Substrate charge transfer drives the absorption site of metal-phthalocyanines and porphyrins on coinage metal surfaces†

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Electronic Supplementary Information

TPP^{2-} & Pc^{2-} ligand fields and frontier electronic structure of MTPP & MPc isolated complexes (M = V, Cr, Mn, Fe, Co, Ni, Cu, and Zn).

ESI.1 TPP^{2-} & Pc^{2-} ligand fields.

A preliminary series of ADF calculations has been carried out to homogeneously compare structural and electronic properties of H_2P, H_2Pz, H_2TPP, and H_2Pc with those of the deprotonated, negatively charged species P^{2-}, Pz^{2-}, TPP^{2-}, and Pc^{2-} (see Figures S1–S4 and Tables S1–S8) by assuming an idealized D_{2h} (D_{4h}) symmetry[1] for the free-base neutral molecules (deprotonated, double charged species). Incidentally, H_2P, P^{2-}, H_2Pz, and Pz^{2-} species have been herein considered to investigate the effects associated with the Ph decoration of C^m H_2P atoms upon the $H_2P \rightarrow H_2TPP$ switching, as well as with the fusion of the benzene ring to Py upon moving from H_2Pz to H_2Pc.

Data reported in Figures S1 and S2, where selected internuclear distances of the neutral species are reported, reveal that the substitution of the four *m*-CH groups with as many N^m atoms affects the pmc molecular structure through the shortening of the $C^{\alpha}–X^m$ bond length and the decreasing of the $N^{Py}\cdots N^{Py}$ and $X^m\cdots X^m$ internuclear distances: in other words, through the shrinking of the coordinative pocket.[2] Consistently with a ligand field stronger in Pc^{2-} than in TPP^{2-},[3-5] analogous considerations hold for the charged species (see Figures S3 and S4).[I] Besides structural effects, information about nature and strength of the electronic perturbations induced by the substitution of the *m*-CH groups with N^m atoms can be gained by referring to Figure S5 where the energy position of the H_2P, H_2Pz, H_2TPP, and H_2Pc FMOs[9] is compared with that of the Py and *i*-Ind HOMOs whose 3D CPs are displayed in Figure S6 (optimized Cartesian coordinates of the C_{2v} Py and *i*-Ind molecules are reported in Tables S9 –S10). The first thing to be noted is the upward energy shift of the *i*-Ind $2a_2$ HOMO compared to the Py $1a_2$ one as a consequence of the antibonding interaction between Py-based and benzene-based HOMOs (see Figure S6).[II] This evidence perfectly agrees with the IEs values of the Py $1a_2$ and *i*-Ind $2a_2$ HOMOs (8.21 and 7.3 eV, respectively),[10-11] quantitatively reproduced (8.39 and 7.18 eV, respectively) by exploiting the Slater TS formalism,[12] a method which allows the evaluation of the excitation/ionization energies through a fictitious transition state in which the occupation numbers of the various SOs are halfway between those of the initial and final states.

Upon moving from the C_{2v} Py to the D_{2h} H_2P,[13] the four SALCs generated by the Py $1a_2$ HOMO ($b_{2g} + b_{3g} + 2 \times a_u$) will interact with the C^m π SALCs ($b_{2g} + b_{3g} + a_u + b_{1u}$) of the same symmetry. Among H_2P a_u, b_{2g}, and b_{3g} MOs, the FMOs related to the Py $1a_2$ HOMO and having contributions from the C^m π SALCs are the occupied/unoccupied $1a_u$, $2a_u$, $2b_{2g}$, $2b_{3g}$/$3a_u$, $4b_{2g}$, $4b_{3g}$ MOs (see Figures S5, S8, and S9); in addition, the frontier energy region includes the $5b_{1u}$ HOMO, strongly localized on the C^m $2p_z$ AOs (see Figure S8) and very close in energy to the $2a_u$ MO (see Figure S5).

The gas-phase HeI PE spectrum of H_2P, first recorded in the late 1980s by Dupuis et al.,[14] shows a prominent peak at 6.9 eV with two evident shoulders on its higher IE side at 7.1 and 7.2 eV. In agreement with theoretical outcomes reported by Ortí and Brédas,[15] Ghosh and Vangberg,[16] and Piet et al.,[17] our TS calculations assign thse structures to the $2a_u$ and $5b_{1u}$ MOs (see Figure S5) whose TSIEs are 7.12 and 6.92 eV, respectively. To the best of our knowledge, no measurements of the H_2P EA are present in the literature; nevertheless, the H_2P lowest attachment energy (to a first approximation the negative of the capturing species EA[18]) has been evaluated by exploiting the Slater TS method.[12] The $4b_{2g}$ TSEA value (1.50 eV) is in quite good agreement with the experimental H_2TPP EA (1.69 eV,[19] *vide infra*).

The substitution of methine bridges with N^m atoms in H_2Pz induces a quite uniform and sizable downward shift of all the H_2P FMOs and energy reversal between the HOMO ($5b_{1u}$ in H_2P) and HOMO-1 ($2a_u$ in H_2P), see Figure S5. Unfortunately, no PE data are available in the literature for H_2Pz; nonetheless, the TSIEs of the H_2Pz $2a_u$ HOMO (7.75 eV) and $5b_{1u}$ HOMO-1 (8.32 eV), as well as the TSEA of the H_2Pz $4b_{2g}$ LUMO (2.36 eV), have been computed. Upon moving from H_2Pz to H_2Pc, the blue-shift determined by substituting methine bridges with N^m atoms ($H_2P \rightarrow H_2Pz$; see Figure S5) is partially offset by fused benzene rings in H_2Pc (see Figure S5). In this regard, it is worthwhile to mention that, as expected, the H_2Pz $5b_{1u}$ FMO (localized on the pmc but not related to the *i*-Ind $2a_2$ HOMO) is only tiny affected by the $H_2Pz \rightarrow H_2Pc$ switching.

A bunch of PE data is available in the literature for H_2Pc in the gaseous,[20-23] solid,[20] and film[24] forms. Nardi et al.[24] ultimately assigned the peak having the lowest IE to the ionization from the $4a_u$ HOMO by exploiting the different C/N ASPCS[25] within the Gelius model[26,III] and comparing experimental evidence with theoretical outcomes homogeneous with those herein reported. Additionally, the H_2Pc HeI PE spectrum recorded by Berkowitz in the vapor phase is characterized by a sharp peak at 6.41 eV,[23] reproduced very well by the TSIE of the $4a_u$ HOMO (6.57 eV, see Table S11 and Figure S10).[IV]

Similarly to the GS (see Figure S5), the TSIE of the $7b_{1u}$ MO is significantly higher (7.74 eV, see Table S11) than that of the $4a_u$ HOMO.[IV] Moving to the quasi-degenerate LUMOs $6b_{3g}$ and $6b_{2g}$ (see Figure S5 and Figure S10), their TSEAs (2.30 and 2.26 eV, respectively) are in good agreement with the experimental and theoretical adiabatic EA values (2.07 ± 0.15 and 2.34 eV, respectively) reported by Khatymov et al.[27] and significantly higher than the H_2TPP experimental EA (1.69 eV).[19]

Perturbations induced by the Ph decoration of C^m are almost negligible, being the $^{pmc}\pi$ system perpendicular to that of the Ph fragments.[28] This is further confirmed by looking at the energy position of H_2TPP FMOs upon moving from H_2P to H_2TPP (see Figure S5). Likewise to H_2P, H_2Pz, and H_2Pc, TSIEs and TSEAs of H_2TPP have been herein evaluated for the HOMOs and LUMOs and compared with literature data.[17, 28-31] TSIEs of the $13b_{1u}$ HOMO and the $10a_u$ MO are 6.48 and 6.77 eV (see Table S11 and Figure S10),[IV] respectively, and they agree quantitatively with gas-phase HeI PE data (6.39 and 6.72 eV) recorded by Khandelwal and Roebber.[29] Analogous considerations hold for the TSEAs of the $12b_{3g}$ and $12b_{2g}$ LUMOs (1.68 and 1.68 eV),[IV] which numerically reproduce the H_2TPP experimental EA (1.69 eV).[19]

Some of us have addressed the parenthood between occupied FMOs of H_2TPP/H_2Pc and TPP^{2-}/Pc^{2-} in ref. 32 (see Figure S10).[IV] Ligand-based occupied FMOs cannot be involved in the substrate → adsorbate charge transfer, while the opposite is true for the lowest-lying $12e_g$ and $9b_{1u}$ TPP^{2-} ($6e_g$ and $3b_{1u}$ Pc^{2-}) $^{pmc}\pi^*$ FMOs (see Figure S11, where the energy and localization of the TPP^{2-} and Pc^{2-} lowest-lying $^{pmc}\pi^*$ FMOs are compared with those of the occupied $2a_{1u}$ $^{pmc}\pi$ MO). Berkowitz,[23] in his seminal paper devoted to the investigation of gas-phase PE spectra of H_2Pc and selected MPcs (M = Mg, Fe, Co, Ni, Cu, and Zn), pointed out that, even in the metal-free species and in the MgPc complex, the lowest IE systematically occurs at ~6.4 eV, thus concluding that it corresponds to the electron ejection from a $^{pmc}\pi$ FMO rather than from an M-based MO. As such, Nardi et al.[24] stated that the CuPc $2a_{1u}$ HOMO and the $16b_{1g}$ singly occupied MO (the half-occupied Cu $3d_{x^2-y^2}$-based orbital, Cu–N^{Py} antibonding in nature) are quasi degenerate (ΔE = 0.1 eV) in the GS; nevertheless, the accounting of the electronic structure relaxation upon ionization through Slater TS calculations removes such a quasi-degeneracy (see Figure 2 in the main text).[V] In addition, it must be underlined that nodal properties of a_{1u} MOs imply a node on the D_{4h} σ_v and σ_d symmetry planes,[1] which sterilize the N^{Py} and X^{m} π ($2p_z$) AOs participation to the corresponding MOs (see Figure S11). The inspection of Figure S11 testifies that, even though the $^{pmc}\pi^*$ e_g and b_{1u} MOs, have similar localizations on the pmc of the TPP^{2-} and Pc^{2} ligands, the opposite is true when their energy position relative to the $^{pmc}\pi$ $2a_{1u}$ MO is considered.[VI] More specifically, the relative energies of the Pc^{2-} $^{pmc}\pi^*$ e_g and b_{1u} MOs are lower than the corresponding TPP^{2-} $^{pmc}\pi^*$ MOs, and this is more evident for the b_{1u} MOs because of the nil localization on the N^{Py} $2p_z$ AOs (a consequence of the presence of σ_v nodal planes)[1] and the significant participation of C^{m} (N^{m}) $2p_z$ AOs to the TPP^{2-} (Pc^{2-}) $9b_{1u}$ ($3b_{1u}$) MO. The relative energy position of the $9b_{1u}$ and $3b_{1u}$ MOs in TPP^{2-} and Pc^{2-}, respectively, might determine significant differences in the MTPP and MPc π acceptor capability and then in the substrate $\rightarrow$ adsorbate charge transfer when chemisorption processes are considered. As a whole, the shrinking of the coordinative pocket induced by the presence of N^{m} atoms combined with the energy position of low-lying $^{pmc}\pi^*$ FMOs, more stable in H$_2$Pc than in H$_2$TPP (H$_2$TPP and H$_2$Pc LUMO TSEAs values are 1.68 and 2.30 eV, respectively), provide a convincing explanation of why the Pc^{2-} ligand field is stronger than the TPP^{2-} one.[VII] These results allow us to foresee a stronger substrate $\rightarrow$ adsorbate charge transfer in MPc/CM interfaces than in the MTPP/CM ones, a consequence of the better energy matching between SALCs of the ^{S}CM AOs and MPcs unoccupied FMOs.

ESI.2 Frontier electronic structure of MTPP & MPc isolated complexes (M = V, Cr, Mn, Fe, Co, Ni, Cu, and Zn).

VTPP and VPc. The lack of literature data for the fourfold coordinated VTPP and the synthesis of the D_{4h} VPc in extreme conditions ten years ago[36] must be underlined before anything else. In addition, it may be useful to remember that two papers, published more than forty years ago, report the synthesis and the structural determination of the hexacoordinate complexes [V(OEP)(L)$_2$] (L = PPhMe$_2$,[37-38] THF[38]), and a more recent contribution describes the synthesis of [V(TTP)(L)$_2$] (L = THF) without reporting any structural determination.[39] As such, it is noteworthy that the mean V–N^{Py} bond lengths in [V(OEP)(PphMe$_2$)$_2$] (2.051 Å)[37] and [V(OEP)(THF)$_2$] (2.046 Å)[38] are in quantitative agreement with the V–N^{Py} distance herein optimized for the D_{4h} HS VTPP (2.046 Å, see Table S12; VTPP optimized Cartesian coordinates are reported in Table S13).

