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ARTICLE

Synthesis and spectroscopic behaviour of metal complexes of *meso*-alkylidenyl carbaporphyrinoids and their expanded analogue

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Abstract: Treatment of *meso*-malonylidene-(*m*-benzi)porphyrin and *meso*-malonylidene-(*m*-benzi)pentaphyrin with Pd(II), Au(III), Ni(II) and Ag(I) afforded corresponding metal complexes. The synthesized metal complexes were characterized by spectroscopic means including single crystal X-ray, NMR and mass spectrometry. Most metal complexes were stable in solution. The metal complexes show strong absorption in near IR region.

Introduction

Porphyrin analogues including core-modified porphyrins, isomeric porphyrins, aromatic or nonaromatic porphyrin analogues and expanded congeners have drawn a prodigious amount of attention in recent years owing to their unique chemical characteristics and potential utilities in innumerable application areas that transcend the frontiers of classical chemistry. These systems have been intensively studied due to their diverse applications in supramolecular chemistry and material science.[1] Carbaporphyrinoids,[2] and their metal complexes,[3] pyridine-containing porphyrinoids,[4] and oxa- or thia-benziporphyrinoids[5] have also been synthesized and studied extensively for their unusual spectroscopic properties. Carbaporphyrinoid compound has become a unique macrocyclic platform that is appropriate for exploring organometallic chemistry confined to a particular macrocyclic environment.[6-10] The confined aromatic C-H or π-bonds which are close to the bound metal centre usually enforce an unusual coordination property and inimitable reactivity. Although the *m*-benziporphyrins are one of the most extensively studied carbaporphyrins,[11] many other related systems have been synthesized[12-14] and their coordination properties have been reported.[15] Both *m*-benziporphyrin and 2,6-pyriporphyrin,[4c-d,16] are known to be non-aromatic unless a tautomerizable functionality is present.[17] However, the systems containing exocyclic double bonds at the *meso*-carbon(s) have not yet been fully explored. Since the first report for the oxophlorin containing carbonyl function at a *meso*-positon, only a handful of the corresponding analogues have been reported.[18] *Meso*-alkylidenyl benziporphyrinoids are non-planar, non-aromatic macrocycles which have been reported recently. The compounds displayed unusual prototropy and distinctive conformational irregularities. They adopt non-planar geometry in most cases and exhibit partial cross conjugation of the π-system.

Most of the reported compounds display regioselective protonation where the protonation occurs at the alpha position of the *meso*-carbon. The sites of the protonation are closely related with the existing number of core hydrogens. As a part of our continuing efforts for establishment of the chemistry and the construction of novel *meso*-alkylidenyl carbaporphyrinoid compounds, [19-26] we herein report the synthesis, characterization, metalation chemistry and conformational characteristics of the *meso*-malonylidene carbaporphyrinoids. We have also been contemplating to study their further applications after forming the transition metals complexes.

Results and discussion

The synthesis is based on the recent reports on the preparation and properties of non-aromatic, *meso*-diethylmalonylidene-(*m*-benzi)porphyrin, diethylmalonylidene-(*p*-benzi) porphyrin and diethylmalonylidene-(*m*-benzi)pentaphyrins. Expanded macrocyclic analogues such as oxa-(*m*-benzi)hexaphyrin and thia-(*m*-benzi)hexaphyrin were also isolated as minor products.[19b] As shown in Scheme 1, 2,6-divinyl benzene derivative **1,** was obtained by Knoevenagel condensation of diethyl malonate with isophathalaldehyde,

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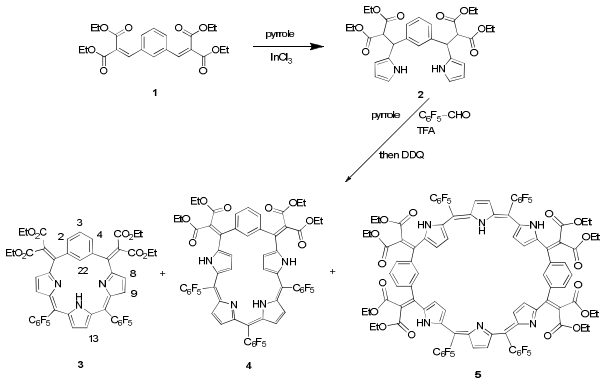
†Electronic supplementary information (ESI) available: ^{1}H, ^{13}C and Uv-Vis spectra of compound **5**, complexes **7a**, **7c**, **7d**, **8** and **9**, 2D spectra data of complex **7a** and **8** (^{1}H-^{1}H COSY, ^{1}H - ^{13}C HMBC and ^{1}H - ^{13}C HSQC) and partial ^{1}H NMR comparison of complex **8** and **9**, ^{1}H NMR acid titrations, X-ray crystal structure of **7a**. ***(CCDC: 1420678)***.

was reacted with pyrrole in the presence of $InCl_3$ to afford the corresponding tripyrrane analogue **2** in high yields.[19]



Scheme 1 Synthesis of *meso*-alkylidenyl carbaporphyrinoids.

