR data, including the primary NMR FID files, for compounds 2-11 (ZIP)

Accession Codes

CCDC 2021819 and 2022192 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data request@ccdc.cam.ac.uk, or by contacting The

Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

- Dandamudi Usharani Department of Food Safety and Analytical Quality Control Laboratory, CSIR-Central Food Technological Research Institute, Mysuru 570020, Karnataka, India; Academy of Scientific and Innovative Research (AcSIR), CSIR-HRDC, Ghaziabad 201002, Uttar Pradesh, India; orcid.org/0000-0001-5728-9421; Email: ushad@cftri.res.in
- Harapriya Rath School of Chemical Sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India; orcid.org/0000-0002-5507-5275; Email: ichr@iacs.res.in

Authors

- Nyancy Halder School of Chemical Sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India
- Krushna Chandra Sahoo School of Chemical Sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India
- Kumar Gourav Department of Food Safety and Analytical Quality Control Laboratory, CSIR-Central Food Technological Research Institute, Mysuru 570020, Karnataka, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.1c00407

Notes

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REFERENCES

(1) (a) Furuta, H.; Asano, T.; Ogawa, T. "N-Confused Porphyrin": A New Isomer of Tetraphenylporphyrin. J. Am. Chem. Soc. **1994**, 116, 767–768. (b) Chmielewski, P. J.; Latos-Grażyński, L.; Rachlewicz, K.; Glowiak, T. Tetra–p-tolylporphyrin with an Inverted Pyrrole Ring: A Novel Isomer of Porphyrin. Angew. Chem., Int. Ed. Engl. **1994**, 33, 779–781.

(2) (a) Maeda, H.; Furuta, H. A dozen years of N-confusion: From synthesis to supramolecular chemistry. *Pure Appl. Chem.* 2006, 78, 29–44. (b) Toganoh, M.; Furuta, H. Blooming of confused porphyrinoids—fusion, expansion, contraction, and more confusion. *Chem. Commun.* 2012, 48, 937–954. (c) Srinivasan, A.; Furuta, H. Confusion approach to porphyrinoid chemistry. *Acc. Chem. Res.* 2005, 38, 10–20. (d) Senge, M. O. Extroverted Confusion—Linus Pauling, Melvin Calvin, and Porphyrin Isomers. *Angew. Chem., Int. Ed.* 2011, 50, 4272–4277. (e) Latos-Grażyński, L. In *Porphyrin Handbook*; Academic Press: San Diego, 2000; Vol. 2.

(3) (a) Furuta, H.; Ishizuka, T.; Osuka, A.; Ogawa, T. N-Fused Porphyrin" from N-Confused Porphyrin. J. Am. Chem. Soc. 1999, 121, 2945–2946. (b) Toganoh, M.; Furuta, H. N-Fused Porphyrin: A

Maverick Member of the Porphyrin Family. *Chem. Lett.* **2019**, *48*, 615–622. (c) Furuta, H.; Maeda, H.; Osuka, A. Doubly N-Confused porphyrin: a new complexing agent capable of stabilizing higher oxidation states. J. Am. Chem. Soc. **2000**, *122*, 803–807.

(4) (a) Wainwright, M. Therapeutic applications of near-infrared dyes. *Color. Technol.* **2010**, *126*, 115–126. (b) Pawlicki, M.; Collins, H. A.; Denning, R. G.; Anderson, H. L. Two-photon Absorption and the design of Two-photon Dyes. *Angew. Chem., Int. Ed.* **2009**, *48*, 3244–3266. (c) Carr, J. A.; Franke, D.; Caram, J. R.; Perkinson, C. F.; Saif, M.; Askoxylakis, V.; Datta, M.; Fukumura, D.; Jain, R. K.; Bawendi, M. G.; Bruns, O. T. Shortwave Infrared Fluorescence imaging with clinically approved near-infrared dye indocyanine green. *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115*, 4465–4470.

(5) Feringa, B. L. The art of building small: From molecular switches to motors (Nobel lecture). *Angew. Chem., Int. Ed.* **2017**, *56*, 11060–11078.

(6) (a) Halder, N.; Sangeetha, M.; Usharani, D.; Rath, H. Redox-Associated Variation of Hückel Aromaticity from Lactam-Embedded Smallest Antiaromatic trans-Doubly N-Confused Porphyrins: Synthesis and Characterization. J. Org. Chem. 2020, 85, 2059–2067. (b) Sahoo, S.; Sangeetha, M.; Bera, S.; Usharani, D.; Rath, H. Targeted synthesis of meso-aryl substituted aromatic trans-doubly N-Confused dithia/diselena [18] porphyrins (1.1.1.1) with NIR absorption: spectroscopic and theoretical characterization. Org. Biomol. Chem. 2020, 18, 6058–6062.