The electronic configuration of the isolated V^{II} ion is $3d^3$ and, in principle, the three 3d electrons may be distributed in 120 ($\frac{10!}{3! \times 7!}$) different ways among the ten 3d-based SOs. Nonetheless, the V^{II} $^{\sigma}e_g$-like $^{\sigma}b_{1g}$ SOs, V–N^{Py} antibonding in nature, can be safely disregarded because of their high energy position (*vide infra*). In the hypothetical VTPP, the three 3d electrons can be then distributed in 56 ($\frac{8!}{3! \times 5!}$) different ways, straightforwardly grouping in the $^4A_{2g}$, $^4B_{1g}$, ^4E_g, 3 × $^2A_{1g}$, 2 × $^2A_{3g}$, $^2B_{2g}$, 7 × ^2E_g states by exploiting the spin factoring method.[40] The HS state herein assumed is based on the evidence that: i) VPc is characterized by a V^{II} HS GS (^4E_g)[41-42] and ii) the TPP^{2-} ligand field is weaker than the Pc^{2-} one.[3-5] Analogously to VPc,[41-42] the ADF ^4E_g term corresponds to the VTPP GS, more stable than $^4B_{1g}$ and $^4A_{2g}$ states by 123 and 278 meV (see Table S14), respectively.[VIII-IX] In addition, as anticipated, the VTPP $^{\sigma}e_g$-like $12b_{1g}$ SOs are significantly higher in energy (> 2 eV) than the VTPP $^{\pi}t_{2g}$-like $12e_g^{\uparrow}$ highest occupied SOs. Finally, VTPP optimized geometrical parameters are negligibly affected by the different occupation numbers of the V 3d-based SOs.

Even though no literature data are available for the isolated VTPP, TS calculations have been run to estimate the IEs of the topmost occupied V 3d-based and $^{pmc}\pi$ orbitals (see Table S11 and the lower panel of Figure 2) as well as the EAs of the lowermost unoccupied V 3d-based and $^{pmc}\pi^*$ orbitals (see Table S15 and the lower panel of Figure 2). Data reported in Tables S11, S15, and Figure 2 reveal that, among the occupied frontier SOs, the V 3d-based $12e_g^{\uparrow}$ SOs have the lowest TSIE, thus mirroring the theoretical outcomes published by some of us for VPc,[41] whose optimized Cartesian coordinates are reported in Table S16. Additionally, all the TSIEs of the VTPP 3d-based SOs are lower than those corresponding to the $^{pmc}\pi$ ones ($12a_{2u}^{\downarrow}$ and $2a_{1u}^{\downarrow}$), whose TSIEs, similarly to H$_2$TPP, are quite close in energy (see Table S11 and Figure 2).

Interestingly, the TSIE of the $2a_{1u}^{\downarrow}$ SO is only tiny affected upon moving from VTPP to VPc while the opposite is true when the VTPP $12a_{2u}^{\downarrow}$ and VPc $6a_{2u}^{\downarrow}$ SOs are considered (see Table S11 and Figure 2). In this regard, it is of some relevance to underline that the pmc localization of the VTPP $12a_{2u}^{\downarrow}$ and VPc $6a_{2u}^{\downarrow}$ SOs is quite similar; thus, the significantly higher TSIE of the $6a_{2u}^{\downarrow}$ SO can be confidently ascribed to the different GS energy position of the two SOs in the ^4E_g VTPP (-5.01 eV) and ^4E_g VPc (-6.60 eV) GS. This is a consequence of the nodal properties of the a_{2u} wavefunctions, symmetric with respect to the σ_d reflection planes (those passing through the X^{m} atoms) in the D_{4h} symmetry point group.[1] By the way, the participation of π ($2p_z$) X^{m} AOs to a_{2u} SOs provides a rationale for the higher stability of the VPc $6a_{2u}^{\downarrow}$ SO (the N^{m} $2p_z$ AOs contribution amounts to 35%; $^{N}\chi$ = 3.04[43-44]) compared to that of the VTPP $12a_{2u}^{\downarrow}$ one (the C^{m} $2p_z$ AOs contribution amounts to 56%; $^{C}\chi$ = 2.55[43-44]).

Before considering the VTPP and VPc LUMO TSEAs, it must be kept in mind that the ^4E_g GS of both complexes is characterized the presence of a single electron in the V $^{\pi}_{\perp}e_g^{\uparrow}$ frontier SOs (see Table S14); thus, the lowest TSEA will correspond to that of the $^{\pi}_{\perp}e_g^{\uparrow}$ SOs (see Table S15 and Figure 2). Moreover, it must be underlined that the VTPP (VPc) $12e_g^{\downarrow}$ ($6e_g^{\downarrow}$) SOs do not correspond to the spin ↓ partners of the V 3d-based $^{\pi}_{\perp}e_g^{\uparrow}$ SOs, but rather to $^{pmc}\pi^*$ orbitals having a contribution from V $3d_{xz}/3d_{yz}$ AOs of 9% and 12% in VTPP and VPc, respectively. Interestingly, VTPP and VPc LUMO TSEAs are larger than those corresponding to the $^{pmc}\pi^*$ MOs (see Table S15 and Figure 2); moreover, the TSEA of the VTPP $12e_g^{\uparrow}$ SOs is significantly lower than that of the VPc $6e_g^{\uparrow}$ ones, tempting us to foresee a higher V^{II} electron acceptor capability in VPc than in VTPP.

As a whole, despite the TPP^{2-} and Pc^{2-} different ligand field strength, VTPP and VPc i) share the same GS term ($^{4}E_g$); ii) consistently with the weaker ligand field of TPP^{-2} compared to the Pc^{2-} one,[5-4] the optimized $V–N^{Py}$ bond length in VTPP is longer than that optimized for VPc (2.046 Å vs. 1.996 Å; see Table S12); iii) quartet states, some of which in Table S14, are all characterized by the occurrence of at least one vacancy in the V $3d_{z^2}$-based MO.

CrTPP and CrPc. The four-coordinate CrTPP was first prepared and characterized in late 1978.[3,45-46] Despite Cr^{II} carries four 3d electrons, which could be distributed in 210 ($\frac{10!}{4! \times 6!}$) different ways among the ten 3d-based SOs, the Cr^{II} $^{\sigma}e_g$-like $^{\sigma}b_{1g}$ SOs, $Cr–N^{Py}$ antibonding, may be safely disregarded because of their energy position (*vide infra*). This means that the four 3d electrons of CrTPP may be distributed in 70 different ways among the remaining eight 3d-based SOs ($\frac{8!}{4! \times 4!}$) factorizable in the $^{5}B_{1g}$, $^{3}A_{1g}$, 3 × $^{3}A_{2g}$, $^{3}B_{1g}$, 5 × $^{3}E_g$, 5 × $^{1}A_{1g}$, $^{1}A_{2g}$, 7 × $^{1}E_g$ states.[40] CrTPP corresponds to a highly reactive Cr^{II} d^4 HS complex (magnetic moments measurements provide $\mu^{298\,K}_{cor} = 4.9\mu_B$)[3] whose GS is uniquely defined by the $^{5}B_{1g}$ spectral term.

The ADF GS configuration (see Table S14) agree with such a picture even if the relative energy position of Cr^{II} occupied 3d-based SOs (the ${}^{\sigma}a^{\uparrow}_{1g}$ SO is more stable than the ${}^{\pi}_{\perp}e^{\uparrow\uparrow}_{g}$ SOs by 196 meV) differs from that obtained by Cook et al. (${}^{\pi}_{\perp}e^{\uparrow\uparrow}_{g}$ SOs are more stable than the ${}^{\sigma}a^{\uparrow}_{1g}$ SO; see Figure S55 of ref. 47) by carrying out DFT calculations, using the 4.1.2 version of the ORCA package,[48] and a different XC functional. As far as the $^{5}B_{1g}$ CrTPP optimized structural parameters are concerned (CrTPP optimized Cartesian coordinates are reported in Table S17), no comparison can be made with data reported by Cook et al.[47] because, even though they claim the geometry optimization of all the structures they considered, no detail about the geometrical parameters of the isolated CrTPP is reported in their contribution. Anyway, the inspection of Table S12 indicates that the optimized ADF $Cr–N^{Py}$ bond length (2.035 Å) quantitatively agrees with the experimental value (2.033 Å) reported by Scheidt and Reed[45-46] and, similarly to the VTPP/VPc pair, it is longer in CrTPP than in the CrPc $^{5}B_{1g}$ GS (1.982 Å;[41] CrPc optimized Cartesian coordinates are reported in Table S18).

Interestingly, the CrTPP GS, independently of the relative position of Cr^{II} occupied 3d-based SOs, is characterized by the Cr^{II} $^{\sigma}e_g$-like $12b_{1g}$ SOs significantly higher in energy (> 3 eV) than the CrTPP HOMO and the empty Cr $3d_{z^2}$-based $25a^{\downarrow}_{1g}$ SO. Moreover, it must be underlined that, analogously to VTPP, the $12e^{\downarrow}_{g}$ SOs do not correspond to the spin ↓ partners of the Cr^{II} $^{\pi}t_{2g}$-like ${}^{\pi}_{\perp}e_{g}$ SOs, but rather to the $^{pmc}\pi^*$ orbitals having a minute contribution (7%) from the Cr^{II} $3d_{xz}/3d_{yz}$ AOs.

Despite several synthetic routes reported in the literature for CrPc,[49-51] the lack of any single crystal X-ray structure must be stressed. Some of us have thoroughly considered the electronic properties of CrPc in ref. 41 (occupation numbers of Cr^{II} 3d-based SOs and their relative energy position mirror the CrTPP ones; see Table S14); thus, we will limit ourselves to reminding here that, even though the $^{5}B_{1g}$ GS has been experimentally revealed[49,52] and theoretically predicted,[41,53] the localization of the occupied frontier SOs is still controversial. Indeed, numerical experiments carried out by Arillo-Flores et al.[53] are consistent with the absence of any contribution from Cr^{II} 3d AOs to the HOMO and LUMO, mainly localized on the pmc, which is certainly correct for the Cr-free $2a_{1u}$ HOMO, but only partially true for the $6e^{\downarrow}_{g}$ lowest unoccupied SOs whose localization on the Cr $3d_{xz}$ and $3d_{yz}$ AOs, similarly to the CrTPP $12e^{\downarrow}_{g}$ SO, is tiny but not negligible (10%). As such, it is noteworthy that, differently from VPc, whose three highest lying SOs are V 3d-based orbitals, the CrPc HOMO is the Cr-free, $2a_{1u}$ $^{pmc}\pi$ MO.

Even though the IEs of CrTPP and CrPc frontier SOs have never been measured, the inspection of Table S11 and Figure 2 is particularly interesting because it reveals that, contrary to VTPP and VPc, the lowest TSIEs correspond to the ionization from $^{pmc}\pi$ MOs (the Cr-free, CrTPP $12a^{\downarrow}_{2u}$ and CrPc $2a^{\downarrow}_{1u}$ SOs). In this regard, it is noteworthy that the GS CrTPP HOMO and HOMO-1 are the Cr^{II} ${}^{\pi}_{\perp}e_{g}$ ($12e^{\uparrow\uparrow}_{g}$) and $^{\sigma}a_{1g}$ ($25a^{\uparrow}_{1g}$) SOs, respectively, thus indicating a strong relaxation upon ionization of the Cr 3d-based SOs.[V]

Two further points deserve to be underlined upon moving from V^{II} to Cr^{II}: i) the quite large and constant (*vide infra*) ΔTSIE between the $12a^{\downarrow}_{2u}$ and $6a^{\downarrow}_{2u}$ TSIEs (~1.5 eV, see Table S11 and Figure 2); ii) LUMO TSEAs are very different (see Table S15 and Figure 2) and this has to be ultimately traced back to the different nature and localization of the LUMO in V^{II} and Cr^{II} complexes.

MnTPP and MnPc. The four-coordinate MnTPP was prepared and characterized by the Scheidt group[54] as almost contemporary of CrTPP[45] and, similarly to Cr^{II} in CrTPP, Mn^{II} has an HS configuration ($\mu^{298\,K}_{cor} = 6.0\mu_B$);[3,54] i.e., the five Mn^{II} 3d electrons are homogeneously distributed among the five 3d AOs and the D_{4h} MnTPP GS corresponds to the $^{6}A_{1g}$ state. As far as the remaining quartet and doublet states are concerned, they are 3 × $^{4}A_{1g}$, 3 × $^{4}A_{2g}$, 3 × $^{4}B_{1g}$, 3 × $^{4}B_{2g}$, 6 × $^{4}E_g$, 11 × $^{2}A_{1g}$, 8 × $^{2}A_{2g}$, 10 × $^{2}B_{1g}$, 10 × $^{2}B_{2g}$, 18 × $^{2}E_g$, for the total of 252 ($\frac{10!}{5! \times 5!}$) different ways of distributing the five 3d electrons among the ten 3d-based SOs.[40] The MnTPP HS $^{6}A_{1g}$ GS, combined with the experimental and theoretical evidence that MnPc has an IS state,[3-4,41,55-56] ultimately confirms the weaker ligand field of TPP^{2-} compared to that of Pc^{2-}.

