

Monothia [22]pentaphyrin(2.0.1.1.0): A core modified isomer of Sapphyrin

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A novel 22 π -aromatic sapphyrin isomer endowed with acene moiety is designed and realized for the first time as its core-modified mono-thia analogue. This macrocycle exhibits absorption and emission in the near infrared region. It was diprotonated under strong acidic condition, then it binds anion like sapphyrin. It shows unusual coordination chemistry by acting as a neutral ligand to undergo large out-of-plane deformation to bind Pd (II) ion.

Porphyrins in association with various metal ions perform vital functions in nature. Therefore, a great deal of attention was focused upon synthetic porphyrins, initiated by Fischer.¹ It took almost another sixty years to synthesize the first constitutional isomer of porphyrin, namely porphycene.² Subsequently, several porphyrin isomers were realized.³ Separately, expanded porphyrins first noticed by Woodward, but reported by Johnson as its core-modified analogues and named as sapphyrin.⁴ While initial efforts towards its coordination with metal ions were found not promising, however, Sessler unexpectedly found anion coordination by sapphyrin in its diprotonated state and subsequently established it as a versatile host for anions.⁵ They have also been studied as potential PDT agents.⁶ This initiated great interest in the chemistry of expanded porphyrins, which has emerged as one of the widely explored research topics in the last few decades.⁷ Further, closely related carbaporphyrinoids and N-confused porphyrinoids opened the avenue towards their organometallic chemistry.⁸

While the chemistry of isomeric porphyrins, in particular, porphycene and N-confused porphyrins has seen a great development in last three decades, that in case of expanded porphyrins is very limited.⁹ For example, in case of widely explored sapphyrins, there are only few reports with regard to its isomers.¹⁰ Core-modification strategy is again employed here as it has emerged as a versatile approach to realize new porphyrinoids owing to easy access to the desired building blocks.^{4a,7g,8} Further, the presence of other heteroatoms provide structural diversity leading to

unique photophysical and nonlinear optical properties.¹¹ Ozaphyrin is the first sapphyrin isomer to be reported by Iler's group as its core-modified analogues,^{10a,10b} followed by Sessler,^{10c} who reported an all-aza [22]pentaphyrin(2.1.0.0.1) possessing a *trans*-double bond, along with its dichloride salt (Figure 1). Subsequently, Furuta and coworkers realized the N-confused sapphyrin as another constitutional isomer of