(7) Szyszko, B.; Latos-Grazyński, L. Core chemistry and skeletal rearrangements of porphyrinoids and metalloporphyrinoids. *Chem. Soc. Rev.* **2015**, *44*, 3588–3616.

(8) (a) Rieger, R.; Müllen, K. Forever young: polycyclic aromatic hydrocarbons as model cases for structural and optical studies. *J. Phys. Org. Chem.* **2010**, *23*, 315–325. (b) Dodziuk, H. *Strained Hydrocarbons: Beyond the van't Hoff and Le Bel Hypothesis*; Wiley-VCH: Weinheim, 2009. (c) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH: New York, 1997. (d) Pascal, R. A. Twisted acenes. *Chem. Rev.* **2006**, *106*, 4809–4819. (e) Tsefrikas, V. M.; Scott, L. T. Geodesic polyarenes by flash vacuum pyrolysis. *Chem. Rev.* **2006**, *106*, 4868–4884. (f) Wu, Y.-T.; Siegel, J. S. Aromatic molecular-bowl hydrocarbons: synthetic derivatives, their structures, and physical properties. *Chem. Rev.* **2006**, *106*, 4843–4867.

(9) (a) Wang, K. K. Twisted Arenes. In Polyarenes I; Springer, 2012; pp 31-61. (b) Lu, J.; Ho, D. M.; Vogelaar, N. J.; Kraml, C. M.; Pascal, R. A. A pentacene with a 1440 twist. J. Am. Chem. Soc. 2004, 126, 11168-11169. (c) Schuster, I. I.; Craciun, L.; Ho, D. M.; Pascal, R. A., Jr Synthesis of a strained, air-sensitive, polycyclic aromatic hydrocarbon by means of a new 1, 4-benzadiyne equivalent. Tetrahedron 2002, 58, 8875-8882. (d) Qiao, X.; Ho, D. M.; Pascal, R. A., Jr An extraordinarily twisted polycyclic aromatic hydrocarbon. Angew. Chem., Int. Ed. Engl. 1997, 36, 1531-1532. (e) Qiao, X.; Padula, M. A.; Ho, D. M.; Vogelaar, N. J.; Schutt, C. E.; Pascal, R. A. Octaphenylnaphthalene and decaphenylanthracene. J. Am. Chem. Soc. 1996, 118, 741-745. (f) Smyth, N.; Van Engen, D.; Pascal, R. A., Jr Synthesis of longitudinally twisted polycyclic aromatic hydrocarbons via a highly substituted aryne. J. Org. Chem. 1990, 55, 1937-1940. (g) Pascal, R. A., Jr; McMillan, W. D.; Van Engen, D.; Eason, R. G. Synthesis and structure of longitudinally twisted polycyclic aromatic hydrocarbons. J. Am. Chem. Soc. 1987, 109, 4660-4665.

(10) (a) Nemykin, V. N.; Rohde, G. T.; Barrett, C. D.; Hadt, R. G.; Bizzarri, C.; Galloni, P.; Floris, B.; Nowik, I.; Herber, R. H.; Marrani, A. G.; et al. Electron-transfer processes in metal-free tetraferrocenylporphyrin. Understanding internal interactions to access mixedvalence states potentially useful for quantum cellular automata. J. Am. Chem. Soc. 2009, 131, 14969–14978. (b) Vecchi, A.; Gatto, E.; Floris, B.; Conte, V.; Venanzi, M.; Nemykin, V. N.; Galloni, P. Tetraferrocenylporphyrins as active components of self-assembled monolayers on gold surface. Chem. Commun. 2012, 48, 5145–5147. (11) Halterman, R. L. Synthesis and applications of chiral

cyclopentadienylmetal complexes. *Chem. Rev.* **1992**, *92*, 965–994. (12) (a) van Staveren, D. R.; Weyhermuller, T.; Metzler-Nolte, N.