The D_{4h} MnTPP free molecule has been herein investigated by running a series of ADF numerical experiments assuming either a HS (five unpaired electrons) or an IS (three unpaired electrons) state. Preliminary HS calculations have been carried out by adopting the same setup exploited for lighter MTPP and imposing either no constraint or the presence of five unpaired electrons in the Mn 3d-based SOs. Calculations slightly converged to a non-Aufbau SOs occupation; moreover, in contrast with the experimental evidence,[3,54] the $^{6}A_{1g}$ HS state resulted less stable than the $^{4}A_{2g}$ and $^{4}E_g$ IS states. A further series of numerical experiments has been then carried out by adopting the hybrid B3LYP[57-59] XC functional (see the Computational details section in the main text). The better treatment of the exchange potential allowed, even in the absence of any constraint, a smooth and fast convergence for the $^{6}A_{1g}$ HS state (see Table S14), more stable than B3LYP $^{4}A_{2g}$ ($[{}^{\pi}_{\perp}e^{\uparrow\uparrow}_{g}\,{}^{\sigma}a^{\uparrow}_{1g}\,{}^{\pi}_{||}b^{\uparrow}_{2g}\,{}^{\pi}_{||}b^{\downarrow}_{2g}]$),[VIII] $^{4}B_{1g}$ ($[{}^{\pi}_{||}b^{\uparrow}_{2g}\,{}^{\pi}_{\perp}e^{\uparrow\uparrow}_{g}\,{}^{\sigma}a^{\uparrow}_{1g}\,{}^{\sigma}a^{\downarrow}_{1g}]$),[VIII] and $^{4}E_g$ ($[{}^{\pi}_{||}b^{\uparrow}_{2g}\,{}^{\pi}_{\perp}e^{\uparrow\uparrow}_{g}\,{}^{\sigma}a^{\uparrow}_{1g}\,{}^{\pi}_{\perp}e^{\downarrow}_{g}]$)[VIII] IS states by 188, 421, and 622 meV, respectively. As conceivable, the optimized $^{6}A_{1g}$ GS $Mn–Ni^{Py}$ bond length results a bit longer (2.095 Å, see Table S12) than those optimized for the $^{4}A_{2g}$ (2.031 Å), $^{4}B_{1g}$ (2.029 Å), and $^{4}E_g$ (2.011 Å) states, as a consequence of the occupation of the Mn^{II} $^{\sigma}e_g$-like ${}^{\sigma}b^{\uparrow}_{1g}$ SO, $Mn–N^{Py}$ antibonding in character

(MnTPP B3LYP optimized Cartesian coordinates are reported in Table S19).[X] In this regard, it must be mentioned that Scheidt and Reed, in their review devoted to the spin-state/stereochemical relationships in Fe porphyrins,[60] explicitly underlined the Mn discontinuity, assigned to the Mn HS configuration, in the M-N bond length decreasing upon moving from CrTPP to NiTPP (an effect of increasing effective nuclear charge).

Differently from VTPP and CrTPP, gas-phase HeI PE data are available for most of the remaining MTPP herein considered;[29] moreover, experimental information about the MnTPP EA is also accessible.[61] Despite this seemingly valuable asset, several points must be underlined before attempting a comparison between experiment[29,61] and theory: i) Khandelwal and Roebber recorded the gas-phase PE spectra of the H_2TPP and MTPP (M = Mg, Mn, Fe, Ni, Cu, and Zn) but the only spectral patterns actually displayed in their paper are those of MgTPP and ZnTPP;[XI] ii) the IE position of H_2TPP and MTPP (M = Mn, Fe, Ni, and Cu) main features are collected in Table 1 of their contribution;[29] iii) the authors emphasize the close similarity of all the PE spectra and the absence of significant shifts in the IE positions of PE peaks along the investigated series;[XII] iv) gas-phase PE spectra are all recorded at the photon energy of the HeI resonance (21.2 eV), thus preventing the exploitation of the different C, N, and M ASPCS[25] within the Gelius model[26] to assign more confidently the experimental evidence.

MnTPP B3LYP TSIEs reported in Table S11 but not displayed in Figure 2 for the sake of homogeneity are consistent with the presence of two high-lying ${}^{\mathrm{pmc}}\pi$ SOs (the $2a_{1u}^{\downarrow}$ and $12a_{2u}^{\downarrow}$ orbitals) tiny affected upon moving from the free ligand to MTPP complexes;[IV] nevertheless, theoretical outcomes herein reported state that the lowest MnTPP TSIE corresponds to the $\mathrm{Mn^{II}}$-based ${}^{\sigma}e_g$-like ($12b_{1g}^{\uparrow}$) SO, Mn–N^{Py} antibonding. Experimental evidence pertinent to MnPc (*vide infra*) and drawbacks affecting the MTPP PE data collected by Khandelwal and Roebber half a century ago[29] would then make desirable further gas-phase IE measurements at different photon energies to wrap up this matter.

As far as the MnTPP EA determination is concerned, the experimental value (1.6 ± 0.1 eV)[61] qualitatively agrees with the TSEA of the ligand-based $12e_g^{\downarrow}$ SO (1.33 eV, see Table S15); nevertheless, it has to be stressed that Buytendyk et al.[61] did not provide any specific assignment of the adiabatic EA they measured.

Likewise VPc and CrPc, the electronic properties of the IS MnPc free molecule have been thoroughly described by some of us in ref. 41; thus, we herein limit to reminding that MnPc, at variance to MnTPP, carries only three unpaired electrons ($\mu_{cor}^{298\,K} = 4.34\mu_B$)[3] and its ${}^4E_g$ GS (see Table S14)[XIII] agrees with DV-Xα calculations[62] and experimental least-square population[63] (MnPc optimized Cartesian coordinates are reported in Table S20). In this regard, it must be noted that CASSCF calculations carried out by Wallace et al.[56] point to a [${}_{||}^{\pi}b_{2g}^{\uparrow\downarrow}\,{}_{\perp}^{\pi}e_g^{\uparrow\uparrow}\,{}^{\sigma}a_{1g}^{\uparrow}$][VIII] configuration (${}^4A_{2g}$) explicitly excluded by Reynolds and Figgis because of the high observed $3d_{z^2}$ spin population.[62] In addition, Wallace et al. themselves agree that the MnPc GS corresponds to the ${}^4A_{2g}$ eventually mixed with a low-lying ${}^4E_g$ excited state.[XIV]

Similarly to lighter complexes, the Mn–N^{Py} bond length corresponding to the MnPc GS (1.952 Å, see Table S12 and Table S20) is, in agreement with the experimental evidence,[4] significantly shorter than that characterizing the MnTPP GS as a consequence of the bareness of the $\mathrm{Mn^{II}}$-based ${}^{\sigma}e_g$-like ${}^{\sigma}b_{1g}^{\uparrow}$ SO determined by the stronger Pc^{2-} ligand field.

Despite the MnPc IS state, its lowest TSIE corresponds to the Mn 3d-based $6e_g^{\downarrow}$ SO at ~600 meV from the $2a_{1u}^{\downarrow}$ TSIE, tiny affected along the whole MTPP/MPc series (see Table S11 and Figure 2). This result, perfectly in tune with experimental and theoretical data reported by Grobosch et al.[64] and Bidermane et al.,[65] arouses further suspicion about the experimental evidence reported by Khandelwal and Roebber for MnTPP.[29]

A few additional points must be underlined before tackling isolated FeTPP and FePc molecules: i) the fairly constant ΔTSIE between the $12a_{2u}^{\downarrow}$ and $6a_{2u}^{\downarrow}$ TSIEs upon moving from MTPP to MPc (~1.5 eV, see Table S11); ii) both the HS MnTPP and the IS MnPc GS carry a vacancy in the ${}^{\sigma}e_g$-like ${}^{\sigma}a_{1g}^{\downarrow}$ SO (the $25a_{1g}^{\downarrow}$ and $21a_{1g}^{\downarrow}$ ones in MnTPP and MnPc, respectively); iii) the highest MnPc TSEA (2.84 eV, see Table S15 and Figure 2) corresponds to a ${}^{\mathrm{pmc}}\pi^*$ SO.[XV] The outcomes herein reported shed then new light on the qualitative assignment proposed by Yoshida et al. for their IPS results.[66,XVI]

FeTPP and FePc. FeTPP was first synthesized and characterized in the middle of the seventies by the Reed group.[67] Despite $\mathrm{Fe^{II}}$ has a $3d^6$ configuration, which may generate HS (S = 2), IS (S = 1), and LS (S = 0) states, stereochemical data, outcomes of Mossbauer spectroscopy recorded in different applied magnetic fields at temperature ranging from 4.2 to 300 K and magnetic moment measurements at RT prompted Collman et al.[67] to point a FeTPP IS GS. Among the $4 \times {}^3A_{1g} + 7 \times {}^3A_{2g} + 2 \times {}^3B_{1g} + 2 \times {}^3B_{2g} + 15 \times {}^3E_g$ IS states, including 135 of the $\frac{10!}{6! \times 4!} = 210$ microstates, those having unoccupied $\mathrm{Fe^{II}}$ ${}^{\sigma}b_{1g}$ SOs are only 18 (${}^3A_{2g} + {}^3B_{2g} + 2 \times {}^3E_g$).[40] Information about their relative energy has been obtained by carrying out a series of numerical experiments for the constrained electronic configurations [${}^{\sigma}a_{1g}^{\uparrow\downarrow}\,{}^{\pi}b_{2g}^{\uparrow\downarrow}\,{}^{\pi}e_g^{\uparrow\uparrow}$] (${}^3A_{2g}$), [${}^{\sigma}a_{1g}^{\uparrow}\,{}^{\pi}b_{2g}^{\uparrow}\,{}^{\pi}e_g^{\uparrow\uparrow\downarrow\downarrow}$] (${}^3B_{2g}$), [${}^{\sigma}a_{1g}^{\uparrow}\,{}^{\pi}b_{2g}^{\uparrow\downarrow}\,{}^{\pi}e_g^{\uparrow\uparrow\downarrow}$] (${}^3E_g^{(1)}$) and [${}^{\sigma}a_{1g}^{\uparrow\downarrow}\,{}^{\pi}b_{2g}^{\uparrow}\,{}^{\pi}e_g^{\uparrow\uparrow\downarrow}$] (${}^3E_g^{(2)}$). According to literature experimental[67-71] and theoretical results[72-73] the FeTPP ADF GS is the ${}^3A_{2g}$ state (see Table S14; FeTPP optimized Cartesian coordinates are reported in Table S21). In this regard, it is noteworthy that RASPT2 calculations carried out by Vancoillie et al.[74] on FeP indicate a ${}^3A_{2g}$ GS and ascribe the FeTPP high magnetic moment ($4.4\mu_B$) to spin-orbit coupling with the very close ${}^5A_{1g}$ and ${}^3E_g$ states.

Before going on, it is worthwhile mentioning that Nachtigallová et al.,[75] based on ^{57}Fe Mössbauer spectroscopy of FePc in crystalline form and in frozen monochlorobenzene and superconducting quantum interference device magnetic measurements coupled to state-of-the-art computational methods (CASPT2 and DMRG) assigned a S = 2 GS to the FePc isolated molecule. The awareness that Pc^{2-} generates a stronger ligand field than TPP^{2-} casts the doubt that a S = 2 GS might characterize the isolated FeTPP too. A further series of numerical experiments on the free FeTPP have been then carried out by assuming either S = 1 or S = 2, adopting the hybrid B3LYP exchange-correlation potential,[57-59] and avoiding any constraint on the Fe 3d-based MO occupation numbers. Analogously to the BP86 outcomes, the B3LYP FeTPP GS corresponds to the ${}^3A_{2g}$ state, more stable than the ${}^5A_{1g}$ one by 203 meV.