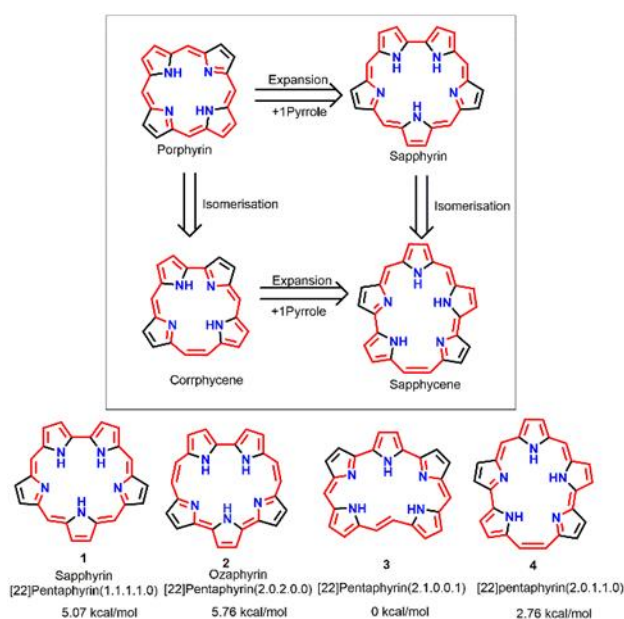


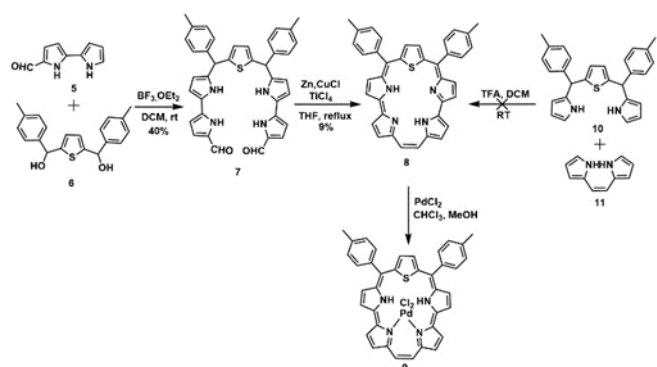
Figure 1: Schematic relation between porphyrin, corphycene, sapphyrin and the designed new sapphyrin isomer (top), along with relative energies of all-aza sapphyrin and its realized isomers (bottom).

sapphyrin.^{10d} However, no further studies found in literature.

Porphycene and expanded porphyrinoids endowed with acene moieties display intense Q- bands owing to their large Δ -LUMO values.¹² We are interested in this class of macrocycles¹³ as they are attractive as photosensitizers and near infrared dyes.^{14,9b} Herein, we have designed and synthesized a new sapphyrin isomer, namely [22]pentaphyrin(2.0.1.1.0) as its core-modified monothia analogue. The preliminary DFT computational analysis of all-aza analogues of sapphyrin and other isomers using B3LYP/6-31G+(d,p) revealed [22]pentaphyrin(2.1.0.0.1) has the lowest energy

followed by our newly proposed isomer [22]pentaphyrin(2.0.1.1.0), on the other hand, ozaphyrin has the highest energy followed by sapphyrin (Figure 1).¹⁵ Further, its complexation with both metal ions and anions in diprotonated state are explored.

We have adopted the core modification strategy to achieve our target. The synthetic strategy envisioned is similar to that for corrphycene viz. McMurry coupling of an open chain pentapyrrolic dialdehyde, which in addition minimizes the chance of formation of other by-products thus, simplifying the purification process.^{3a} Synthesis of the desired precursor involved acid-promoted condensation of monoformylbipyrrole **5** and 2,5-thiophene bis-carbinol **6** to obtain diformyl thiapentapyrrane **7**. An intramolecular reductive McMurry coupling of **7**, followed by open air oxidation resulted in desired macrocycle **8** (Scheme 1). The macrocycle was isolated as a green band from silica gel column in 9% yield. Whereas, the acid-mediated oxidative coupling of thiatripyrromethane and dipyrroethene in dichloromethane with borontrifluoride etherate did not provide the desired macrocycle **8**. The new sapphyrin isomer has been fully characterized by standard spectroscopic analysis like UV-vis-NIR spectroscopy, NMR spectroscopy, high resolution mass spectrometry (HRMS), and single crystal x-ray diffraction analysis.



Scheme 1: Synthesis of sapphyrins **8** and its Pd(II)-complex **9**.

The first evidence of cyclization and aromatization was realized from the UV-vis-NIR absorption spectrum. The absorption spectrum of **8** exhibits very high molar absorptivity with Soret band at 447 nm accompanied with a shoulder on the lower energy side at 467 nm and several lower energy Q bands (Figure 2a).