The ^{1}H NMR spectrum of the isolated tripyrrane indicated the formation of a diastereomeric mixture which was directly used to the next step without further purification. Then '3+1' type condensation with pyrrole and pentafluorobenzaldehyde in the presence of catalytic amount of trifluoroacetic acid, followed by DDQ oxidation afforded three products **3**, **4** and **5** in 8%, 10% and 2% yields, [23,26] respectively.

The ^{1}H NMR spectrum of macrocycle **5** revealed that the signals for the three pyrrole N-Hs appeared at 13.30 ppm and 11.14 ppm as singlets. Large down-field shifts of the N-H signals indicate existence of the intramolecular hydrogen bonding between pyrrole N-H and carbonyl group suggesting inverted conformation of four pyrrole rings adjacent to the carbonyl groups. Another signal of the pyrrole N-Hs appeared at 8.76 ppm as a singlet.

The UV-Vis spectra of expanded analogue **5** depicted similar shape of absorption pattern as **3** and **4** (Fig. 5S, ESI†). When a solution of expanded porphyrin **5** was titrated with trifluoroactetic acid in acetonitrile, a dramatic colour change from red to purple and noticeable spectral changes were observed (Fig. 1).

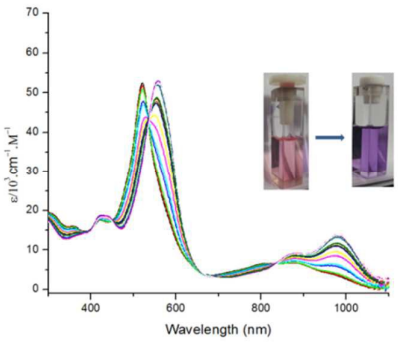
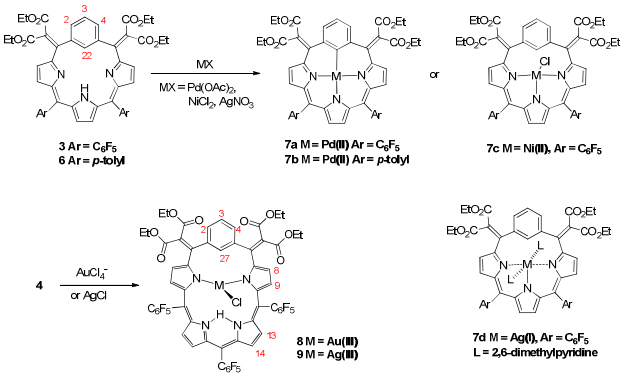


Fig. 1 UV-Vis spectral changes of compound **5** (2.06 x 10^{-5} M, in CH_3CN) observed upon incremental addition of TFA from 0.25 - 100 equiv. The original pinkish red solution became purple upon addition of TFA.

The intensity of the Soret-like absorption band that originally appeared at 510 nm was seen to decrease and then red shifted with gradual increase to 576 nm while it resulted in highly red shifted Q-bands from 810 nm to 890 nm and 990 nm. The original free-base spectrum was fully recovered upon addition of excess triethylamine indicating the reversible nature of the protonation-deprotonation process. These spectral changes are associated with clear isosbestic points.

The syntheses of metal complexes were straight forward and most of the metalation reactions were performed by stirring the free base ligand with appropriate metal salts (Scheme 2). Although most of the synthesized metal complexes are highly stable yet axial ligands are required for stabilization in some cases. The metalation reaction was easily monitored by TLC due to a dramatic color change during the reaction. The reaction of *m*-benziporphyrin **3** with Pd(II), Ni(II), and Ag(I) went quite smoothly giving the corresponding metal complexes.



Scheme 2 Synthesis of metal complexes of porphyrin **3**, **4** and **6.**

Reaction of palladium(II) chloride with *m*-benziporphyrin **3** in acetonitrile results in the formation of the four coordinated palladium(II) complex **7a** (Scheme 2). A single crystal X-ray structure of the *m*-benziporphyrin palladium (II) complex **7a** (Cc point group) is obtained by slow evaporation of dichloromethane solution is depicted in (Fig. 2). The solid state structural analysis indicates that the complex adopts a distorted square planar geometry with three Pd-N and one Pd-C bond. Undoubtedly this distortion reflects a need to minimize the steric hindrance between the two pyrrole rings and the benzene ring and bulky diethyl malonyl group at *meso* position. Thus the observed distortion from planarity may explain partly why **7a** exist as a stable species. The crystallographic data of **7a** is presented in the ESI† (Table 1S and Fig. 16S). The average Pd-N bond length is ~2.0 Å, whereas the Pd - C (22) bond length is found to be 2.02 Å.