(12) (a) van Staveren, D. R.; Weyhermuller, T.; Metzler-Nolte, N. Organometallic β -turn, N. M.-N. mimetics. A structural and

spectroscopic study of inter-strand hydrogen bonding in ferrocene and cobaltocenium conjugates of amino acids and dipeptides. *J. Chem. Soc., Dalton Trans.* 2003, 210–220. (b) Kirin, S. I.; Kraatz, H.-B.; Metzler-Nolte, N. Systematizing structural motifs and nomenclature in 1, n'-disubstituted ferrocene peptides. *Chem. Soc. Rev.* 2006, 35, 348–354.

pubs.acs.org/joc

(13) (a) Nakano, T.; Okamoto, Y. Synthetic helical polymers: conformation and function. *Chem. Rev.* 2001, 101, 4013-4038.
(b) Corradini, P.; Guerra, G.; Cavallo, L. Do New Century Catalysts Unravel the Mechanism of Stereocontrol of Old Ziegler- Natta Catalysts? *Acc. Chem. Res.* 2004, *37*, 231-241.

(14) Toganoh, M.; Sato, A.; Furuta, H. Double-Decker Ferrocene-Type Complex of N-Fused Porphyrin: A Model of π -Extended Ferrocene? *Angew. Chem., Int. Ed.* **2011**, *50*, 2752–2755.

(15) (a) Simkowa, I.; Latos-Grażyński, L.; Stępień, M. π Conjugation Transmitted across a d Electron Metallocene in Ferrocenothiaporphyrin Macrocycles. Angew. Chem., Int. Ed. 2010, 49, 7665-7669. (b) Stępień, M.; Simkowa, I.; Latos-Grażyński, L. Helicinal Porphyrinoids: Incorporation of Ferrocene Subunits into Macrocyclic Structures. Eur. J. Org. Chem. 2008, 2008, 2601-2611. (c) Ramakrishnan, S.; Anju, K. S.; Thomas, A. P.; Suresh, E.; Srinivasan, A. Calix [n] metallocenyl [m] phyrins (n = 1, 2 and m = 2, 24): aryl vs. alkyl. Chem. Commun. 2010, 46, 4746-4748. (d) Chatterjee, T.; Theophall, G. G.; Silva, K. I.; Lakshmi, K. V.; Ravikanth, M. Synthesis and Quantum Mechanical Studies of a Highly Stable Ferrocene-Incorporated Expanded Porphyrin. Inorg. Chem. 2016, 55, 6873-6881. (e) Grocka, I.; Latos-Grażyński, L.; Stępień, M. Ruthenocenoporphyrinoids: Conformation determines Macrocyclic π -conjugation Transmitted across a d Electron Metallocene. Angew. Chem., Int. Ed. 2013, 52, 1044-1048.

(16) Punnagai, M.; Narahari Sastry, G. Theoretical study on the structure and stability of ring inverted porphyrin isomers. J. Mol. Struct.: THEOCHEM 2004, 684, 21–28.

(17) Toganoh, M.; Furuta, H. Theoretical study on rotation of pyrrole rings in porphyrin and N-Confused porphyrin. *J. Phys. Chem.* A **2009**, *113*, 13953–13963.

(18) Lu, Y.; Plocher, E.; Hu, Q. S. Synthesis of Novel Bisphosphine-Containing Polymers and Their Applications as Bidentate Ligands for Nickel (0)-Catalyzed Cross-Coupling Reactions. *Adv. Synth. Catal.* **2006**, 348, 841–845.

(19) (a) Gouterman, M.; Wagnière, G. H.; Snyder, L. C. Spectra of porphyrins: Part II. Four orbital model. *J. Mol. Spectrosc.* **1963**, *11*, 108–127. (b) Lee, J. S.; Lim, J. M.; Toganoh, M.; Furuta, H.; Kim, D. Comparative spectroscopic studies on porphyrin derivatives: electronic perturbation of N-Confused and N-fused porphyrins. *Chem. Commun.* **2010**, *46*, 285–287.

(20) Higashino, T.; Osuka, A. Phosphorus complexes of a triply-fused [24]pentaphyrin. *Chem. Sci.* **2012**, *3*, 103–107.

(21) Average bond lengths for C-N and C=N are 1.47 and 1.36 Å, respectively. March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 19.

(22) Elschenbroich, C. Organometallics; John Wiley & Sons, 2016.

