Structure-sensitive marker bands of metallocorroles: A resonance Raman study of manganese and gold corrole derivatives☆

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ABSTRACT

Soret-excited resonance Raman spectra (λ_{ex} 413.1 nm) were acquired for manganese(III) and gold(III) tris(pentafluorophenyl)corrole, each as four different isotopomeric samples: natural abundance, fully pyrrole-^{15}N-substituted, fully *meso*-^{13}C-substituted, and fully pyrrole-^{15}N-*meso*-^{13}C-substituted. The spectra were modeled with density functional theory-based vibrational analyses, which in general did an excellent job of reproducing both the absolute frequencies and isotope shifts. The results led to the assignment and visualization of approximately 10 prominent Raman bands. A key finding was that the bands could be categorized into two broad classes: Class A, exhibiting large ^{15}N isotope shifts, assignable to vibrations with predominant C_α-N character, and Class B, exhibiting large *meso*-^{13}C isotope shifts, assignable to vibrations with predominant C_α-C_{meso} character. Preliminary evidence suggests that the class A bands may serve as core size markers, while class B bands may correlate with the innocence or otherwise of the corrole macrocycle.

1. Introduction

Ever since the discovery of simple, one-pot syntheses of corroles, their chemistry has grown by leaps and bounds [1,2]. Today, the coordination chemistry of corroles is comparable in breadth and depth to that of porphyrins [3–6]. The same can be said for applications of corroles in the biomedical and technological arenas – cancer imaging and therapy [7], chemical sensors [8], and catalytic small-molecule [9], to name a handful. Vibrational spectroscopy can potentially afford deep insights into many aspects of corrole-based science and technology. Unlike for porphyrins [1–15], however, detailed IR and resonance Raman (RR) spectroscopic studies of corroles remain few and far between [16–20]. In 2015, we began a collaborative RR study of isotopically labeled manganese(III) and gold(III) corroles with the late James Terner (Jim) with a view to identifying structure-sensitive marker bands. The choice of Mn [21–23] and Au [24–33] corroles was dictated by the fact that both are paradigmatic, four-coordinate, innocent M(III) complexes, which should aid in the identification of core size marker bands. With Jim's death in March 2018, the project was sadly interrupted. The RR data he left behind has now been modeled and partially assigned with density functional theory (DFT) calculations. The results

provide one of the first, systematic studies of the skeletal vibrations of metallocorroles, including the question of structure-sensitive marker bands.
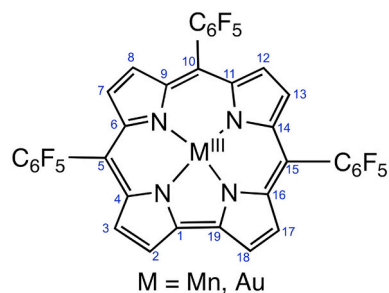
One of us (AG) first met Jim at the first International Conference on Porphyrins and Phthalocyanines (ICPP) in Dijon, France, in 2000. An authority on heme proteins, Jim was singularly respected as one who had correctly established the symmetry states and vibrational signatures of the high-valent Compound I [34,35] and Compound II [36–39] intermediates of heme proteins and model compounds (the definitive work on Compound II intermediates of heme-thiolate proteins came later from the work of Green et al. [40]). At AG's invitation, he wrote a series of critical reviews on the subject in the *Journal of Porphyrins and Phthalocyanines* [41,42], the *Journal of Biological Inorganic Chemistry* [43,44], and the *Journal of Inorganic Biochemistry* [34,45]. He also brought to bear his formidable skills as a Raman spectroscopist to another subtle problem – spin-admixed ferrihemes [46] – as well as to improved measurement of the oxygen saturation of blood [47–49]. Over the years, we enjoyed a deep friendship and many stimulating discussions at ICPP and other conferences (where we were often accompanied by our sons). In 2014, we formally collaborated for the first time, when Terner helped clarify the vibrational signatures of osmium-nitrido

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Scheme 1. Metallocorroles studied in this work, along with skeletal atom numbering.

corroles [50], in an early contribution to the now-vibrant field of 5d metallocorroles [4–6]. Unfortunately, we were destined to collaborate only once more, resulting in the findings described below.

2. Results and discussion

Two metallocorroles – Mn[TPFPC] and Au[TPFPC] [Scheme 1; TPFPC = *meso*-tris(pentafluorophenyl)corrole] – were each studied in 4 different isotopomeric forms: natural abundance, fully pyrrole-^{15}N-substituted, fully *meso*-^{13}C-substituted, and fully pyrrole-^{15}N-*meso*-^{13}C-substituted. Both molecules were optimized under a C_2 symmetry constraint, which resulted in no imaginary frequencies. Fig. 1 depicts the Soret-excited (λ_{ex} = 413.1 nm) RR spectra of all eight species over 250–2000 cm^{-1}. Table 1 lists the frequencies of potential structure-sensitive RR bands and potential scalar-relativistic DFT (ZORA-BP86-D3/ZORA-STO-TZ2P) counterparts. Table 2 recasts the data in the form of isotope shifts and identifies calculated vibrations whose isotope shifts best match the experimental values. Fig. 2 depicts selected optimized geometries of the two molecules; only marginal differences were observed for the C_α-C_β and C_β-C_β bonds between the two molecules. Figs. 3-8 present visual depictions of selected, calculated eigenvectors. The results underscore the following points.

The main conclusion arising out of the data is that majority of the prominent vibrations in the Raman spectra may be categorized into two broad classes: class A, with larger ^{15}N isotope shifts but small *meso*-^{13}C isotope shifts, and class B, with larger *meso*-^{13}C isotope shifts but smaller ^{15}N isotope shifts. The calculated results provide broad support for this finding: class A vibrations involve predominantly C_α-N stretching, whereas class B vibrations involve predominantly C_α-C_{meso} stretching. Given the low symmetry of the corrole macrocycle, several vibrations, understandably, involve both C_α-N and C_α-C_{meso} character, but one