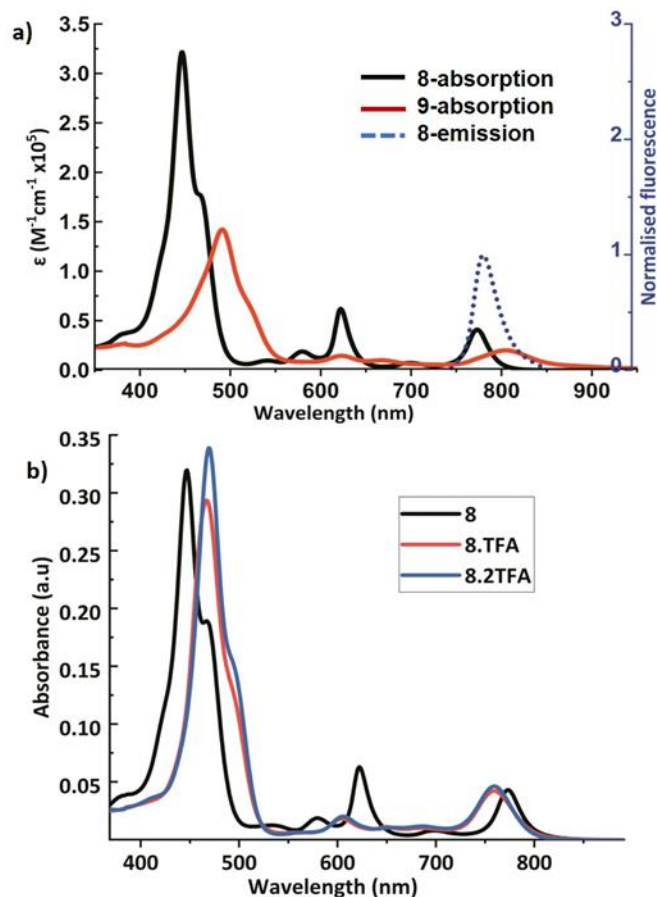


Figure 2: (a) UV-vis-NIR spectra of **8** (black), **9** (red) and emission spectrum of **8** (blue); (b) UV-vis-NIR spectra of sapphyrins **8** and its TFA salts in CHCl_3 .

Unlike sapphyrin, macrocycle **8** exhibits intense Q bands in the lower energy region. The absorption coefficient of the most intense Q band is approximately 20% of that of the Soret band, which is almost more than double than that in case of corrphycene (<10%).^{3a} The lowest energy Q band of **8** appears at 773 nm in chloroform, which is more bathochromically shifted relative to monothiasapphyrin (691 nm) and monothiazozapphyrin (755 nm).^{16,10b} Further, freebase **8** exhibited weak near infrared (NIR) emission at 780 nm indicating its potential utility in NIR diagnostics (Figure 2a, S19).¹⁷

¹H NMR spectrum of **8** exhibits four sets of pyrrole β -protons, one set of thiophene β -protons, and a set of *meso*-protons in the downfield region from 9.42 to 10.48 ppm (Figure 3b). This indicates the thiophene ring is not inverted and all the heteroatoms are directed towards the core. The two NH protons could not be observed at room temperature due to fluxional behaviour. However, both the NH resonances appeared at 5.4 ppm as a single broad peak upon lowering the