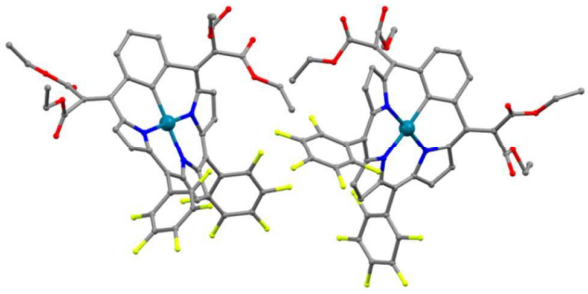


Fig. 2 Solid state structure of *m*-benzi porphyrin Pd(II) complex **7a** from X-ray diffraction analysis: the two structures shows racemic form. Selected bond lengths [Å]: Pd (1)–N (11) 2.004 (15), Pd (1)–N (12) 2.045 (15), Pd (1)–N (13) 1.962 (17), Pd (1)–C (121) 2.020 (17).

The unambiguous confirmation of the structural characterization was supported by 2D NMR spectroscopy including ^{1}H – ^{1}H COSY, ^{1}H – ^{13}C HSQC and ^{1}H - ^{13}C HMBC experiments (Fig. 10S-15S, ESI†). The down field change in ^{13}C NMR spectrum of the sp^2 C-22 from 122.37 ppm to 126.36 ppm and the disappearance of the peak at 7.61 ppm in the ^{1}H NMR spectrum of Pd(II)-complex **7a** revealed the existence of the Ar(C-22)-Pd(II) bond (Fig. 3). The single resonance line corresponding to the Ar-H shown at 7.58 ppm in **6** disappeared upon complexation. Thereafter, reappeared at 7.16 ppm upon addition of acid (trifluoroacetic acid) (Fig. 4). On the other hand, no evidence for the cleavage of the Ar(C)-Pd(II) bond was observed in the case of complex **7a**. These observations indicate that the *meso*-substituents greatly influence the stability of the metal complexes.

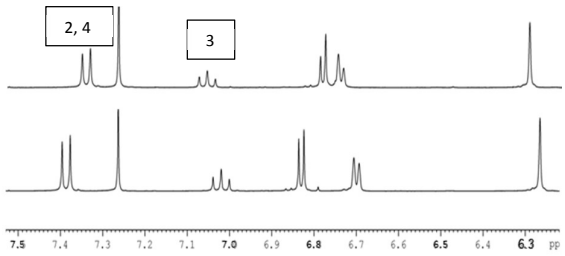


Fig. 3 ^{1}H NMR spectra of Pd(II) complex **7a** (top) and after addition of excess TFA (~30 equiv.) in $CDCl_3$.

Ni(II)-complex **7c** and Ag(I)-complex **7d** were also readily formed upon treatment with $NiCl_2$ or $AgNO_3$, respectively. Ni(II)-porphyrins devoid of axial ligands and square planar geometry are always diamagnetic (low spin, LS, S=0), while upon axial coordination of ligands paramagnetic (high spin, HS, S=1) Ni-complex is formed having square-pyramidal or octahedral geometry.[7c,27] In our case the presence of bulky *meso*-alkylidenyl exocyclic double bond drives the Ni(II)-complex to form only high spin and paramagnetic complex. The MALDI-TOF spectrum of the Ni-complex **7c** shows a peak at 1082.08 corresponding to a chloride bound complex. No evidence for the formation of Ar(C)-Ni(II) bond was seen(Fig. 18S, ESI†). However, Ag(I) complex **7d** requires axial ligands such as two molecules of pyridine for stabilization. ^{1}H NMR spectral analysis indicates the axial coordination of two molecules of pyridine (Fig. 19S-20S, ESI†).