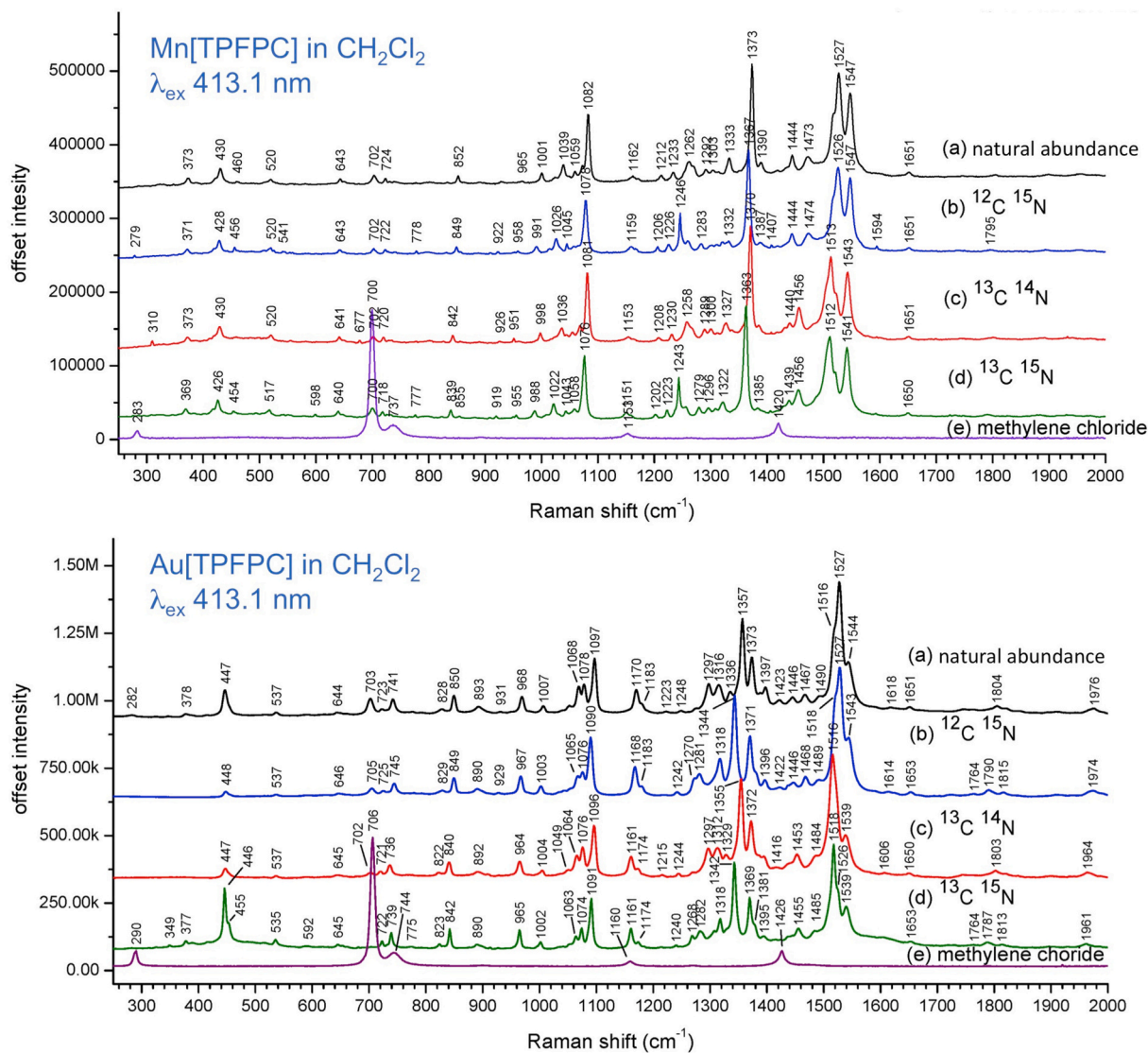**Fig. 1.** Resonance Raman spectra (λ_{ex} 413.1 nm) of Mn[TPFPC] and Au[TPFPC] in dichloromethane.

Table 1

Selected RR frequencies (ν_{RR}, cm^{-1}) in CH$_2$Cl$_2$ and potential DFT counterparts (ν_{DFT}, cm^{-1}) for different isotopomers.

Metal	ν_{RR}				ν_{DFT}				ν_{RR}/ν_{DFT}			
	$^{12}C^{14}N$	$^{13}C^{14}N$	$^{12}C^{15}N$	$^{13}C^{15}N$	$^{12}C^{14}N$	$^{13}C^{14}N$	$^{12}C^{15}N$	$^{13}C^{15}N$	$^{12}C^{14}N$	$^{13}C^{14}N$	$^{12}C^{15}N$	$^{13}C^{15}N$
Au	447	447	448	446	440.0	439.7	438.1	437.8	1.0158	1.0166	1.0226	1.0188
Mn	430	430	428	426	415.9	416.0	415.0	415.1	1.0339	1.0337	1.0313	1.0263
Au	537	537	537	535	531.5	530.8	528.2	527.7	1.0104	1.0116	1.0166	1.0139
Mn	520	520	520	517	518.2	517.8	515.7	515.3	1.0035	1.0042	1.0083	1.0033
Au	850	840	849	842	845.5	836.8	843.1	834.7	1.0054	1.0038	1.0070	1.0087
					848.1	838.9	844.7	835.7	1.0023	1.0013	1.0051	1.0075
Mn	852	842	849	839	847.8	840.3	845.0	837.9	1.0050	1.0020	1.0047	1.0013
					849.7	841.7	846.1	838.3	1.0027	1.0004	1.0034	1.0008
Au	1007	1004	1003	1002	1001.4	999.8	995.1	993.4	1.0056	1.0042	1.0080	1.0086
Mn	1001	998	991	988	996.5	994.8	987.5	985.9	1.0045	1.0032	1.0035	1.0021
Au	1097	1096	1090	1091	1092.0	1091.9	1083.9	1083.8	1.0046	1.0037	1.0056	1.0066
Mn	1082	1081	1078	1076	1081.3	1081.1	1076.7	1076.4	1.0006	0.9999	1.0012	0.9996
Au	1170	1161	1168	1161	1168.4	1160.3	1165.1	1156.3	1.0013	1.0006	1.0025	1.0040
Mn	1162	1153	1159	1151	1157.7	1149.8	1153.2	1145.5	1.0037	1.0028	1.0051	1.0048
Au	1297	1297	1281	1282	1282.9	1282.1	1267.1	1267.0	1.0110	1.0116	1.0110	1.0118
					1286.7	1284.3	1284.3	1282.6	1.0080	1.0099	0.9974	0.9995
					1294.9	1293.4	1283.6	1282.7	1.0016	1.0028	0.9980	0.9995
Mn	1292	1289	1283	1279	1238.1	1237.5	1226.9	1226.2	1.0193	1.0166	1.0156	1.0137
					1281.6	1280.6	1279.4	1278.6	0.9847	0.9824	0.9739	0.9722
					1258.4	1257.6	1248.9	1248.4	1.0029	1.0003	0.9977	0.9957
Au	1357	1355	1343	1342	1362.2	1361.3	1355.3	1353.5	0.9962	0.9953	0.9909	0.9915
					1377.3	1374.6	1368.9	1365.5	0.9853	0.9858	0.9810	0.9828
Mn	1373	1370	1367	1363	1361.1	1357.1	1355.0	1350.1	1.0087	1.0095	1.0089	1.0096
					1373.3	1368.4	1371.6	1366.6	0.9998	1.0012	0.9966	0.9974
Au	1467	1453	1468	1455	1471.5	1463.8	1470.3	1462.9	0.9969	0.9926	0.9984	0.9946
					1472.6	1465.1	1470.3	1464.4	0.9962	0.9918	0.9985	0.9936
Mn	1473	1456	1474	1456	1478.0	1469.0	1477.6	1468.4	0.9966	0.9912	0.9976	0.9916
					1481.7	1476.0	1481.6	1475.6	0.9941	0.9864	0.9949	0.9867
Au	1527	1516	1527	1518	1503.6	1487.8	1501.7	1486.8	1.0155	1.0189	1.0168	1.0210
					1508.5	1499.9	1507.0	1497.1	1.0123	1.0107	1.0133	1.0140
Mn	1527	1513	1526	1512	1505.9	1500.9	1505.1	1500.1	1.0140	1.0081	1.0139	1.0079
					1518.8	1496.0	1518.4	1495.4	1.0054	1.0114	1.0050	1.0111
Au	1544	1539	1543	1539	1515.9	1511.2	1514.8	1510.0	1.0185	1.0184	1.0186	1.0192
					1531.9	1528.7	1531.0	1527.9	1.0079	1.0067	1.0078	1.0072
Mn	1547	1543	1547	1541	1518.9	1512.6	1518.3	1512.0	1.0185	1.0201	1.0189	1.0192
					1555.2	1553.5	1555.1	1553.4	0.9947	0.9932	0.9948	0.9920

Table 2

Experimentally observed ^{15}N and *meso*-^{13}C isotope shifts of key structure-sensitive bands and the most plausible DFT assignments.