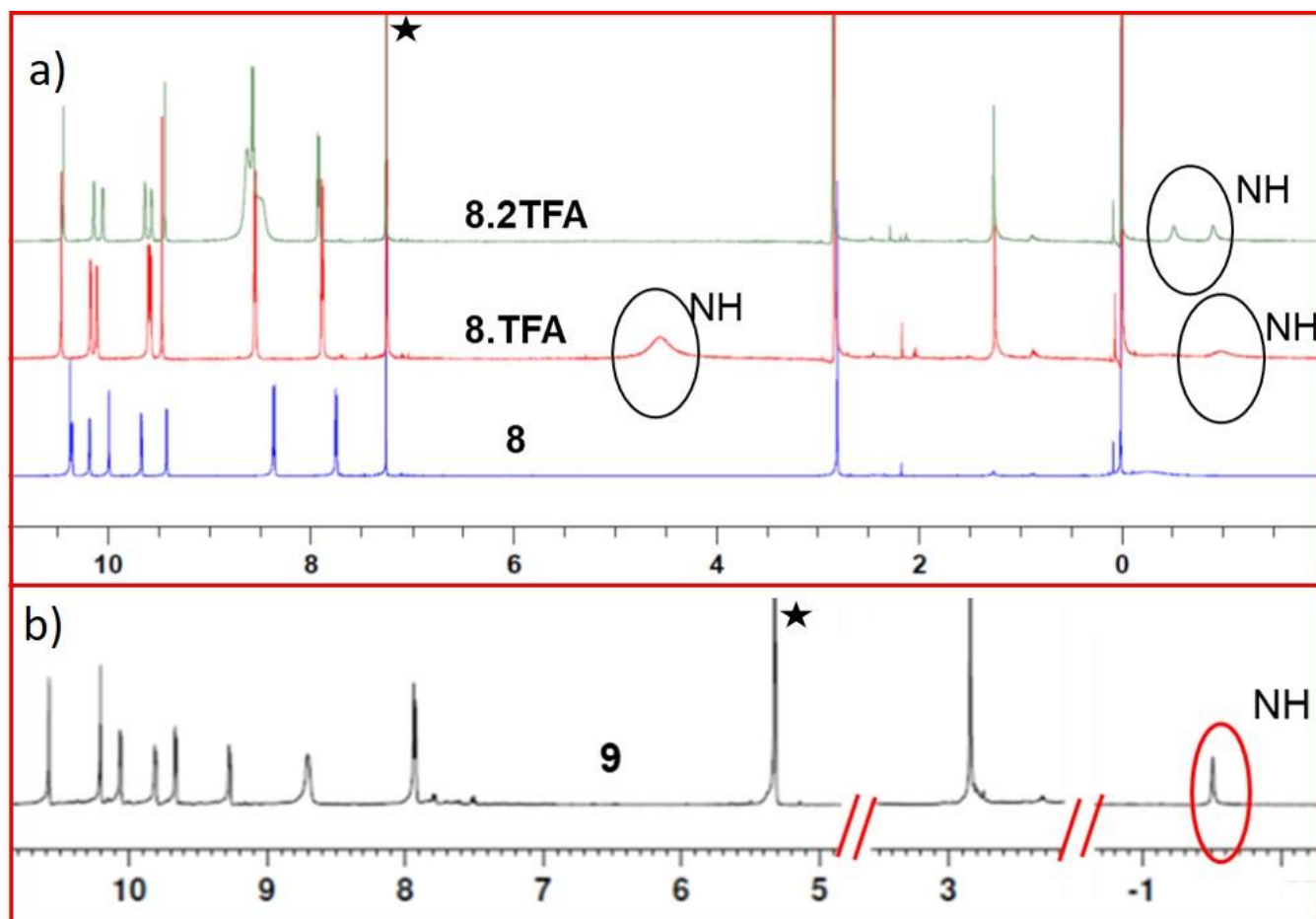


Figure 3: ^1H NMR spectra of (a) titration of TFA with sapphyrene **8** in CDCl_3 ; (b) **9** in CD_2Cl_2 (* residual solvents peak).

temperature to $-30\text{ }^\circ\text{C}$ in the NMR spectrum (Figure S11). The downfield shift of NH peaks is noteworthy and attributed to the possible existence of strong $\text{NH}\cdots\text{N}$ hydrogen bonding in **8** having acene moiety, as both oxa- and thia- ozaphyrins endowed with acenes displayed NH resonances in the shielded region like sapphyrins.^{16,10b} Thus, macrocycle **8** behaved more like porphycene (having large downfield shifted NH resonances owing to strong $\text{NH}\cdots\text{N}$ hydrogen bonding),^{9e} which prompted us to name this new sapphyrin isomer as sapphyrene. Despite strong $\text{NH}\cdots\text{N}$ hydrogen bonding, we were intrigued by the absence of NH resonances under ambient conditions. Further, variable temperature ^1H NMR spectra up to $-70\text{ }^\circ\text{C}$ (in toluene- d_8) could not resolve the two NHs. However, tautomeric equilibrium could be arrested by protonation. ^1H NMR titration experiment of **8** with TFA clearly showed separation of non-equivalent NHs (Figure 3a, S12). Both the NHs are confirmed by deuterium exchange analysis (Figure S13). Interestingly, both monoproteination and

diproteination could be distinctly observed in the experiment. Monoproteinated species showed two different NH resonances, with one in the shielded (-0.96 ppm) and another in downfield region (4.56 ppm). This is a very unusual trend and not noticed in case of porphycenes and may be attributed to the possible unsymmetric nature of the core, owing to which the stronger $\text{N3H}\cdots\text{N2}$ hydrogen bonding is retained. This is well supported by theoretical calculations, which shows less energy for protonation at N4 (Table S2). Upon diproteination, both NH resonances appeared in the shielded region at -0.50 and -0.91 ppm due to interruption in hydrogen bonding (Figure S12).