As far as the FeTPP structural parameters are concerned, the agreement between the experimental Fe–N^{Py} bond length[67] and the ADF BP86 one is satisfactory (see Table S12); in addition: i) the Fe–N^{Py} bond length value reported in Table S12 well agree with the B3LYP one estimated by Shah et al. (2.01 Å),[76] ii) minor variations are present among the triplets of different symmetry. As such, it is noteworthy that although the ΔE between the $^3E_g^{(1)}$ state and the $^3A_{2g}$ GS is of the level of uncertainty of the numerical experiments herein carried out (see Table S14), the TSIEs of the Fe^{II} 3d-based $^{\sigma}e_g$-like $25a_{1g}$ and $^{\pi}t_{2g}$-like $12e_g$ SOs are significantly different in the two cases (compare data reported in Table S11 with those included in the note XVII). Even more specifically, the lowest $^3A_{2g}$ ($^3E_g^{(1)}$) TSIE corresponds to the ionization from the $25a^{\downarrow}_{1g}$ ($12e^{\downarrow}_{g}$) SO. At variance to that, the Fe^{II} $^{\pi}t_{2g}$-like $19b^{\uparrow}_{2g}/19b^{\downarrow}_{2g}$ and the pmc-based $2a^{\uparrow}_{1u}/2a^{\downarrow}_{1u}$ and $12a^{\uparrow}_{2u}/12a^{\downarrow}_{2u}$ π orbitals are filled independently of the GS symmetry, and corresponding TSIEs are negligibly affected upon the $^3A_{2g} \rightarrow {}^3E_g^{(1)}$ GS switching. Unfortunately, any comparison with the experiment is hampered by the hitches affecting the Khandelwal and Roebber PE data;[29] there is however further evidence that might turn out as conclusive of the $^3A_{2g}$ FeTPP GS. BP86 ADF outcomes indicate that the empty $12e^{\downarrow}_{g}$ LUMO of the $^3A_{2g}$ GS corresponds to a $^{pmc}\pi^*$ SO, while the half-occupied $12e^{\downarrow}_{g}$ LUMO of the $^3E_g^{(1)}$ is strongly (67%) localized on the Fe^{II} ${}^{\pi}_{\perp}e_g$ AOs. The $^3A_{2g}$ LUMO TSEA is 1.85 eV (see Table S15), which numerically agrees with the experimental EA value reported by Chen et al. (1.87 eV),[77] while the $^3E_g^{(1)}$ LUMO TSEA is 2.22 eV.[XVII]

Despite the FePc first synthetic route being due to the Linstead group and dating back to the mid-thirties,[78-84] both its spin state (S = 1 vs. S = 2) and the GS symmetry are still debated.[4,41,55-56,75,85-90] Most of the literature DFT data indicate a S = 1 state (occupation numbers of the Fe^{II} 3d-based SOs are highly sensitive to the adopted XC functional and basis set),[41,85-86,90] the same S = 1 value is predicted by CASSCF calculations carried out by Wallace et al.,[56,XIV,XVIII-XIX] while CASPT2 and DMRG methods assigned a S = 2 GS to the isolated FePc.[75]

ADF outcomes, independently of their non-relativistic[41] or quasi-relativistic[86] nature, point to a $^3A_{2g}$ IS GS very close to the $^3E_g^{(1)}$ and $^3B_{2g}$ states (see Table S14). Moreover, alike FeTPP, the FePc $^3E_g^{(2)}$ state is much higher in energy (532 meV) and it implies a non-Aufbau filling of one-electron energy levels. The agreement between experimental and optimized structural parameters (see Table S12; the $^3A_{2g}$ FePc optimized Cartesian coordinates are reported in Table S22) is satisfactory and substantially independent of the GS symmetry.

Similarly to FeTPP and just for the sake of completeness, besides BP86[57-58] calculations, B3LYP[57-59] numerical experiments have been run also for FePc within the assumption of S = 1 or S = 2; the $^3B_{2g}$ GS was found more stable than the $^5A_{1g}$ state by 207 meV.

Several authors have tackled the study of the FePc PE valence band,[20-23,65,90] whose lowest IE region is characterized by the presence of a sharp band at 6.36 eV, assigned to the ionization from a $^{pmc}\pi$ MO, having an evident broad shoulder on its higher IE side (6.88 eV), which Berkowitz assigned to the ionization from a Fe^{II} 3d-like orbital.[23] BP86[57-58] FePc TSIEs values reported in Table S11 and displayed in Figure 2 perfectly agree with the experimental evidence obtained by Berkowitz[23] and Bidermane et al.[65] and allow us to assign the sharp peak at 6.36 eV to the ionization from the $2a^{\downarrow}_{1u}$ $^{pmc}\pi$ SO (see Figure S11), whose TSIE is substantially the same along the whole MPc series herein considered (see the upper panel of Figure 2). As far as the broad shoulder at 6.88 eV is concerned, in tune with its relative intensity increase upon changing the ionizing source (HeI → HeII → AlKα; see Figure 13 of ref. 23),[III] this is assigned to the ionization from the closely spaced Fe^{II} $^{\sigma}e_g$-like $^{\sigma}a_{1g}$ ($21a^{\downarrow}_{1g}$) and ${}^{\pi}_{\|}b_{2g}$ ($14b^{\downarrow}_{2g}$) SOs.

The HeI PE spectra of H_2Pc and MPc molecules investigated by Berkowitz[23] are also characterized by a broad band whose IE ranges between 8 and 9 eV. Data pertaining to the IS FePc (see Table S11 and the upper panel of Figure 2) prompts us to ascribe this spectral feature to the ionization from the $6a^{\downarrow}_{2u}$ $^{pmc}\pi$ SO (the lower IE side) and the Fe^{II} ${}^{\pi}_{\perp}e_g$ ($6e^{\uparrow}_{g}$) SOs. As a final remark, let us mention that TSIE calculations have been also run for the $^3E_g^{(1)}$ state but the agreement between experiment and theory was worse with the lowest TSIE (6.49 eV) corresponding to the ionization from the Fe^{II} ${}^{\pi}_{\perp}e_g$ SO (the $2a^{\downarrow}_{1u}$ SO TSIE = 6.53 eV).

Moving to the FePc unoccupied electronic states, to the best of the authors' knowledge, the only study specifically devoted to this subject is that published by Yoshida et al.[66] who indirectly measured the energy of the FePc EA levels through IPS and assigned them by referring to the EHT results obtained by Schaffer et al.[91] and the DV-Xα outcomes of Reynolds and Figgis.[62] The comparison with TSEAs reported in Table S15 and Figure 2 is somewhat tainted by the starting assumptions of Yoshida et al.[66] that the FePc GS might be either of symmetry E_g or B_{2g}, with the empty Fe-based SOs corresponding to the ${}^{\pi}_{\perp}e^{\downarrow}_{g}$, $^{\sigma}a^{\downarrow}_{1g}$, $^{\sigma}b^{\uparrow}_{1g}$, and $^{\sigma}b^{\downarrow}_{1g}$ orbitals in the former case and to the ${}^{\pi}_{\|}b^{\downarrow}_{2g}$, $^{\sigma}a^{\downarrow}_{1g}$, $^{\sigma}b^{\uparrow}_{1g}$, and $^{\sigma}b^{\downarrow}_{1g}$ orbitals in the latter. In other words, the FePc first affinity levels are all Fe 3d-based.[XVII] In this regard, despite the agreement between the highest FePc TSEA herein reported (2.61 eV; see Table S15 and Figure 2) and the first EA computed by Liao et al.[86] (2.92 eV),[XX] it must underline that the unoccupied $6e^{\downarrow}_{g}$ SOs do not correspond to the spin ↓ Fe-based ${}^{\pi}_{\perp}e^{\uparrow}_{g}$ partner but, similarly to lighter MPc (*vide supra*), to $^{pmc}\pi^*$ SOs.

CoTPP and CoPc. CoTPP is a LS magnetic molecule first synthesized and spectroscopically characterized by Rothemund and Menotti at the end of the forties,[92] while its molecular stereochemistry has been determined much more recently by the Scheidt group.[93] The three holes present in the Co^{II} 3d SOs determine the same number of microstates (120) and the same grouping valid for V^{II} in VTPP; nevertheless, both experimental[93-97] and theoretical[72-73,94,98] evidence are consistent with a CoTPP $^2A_{1g}$ LS GS generated by the $^{\pi}t^{6}_{2g}$-$^{\sigma}e^{1}_{g}$-like configuration (see Table S14). Incidentally, the ^2E_g LS state generated by the $^{\pi}t^{5}_{2g}$-$^{\sigma}e^{2}_{g}$-like configuration is less stable than the $^2A_{1g}$ GS by 172 meV (see Table S14).

The outcomes of the present BP86 numerical experiments well-agree with the literature results concerning the CoTPP GS symmetry, the spin multiplicity[72-73,93-94,98] and the structural parameters (CoTPP optimized Cartesian coordinates are reported in Table S23).[45,76,93] As such, the inspection of Table S12 reveals that our ADF results perfectly reproduce the progressive M–N^{Py} bond length decreasing upon moving from CrTPP to NiTPP (with the MnTPP anomaly).[60]

To the best of the authors' knowledge, no gas-phase PE data is available for CoTPP (Khandelwal and Roebber investigated the TPP^{2-} complexes of the Mg, Mn, Fe, Ni, Cu, and Zn).[29] Nevertheless, it is worth mentioning that i) Nakato et al.[98] estimated the lowest-lying gas-phase CoTPP IE by photocurrent measurements in non-polar solvents by concluding that photo-ejection involved a $^{pmc}\pi$ orbital; ii) Scudiero et al.[100] recorded the HeI PE spectra of a 4 nm film of CoTPP vapor-deposited on a clean polycrystalline gold surface.[XXI] With specific reference to the Scudiero et al.[100] measurements, the IE region extending from ~6.0 to ~7.5 eV is characterized by the presence of a rather weak and broad band centered at 6.6 eV followed by an even weaker feature, not mentioned by the authors but hardly ascribable to the background noise, at ~7.5 eV (see the Figure 5 inset of ref. 100). A further broad and rather intense PE band lies at 8.8 eV. The agreement between CoTPP TSIEs reported in Table S11 and Figure 2 and the experimental evidence[98-100] is very satisfactory. The lowest IE peak is assigned with confidence to the ionization from the quasi-degenerate ${}^{\mathrm{pmc}}\pi$ $12a_{2u}^{\downarrow}$ and $2a_{1u}^{\downarrow}$ SOs, while the higher IE side of the peak centered at 6.6 eV and the IE spectral region extending till ~7.5 eV should include the ionizations from the Co 3d-based ${}^{\pi}\mathrm{t}_{2g}$-like SOs. The $25a_{1g}^{\uparrow}$ SO TSIE is 8.94 eV and we tentatively assign it to the feature revealed by Scudiero et al. at 8.8 eV.[100] The peculiar IE of the $25a_{1g}^{\uparrow}$ SO (the GS HOMO) is a consequence of the very strong relaxation upon ionization determined by its lone pair nature (the contribution of the Co $3\mathrm{d}_{z^2}$ AO to the ${}^{\sigma}\mathrm{e}_g$-like $25a_{1g}^{\uparrow}$ SO amounts to 87%).[V]

An interesting issue concerns the CoTPP EA. Scudiero et al.,[100] based on STM and STM-OMTS results collected for sub-ML films of CoTPP on polycrystalline gold, assigned the first affinity level (3.5 eV below the vacuum level) as due to the ${}^{\mathrm{pmc}}\pi^*$ LUMO, while the CoTPP lowest TSEA herein computed (see Table S15 and Figure 2) corresponds to the fulfillment of the ${}^{\sigma}\mathrm{e}_g$-like $25\mathrm{a}_{1g}$ MO. The disagreement is total, and it involves not only the absolute energy values (3.5 vs. 2.13 eV) but also the nature of the SO involved in the extra electron capture. Nevertheless, we cannot be silent about the experimental evidence reported by Felton and Linschitz on several MTPP complexes in DMF or DMSO solutions,[101] and by Niwa for CoTPP and CuTPP.[102] The polarograms recorded by Felton and Linschitz[101] are characterized by two main waves corresponding, for the most part, to one-electron reductions. As such, it has been underlined by the authors that the electron addition usually involved ${}^{\mathrm{pmc}}\pi^*$ orbitals except for CoTPP, where the reduction occurs in a $\mathrm{Co^{II}}$-based orbital.[101] Additionally, the Co 2p PE spectra of Na/CoTPP collected by Niwa revealed that Na reduced CoTPP by generating the $\mathrm{Co^{I}}$ species.[102]

CoPc was first synthesized in late 1936 by the Linstead group[78] and much more recently structurally characterized by X-ray and neutron diffraction.[103-104] Not surprisingly, the CoPc LS state is unanimously accepted[52,55-56,62,86,89,105-107] (the Pc^{2-} ligand field is stronger than the TPP^{2-} one), while the opposite is true as far as the CoPc GS symmetry is concerned: Reynolds and Figgis,[62] Kroll et al.,[89] Wallace et al.,[56] Liao and Scheiner,[105] and Rosa and Baerends[106] point toward a ${}^2\mathrm{A}_{1g}$ (${}^{\pi}t_{2g}^{6}$-${}^{\sigma}e_{g}^{1}$-like) GS, while Liao and Scheiner[86] and Liang et al.[107] indicate a ${}^2\mathrm{E}_g$ (${}^{\pi}t_{2g}^{5}$-${}^{\sigma}e_{g}^{2}$-like) GS. The outcomes of our ADF BP86 numerical experiments (CoPc optimized Cartesian coordinates are reported in Table S24) are consistent with a ${}^2\mathrm{A}_{1g}$ GS generated by the ${}^{\pi}t_{2g}^{6}$-${}^{\sigma}e_{g}^{1}$-like configuration, more stable than the ${}^2\mathrm{E}_g$ (${}^{\pi}t_{2g}^{5}$-${}^{\sigma}e_{g}^{2}$-like) state by 231 meV (see Table S14) and in good agreement with literature results concerning CoPc GS symmetry, spin multiplicity, and structural parameters.[103] As such, the inspection of Table S12 reveals that the progressive M–$\mathrm{N^{Py}}$ bond length decreasing upon moving from MnPc to NiPc is well reproduced by ADF results.