(23) (a) Sessler, J. L.; Cho, D.-G.; Stępień, M.; Lynch, V.; Waluk, J.; Yoon, Z. S.; Kim, D. Inverted sapphyrin: A new family of doubly N-Confused expanded porphyrins. J. Am. Chem. Soc. 2006, 128, 12640– 12641. (b) Chmielewski, P. J.; Latos-Grażyński, L. N-methyltetraphenylporphyrin with an inverted N-methylpyrrole ring: the first isomer of N-methyltetraphenylporphyrin. J. Chem. Soc., Perkin Trans. 2 1995, 503–509. (c) Hong, J.-H.; Aslam, A. S.; Ishida, M.; Mori, S.; Furuta, H.; Cho, D.-G. 2-(Naphthalen-1-yl) thiophene as a New Motif for Porphyrinoids: Meso-Fused Carbaporphyrin. J. Am. Chem. Soc. 2016, 138, 4992–4995.

(24) Yamasumi, K.; Notsuka, Y.; Yamaoka, Y.; Mori, S.; Ishida, M.; Furuta, H. Synthesis of Helically π -Extended N-Confused Porphyrin Dimer via meso-Bipyrrole-Bridge with Near-Infrared-II Absorption Capability. *Chem. - Eur. J.* **2020**, *26*, 13590–13594.

(25) (a) Becke, A. D. A new mixing of Hartree-Fock and local density-functional theories. J. Chem. Phys. 1993, 98, 1372-1377.
(b) Becke, A. D. Density-functional thermochemistry. I. The effect of

Article

the exchange-only gradient correction. J. Chem. Phys. **1992**, 96, 2155–2160. (c) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B: Condens. Matter Mater. Phys. **1988**, 37, 785. (d) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. J. Chem. Phys. **1985**, 82, 270–283. (e) Wadt, W. R.; Hay, P. J. Ab initio effective core potentials for molecular calculations. In Methods of Electronic Structure Theory; Springer, 1977; pp 1–27.

(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Hevd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 16, Rev. C.01; Gaussian, Inc.: Wallingford, CT, 2016.

(27) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; van Eikema Hommes, N. J. R. Nucleus-independent chemical shifts: a simple and efficient aromaticity probe. *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.

(28) Geuenich, D.; Hess, K.; Köhler, F.; Herges, R. Anisotropy of the induced current density (ACID), a general method to quantify and visualize electronic delocalization. *Chem. Rev.* **2005**, *105*, 3758–3772.

(29) (a) Srinivasan, A.; Toganoh, M.; Niino, T.; Osuka, A.; Furuta, H. Synthesis of N-Confused tetraphenylporphyrin rhodium complexes having versatile metal oxidation states. *Inorg. Chem.* 2008, 47, 11305–11313. (b) Srinivasan, A.; Furuta, H.; Osuka, A. The first bis-Rh(I) metal complex of N-Confused porphyrin. *Chem. Commun.* 2001, 1666–1667.

(30) Spek, A. L. PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71*, 9–18.

(31) (a) Adamo, C.; Jacquemin, D. The calculations of excited-state properties with Time-Dependent Density Functional Theory. *Chem. Soc. Rev.* **2013**, *42*, 845–856. (b) Scalmani, G.; Frisch, M. J.; Mennucci, B.; Tomasi, J.; Cammi, R.; Barone, V. Geometries and properties of excited states in the gas phase and in solution: Theory and application of a time-dependent density functional theory polarizable continuum model. *J. Chem. Phys.* **2006**, *124*, 1–15.

(32) (a) Miertus, S.; Tomasi, J. Approximate evaluations of the electrostatic free energy and internal energy changes in solution processes. *Chem. Phys.* **1982**, *65*, 239–245. (b) Cossi, M.; Barone, V. Solvent effect on vertical electronic transitions by the polarizable continuum model. *J. Chem. Phys.* **2000**, *112*, 2427–2435.

(33) (a) Wolinski, K.; Hinton, J. F.; Pulay, P. Efficient implementation of the gauge-independent atomic orbital method for NMR chemical shift calculations. *J. Am. Chem. Soc.* **1990**, *112*, 8251–8260. (b) London, F. Théorie quantique des courants interatomiques dans les combinaisons aromatiques. *J. Phys. Radium* **1937**, *8*, 397–409.

(34) (a) Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. A comparison of models for calculating nuclear magnetic resonance shielding tensors. *J. Chem. Phys.* **1996**, *104*, 5497–5509. (b) Keith, T. A.; Bader, R. F. W. Calculation of magnetic response properties using a continuous set of gauge transformations. *Chem. Phys. Lett.* **1993**, *210*, 223–231.