The inward disposition of all heteroatoms in freebase **8** could be unequivocally assigned via solid state structural elucidation through single crystal x-ray diffraction analysis (crystals were obtained from slow evaporation of chloroform solution). The structure revealed a slight nonplanar structure with maximum mean plane deviations occurring at the C_β -positions of the

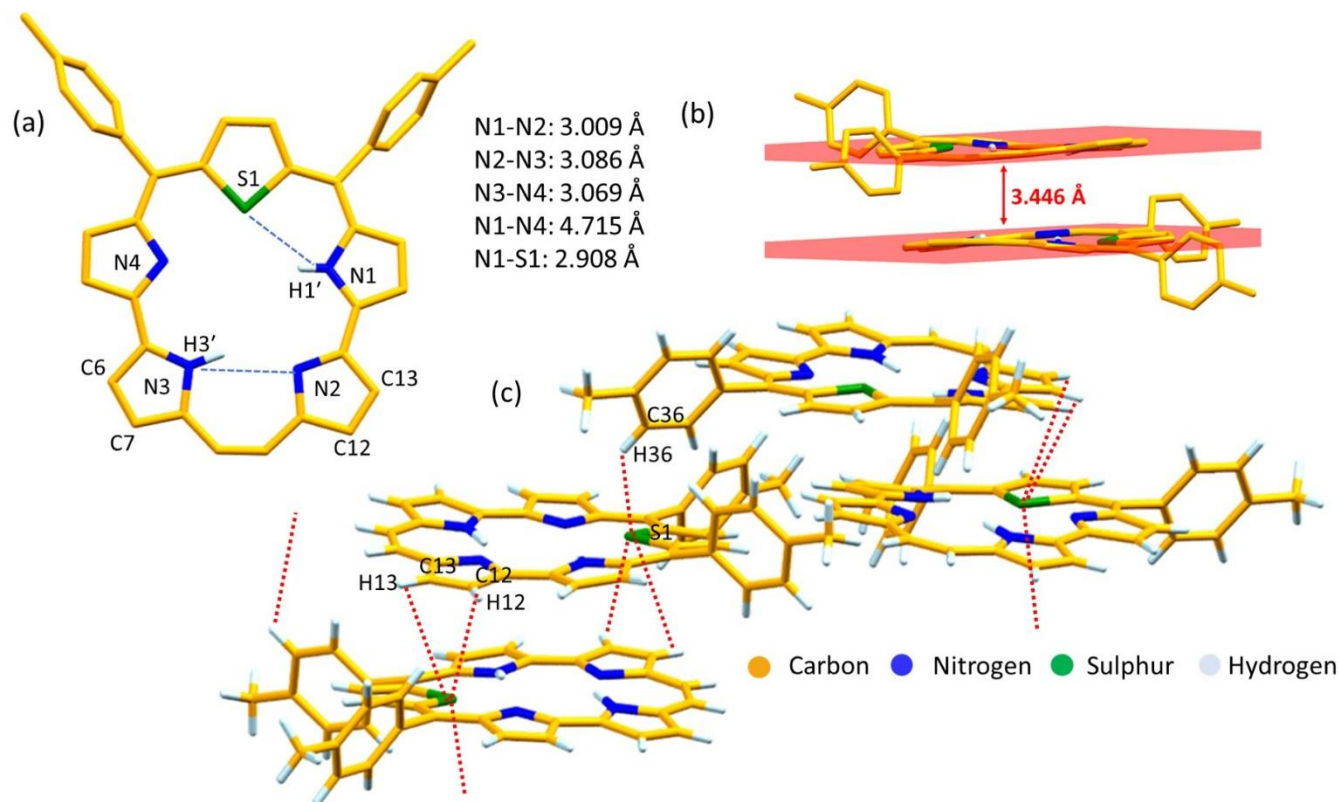


Figure 4: Molecular structure of **8** (a) front view; (b) side view showing interplanar distance; (c) packing diagram showing intermolecular interaction S.