Metal	$\nu_{unlabelled}$ (cm^{-1})	$\Delta\nu_{15N}$ (cm^{-1})	$\nu_{meso\text{-}13C}$ (cm^{-1})	$\Delta\nu_{13C}$ (cm^{-1})	$\Delta\nu_{15N}$ (cm^{-1})[a]	ν_{DFT} (cm^{-1})
Group A: Vibrational modes with substantial/predominant C$_\alpha$-N character						
Mn	1373	−6	1370	−3	−7	1361.1
Au	1357	−14	1355	−2	−13	1362.2
Mn	1292	−9	1289	−3	−15	1281.6
Au	1297	−16	1297	−0	−15	1286.7
Mn	1082	−4	1081	−1	−5	1082.7
Au	1097	−7	1096	−1	−5	1092.0
Mn	1001	−10	998	−3	−10	996.5
Au	1007	−4	1004	−3	−2	1001.4
Group B: Vibrational modes with substantial/predominant C$_\alpha$-C$_{meso}$ character						
Mn	1547	0	1543	−4	−1	1555.2
Au	1544	−1	1539	−5	0	1531.9
Mn	1527	−1	1513	−14	−1	1518.9
Au	1527	0	1516	−11	0	1515.9
Mn	1473	1	1456	−17	−3	1481.7
Au	1467	1	1453	−14	−2	1472.6
Mn	1162	−3	1153	−9	−2	1157.7
Au	1170	−2	1161	−9	0	1168.4
Mn	852	−3	842	−10	−3	847.8
Au	850	−1	840	−10	−2	845.5

usually predominates. Importantly, these two classes do not refer to the irreducible representations of the C_2 point group. The great majority of the observed Raman-active vibrations appear to belong to the A irrep; however, certain vibrations belonging to the B irrep are potentially also Raman-active.

Table 2 identifies four vibrations with predominant or substantial C$_\alpha$-N character, all in the 950–1400 cm^{-1} range. Of these, only the vibration around 1360 cm^{-1} can be described as a breathing mode; the other three vibrations preferentially involve only one of the two symmetry-distinct pairs of central nitrogens. For all four vibrations, ν_{DFT} is slightly higher for Au than for Mn, suggesting stronger metal-nitrogen bonds with higher stretching force-constants for Au (even though kinematic considerations might have suggested the reverse). However, the complex interplay of kinematic and dynamic factors in these complexes makes such an interpretation uncertain. Be that as it may, these four vibrations appear most suited as core size markers.

Of the five vibrations identified as having predominant or substantial C$_\alpha$-C$_{meso}$ character, the highest-frequency vibration, with ν_{DFT} (Mn, Au) = 1555.2, 1531.9 cm^{-1}, also has substantial C1-C19 (direct pyrrole-pyrrole linkage) character. Preliminary evidence from an earlier IR and DFT studies of Fe corroles suggest that the vibrations may serve as markers for a noninnocent macrocycle in metallocorroles (which exhibit characteristic bond length alternations for the corrole skeleton). However, vibrational analyses of a wider range of compounds, and appropriate isotopomers, are warranted before such studies can be considered
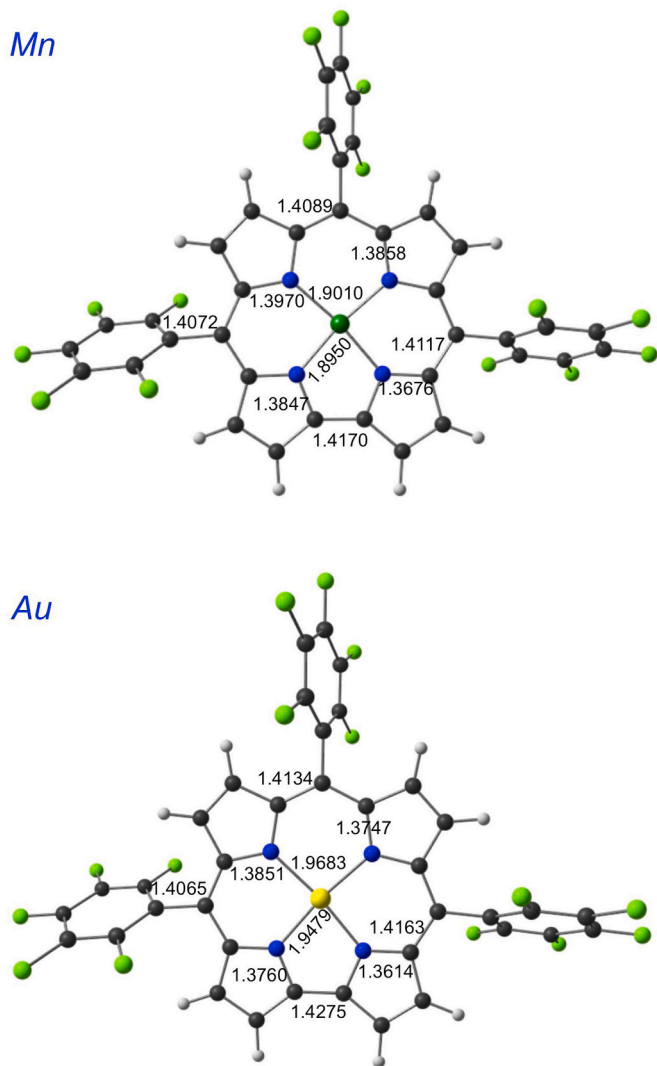
Mn

1.4089
1.3858
1.3970 1.9010
1.4072
1.4117
1.8950
1.3847 1.3676
1.4170

Au

1.4134
1.3747
1.3851 1.9683
1.4065
1.4163
1.9479
1.3760 1.3614
1.4275

Fig. 2. Selected distances (Å) in the optimized geometries of Mn[TPFPC] and Au[TPFPC]. Note that the Au—N distances are 0.05 Å or more longer than the corresponding Mn—N distances.

widely useful.

3. Conclusion

A combined resonance Raman and DFT study of planar Mn(III) and Au(III) corroles has led to the assignment of approximately ten prominent bands, filling a significant knowledge gap relative to the physicochemical properties of metallocorroles. Based on ^{15}N and *meso*-^{13}C isotope shifts, the bands fall into two major classes: class A, with predominant or substantial C_α-N character, and class B, with predominant or substantial C_α-C_{meso} character. The former appear more relevant as core size marker bands, while the latter may shed light on the innocence or noninnocence of the corrole macrocycle. That said, the increased mixing of internal coordinates in corrole normal modes (relative to porphyrins) may ultimately limit their use as geometric and electronic markers.

4. Experimental section

4.1. Synthetic methods

N,N-dimethylformamide (carbonyl-^{13}C, 99%) and pyrrole-[15]N (98%) were purchased from Cambridge Isotopes Laboratories, Inc., and used as received. Silica (150 Å pore size, 35–70 μm particle size, Davisil) was used for flash chromatography and silica gel 60 preparative thin-layer chromatographic (PTLC) plates (20 × 20 cm; 0.5 mm thick, Merck) for further purification. Pentafluorobenzaldehyde-[13]CHO was prepared as previously reported [51], as were free-base tris(pentafluorophenyl) corrole, H_3[TPFPC] [52,53], and its *meso*-^{13}C, pyrrole-^{15}N, and *meso*-^{13}C-pyrrole-[15]N -labeled analogues. Natural-abundance and labeled Mn[TPFPC] [22] and Au[TPFPC] [26,31] were also prepared as previously reported, with minor modifications for the Au complex.

Gold acetate (5 eq, 141 mg, 0.37 mmol) was added to a pyridine (10 mL) solution of H_3[TPFPC] (60 mg, 0.075 mmol). The reaction mixture was stirred overnight, followed by evaporation of the solvent. The residue was chromatographed on a silica gel column with 4:1 n-hexane/ CH_2Cl_2, yielding Au[TPFPC] as the first red band. PTLC with 3:1 hexane/CH_2Cl_2 yielded the pure complex as the first scarlet band (3.8 mg, 5.2%), with spectroscopic data matching those reported earlier [31].