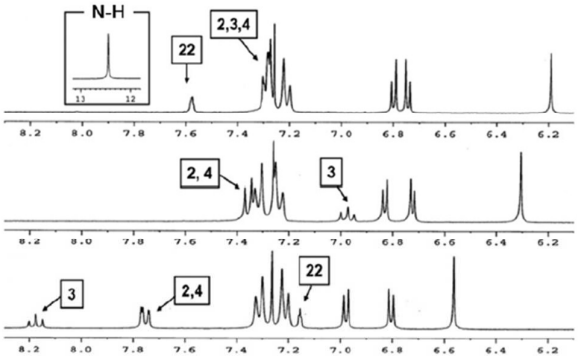
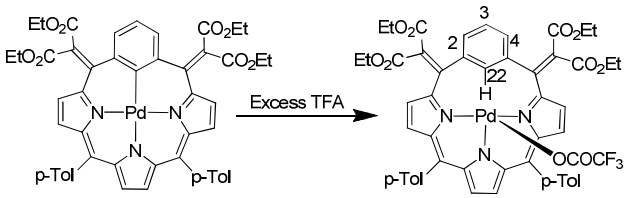


Fig. 4 ^{1}H NMR spectra of free base porphyrin **6** (top), *m*-benziporphyrin Pd (II) complex **7b** (middle) and after addition of TFA (~20 equiv.) to **7b** (bottom) in $CDCl_3$. The disappearance of the Ar-H (22) is clearly seen.



Scheme 3 Re-protonation of **7b** upon titration with excess TFA (which was previously reported on ref 26)

Figure 5 shows the absorption spectra of compounds **6**, **7b** and their corresponding protonated forms. Dramatic spectral changes were observed on the protonation of porphyrin **6**. Pd(II)-complex **7b** displayed a highly red shifted Q-band at 756 nm which further red-shifted to 820 nm upon protonation.

Au(III)-complex **8** was also synthesized by reacting $Na[AuCl_4]•2H_2O$ with **4**. The analytically pure product was obtained by column chromatography on basic alumina (grade 3). Subsequent recrystallization from chloroform/methanol afforded dark green solid in 33% yield. The MALDI-TOF and high resolution mass spectra clearly indicate the incorporation of one Au(III) and one chloride (Fig. 23S, ESI†). Significant down field shift for all the β-pyrrole-Hs was observed in the ^{1}H NMR spectrum of **8** and only a single pyrrole N-H signal was observed at 14.16 ppm, which is similar to those of compound **4** (Fig. 6). Substantial down field shifts of the Ar-Hs strongly suggest the existence of π-back bonding interaction between the phenyl group and bound Au(III). The symmetric nature of ^{1}H NMR spectrum also suggests that the inverted pyrrole units in free base **4** be reinverted to form the Au(III) complex.

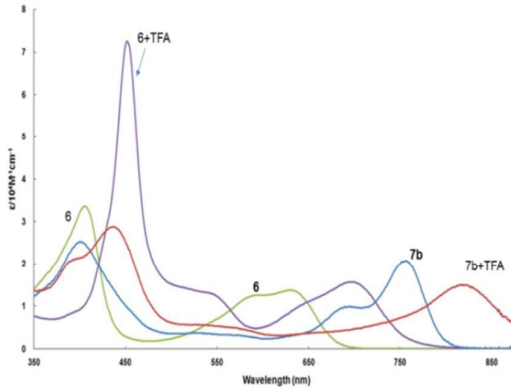


Fig. 5 UV-Vis absorption spectra of **6** (green), **7b** (blue), **6**+ excess TFA (violet) and **7b** + excess TFA (red) in acetonitrile.

The explicit confirmation of the structural characterization was obtained by 2D NMR spectroscopy including ^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC and ^{1}H-^{13}C HMBC experiments (Fig. 24S-29S, ESI†). For instance, in compound **8**, two doublets appearing at 6.65 ppm (J = 4.40 Hz, 2H (13, 19)) and 6.41 ppm (J = 4.38 Hz, 2H (14, 18)) in the ^{1}H NMR spectrum are assigned as β-pyrrole-Hs that hold the core NH (Fig. 6). This was further confirmed by ^{1}H – ^{13}C HMBC spectra which displayed a cross peak correlation between β-pyrrole-C and core N–H. Furthermore, along with the cross-peak between carbonyl of malonyl and β-pyrrole-Hs, the cross-peak between *meso*-alkenyl carbon and β-pyrrole-Hs appearing as a doublet at 7.77 ppm on ^{1}H – ^{13}C HMBC led us to conclude that the further downfield hydrogen must be attached to the β-carbon adjacent to the *meso*-alkenyl group (i.e., for C-8 and C-24).