dipyrroethene pyrroles (Figure 4). C6 and C7 exhibit positive deviations of 0.210 and 0.269 Å, respectively from the mean sapphyrcene plane (excluding tolyl substituents), whereas, C12 and C13 show negative deviations of 0.183 and 0.218 Å, respectively. The amino protons could not be assigned to any two particular nitrogens due to rapid tautomerization. These were fixed at *trans*-pyrrolic nitrogens (N1 and N3), which provided lowest reliability factor (R-factor). The N4 core of **8** is trapezoidal having core size (N2-N4 distance) of 4.901 Å, which is comparable to that of monooxaozaphyrin (4.928 Å).^{10a} Further analysis revealed N-N bipyrrrolic distances are slightly different (N1-N2: 3.009 Å and N3-N4: 3.069 Å). This could be attributed to a surprisingly strong N1-H1'...S1 intramolecular hydrogen bonding (N1-S1: 2.908 Å), in addition to the corresponding N3-H3'...N2 hydrogen bond (N3-N2: 3.086 Å), possibly making the *trans*-NH tautomer to be the most stable conformation. The presence of the additional strong N-H...S hydrogen bonding probably facilitated the rate of proton transfer in solution state, thus complying with fluxional behaviour observed in ¹H NMR spectrum under ambient

condition. Further, packing diagram revealed π - π stacking with an interplanar distance of 3.446 Å where the core is aligned in a staggered manner with thiophene rings aligned in opposite direction to each other (Figure 4).

Upon protonation with different acids, we observed UV-vis-NIR absorption spectral changes. Absorption coefficient increased after protonation. Bathochromic shift in the Soret band and hypsochromic shift in Q bands along with a change in Q-band pattern were observed for TFA, HCl, HF and perchloric acids (Figure S14). With TFA, both monoprotection and diprotection are observed with λ_{max} of the Soret band shifted to 465 and 470 nm, respectively (Figure 2, S15). Anion binding of **8.2TFA** with TBAF, shows a gradual blue shift in the Soret band indicating fluoride ion binding. However, upon addition of excess TBAF (15 equivalent), it regenerated the freebase **8** absorption spectrum (Figure S17), possibly indicating deprotonation caused by the water molecules accumulated from the salt TBAF.3H₂O.

To check further the stability of possible tautomeric conformation that we have envisioned in the solid and solution phase, we have performed computational energy calculation of all the possible tautomers of freebase **8** using DFT/B3LYP/6-31G+(d,p).¹⁵ Data revealed the *trans*-NH tautomer to be the most stable form. Surprisingly, tautomer with *cis*-NH in the dipyrroethene (*cis*-3) is more stable than the one having NHs on one of the bipyrrrole (*cis*-2), whereas the tautomer having NH on the two internal pyrrolic units (*cis*-1) is the least stable one (Table S1). The latter can be ascribed to the greater distortion in the macrocycle, where the thiophene ring and the two pyrrole moieties having NHs are on the opposite sides of the molecular plane.

The interesting structural attributes of **8** prompted us to embark on exploring its coordination chemistry. The reaction of macrocycle **8** with palladium(II) chloride resulted in facile metalation, where the resultant complex **9** exhibited unusually red-shifted broad Soret-type band at 491 nm with reduced intensity along with three broad Q-type bands at 623, 667 and 804 nm (Figure 2a). But the mass analysis did not match to regular N4-coordinated Pd-complex (observed *m/z*: 713.0754). ¹H NMR spectral analysis of **9** displayed presence of all the *meso* and β -protons between 7.5 to 10.5 ppm along with two protons in the shielded region at -1.56 ppm, which exchanged with deuterium oxide, confirming the presence of two NH protons inside the core. Fortunately, we could elucidate its structure unequivocally in solid state (crystals obtained by slow evaporation of dichloromethane solution) through single crystal x-ray diffraction analysis (Figure 5a). The solid state structure of **9** revealed a unique coordination mode, where the sapphyrene is behaving as a neutral bidentate ligand. Palladium binds to the macrocycle through imine nitrogens of dipyrroethene side. The other two coordination sites of palladium as well as the charge neutrality were satisfied by two chloride ions. This makes the complex much more distorted from planarity and adopts a highly saddle distorted conformation. Though this kind of seven-membered palladium(II) metallacycle has been observed in triphyrin and porphycene,^{18b,19} but this is unprecedented in expanded porphyrinoids. Palladium