The situation is a bit more complicated when CoPc TSIEs (TSEA) reported in Table S11 (Table S15) and displayed in Figure 2 are compared with literature PES[23] (IPS[66] and OMTS[108-109]) measurements. Like all the MPc investigated by Berkowitz,[23] the HeI PE spectrum of gaseous CoPc is characterized by a sharp peak occurring at ~6.4 eV and assigned with confidence to the ionization from the $2a_{1u}^{\downarrow}$ ${}^{\mathrm{pmc}}\pi$ SO. The CoPc lower IE region, and the same holds for NiPc, ZnPc, and even MgPc (*vide infra*), also includes a weak shoulder on the higher IE side of the lowest lying peak (~6.5 eV). Differently from Rosa and Baerends,[106] the systematic presence of this shoulder at the *same* IE and the comparison of experimental data with CoPc TSIEs reported in Table S11 and Figure 2 lead us to exclude any contribution to this feature due to ionization from i) the $6a_{2u}^{\downarrow}$ ${}^{\mathrm{pmc}}\pi$ SO, ii) $\mathrm{Co^{II}}$ ${}^{\pi}\mathrm{t}_{2g}$-like SOs, iii) the $\mathrm{Co^{II}}$ ${}^{\sigma}\mathrm{e}_g$-like ${}^{\sigma}a_{1g}^{\uparrow}$ ($21a_{1g}^{\uparrow}$) SO, strongly localized on the $\mathrm{Co^{II}}$ $3\mathrm{d}_{z^2}$ AO (84%). The asymmetry of the lowest-lying peak could then be generated by a vibrational progression of the ${}^3\mathrm{A}_{1u}$ excited state. To look into this matter, the Cartesian coordinates of the $\mathrm{CoPc^+}$ species carrying an empty $2a_{1u}^{\downarrow}$ ${}^{\mathrm{pmc}}\pi$ SO have been optimized (see Table S25 and Figure S12a where the licorice representation of the CoPc and $\mathrm{CoPc^+}$ optimized structures are superimposed), and the corresponding vibrational parameters have been compared with those of the neutral molecule (see Table S26).

The presence of 57 atoms characterizes both MPc and $\mathrm{MPc^+}$ (see the lower panel of Figure 1); in the $\mathrm{D_{4h}}$ symmetry, the (3 × 57 – 6) = 165 normal vibration modes[1] can be factorized in $14\mathrm{A}_{1g} + 13\mathrm{A}_{2g} + 14\mathrm{B}_{1g} + 14\mathrm{B}_{2g} + 13\mathrm{E}_g + 6\mathrm{A}_{1u} + 8\mathrm{A}_{2u} + 7\mathrm{B}_{1u} + 7\mathrm{B}_{2u} + 28\mathrm{E}_u$ with A_{1g}, B_{1g}, B_{2g}, and E_g (A_{2u} and E_u) modes being Raman (IR) active. The ΔE between the PE peak assigned to the ionization from the $2a_{1u}^{\downarrow}$ ${}^{\mathrm{pmc}}\pi$ SO and the shoulder on its higher IE side amounts to 190 meV (1532 $\mathrm{cm^{-1}}$, see Table 1 of ref. 23).

The IR absorption spectra of the $\mathrm{H_2Pc}$ free base and its M derivatives ($Z^{\mathrm{M}} = 26 - 30, 46, 78$) were recorded in late 1970 by Kobayachi et al.[110] and thoroughly assigned by Liu et al.[111] A common spectral feature of the MPc IR spectra is a strong band having $1480\ \mathrm{cm^{-1}} \leq \nu \leq 1520\ \mathrm{cm^{-1}}$, assigned to the 138th and 139th degenerate IR active normal mode ($22\mathrm{e}_u$), and corresponding to the $\mathrm{C^{\alpha}}$–$\mathrm{N^{Py}}$–$\mathrm{C^{\alpha}}$, $\mathrm{C^{\alpha}}$–N^{m} stretchings and C–H || bending.[111] Experimental and theoretical ν values of the $22\mathrm{e}_u$ normal mode for the CoPc ${}^2\mathrm{A}_{1g}$ GS and the $\mathrm{CoPc^+}$ ${}^3\mathrm{A}_{1u}$ excited state are compared in Table S26. The agreement between theory and experiment is more than satisfactory for CoPc but only decent for $\mathrm{CoPc^+}$ (the IE uncertainty of MPc HeI gas-phase PE bands is ~1×10^{-2} eV, i.e., ~80 $\mathrm{cm^{-1}}$); moreover, consistently with the almost perfect superimposibility of the CoPc ${}^2\mathrm{A}_{1g}$ and $\mathrm{CoPc^+}$ ${}^3\mathrm{A}_{1u}$ optimized structures (see Figure S12a), the ν^{22e_u} values estimated for the CoPc ${}^2\mathrm{A}_{1g}$ GS and the $\mathrm{CoPc^+}$ ${}^3\mathrm{A}_{1u}$ state are almost degenerate.

Coming back to the CoPc HeI gas-phase PE spectrum recorded by Berkowitz,[23] the $6.7 \leq \mathrm{IE} \leq 7.9$ region does not seem to include any spectral feature (see Figure 4 and Table 1 of ref. 23); moreover, the author does not mention the presence of an evident shoulder on the lower IE side of the intense and broad peak centered at 8.83 eV. In contrast to that, the PE spectra of the valence band region of a CoPc multilayer film[XXI] deposited on Ag(100) and recorded by using two different photon energies (126 and 25 eV)[112] are characterized by an evident peak at 7.4 eV (see Figure 1 of ref. 112) whose relative intensity dramatically increases upon switching the photon energy from 25 to 126 eV.[III] Incidentally, the same holds for the higher IE side of the spectral feature centered at 8.83 eV, which splits into two components at the photon energy of 126 eV (see Figure 1 of ref. 112). Based on this evidence, Salomon et al.

assigned the peak at 7.4 eV and the higher IE side of the broad and intense spectral feature centered at 8.83 eV to the ionization from SOs having major contributions from Co^{II} 3d-based SOs.[112] TSIEs reported in Table S11 combined with ASPCS values[25] for photon energies of 25 and 126 eV[III] allow us to propose a detailed assignment of photoemission processes taking place in the CoPc valence band region: i) the feature at 7.4 eV is assigned with confidence to the ionization from Co^{II} ${}^{\pi}_{\parallel}b_{2g}$ and ${}^{\pi}_{\perp}e_{g}$ ($14b_{2g} + 6e_g$) SOs; ii) the lower and higher IE sides of the broad peak centered at 8.83 eV are assigned to the ionizations from the $6a_{2u}^{\downarrow}$ $^{pmc}\pi$ SO and the $^{\sigma}a_{1g}$ ($21a_{1g}^{\uparrow}$) SO, strongly localized (84%) on the Co^{II} $3d_{z^2}$ AO, respectively.[III]

The CoPc first affinity level is again a tricky subject. Yoshida et al.[66] assigned it to the Co^{II} 3d-based $^{\sigma}e_g$-like $16b_{1g}^{\uparrow}/16b_{1g}^{\downarrow}$ SOs, while the Hipps' group, based on OMTS measurements,[108] proposed to assign the lowest lying feature (3.7 eV) of the STM and tunnel-diode spectra to the reduction of the $^{pmc}\pi^*$ LUMO. Even though Hipps and Mazur[109] emphasized that EAs, IEs, reduction, and oxidation potentials in condensed phases may be different from the gas-phase values by as much as 2 eV, we cannot avoid underlining that, ADF BP86 results herein reported indicate that the CoPc LUMO corresponds to the Co^{II} $^{\sigma}a_{1g}$ ($21a_{1g}^{\downarrow}$) SO whose TSEA (3.00 eV) is the highest among those reported in Table S15. In addition, it is noteworthy that the TSEA of the $^{pmc}\pi^*$ $7e_{1g}^{\uparrow}$ LUMO+1 amounts to 2.17 eV.

NiTPP and NiPc. Similarly to CoTPP, NiTPP is a LS molecule first synthesized by Rothemund and Menotti[92] and structurally characterized many years later.[113] The two holes present in the Ni^{II} 3d SOs determine 45 ($\frac{10!}{2! \times 8!}$) microstates, which can be grouped in $3 \times {}^3A_{2g} + {}^3B_{2g} + 3 \times {}^3E_g + 4 \times {}^1A_{1g} + {}^1A_{2g} + 2 \times {}^1B_{1g} + 2 \times {}^1B_{2g} + 3 \times {}^1E_g$ states;[40] nevertheless, the NiTPP diamagnetic nature, with the central $3d^8$ Ni^{II} species carrying vacancies in the $^{\sigma}e_g$-like $^{\sigma}b_{1g}$ SOs, and its $^1A_{1g}$ GS are unanimously accepted.[46,56,72] In addition, the ${}_{\pi}t_{2g}^{6}\text{-}{}_{\sigma}e_{g}^{2}$-like closed shell configuration makes NiTPP, among the complexes so far considered, the first species whose M $3d_{z^2}$-based MO is wholly occupied and unavailable to be involved in any substrate → adsorbate charge transfer processes.[114,XXII]

ADF BP86 numerical experiments agree with the literature results concerning the NiTPP GS symmetry and spin multiplicity. Regarding the optimized geometrical parameters (NiTPP optimized Cartesian coordinates are reported in Table S27), the Ni–N^{Py} bond length (see Table S12) matches the B3LYP one estimated by Shah et al. (1.97 Å);[76] nevertheless, the poor agreement with the only NiTPP structural determination available in the literature[113] cannot be concealed. As such, McLean et al.[113] underlined that the D_{4h} symmetry they initially adopted to refine their extended NEXAFS spectra to optimize the NiTPP geometry produced some unrealistic bond distance.

Even though the only NiTPP gas-phase PE data in the literature are those collected by Khandelwal and Roebber,[29] Scudiero et al.[100] recorded the HeI PE spectra of a 4 nm film of NiTPP vapor-deposited on a clean polycrystalline gold surface.[XXI] With specific reference to the Scudiero et al. measurements,[100] the IE region extending from ~6.0 to ~7.5 eV is characterized by the presence of two broad and rather weak bands centered at 6.5 and 7.2 eV, both of them highly asymmetric, the former with an evident shoulder on its higher IE side, the latter with a with an equally evident shoulder on its lower IE side (see the inset of Figure 2 of ref. 100). A further broad, intense, and quite symmetric feature lies at 8.7 eV. The comparison of experimental evidence with the NiTPP TSIEs reported in Table S11 and displayed in Figure 2 is very satisfactory. The lowest IE peak and the shoulder on its higher IE side are assigned with confidence to the ionization from the quasi-degenerate $^{pmc}\pi$ $12a_{2u}^{\downarrow}$ and $2a_{1u}^{\downarrow}$ SOs, while the second peak and its shoulder on the lower IE side should include both the ionizations from the Ni^{II} $^{\pi}t_{2g}$-like ${}^{\pi}_{\perp}e_{g}$ ($12e_{g}^{\downarrow}$) and $^{\sigma}e_g$-like $^{\sigma}a_{1g}$ ($25a_{1g}^{\downarrow}$) SOs. As such, it has to be noted that, not surprisingly, the $25a_{1g}^{\downarrow}$ TSIEs in FeTPP and NiTPP are lower (the GS $25a_{1g}$ MO is completely occupied in both cases) than the $25a_{1g}^{\uparrow}$ one in MnTPP and CoTPP (see Table S11 and Figure 2), independently of the $25a_{1g}$ MO lone-pair nature (the Ni^{II} $3d_{z^2}$ AO contribution to the $25a_{1g}$ is 89%). As far as the ionization from the third Ni^{II} $^{\pi}t_{2g}$-like SO is concerned (the $12b_{2g}^{\downarrow}$ SO), it should be hidden under the symmetric feature lying at 8.7 eV.