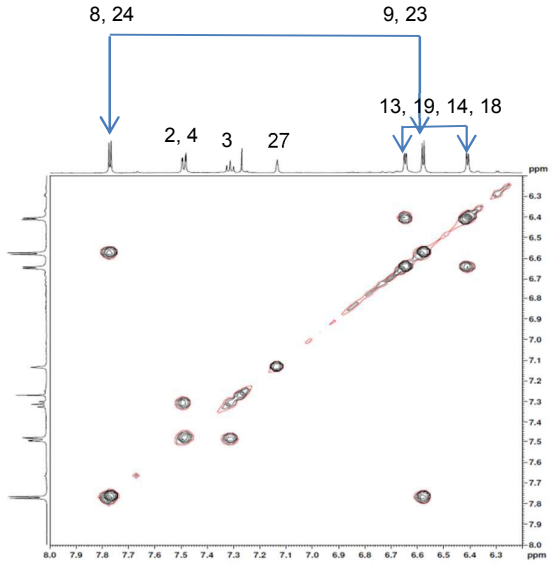


Fig. 6 Selected region of ^{1}H-^{1}H COSY spectrum of m-benzipentaphyrin Au(III) complex **8**.

When comparing the ^{1}H NMR spectra of the free base **4** and Au(III) complex **8** at room temperature, it is clear that although the spectra are similar, the key difference is most notably the number and position of pyrrolic NH and β-protons (Fig. 7). Free base has three NH protons at 11.19 ppm (2H) and 9.99 ppm (1H) which disappear completely in case of complex **8** whereas only one NH proton signal is shown at highly down field shifted due to H-bonding with nitrogen and the presence of bound chloride ion.

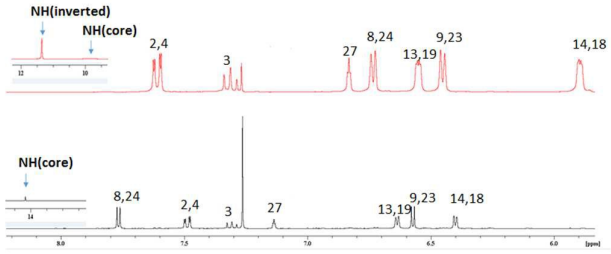


Fig. 7 Partial ^{1}H NMR spectra of benzipentaphyrin **4** (top) and **8** (bottom) taken in $CDCl_3$ at 300 K.

When benzipentaphyrin **4** was refluxed in the presence of excess AgCl in acetonitrile, the initial green reaction mixture turned into dark green over an hour period. Following workup and column chromatography on alumina afforded the Ag(III) complex **9** in 34% yield. The MALDI-TOF and high resolution mass spectra clearly indicate the incorporation of one Ag(III) and one bound chloride (Fig. 33S, ESI†). The ^{1}H NMR spectrum clearly indicates the symmetric nature of the complex. Interestingly, the UV-Vis spectrum of complex **9** was almost identical to that of Au(III)-complex **8**, except having slightly less molar absorptivity.

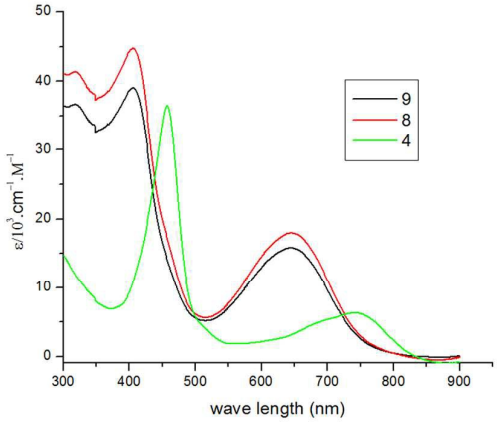


Fig. 8 UV-Vis absorption spectra of *m*-benzipentaphyrin **4** (green) (33.0 μM), Au(III) complex **8** (red) (27.7 μM), Ag(III) complex **9** (black) (28.7 μM) in acetonitrile

Conclusions

In summary, we have successfully synthesized and characterized the metal complexes of the *meso*-malonylidenyl carbaporphyrinoids. The Pd(II) complexes **7a**, **7b**, and Ni(II) complexes **7c** were very stable even in acidic media whereas Ag(I) complex **7d** was rather unstable and demetalated. The *m*-benzipentaphyrin **4** readily form Au(III) or Ag(III) complex under mild conditions. A convenient access to these metal complexes makes this approach appealing for the application in various metalloporphyrins catalysed reactions such as oxidation and catalysis. The studies presented here demonstrate that *meso*-alkylidenyl carbaporphyrinoids can accommodate various metal ions and be amenable to further modification, including self-assembly. Work along these lines is currently under progress.