Electrospray ionization (ESI) mass spectra were recorded in the positive mode on an LTQ Orbitrap XL spectrometer for all isotopomeric complexes. Infrared spectra were obtained on dry, solid samples via attenuated total reflection on a Varian 700e FT-IR spectrometer.

4.2. Resonance Raman measurements

Resonance Raman spectra were obtained as previously reported [50], using a Coherent Sabre DBW krypton ion laser, generally with an excitation wavelength of 413.1 nm. Samples were prepared by placing microgram quantities of the solid compounds inside melting point capillaries, and adding dichloromethane to obtain an optical density of approximately 1.0 at the wavelength of the laser. A laser power of ~0.7 mW was focused to a 100 μ diameter spot at the sample. Raman signal was collected at 90 degrees with a Canon f/0.95 50 mm camera lens and focused onto a 75 μ slit aperture of a 0.5 m Spex (Horiba) model 1870 spectrograph containing a single Jobin Yvon (Horiba) 1200 lines/mm holographic grating. Kaiser Optical holographic filters were used to filter the laser scattered light when necessary. Mounted on the spectrograph was a liquid nitrogen cooled Pylon CCD detector from Princeton Instruments. Indene and toluene were used for wavelength calibration.

4.3. DFT calculations

The structures were optimized in gas phase with the scalar ZORA [54,55] Hamiltonian, the BP86 [56,57] exchange-correlation functional, Grimme's D3 [58,59] dispersion corrections and all-electron Slater-type TZ2P basis sets, all as implemented in the ADF program system [60]. The tightest practicable criteria were used for both SCF and geometry cycles as well as for frequency analyses; the latter established the optimized structures as true minima.
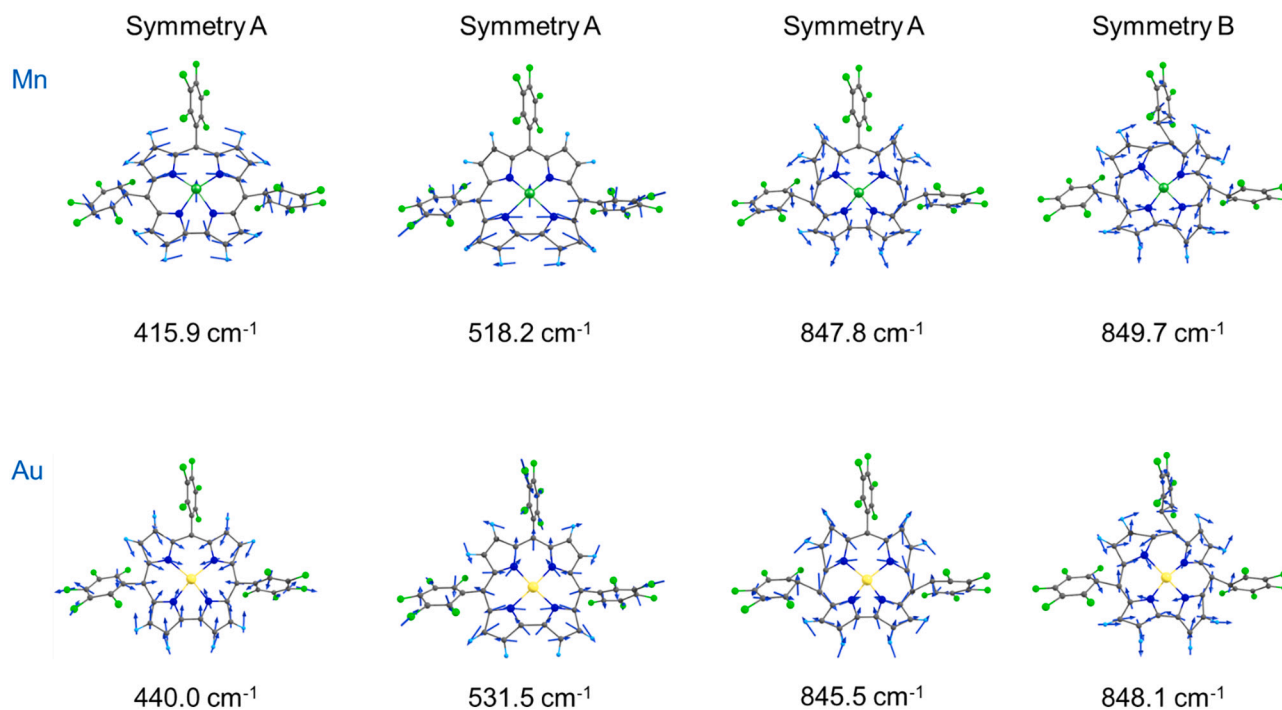
Fig. 3. Eigenvectors and corresponding DFT frequencies for potential structure-sensitive RR bands below 900 cm^{-1}. The frequencies refer to the ^{12}C^{14}N column under ν_{DFT} in Table 1.
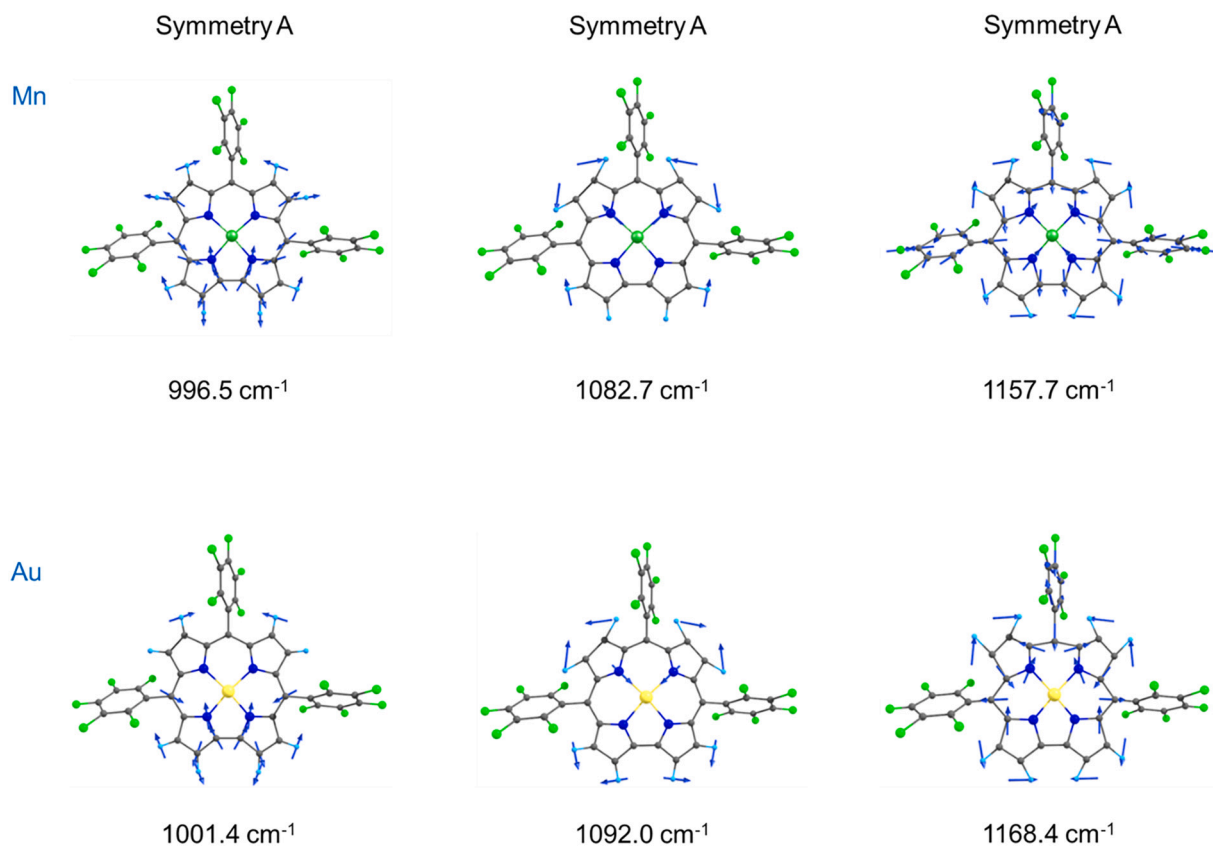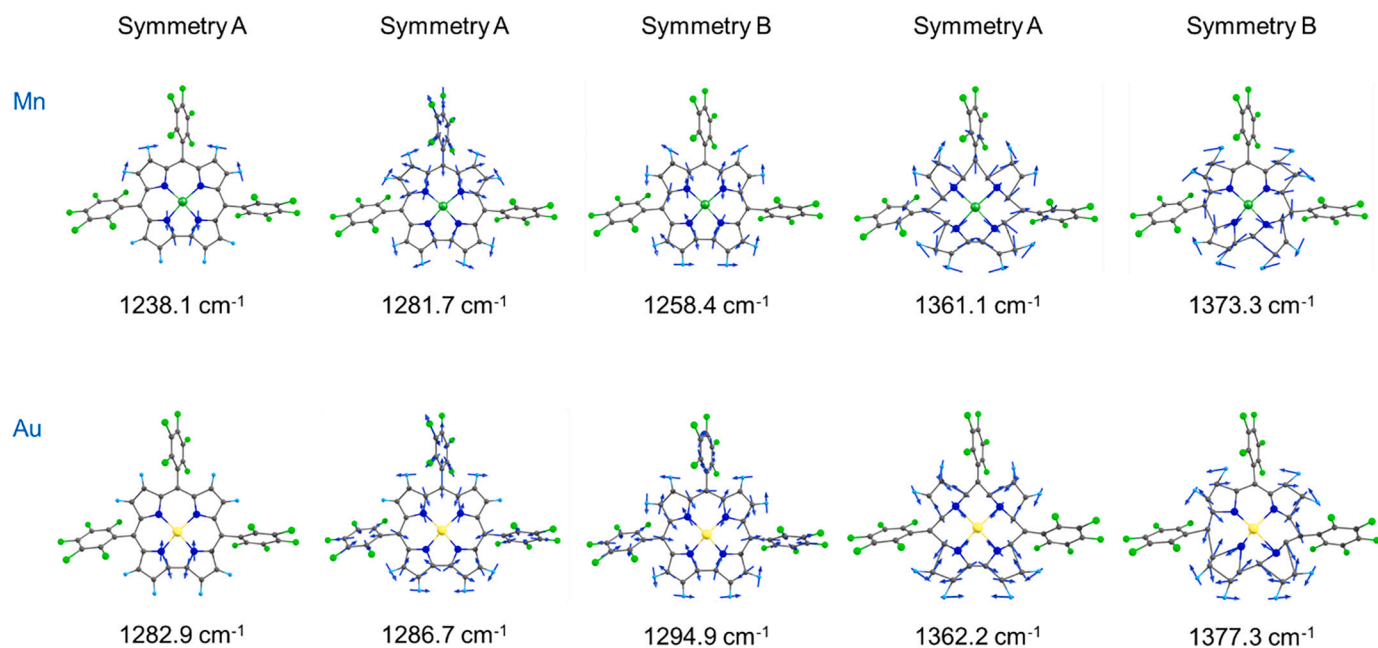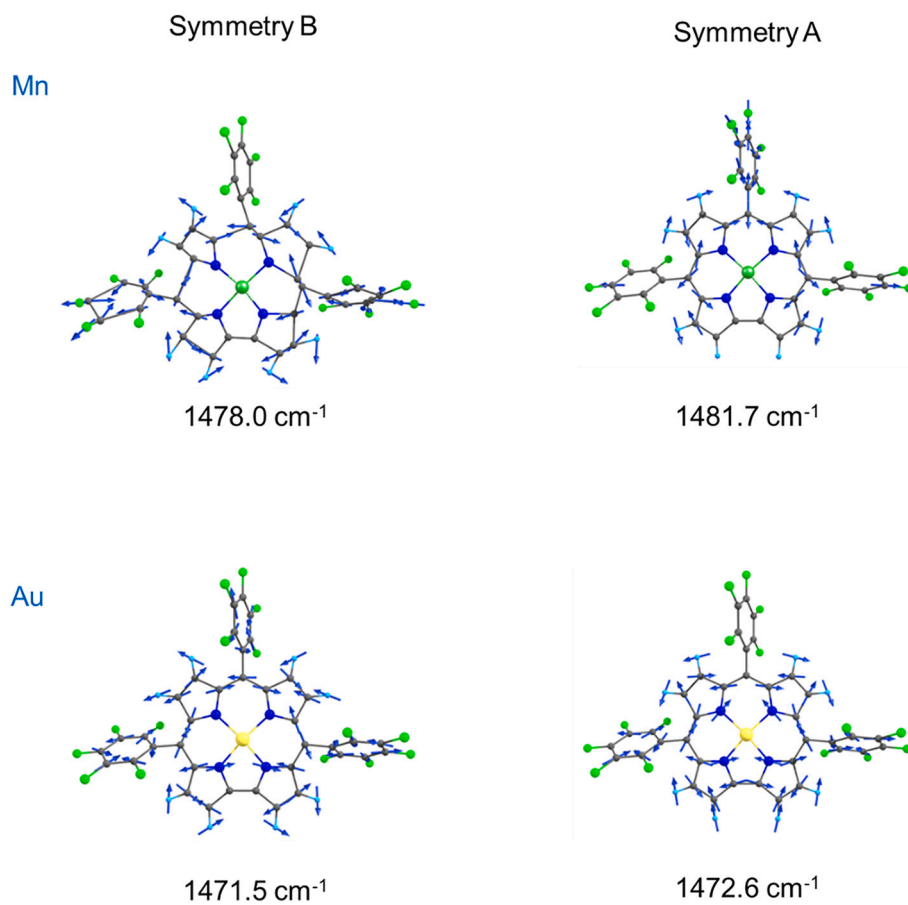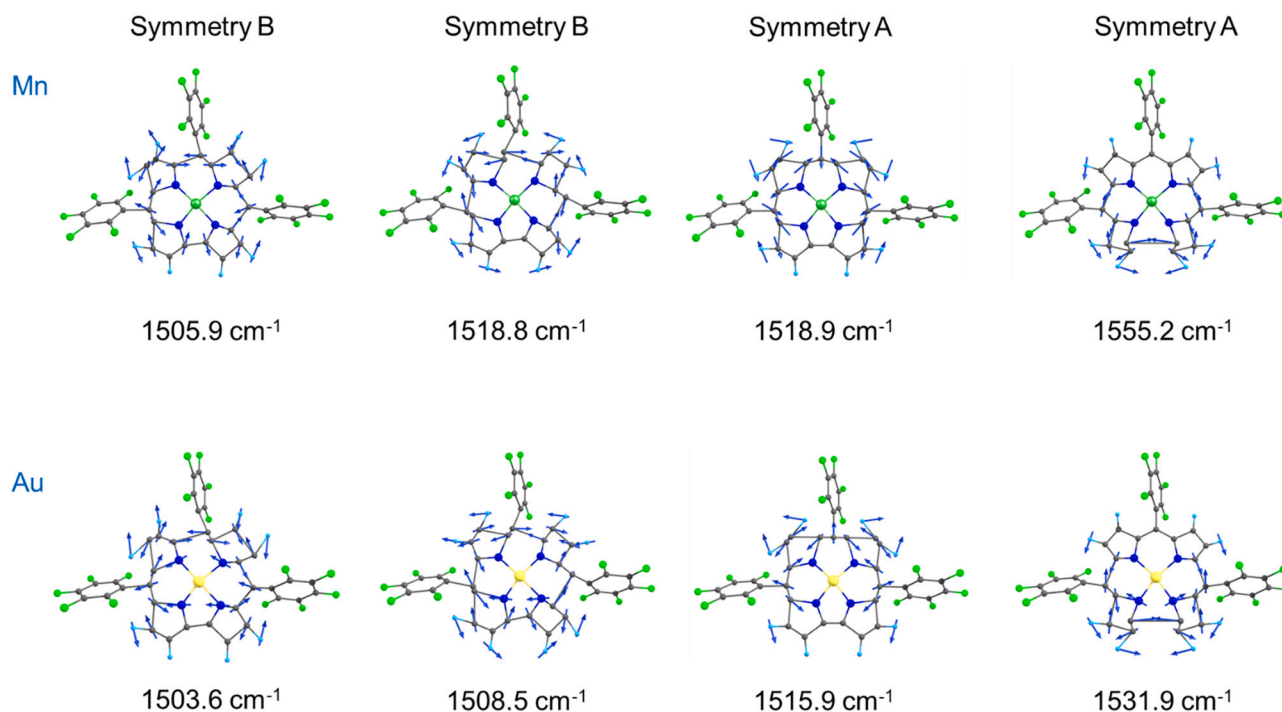