Similarly to CoTPP, there is no consensus about the energy and the assignment of the NiTPP first affinity level. Scudiero et al.[100] and Chen et al.[19] ascribed the first affinity level to a $^{pmc}\pi^*$ orbital without indicating if corresponded to the $13e_g$ or $9b_1$ $^{pmc}\pi^*$ MOs, while Lexa et al.[115] pointed out that the one-electron electrochemical reduction of NiTPP generates a Ni^{I} complex rather than the anion of Ni^{II}TPP by populating the Ni^{II} $^{\sigma}e_g$-like $^{\sigma}b_{1g}$ $13b_{1g}^{\uparrow}$ virtual SO. In addition, STM-OMTS and IETS-OMTS outcomes reported by Scudiero et al.[100] locate the lowest unoccupied π^* MO near 3.4 eV below the vacuum level, while Chen et al.[19] report, for the first EA, a value of 1.51 eV. Moving to the literature theoretical results, Liao and Scheiner[72] evaluated the relative energies of the NiTPP$^-$ ^2E_g ($^{\pi}t_{2g}^{6}{}_{\sigma}e_{g}^{2}e_{g}^{1}$, 0 meV) and $^2B_{1g}$ ($^{\pi}t_{2g}^{6}{}_{\sigma}e_{g}^{3}$, 80 meV) states, the former (latter) corresponding to the Ni^{II}TPP (Ni^{I}TPP) anion (radical) whose unpaired electron occupies the $^{pmc}\pi^*$ (Ni^{II} $3d_{x^2-y^2}$-based) $13e_{1g}^{\uparrow}$ ($12b_{1g}^{\uparrow}$) SO.

ADF BP86 outcomes of our numerical experiments indicate that the NiTPP GS LUMO and LUMO+1 correspond to the Ni^{II} $^{\sigma}e_g$-like $3d_{x^2-y^2}$-based $12b_{1g}$ and the $^{pmc}\pi^*$ $13e_g$ MOs, respectively ($\Delta E = 350$ meV). Interestingly, their TSEA values are not only very similar but the $13e_{1g}^{\uparrow}$ TSEA (1.53 eV) is higher than the $12b_{1g}^{\uparrow}$ one (1.47 eV, see Table S15 and Figure 2). As a whole, besides the unsurprising agreement between our results and those reported by Liao and Scheiner,[72] theoretical outcomes herein reported perfectly match both the energy and the assignment of the NiTPP first affinity level reported by Chen et al.[19]

NiPc was first synthesized[78] and structurally characterized[116] by the Linstead group in the mid-thirties; however, a much more recent structural determination of the isolated NiPc molecule is present in the literature.[117] Similarly to NiTPP, NiPc is a closed shell molecule whose GS symmetry and spin multiplicity ($^1A_{1g}$) are unanimously accepted.[52,55-56,86,89,105-106] The outcomes of our ADF BP86 numerical experiments (NiPc optimized Cartesian coordinates are reported in Table S28) are consistent with the $^1A_{1g}$ GS ($^{\pi}t_{2g}^{6}\text{-}{}^{\sigma}e_{g}^{2}$-like) and reproduce quantitatively the structural data of Tverdova et al.[117] (see Table S12).

As already mentioned, the lower IE region of the CoPc and NiPc HeI PE spectra are very similar.[23] More specifically, the spectral feature at the lowest IE corresponds to a sharp peak at 6.38 eV with a shoulder on its higher IE side (6.55 eV). The inspection of the NiPc TSIEs reported in Table S11 and the assignment we proposed for the FePc and CoPc lower IE region of corresponding HeI PE spectra prompt us to ascribe the peak at 6.38 eV and its shoulder at 6.55 eV to the ionization from the $2a_{1u}^{\downarrow}$ $^{pmc}\pi$ SO and to the 22e$_u$ normal mode of the NiPc$^+$ $^2A_{1u}$ excited state (see Table S26), respectively. As in CoPc, the optimized structures of the NiPc $^1A_{1g}$ and NiPc$^+$ $^2A_{1u}$ states (the optimized Cartesian coordinates for NiPc carrying an electron vacancy in the 2a$_{1u}$ MO are reported in Table S29) are perfectly superimposable (see Figure S12b) and the ν^{22e_u} values estimated for the $^1A_{1g}$ GS and the $^2A_{1u}$ excited state are almost degenerate. The agreement between theory and experiment[110] is excellent for NiPc but only decent for NiPc$^+$. As such, it must reiterate that the shoulder IE location in Figure 5 of ref. 23 is a matter of taste and the IE uncertainty of the MPc HeI gas-phase PE bands is ~1×10^{-2} eV (80 cm^{-1}).

Before addressing NiPc spectral features extending beyond 7 eV, it must be pointed out that the assignment we propose for the shoulder at 6.55 eV is in evident contrast with the one suggested by Rosa and Baerends.[106] Despite the ΔE between the peak at the lowest IE, systematically found at ~6.4 eV, and its shoulder on the higher IE side being the *same* (~150 meV) for MgPc, CoPc, NiPc, and ZnPc,[23] they proposed to ascribe the shoulder to the ionization from different MOs along the series.[106]

The 7.5 eV ≤ IE ≤ 10.0 eV region of the NiPc HeI gas-phase PE spectrum recorded by Berkowitz includes two well-defined spectral features: a weak peak[23] at 7.75 eV and a broad, intense, and structured band centered at 8.81 eV with evident shoulders on its lower and higher IE sides. In addition, Berkowitz[23] compared and aligned his gas-phase data with the X-ray PE outcomes recorded by Höchst et al.[22] by using a monochromatized AlKα radiation (1487 eV) and agreed with the qualitative assignment they proposed (see Figure 11 of ref. 23). In more detail, the weak peak at 7.75 eV was associated to the ionization from the Ni^{II} $^{\sigma}e_g$-like 21a$_{1g}$ MO while the shoulder on the lower (higher) IE side of the broad and intense band centered at 8.81 eV was assigned to the ionization from the ${}^{\pi}_{\perp}t_{2g}$-like (${}^{\pi}_{\parallel}t_{2g}$-like) MOs. As such, it must be noted that the energy order of ionizations from Ni^{II} 3d-based MOs proposed by Höchst et al.[22] and shared by Berkowitz[23] is that corresponding to the NiPc GS; i.e., no relaxation upon ionization was considered.[V]

NiPc TSIEs reported in Table S11 prompt us to assign the weak peak at 7.75 eV, whose relative intensity dramatically increases upon moving from the HeI to the AlKα ionizing source,[25] to the ionization from the Ni^{II} ${}^{\pi}_{\perp}t_{2g}$-like $6e_g^{\downarrow}$ SOs. The following band will then include ionizations from the $6a_{2u}^{\downarrow}$ $^{pmc}\pi$ SO, the ${}^{\pi}_{\parallel}t_{2g}$-like $6b_{2g}^{\downarrow}$ SO, and the $^{\sigma}e_g$-like $21a_{1g}^{\downarrow}$ SO whose lone pair character is once again confirmed (the Ni^{II} 3d$_{z^2}$ participation to the $21a_{1g}^{\downarrow}$ SO is 87%).[V]

Similarly to NiTPP, the $16b_{1g}^{\uparrow}$ LUMO TSEA (1.88 in Table S15 and Figure 2) is not the TSEA largest value, corresponding to the $^{pmc}\pi^*$ $7e_g^{\uparrow}$ SO (2.19 eV). This evidence obviously agrees with theoretical data reported by Liao and Scheiner,[86] but reproduces only qualitatively the literature's experimental results.[66,118] More specifically, the lowest lying peak of the IPS spectra of NiPc thin films[66] and NiPc/Ag(111)[118] lies at ~1 eV above the Fermi level, and has been tentatively assigned to the unresolved superposition of the $^{\sigma}e_g$-like $16b_{1g}^{\uparrow}$ and $^{pmc}\pi^*$ $7e_g^{\uparrow}$ SOs.[118] In addition, the lowest lying resonance of the NEXAFS spectra of NiPc thin films at the C, N K-edge and Ni L$_{2,3}$-edges has been assigned to transition from SALC of C and N 1s AOs and from the Ni 2p AOs to the quasi-degenerate 7e$_g$ $^{pmc}\pi^*$ and Ni $^{\sigma}e_g$-like 16b$_{1g}$ SOs.

CuTPP and CuPc. Analogously to other MTPP herein considered, CuTPP has been firstly synthesized by Rothemund and Menotti[92] and structurally characterized several years later.[119] CuTPP is an open-shell molecule with its single unpaired electron occupying the Cu $^{\sigma}e_g$-like $12b_{1g}^{\uparrow}$ SO and then having a $^2B_{1g}$ GS. As a part of a systematic investigation of the electronic properties of materials usually labeled as energy-targeted, some of us thoroughly investigated in the past the occupied and empty electronic structure of CuTPP[5,32] and CuPc films[120-122,XXI] deposited on gold by combining UV and X-ray PE spectroscopy, NEXAFS spectroscopy at the C and N K-edges and Cu L$_{2,3}$-edges with the outcomes of DFT and time-dependent DFT calculations; in the following, we will then limit ourselves to reminding the main literature results (CuTPP Cartesian coordinates herein reported in Table S30 just for the sake of completeness are those optimized in ref. 32). Moreover, a thorough comparison between theory and experiment has been already addressed in ref. 32 and will therefore not be considered further.

To the best of the authors' knowledge, the only gas-phase PE data available for CuTPP are those reported by Khandelwal and Roebber,[29] while Mangione et al.[32] recorded the HeI and X-ray PE spectra of CuTPP thin films on Au(111).[XXI] In both cases,[29,32] the valence IE region is characterized by the presence of a low-lying spectral feature at ~6.5 eV, resolved in two distinct peaks at 6.49 and 6.66 eV in the gas-phase spectrum,[29] followed by a broad and structured band centered at 8.5 eV with an evident shoulder on its lower IE side[32] (in Table 1 of ref. 29 the IEs of two peaks at 7.77 and 8.78 eV are reported without providing any further information). Khandelwal and Roebber[29] proposed to assign the closely spaced first and second peak of the CuTPP HeI spectrum to the ionization from an a$_{2u}$ MO (6.49 eV) and an a$_{1u}$ MO (6.66 eV), and similarly to MnTPP (*vide supra*), they said nothing about the $^{\sigma}e_g$-like $^{\sigma}b_{1g}$ IE position. As such, the ADF BP86 CuTPP GS indicates that the half-occupied $^{\sigma}b_{1g}$ HOMO and the 2a$_{1u}$ and 12a$_{2u}$ $^{pmc}\pi$ MOs lye within 300 meV; nevertheless, the accounting of the electronic structure relaxation upon ionization through TS calculations reliefs such a quasi-degeneracy (see Table S11 and Figure 2). In this regard, it must be underlined that Ellis and Berkovitch-Yellin[123] carried out TS numerical experiments on CuP without mentioning any differential relaxation of the outermost ...$(^{\pi}a_{1u})^2(^{\pi}a_{2u})^2(^{\sigma}b_{1g})^1$ MOs able to modify the GS energy order.

Besides the agreement with the Khandelwal and Roebber outcomes,[29] the theoretical results herein reported provide information about the IE positions of all the Cu 3d-based SOs; the $12b_{1g}^{\uparrow}$ SO should be realistically hidden under the higher IE side of the lowest lying feature centred at 6.3 eV in the CuTPP HeI PE spectrum recorded by Mangione et al. (see Figure 2 of ref. 32), while ionizations from the $^{\sigma}e_g$-like $^{\sigma}a_{1g}$ and $^{\pi}t_{2g}$-like SOs (see Table S11 and Figure 2) should contribute to the higher IE side of the broad and structured band centred at 8.5 eV generated, together with its evident shoulder, from photoemission processes involving $^{Ph}\pi$ and $^{Py}\pi$ MOs (see the CuTPP GS partial density of state reported in Figure 2 of ref. 32). Unfortunately, photoemission processes taking place in the CuTPP valence region has not been investigated by using ionizing source of different energies; the proposed assignment cannot be then confirmed by exploiting the band relative intensity variations upon changing the ionizing source energy.[25]

No CuTPP EA determination is present in literature; nevertheless, it can be of some interest to point out that the first affinity level is, in agreement with theoretical results reported by Liao and Scheiner,[72] the $^{pmc}\pi^*$ $13e_g^{\uparrow}$ SO whose TSEA (1.61 eV, see Table S15 and Figure 2) is similar to that estimated for the H_2TPP free base (*vide supra*).