Experimental Section

Unless noted otherwise specified, all reagents were purchased from commercial supplies and used without further purification. Pyrrole was distilled at atmospheric pressure over CaH_2. All reactions were carried out with standard Schlenk techniques under an N_2 atmosphere and monitored by TLC until the complete consumption of starting materials. ^{1}H NMR and proton coupled ^{13}C NMR spectra were recorded on 400 MHz and 100 MHz respectively, using TMS as the internal standard. Chemical shifts for ^{1}H and ^{13}C NMR were reported in ppm and referenced with the residual solvent protons in $CDCl_3$ (δ 7.26, 77.73 ppm) or in DMSO-d_6 (δ 2.50 ppm) using TMS as the internal standards. Coupling constants (J) are reported in hertz (Hz). High resolution mass spectra were obtained on a Voyager-DE STR MALDI-TOF mass spectrometer. Thin-layer chromatography was performed on Merck pre-coated silica gel 60 F_{254} plates. Silica gel (Merck, 70–230 and 230–400 mesh) was used for column chromatography in air. Compound **1**, **2**, **3**, and **4** were synthesized according to literature procedures.[19, 23, 26] All spectroscopic data for these compounds were in good agreement with those reported in the literature.

General synthesis of the expanded porphyrin 5: Compound **2** (0.51 g, 0.92 mmol) was dissolved in dry dichloromethane (450 ml) and then distilled pyrrole (0.07 ml, 1.02 mmol), pentafluorobenzaldehyde (0.5 ml, 2.18 mmol), and TFA (0.04 ml, 0.45 mmol) were added and the reaction mixture was allowed to stir for 7 days at room temperature in the absence of air and light. Then the reaction mixture was oxidized with 2, 3-dichloro-5, 6-dicyano benzoquinone (DDQ) (0.79 g, 3.48 mmol) for an hour and then treated with TEA (0.45 ml, 3.23 mmol). After quenching with brine (100 ml) the aqueous layer extracted with DCM (50 ml x 4). The organic layers were combined and dried over Na_2SO_4 filtered and concentrated under reduced pressure. The mixture was chromatographed on silica, eluting first with CH_2Cl_2/EtOAc (50/1), CH_2Cl_2/EtOAc (50/5) and then with CH_2Cl_2/EtOAc (50/10) in order to isolate three different products **3, 4** and the minor product **5**.

Compound 3: 0.084 g (yield: 8%)[23]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.19 (br, s, 1H), 7.61 (s, 1H), 7.36-7.32 (t, 1H, *J* = 8.21 Hz), 7.27-725 (m, 2H), 6.84-6.82 (d, *J* = 4.84 Hz, 2H), 6.65-6.63 (d, 2H, *J* = 4.84 Hz), 6.11-6.09 (d, 2H, *J* = 0.75 Hz), 4.21-4.18 (q, 4H, *J* = 7.13 Hz), 4.15-4.11 (q, 4H, *J* = 7.09 Hz), 1.30-1.23 (t, 6H, *J* = 7.13 Hz), 1.03-0.98 (t, 6H, *J* = 7.09 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.70, 165.25, 164.44, 153.94, 147.56, 138.71, 137.55, 133.96, 130.49, 129.65, 128.78, 128.42, 128.00, 122.37, 122.19, 62.30, 61.76, 13.80, 13.77; MALDI-TOF MS Calcd. for $C_{48}H_{31}F_{10}N_3O_8$ exact mass 967.20, Found 968.22.

Compound 4: 0.09 g (yield 10%)[24]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 11.19 (br, s, 2H), 9.99 (br, s, 1H), 7.60-7.58 (dd, 2H, *J* = 1.71 Hz, *J* = 1.71 Hz), 7.33-7.29 (t, 1H, *J* = 7.71 Hz), 6.83 (s, 1H), 6.75-6.73 (d, 2H, *J* = 5.12 Hz), 6.58-6.55 (d, 2H, *J* = 3.93 Hz), 6.48-6.44 (d, 2H, *J* = 5.12 Hz), 5.92-5.89 (d, 2H, *J* = 3.93 Hz,), 4.19-4.14 (q, 4H, *J* = 7.13 Hz), 3.99-3.97 (q, 4H, *J* = 7.10 Hz), 1.29-1.26 (t, 6H, *J* = 7.13 Hz), 1.03-0.99 (t, 6H, *J* = 7.13 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.31, 165.63, 159.55, 150.46, 144.03, 138.41, 137.45, 135.94, 133.15, 131.79, 129.49, 128.92, 125.84, 124.82, 119.33, 116.97, 107.41, 93.16, 61.98, 61.24, 13.88, 13.63; MALDI-TOF MS Calcd. for $C_{59}H_{35}F_{15}N_4O_8$ exact mass 1212.22, Found 1212.26.