Fig. 4. Eigenvectors and corresponding DFT frequencies for potential structure-sensitive RR bands in the 900–1200 cm^{-1} region. The frequencies refer to the ^{12}C^{14}N column under ν_{DFT} in Table 1.

Fig. 5. Eigenvectors and corresponding DFT frequencies for potential structure-sensitive RR bands in the 1200–1400 cm^{-1} region. The frequencies refer to the ^{12}C^{14}N column under ν_{DFT} in Table 1.

Fig. 6. Eigenvectors and corresponding DFT frequencies for potential structure-sensitive RR bands in the 1400–1500 cm^{-1} region. The frequencies refer to the ^{12}C^{14}N column under ν_{DFT} in Table 1.

Symmetry B	Symmetry B	Symmetry A	Symmetry A

Mn

1505.9 cm^{-1} | 1518.8 cm^{-1} | 1518.9 cm^{-1} | 1555.2 cm^{-1}

Au

1503.6 cm^{-1} | 1508.5 cm^{-1} | 1515.9 cm^{-1} | 1531.9 cm^{-1}

Fig. 7. Eigenvectors and corresponding DFT frequencies for potential structure-sensitive RR bands in the 1500–1500 cm^{-1} region. The frequencies refer to the $^{12}C^{14}N$ column under ν_{DFT} in Table 1.

Mn

697.8 cm^{-1} | 1016.4 cm^{-1} | 1063.1 cm^{-1}

Au

685.0 cm^{-1} | 1028.7 cm^{-1} | 1075.0 cm^{-1}

Fig. 8. Eigenvectors and corresponding DFT frequencies for potential structure-sensitive IR bands. The frequencies refer to the $^{12}C^{14}N$ column under ν_{DFT} in Table 2.

Declaration of Competing Interest

None.

Appendix A. ESI mass spectra

Fig. A1. Positive-mode ESI mass spectrum of natural-abundance Au[TPFPC]. Insert: Detail of the molecular ion peak (top) and simulation (bottom). Molecular formula: $N_4F_{15}C_{37}H_8Au$.
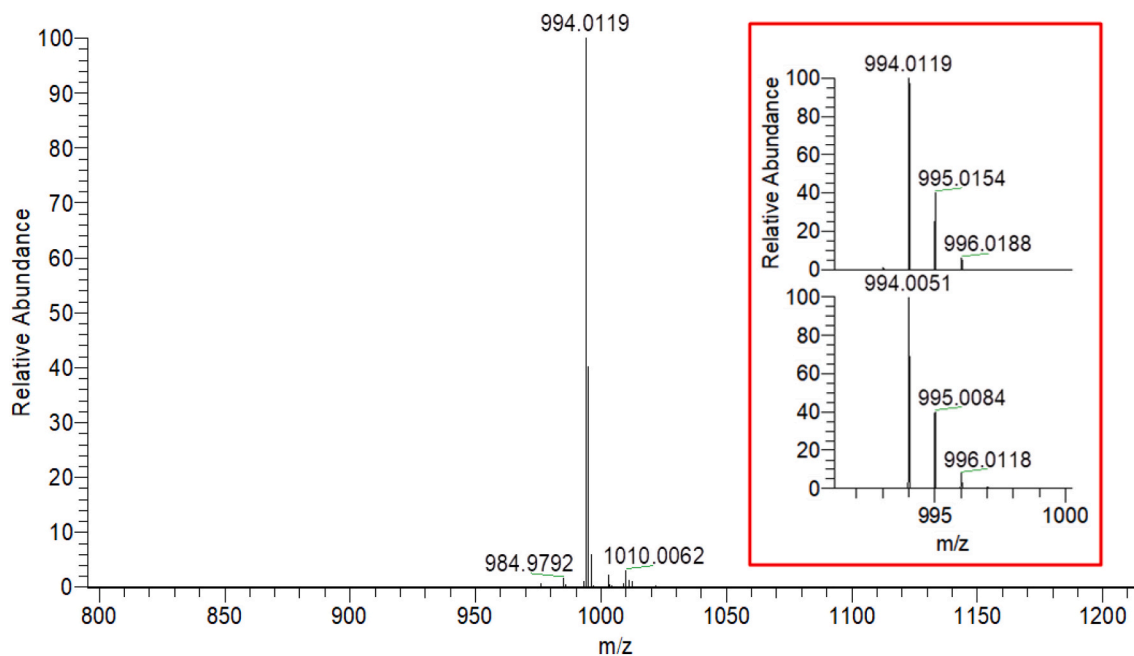