CuPc, first synthesized by the Linstead group,[78] is known to crystallize into various polymorphs[124] but it is also one of the few unsubstituted MPc investigated by GED.[125] As such, the optimized Cartesian coordinates reported in Table S31 only for completeness are those optimized in ref. 24 and for this reason, any comparison with the experiment will be herein avoided. CuPc is an open-shell molecule with its single unpaired electron occupying the Cu $^{\sigma}e_g$-like $16b_{1g}^{\uparrow}$ SO[24,56,120-122] and then sharing with CuTPP the same GS symmetry and spin multiplicity ($^2B_{1g}$) even though with a different SOs ordering (see Table S14). The CuPc valence band has been investigated using ionizing sources of different energies in the gas-phase[23] and as-deposited thin films[21-22,24,121-122] on inert substrates.[XXI] The gas-phase CuPc valence IE region is characterized by the presence of a sharp peak at 6.38 eV, followed by a weak peak at 7.45 eV and a broad, intense, and structured band centered at 8.79 eV with evident shoulders on the lower (8.31 eV) and higher (9.39 eV) IE sides.[23] The agreement between the experimental evidence and TSIEs reported in Table S11 and Figure 2 is noticeable. In more detail, the sharp peak at 6.38 eV is confidently assigned to the ionization from the $2a_{1u}$ $^{pmc}\pi$ HOMO. In this regard, it must be noted that the Cu $^{\sigma}e_g$-like $16b_{1g}^{\uparrow}$ SO and the $2a_{1u}$ $^{pmc}\pi$ MO are closely spaced in the GS. [24,56] Still, such a quasi-degeneracy is relieved by accounting for the different relaxation upon ionization undergone by Cu 3d-based and $^{pmc}\pi$ MOs (see Table S11 and Figure 2).[V]

Although the CuPc HeI spectrum does not reveal any weak feature on the higher IE side of the sharp peak at 6.38 eV, the analysis of vibrational parameters of the $^2B_{1g}$ CuPc GS and $^3B_{1u}$ state of the CuPc$^+$ species, optimized by assuming a vacancy in the $2a_{1u}$ MO (see Table S32), has been carried out. As expected, optimized structures of the CuPc $^2B_{1g}$ GS and CuPc$^+$ $^3B_{1u}$ state are superimposable (see Figure S12c) and the ν^{22e_u} values estimated for the $^2B_{1g}$ GS and the $^3B_{1u}$ excited state are degenerate (see Table S26). As already found for CoPc and NiPc, the agreement between theory and experiment[110] is excellent for the neutral species. At the same time, no comparison can be done for the CuPc$^+$ species as a consequence of the lack of experimental evidence.

Moving toward the higher IE region, we propose to assign the weak peak at 7.45 eV[23] to the ionization from the Cu $^{\sigma}e_g$-like $16b_{1g}^{\uparrow}$ SO. The comparison of the aligned X-ray PE spectrum of thin-film CuPc with the HeI and HeII gas phase spectra of CuPc[21-23] does not provide useful information about the proposed assignment because of the high noise-to-signal ratio, which prevents the possibility of appreciating intensity variations upon changing the ionizing source. At variance to that, valence band spectra from CuPc film taken at hν = 21.2 and 90.0 eV,[24] strongly support the proposed assignment. Analogous considerations hold for the broad, intense, and structured band centered at 8.79 eV, which should include, besides ionizations from occupied $^{\pi}t_{2g}$-like and $^{\sigma}e_g$-like MOs, the photoemission from $^{Py}\pi$ orbitals.

CuPc has been the object of several IPS studies.[109,126-128] To date, the most precise determination of the CuPc first affinity level is that of Yoshida,[126] who determined a value of 2.92 ± 0.07 eV. Even though he did not propose any assignment for such a level, the claimed agreement with experimental and theoretical data reported by Zahn et al.[127] allows us to presume that it corresponds, in agreement with theoretical data reported in Table S15 and displayed in Figure 2, to the $7e_g$ $^{pmc}\pi^*$ SO. As such, it must be noted that Liao and Scheiner pointed out that calculated MPc electron affinities are all rather negative (> 1.7 eV) with FePc and CoPc showing the strongest attraction of an electron and CuPc the weakest.[86] This consideration sounds rather odd because, even though the TSEA of the $16^{\sigma}b_{1g}^{\downarrow}$ SO (1.78 eV, see Table S15 and Figure 2) numerically agrees with the CuPc EA they estimated (1.74 eV), the TSEA of the ^{pmc} $7e_g^{\uparrow}$ π^* SO is higher (2.25 eV, see Table S15 and Figure 2) and in qualitative agreement with the IPS determination of Yoshida.[126]

ZnTPP and ZnPc. Similarly to many of the MTPP herein considered, ZnTPP was first synthesized by Rothemund and Menotti[92] but structurally characterized only several years later.[129-130] ZnTPP is a closed-shell molecule (the optimized Cartesian coordinates of the ZnTPP $^1A_{1g}$ GS are reported in Table S33) whose $^{\pi}t_{2g}$-like and $^{\sigma}e_g$-like MOs are completely occupied, core-like in character, closely spaced (GS $^{\sigma}e_g$-like + $^{\pi}t_{2g}$-like MOs cover and energy range < 500 meV), and scarcely involved in the Zn–N^{Py} interaction (the participation of Zn 3d AOs to the $21a_{1g}$, $8b_{1g}$, $16b_{2g}$, and $6e_g$ MOs amounts to 70, 64, 82, and 81%, respectively). According to that, the optimized Zn–N^{Py} bond distance (see Table S12) is the longest along the investigated series and quantitatively reproduces the B3LYP one estimated by Shah et al. (2.07 Å)[76] as well as the bond length measured by Dechan et al (2.048 Å).[130]

The ZnTPP occupied valence region has been investigated both by gas-phase PES[29] as well as by photocurrent measurements in non-polar solvents.[98] Due to the core-like nature of the Zn^{II} 3d-based MOs, we have only reported in Table S11 the TSIEs of the quasi-degenerate $12a_{2u}$ HOMO and $2a_{1u}$ $^{pmc}\pi$ MO whose GS energies are 5.05 and 5.23 eV, respectively. The lowest IE region of the gas-phase PE spectrum recorded by Khandelwal and Roebber, one of the two displayed among the several MTPP they investigated in ref. 29, is characterized by the presence of two closely spaced sharp peaks at 6.42 and 6.62 eV assigned by the authors to the ionization from an a_{2u} and an a_{1u} orbital respectively. The agreement with TSIE values reported in Table S11 is remarkable and wraps up this matter.

As in other MTPP herein considered, the most relevant controversies concern the energy and nature of the first affinity level. To the best of the authors' knowledge, no experimental determination of the ZnTPP EA is available in the literature. However, Liao and Scheiner,[72,131] estimated an EA value of 1.6 eV in perfect in agreement with the present value reported in Table S15 and displayed in Figure 2.

As most of the MPc herein considered (VPc[36] and CrPc[49] are the exceptions), ZnPc was first synthesized by the Linstead group[78] and structurally characterized many years later by the Scheidt group[132] (optimized Cartesian coordinates of the closed-shell ZnPc $^1A_{1g}$ GS are reported in Table S34). The agreement between experiment and theory is satisfactory with the Zn–N^{Py} optimized bond length corresponding to the longest one along the series (see Table S12). Similarly to ZnTPP, the ZnPc $^{\pi}t_{2g}$-like and $^{\sigma}e_g$-like MOs are completely occupied, core-like in character, but not as closely spaced as those of ZnTPP. More specifically, the GS $^{\pi}t_{2g}$-like MOs lie at 11.64 ($1e_g$) and 10.91 ($12b_{2g}$) eV, while the GS energies of the $^{\sigma}e_g$-like MOs are 11.37 ($17a_{1g}$) eV and 12.17 ($12b_{1g}$) eV; i.e., the energy range covered by GS $^{\sigma}e_g$-like + $^{\pi}t_{2g}$-like MOs in ZnPc is almost three times that of ZnTPP. In addition, despite their core-like nature, the lone-pair character of the Zn^{II} 3d-based MOs in ZnPc (the

Zn 3d AOs participation to the $17a_{1g}$, $12b_{1g}$, $12b_{2g}$, and $1e_g$ MOs amounts to 36, 40, 72, and 52%, respectively) is less marked than in ZnTPP.

Among the MPc investigated by Berkowitz in the gas-phase,[23] ZnPc is the heaviest one and its lowest IE region is characterized by the presence of a single sharp peak at 6.37 eV assigned by Berkowitz to the $2a_{1u}$ $^{pmc}\pi$ MO. Moreover, likely CoPc and NiPc, the higher IE side of the sharp peak at 6.37 eV is characterized by the presence of a shoulder, placed by Berkowitz at ~6.5 eV (see Table 1 of ref. 23). Analogously to H_2Pc and the other MPcs herein considered, the agreement between experiment and the $2a_{1u}$ TSIE reported in Table S11 and displayed in Figure 2 is remarkable.

Similarly to CoPc, NiPc, and CuPc, vibrational parameters of the ZnPc $^1A_{1g}$ GS and $^2A_{1u}$ state of $ZnPc^+$ species whose molecular structure has been optimized by assuming a vacancy in the $2a_{1u}$ MO (see Table S35), have been estimated. As expected, optimized structures of the ZnPc $^1A_{1g}$ GS and $ZnPc^+$ $^2A_{1u}$ are superimposable (see Figure S12d) and the ν^{22e_u} values estimated for the $^1A_{1g}$ GS and the $^2A_{1u}$ excited state are degenerate (see Table S26). The agreement between theory and experiment[110] is similar to that obtained for lighter MPc (see Table S26) while the opposite is true when the estimated $ZnPc^+$ ν^{22e_u} is compared with the shoulder IE position. As such, it has to be kept in mind that the uncertainty of the shoulder IE position is of the order of 0.1 eV, which means 800 cm^{-1}.

At our knowledge, only one determination of the ZnPc EA value (3.34 eV) is present in the literature;[133] even though it has to be noted that Gao and Khan did not provide any information about the first affinity level nature. The numerical agreement between the highest ZnPc TSEA (see Table S15 and Figure 2) and IPS[133] measurements is rather poor; nevertheless, it has to be mentioned that our results are perfectly in agreement with those reported by Liao and Scheiner.[86]

Notes and references

I. In a simple crystal field approach,[6-8] the potential for four point charges at a distance R from the origin O and lying on the ±OX and ±OY axes (D_{4h} arrangement) depends on the inverse of the third and fifth power of R (see Table 8.2 of Ref. 6).

II. The bonding interaction between the Py-based and benzene-based HOMOs is accounted for the *i*-Ind $1a_2$ MO (see Figure S7).

III. Within the Gelius model,[26] the photoionization cross-section σ_p of the pth MO is $\sigma_p = \sum_{\nu,nl} c^{p}_{nl,\nu}\sigma^{\nu}_{nl}$ where (n^l) sums over the states localized on the atomic centers ν and contributing to the pth MO. As far as the σ^{ν}_{nl} are concerned, they correspond to the ASPCS,[25] while the $c^{p}_{nl,\nu}$ coefficients account for the MO occupancy.

IV. Upon the $D_{2h} \rightarrow D_{4h}$ switching, the following correlations hold between irreducible representations (*ir*): $(B_{2g} + B_{3g}) \rightarrow E_g$; A_u (C_2') $\rightarrow A_{1u}$; A_u (C_2') $\rightarrow B_{1u}$; B_{1u} (C_2') $\rightarrow A_{2u}$ (see Appendix 3 of ref. 1).

V. Limitations of the Koopmans' theorem[33] arising from larger relaxation effects during the ionization processes for 3d M-like MOs with respect to the delocalized ones are well known.[34]

VI. The double degenerate TPP^{2-} (Pc^{2-}) $12e_g$ ($6e_g$) MO corresponds to the TPP^{2-} (Pc^{2-}) LUMO.

VII. The position of ligands in the spectrochemical series[6-8] is determined largely by their donor atoms, so implying the following sequence: I < Br < Cl < S < F < O < N < C, which is in order of π-acceptor capability.[35]

VIII. Electronic configurations are throughout reported with energy ordered SOs.

IX. The VPc $^4B_{1g}$ and $^4A_{2g}$ states are 78 and 75 meV less stable than the ^4E_g GS, respectively (see Table S14).[41]

X. V–N^{Py} and Cr–N^{Py} bond lengths of the ^4E_g VTPP and $^5B_{1g}$ CrTPP GSs have been also optimized by adopting the hybrid B3LYP functional.[57-59] BP86 lengths are shorter than the B3LYP ones by 0.002 and 0.019 Å in VTPP and CrTPP, respectively.

XI. To the best of the authors' knowledge, gas-phase PE data reported by Khandelwal and Roebber[29] are the only ones available in the literature for the isolated MnTPP molecule.

XII. Khandelwal and Roebber[29] claim to have verified the absence of decomposition processes in the ionizing chamber.

XIII. $^4A_{2g}$ and $^4B_{1g}$ states are computed not only less stable than the ^4E_g GS (see Table S14) but do not imply an Aufbau SO occupation.