Compound 5: 0.045 g (yield 2%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 13.30 (br, 1H), 11.14 (br, 2H), 8.76 (br, 1H), 7.84-7.80 (t, 1H, *J* = 7.6 Hz), 7.54-7.52 (dd, 2H, *J* = 8.02 Hz), 7.51-7.49 (dd, 2H, *J* = 8.02 Hz), 7.37-7.33 (t, 1H, *J* = 7.6 Hz), 7.25 (s, 1H), 7.06-7.05 (d, 1H, *J* = 4.7 Hz), 6.89 (s, 1H), 6.84 (s, 1H), 6.79-6.77 (t, 2H, *J* = 5.4 Hz), 6.67-6.65 (t, 2H, *J* = 4.5 Hz), 6.53-6.52 (d, 1H, *J* = 5.3 Hz), 6.45-6.43 (d, 2H, *J* = 5.3 Hz), 6.37-6.36 (d, 2H, *J* = 4.6 Hz), 5.44 (s, 1H), 4.34-4.30 (t, 4H, *J* = 6.9 Hz), 4.13-4.11 (m, 8H, *J* = 3.8 Hz), 3.95-3.88 (m, 4H, *J* = 7.1 Hz), 1.32-1.24 (m, 12H, *J* = 3.8 Hz), 1.17-1.13 (m, 6H, *J* = 7.1 Hz), 1.09-1.06 (m, 6H, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.63, 166.62, 165.62, 159.55, 150.45, 146.49, 146.98, 144.04, 138.42, 137.41, 135.90, 133.16, 131.78, 129.46, 128.91, 125.84, 124.73, 119.37, 116.96, 113.45, 113.25, 112.66, 112.32, 112.32, 107.40, 93.14, 61.92, 61.48, 61.21, 41.64, 14.00, 13.83, 13.58; MALDI-TOF MS Calcd. for $C_{96}H_{64}F_{20}N_6O_{16}$ exact mass 1939.55, Found 1939.42

Synthesis of complex 7a: Compound **3** (0.11 g, 0.11 mmol) and palladium(II) chloride (0.30 g, 1.69 mmol) were added to dry acetonitrile (22 ml) under nitrogen and refluxed at 80 ^{0}C for 1 hour. After cooling to room temperature the reaction mixture was quenched with brine (30 ml), back extracted with DCM (3 x 50 ml), dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified in column chromatography on silica gel, eluting with DCM/EA (50:1). Recrystallization from EA−Hexane gave the palladium complex **7a** (0.069 g, 57%); ^{1}H NMR (400 MHz, $CDCl_3$,) δ (ppm) 7.39-7.38 (d, 2H, *J* = 7.66 Hz), 7.03-7.00 (t, 1H, *J* = 7.66 Hz), 6.83-6.82 (d, 2H, *J* = 4.86 Hz), 6.70-6.69 (d, 2H, *J* = 4.86 Hz), 6.26 (s, 2H), 4.21-4.17 (q, 4H, *J* = 7.15 Hz), 4.14-4.10 (q, 4H, *J* = 7.11 Hz), 1.23-1.20 (t, 6H, *J* = 7.11 Hz), 1.09-1.07 (t, 6H, *J* = 7.15 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.63, 164.97, 164.29, 149.03, 145.60, 143.86, 141.61, 141.10, 138.55, 138.36, 136.67, 135.67, 130.16, 128.85, 126.89, 126.65, 126.36, 125.27, 111.23, 111.11, 110.98, 62.40, 62.05, 13.79; MALDI-TOF MS Calcd. for $C_{48}H_{29}F_{10}N_3O_8Pd$ exact mass 1071.08, Found 1072.28.

Synthesis of complex 7c: Compound **3** (0.11 g, 0.11 mmol) and nickel(II) chloride (0.30 g, 1.10 mmol) were added to dry acetonitrile (22 ml) under nitrogen and stirred at room temperature for 1 hour. Then the reaction mixture was quenched with brine (30 ml), back extracted with DCM (3 x 50 ml), dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. Recrystallization from MeOH gave the Nickel complex **7c** (0.09 g, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 14.38 (br, s, 1H), 12.53 (s, 2H), 5.83 (s, 3H), 5.18-5.09 (d, 4H), 4.77 (s, 7H), 2.12 (s, 5H), 1.33-0.88 (m, 7H); MALDI-TOF MS Calcd. for $C_{48}H_{29}F_{15}N_3O_8Ni$ exact mass 1023.11, Found 1024.09.