sits 1.065 Å above the mean plane (of the four *meso*-carbons) with Pd-N2 distance 2.026(0) Å. While nitrogens (N2) coordinated to palladium are less distorted from the mean plane, the non-coordinated nitrogens (N1) are relatively more distorted with dihedral angles between mean plane of *meso*-carbons and those of pyrrole A and pyrrole B are 36.79° and 23.11°, respectively (Figure 5c). Further, the dihedral angle between pyrroles coordinating to palladium is 133.9°, which is more than that in case of Pd-triphyrin complex (116.2°).^{18b} Recently, Gross and co-workers reported mono and di Pd(II)sapphyrin complexes. In both the complexes, Pd(II) have been coordinated with the dipyrromethene moiety of sapphyrin to form a six-membered metallacycle along with an η^3 -allylic ligand. Owing to the steric crowding caused by the latter the dipalladium complex showed a non-planar solid-state structure.²⁰ In-core pyrrolic NHs experience hydrogen bonding with thiophene-S (S-N: 2.861 Å) as well as with the chloride ligands on their side (Cl-N: 3.155 Å). The N1-N2 distance (3.128 Å) across the bipyrrrole is elongated in the metallo-derivative compared to that in case of freebase **8**. This type of elongation is a typical attribute observed in case of porphycenes upon complexation due to lack of N-H...N hydrogen bonding.^{3g} Further, molecular packing diagram of the complex showed the solid-state structure is stabilized by intermolecular Cl...H-C (*meso* of another complex) hydrogen bonding (Cl1-C17: 3.487 Å). In addition, a solvent dichloromethane molecule also interacts with sulphur (S1...H20A-C20) of one molecule and palladium of another molecule (Pd...H20B-C20) to further stabilize the crystal packing (Figure S24).

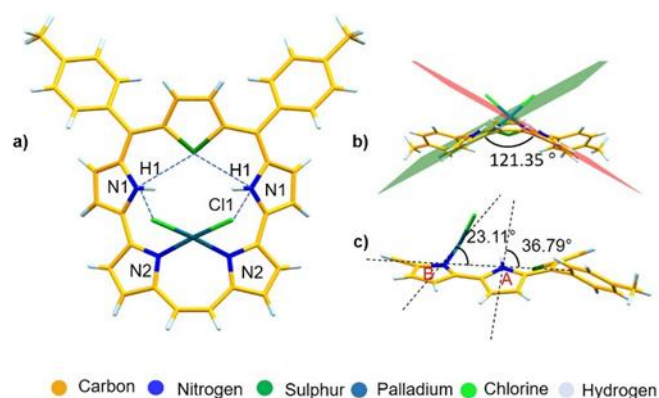


Figure 5: Molecular structure of **9** (a) front view; (b) and (c) side views.

Optimization of palladium complex with seven-membered metallacycle and six-membered metallacycle (Pd binds to bipyrrrolic unit, **9'**) demonstrated **9** as the most stable form with coordination to the dipyrroethene unit as the most suitable mode of binding (Table S3). Further, nucleus-independent chemical shift (NICS(0) and NICS(1)_{zz}) values and harmonic oscillator model of aromaticity (HOMA) indices were calculated using optimized geometries of **8** and **9**.²¹ Both NICS(0) and NICS(1)_{zz} for **9** (-10.1 and -11.9, respectively) revealed a reduction of aromaticity owing to complexation compared to those of freebase **8** (-13.6 and -12.7, respectively) and was further supported by HOMA indices of **8** (0.738) and **9** (0.669), which can be attributed to its large deformation.

In conclusion, we have realized a novel core-modified sapphyrin isomer having attributes of both sapphyrin (anion binding in diprotonated state) and porphycene (intensification of lowest energy absorption band and highly deshielded NH resonances due to intramolecular hydrogen bonding), hence named sapphyrene. The macrocycle displays an unusual coordination ability, where it undergoes large out-of-plane distortion in order to complex with PdCl₂ as a neutral ligand. Further scope of this exciting new sapphyrin isomer is presently under investigation.

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Conflicts of interest

Authors declare no conflicts of interest.

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