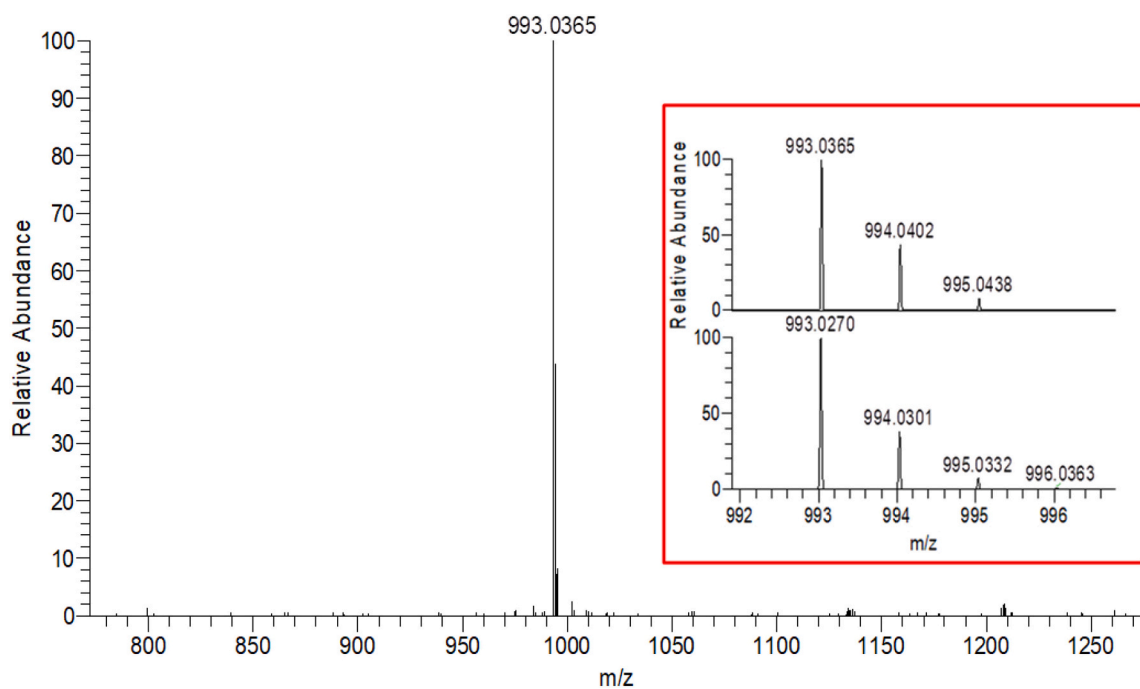**Fig. A2.** Positive-mode ESI mass spectrum of fully pyrrole-^{15}N-substituted Au[TPFPC]. Insert: Detail of the molecular ion peak (top) and simulation (bottom). Molecular formula: $^{15}N_4F_{15}C_{37}H_8Au$.

Fig. A3. Positive-mode ESI mass spectrum of fully *meso*-^{13}C-substituted Au[TPFPC]. Insert: Detail of the molecular ion peak (top) and simulation (bottom). Molecular formula: $^{13}C_3N_4F_{15}C_{34}H_8Au$.
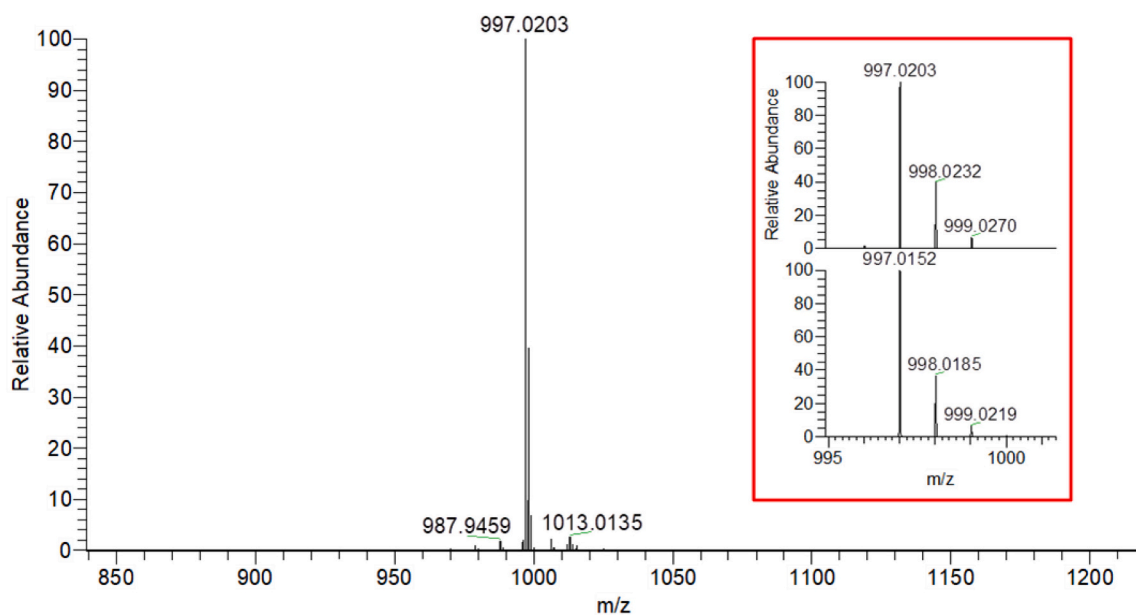

Fig. A4. Positive-mode ESI mass spectrum of fully *meso*-^{13}C- and pyrrole-^{15}N-substituted Au[TPFPC]. Insert: Detail of the molecular ion peak (top) and simulation (bottom). Molecular formula: $^{13}C_3{}^{15}N_4F_{15}C_{34}H_8Au$.
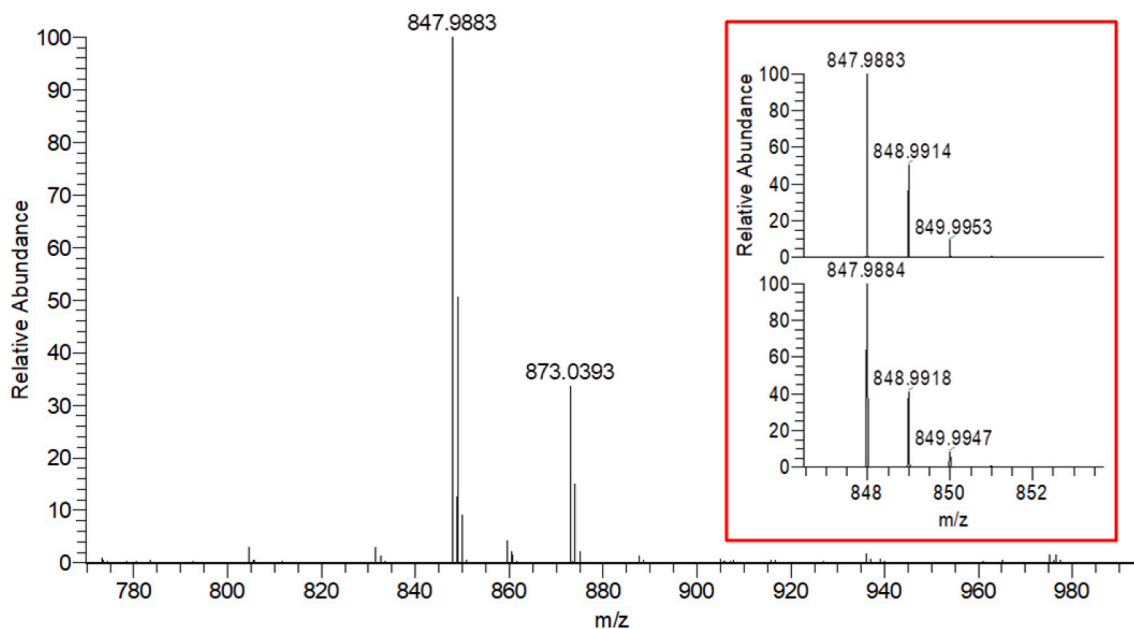
Fig. A5. Positive-mode ESI mass spectrum of natural-abundance Mn[TPFPC]. Insert: Detail of the molecular ion peak (top) and simulation (bottom). Molecular formula: $N_4F_{15}C_{37}H_8Mn$.
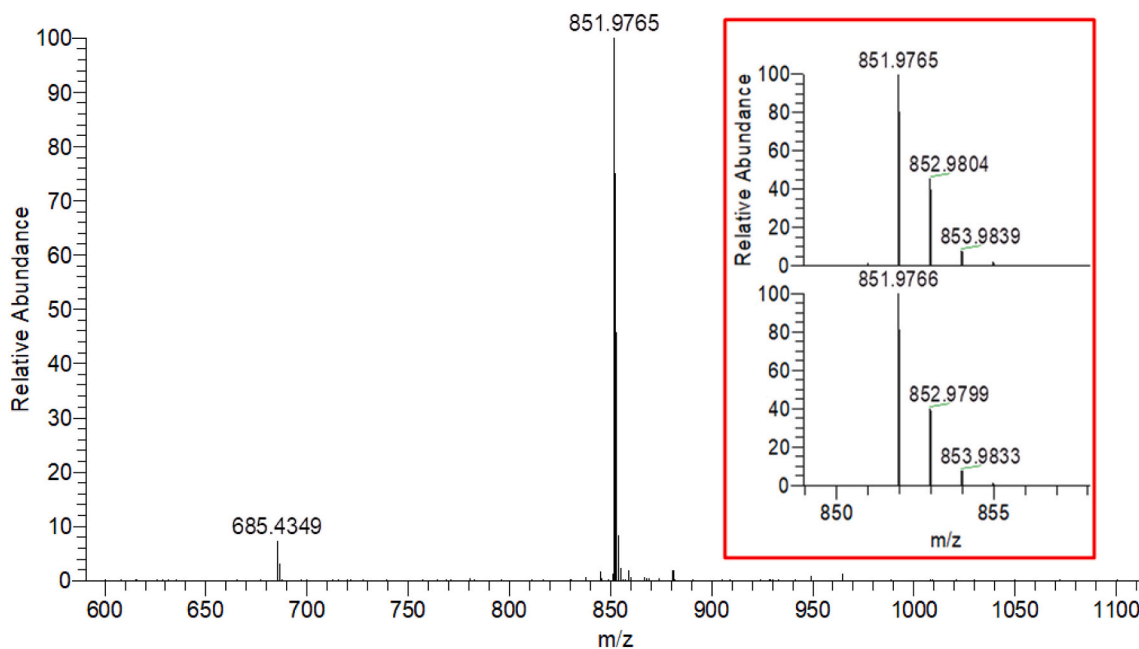