Synthesis of complex 7d: Compound **3** (0.11 g, 0.11 mmol) and Silver nitrate (0.30 g, 1.10 mmol) were added to dry acetonitrile (22 ml) under nitrogen and after stirring for 5 minute at room temperature. 2, 6-Lutidine was added and the stirring continued for 1 hour. Then the reaction mixture was quenched with brine (30 ml), back extracted with DCM (3 x 50 ml), dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. Recrystallization from MeOH gave the silver(I) complex **7d** (0.087 g, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.51 (s, 3H), 7.84 (t, 3H), 6.85 (d, 2H), 6.69 (d, 2H), 6.25 (s, 2H), 4.31-4.29 (m, 4H), 4.10-4.08 (m, 4H), 1.31-1.27 (m, 6H), 1.16-1.13 (m, 6H); MALDI-TOF MS Calcd. for $C_{48}H_{29}F_{15}N_3O_8Ag$ exact mass 1074.62, Found 1074.17.

Synthesis of complex 8: In a 100 mL round bottomed flask, *m*-benzipentaphyrin **4** (9.7 mg, 0.016 mmol), sodium tetrachloroaurate (III) dihydrate (52.6 mg, 0.13 mmol), and potassium carbonate (300 mg) were suspended in chloroform (50 mL). The mixture of reagents was stirred vigorously for 72 h. After this time, solvent was evaporated under reduced pressure and the residue was subjected to chromatography (grade II alumina, dichloromethane). The desired product was eluted after the unreacted free base was totally removed as a yellow band. Subsequent chromatography on alumina (grade II) with dichloromethane/n-hexane (7:3, v/v) as eluent gave **8** (1.3 mg (35%); ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) 14.16 (br, 1H); 7.77-7.76 (d, 2H, *J* = 4.62 Hz); 7.50-7.47 (dd, 2H, *J* = 1.8 Hz); 7.32-7.30 (t, 1H); 7.13 (s, 1H); 6.65-6.64 (d, 2H, *J* = 4.40 Hz); 6.58-6.57 (d, 2H, *J* = 4.63 Hz); 6.41-6.40 (d, 2H, *J* = 4.38 Hz); 4.16-4.15 (q, 4H, *J* = 7.1 Hz); 4.14-4.12 (q, 4H, *J* = 7.1 Hz); 1.19-1.17 (t, 6H, *J* = 7.1 Hz); 1.10-1.08 (t, 6H, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 176.33, 164.82, 163.66, 158.11, 154.17, 146.03, 145.66, 145.54, 144.00, 138.42, 136.74, 136.48, 133.84, 133.77, 131.23, 129.48, 129.11, 128.39, 128.04, 125.91, 125.03, 124.23, 123.64, 111.50, 111.39, 111.28, 61.73, 61.69, 13.72, 13.61; MALDI-TOF MS Calcd. For $C_{59}H_{33}AuClF_{15}N_4O_8$ exact mass 1442.14, found 1444.09.

Synthesis of complex 9: A mixture of benzipentaphyrin **4** (110 mg, 0.11 mmol) and silver(I) chloride (0.3 g, 1.69 mmol) in acetonitrile (22 ml) was stirred under reflux for 1 hr. The mixture was quenched with brine (30 ml) and back extracted with DCM (3 x 50 ml), dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified in column chromatography on silica gel, eluting with DCM/EA (50:1). Recrystallization from chloroform−methanol gave the silver complex **9** (11.1 mg, 34%) as dark green solid; ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) 14.16 (s, 1H); 7.77-7.76 (d, 2H, *J* = 4.75 Hz); 7.50-7.47 (dd, 2H, *J* = 1.8 Hz); 7.33-7.29 (t, 1H); 7.13 (s, 1H); 6.64-6.63 (d, 2H, *J* = 4.44 Hz); 6.58-6.57 (d, 2H, *J* = 4.8 Hz); 6.40-6.39 (d, 2H, *J* = 4.44 Hz); 4.16-4.12 (m, 8H); 1.20-1.16 (t, 6H, *J* = 7.1 Hz); 1.11-1.07 (t, 6H *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) 176.35, 166.63, 166.62, 165.62, 159.55, 150.45, 146.49, 146.98, 144.04, 138.42, 137.41, 135.90, 133.16, 131.78, 129.46, 128.91, 125.84, 124.73, 119.37, 116.96, 113.45, 113.25, 112.66, 112.32, 112.32, 107.40, 93.14, 61.92, 61.48, 61.21, 41.64, 14.00, 13.83, 13.58; MALDI-TOF MS Calcd. For $C_{59}H_{33}AgCl_2F_{15}N_4O_8$ exact mass 1354.67, found 1393.12 (M+Cl+K).

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Graphical Abstract

Metal complexes of *meso*-diethyl malonylidene carbaporphyrinoids have been synthesized and fully characterized.