Fig. A6. Positive-mode ESI mass spectrum of fully pyrrole-^{15}N-substituted Mn[TPFPC]. Insert: Detail of the molecular ion peak (top) and simulation (bottom). Molecular formula: $^{15}N_4F_{15}C_{37}H_8Mn$.
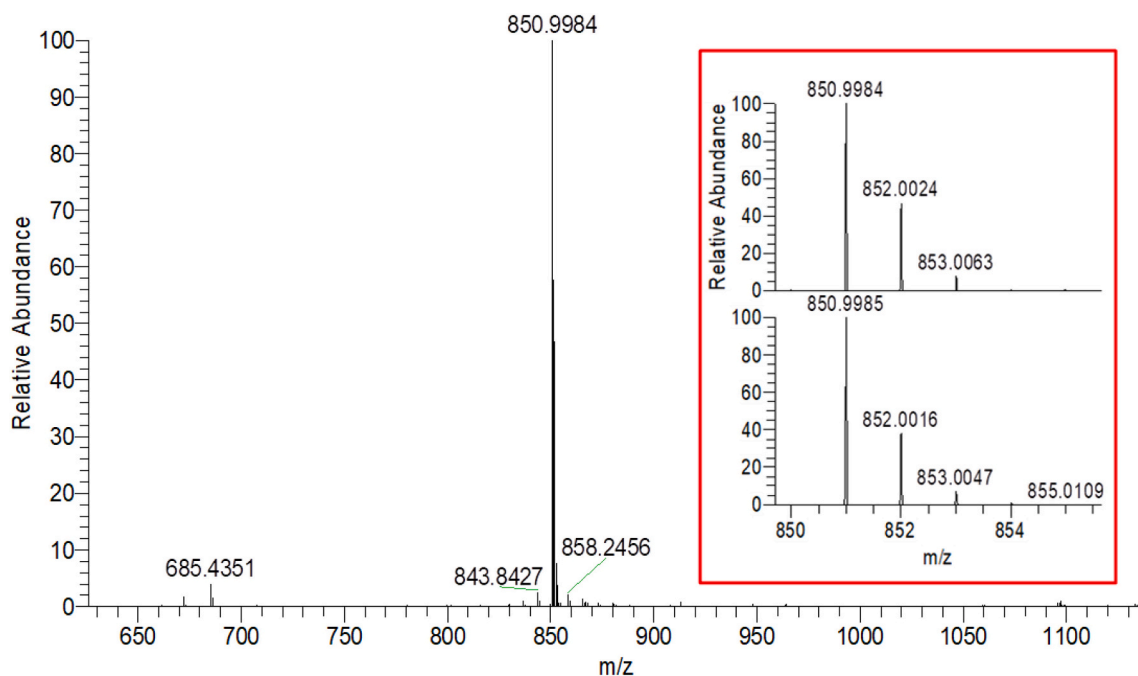
Fig. A7. Positive-mode ESI mass spectrum of fully *meso*-^{13}C-substituted Mn[TPFPC]. Insert: Detail of the molecular ion peak (top) and simulation (bottom). Molecular formula: $^{13}C_3N_4F_{15}C_{34}H_8Mn$.

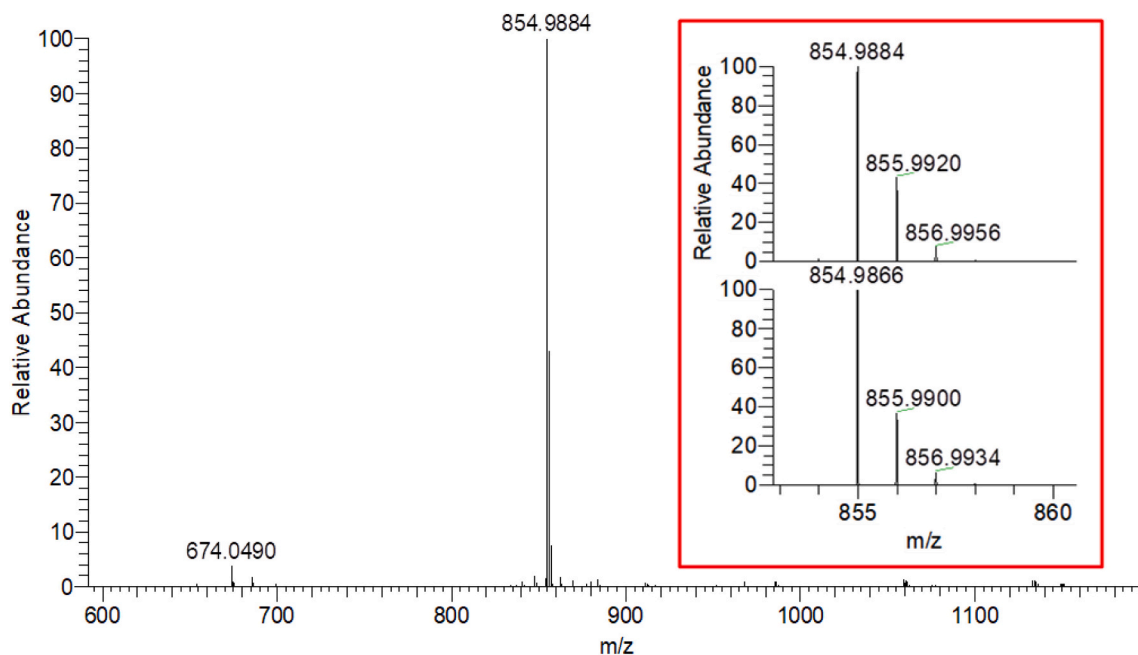**Fig. A8.** Positive-mode ESI mass spectrum of fully *meso*-^{13}C- and pyrrole-^{15}N-substituted Insert: Detail of the molecular ion peak (top) and simulation (bottom). Molecular formula: $^{13}C_3{}^{15}N_4F_{15}C_{34}H_8Mn$.

References

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