XIV. Wallace et al. limited the MPc (M = Mn, Fe, Co, Ni, Cu, Zn) geometry optimization to the closed shell ZnPc, which was used as a template for the remaining species whose geometry was not optimized.[56]

XV. The singly occupied (empty) $6e^{\downarrow}_{g}$ ($7e^{\downarrow}_{g}$) SOs of the MnPc ^4E_g GS correspond to the spin ↓ component of the $^{\pi}_{\perp}e_g$ ($^{pmc}\pi^*$) SOs. The GS energy order is reversed in TSEA calculations.

XVI. Measurements carried out by Yoshida et al.[66] suffer of a quite poor resolution (~1 eV).

XVII. The $^3E_g^{(1)}$ FeTPP (FePc) BP86 TSIEs of the $25a^{\uparrow}_{1g}$, $19b^{\downarrow}_{2g}$, $12e^{\downarrow}_{g}$, $2a^{\downarrow}_{1u}$, and $12a^{\downarrow}_{2u}$ ($21a^{\uparrow}_{1g}$, $14b^{\downarrow}_{2g}$, $6e^{\downarrow}_{g}$, $2a^{\downarrow}_{1u}$, and $6a^{\downarrow}_{2u}$) are 8.19, 6.42, 5.93, 6.70, and 6.58 (8.66, 6.80, 6.49, 6.53, 7.99) eV, respectively. The $^3E_g^{(1)}$ FeTPP (FePc) BP86 TSEA of the $12e^{\downarrow}_{g}$ ($6e^{\downarrow}_{g}$) is 2.22 (3.04) eV.

XVIII. The CASSCF FePc GS ($^3E_g^{(1)}$) and the lowest excited state ($^3A_{2g}$) are quasi-degenerate.[56] Their ΔE amounts to 27 meV with active space comprising the Fe-centered d_{xy}, d_{xz}, d_{yz}, and d_{z^2} orbitals and to 12 meV if the $2a_{1u}$ HOMO and the $7e_g$ LUMO are also included in active space.

XIX. Numerical experiments carried out by Carlotto et al.[85] by using the hybrid B3LYP XC functional with a 20% of the Hartree-Fock exchange and by adopting the def2-TZVP basis set point to the $^3E_g^{(1)}$ GS.

XX. Liao et al.[86] estimated MPc (M = Mg, Fe, Co, Ni, Cu, and Zn) EAs by running ΔSCF quasi-relativistic ADF calculations and adopting the BP86 XC fuctional.

XXI. Multilayers of randomly oriented and weakly interacting MTPP molecules may be representative of the isolated species.[32]

XXII. The $^3A_{2g}$ GS of FeTPP and FePc is associated with the electronic configuration $[e^{\uparrow\uparrow}_{g}b^{\uparrow}_{2g}a^{\uparrow}_{1g}b^{\downarrow}_{2g}a^{\downarrow}_{1g}]^{VIII}$ while their thermally accessible $^3E_g^{(1)}$ excited states are determined by the $[a^{\uparrow}_{1g}b^{\uparrow}_{2g}e^{\uparrow\uparrow}_{g}b^{\downarrow}_{2g}e^{\downarrow}_{g}]^{VIII}$ (FeTPP) and $[a^{\uparrow}_{1g}e^{\uparrow\uparrow}_{g}b^{\uparrow}_{2g}b^{\downarrow}_{2g}e^{\downarrow}_{g}]^{VIII}$ (FePc) configurations, respectively (see Table S14). Tiny perturbations of the ligand field, generated for instance by the substrate presence, could induce GS variations and then different occupation numbers of the Fe^{II} 3d-based SOs.

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Table S1. BP86 Optimized Cartesian Coordinates of H_2P

N	0.000000	2.123088	0.000000
N	0.000000	-2.123088	0.000000
N	-2.030689	0.000000	0.000000
N	2.030689	0.000000	0.000000
C	1.131904	2.904973	0.000000
C	-1.131904	2.904973	0.000000
C	1.131904	-2.904973	0.000000
C	-1.131904	-2.904973	0.000000
C	0.688064	4.271694	0.000000
C	-0.688064	4.271694	0.000000
C	0.688064	-4.271694	0.000000
C	-0.688064	-4.271694	0.000000
C	2.445105	2.428300	0.000000
C	-2.445105	2.428300	0.000000
C	2.445105	-2.428300	0.000000
C	-2.445105	-2.428300	0.000000
C	2.861872	1.088572	0.000000
C	-2.861872	1.088572	0.000000
C	2.861872	-1.088572	0.000000
C	-2.861872	-1.088572	0.000000
C	4.265313	0.680545	0.000000
C	-4.265313	0.680545	0.000000
C	4.265313	-0.680545	0.000000
C	-4.265313	-0.680545	0.000000
H	0.000000	1.099417	0.000000
H	0.000000	-1.099417	0.000000
H	1.353624	5.130435	0.000000
H	-1.353624	5.130435	0.000000
H	1.353624	-5.130435	0.000000
H	-1.353624	-5.130435	0.000000
H	5.117708	1.356546	0.000000
H	-5.117708	1.356546	0.000000
H	5.117708	-1.356546	0.000000
H	-5.117708	-1.356546	0.000000
H	3.225331	3.189733	0.000000
H	-3.225331	3.189733	0.000000
H	3.225331	-3.189733	0.000000
H	-3.225331	-3.189733	0.000000

Table S2. BP86 Optimized Cartesian Coordinates of H_2Pz

N	0.000000	2.000969	0.000000
N	0.000000	-2.000969	0.000000
N	-1.911391	0.000000	0.000000
N	1.911391	0.000000	0.000000
C	1.133009	2.784875	0.000000
C	-1.133009	2.784875	0.000000
C	1.133009	-2.784875	0.000000
C	-1.133009	-2.784875	0.000000
C	0.684713	4.162663	0.000000
C	-0.684713	4.162663	0.000000
C	0.684713	-4.162663	0.000000
C	-0.684713	-4.162663	0.000000
N	2.400001	2.384555	0.000000
N	-2.400001	2.384555	0.000000
N	2.400001	-2.384555	0.000000
N	-2.400001	-2.384555	0.000000
C	2.744748	1.087263	0.000000
C	-2.744748	1.087263	0.000000
C	2.744748	-1.087263	0.000000
C	-2.744748	-1.087263	0.000000
C	4.157448	0.677659	0.000000
C	-4.157448	0.677659	0.000000
C	4.157448	-0.677659	0.000000
C	-4.157448	-0.677659	0.000000
H	0.000000	0.979161	0.000000
H	0.000000	-0.979161	0.000000
H	1.361784	5.011480	0.000000
H	-1.361784	5.011480	0.000000
H	1.361784	-5.011480	0.000000
H	-1.361784	-5.011480	0.000000
H	4.996091	1.368525	0.000000
H	-4.996091	1.368525	0.000000
H	4.996091	-1.368525	0.000000
H	-4.996091	-1.368525	0.000000

Table S3. BP86 Optimized Cartesian Coordinates of H_2TPP

N	0.000000	2.114106	0.000000
N	0.000000	-2.114106	0.000000
N	2.033815	0.000000	0.000000
N	-2.033815	0.000000	0.000000
C	1.133440	2.899658	0.000000
C	-1.133440	2.899658	0.000000
C	1.133440	-2.899658	0.000000
C	-1.133440	-2.899658	0.000000
C	2.867786	1.090666	0.000000
C	2.867786	-1.090666	0.000000
C	-2.867786	1.090666	0.000000
C	-2.867786	-1.090666	0.000000
C	2.463705	2.444330	0.000000
C	2.463705	-2.444330	0.000000
C	-2.463705	2.444330	0.000000
C	-2.463705	-2.444330	0.000000
C	0.687008	4.264688	0.000000
C	0.687008	-4.264688	0.000000
C	-0.687008	4.264688	0.000000
C	-0.687008	-4.264688	0.000000
C	4.269473	0.679579	0.000000
C	4.269473	-0.679579	0.000000
C	-4.269473	0.679579	0.000000
C	-4.269473	-0.679579	0.000000
H	0.000000	1.090826	0.000000
H	0.000000	-1.090826	0.000000
H	1.348372	5.124778	0.000000
H	-1.348372	5.124778	0.000000
H	1.348372	-5.124778	0.000000
H	-1.348372	-5.124778	0.000000
H	5.125555	1.347808	0.000000
H	-5.125555	1.347808	0.000000
H	5.125555	-1.347808	0.000000
H	-5.125555	-1.347808	0.000000
C	3.532014	3.500983	0.000000
C	-3.532014	3.500983	0.000000
C	3.532014	-3.500983	0.000000
C	-3.532014	-3.500983	0.000000
C	4.039349	4.005282	1.208254
C	4.039349	4.005282	-1.208254
C	4.039349	-4.005282	1.208254
C	4.039349	-4.005282	-1.208254
C	-4.039349	4.005282	1.208254
C	-4.039349	4.005282	-1.208254
C	-4.039349	-4.005282	1.208254
C	-4.039349	-4.005282	-1.208254
C	5.031159	4.990554	1.208239
C	5.031159	4.990554	-1.208239
C	5.031159	-4.990554	1.208239
C	5.031159	-4.990554	-1.208239
C	-5.031159	4.990554	1.208239
C	-5.031159	4.990554	-1.208239
C	-5.031159	-4.990554	1.208239
C	-5.031159	-4.990554	-1.208239
C	5.530306	5.485177	0.000000
C	-5.530306	5.485177	0.000000
C	5.530306	-5.485177	0.000000
C	-5.530306	-5.485177	0.000000
H	3.652863	3.617486	2.152394
H	3.652863	3.617486	-2.152394

H	3.652863	-3.617486	2.152394
H	3.652863	-3.617486	-2.152394
H	-3.652863	3.617486	2.152394
H	-3.652863	3.617486	-2.152394
H	-3.652863	-3.617486	2.152394
H	-3.652863	-3.617486	-2.152394
H	5.416132	5.371097	2.155916
H	5.416132	5.371097	-2.155916
H	5.416132	-5.371097	2.155916
H	5.416132	-5.371097	-2.155916
H	-5.416132	5.371097	2.155916
H	-5.416132	5.371097	-2.155916
H	-5.416132	-5.371097	2.155916
H	-5.416132	-5.371097	-2.155916
H	6.305410	6.253473	0.000000
H	-6.305410	6.253473	0.000000
H	6.305410	-6.253473	0.000000
H	-6.305410	-6.253473	0.000000

Table S4. BP86 Optimized Cartesian Coordinates of H_2Pc

N	0.000000	2.032082	0.000000
N	1.946882	0.000000	0.000000
N	0.000000	-2.032082	0.000000
N	-1.946882	0.000000	0.000000
N	2.405456	2.391832	0.000000
N	2.405456	-2.391832	0.000000
N	-2.405456	2.391832	0.000000
N	-2.405456	-2.391832	0.000000
C	2.765577	1.101389	0.000000
C	2.765577	-1.101389	0.000000
C	1.148790	-2.801000	0.000000
C	-1.148790	-2.801000	0.000000
C	-2.765577	-1.101389	0.000000
C	-2.765577	1.101389	0.000000
C	-1.148790	2.801000	0.000000
C	1.148790	2.801000	0.000000
C	4.178958	0.703718	0.000000
C	4.178958	-0.703718	0.000000
C	0.708897	-4.187793	0.000000
C	-0.708897	-4.187793	0.000000
C	-4.178958	-0.703718	0.000000
C	-4.178958	0.703718	0.000000
C	-0.708897	4.187793	0.000000
C	0.708897	4.187793	0.000000
C	5.372123	1.426706	0.000000
C	5.372123	-1.426706	0.000000
C	1.428042	-5.387538	0.000000
C	-1.428042	-5.387538	0.000000
C	-5.372123	-1.426706	0.000000
C	-5.372123	1.426706	0.000000
C	-1.428042	5.387538	0.000000
C	1.428042	5.387538	0.000000
C	6.569807	0.703433	0.000000
C	6.569807	-0.703433	0.000000
C	0.705283	-6.579806	0.000000
C	-0.705283	-6.579806	0.000000
C	-6.569807	-0.703433	0.000000
C	-6.569807	0.703433	0.000000
C	-0.705283	6.579806	0.000000
C	0.705283	6.579806	0.000000
H	0.000000	1.008809	0.000000
H	0.000000	-1.008809	0.000000
H	5.364095	2.517245	0.000000
H	5.364095	-2.517245	0.000000
H	2.518151	-5.379545	0.000000
H	-2.518151	-5.379545	0.000000
H	-5.364095	-2.517245	0.000000
H	-5.364095	2.517245	0.000000
H	-2.518151	5.379545	0.000000
H	2.518151	5.379545	0.000000
H	-1.237619	-7.532357	0.000000
H	1.237619	-7.532357	0.000000
H	7.522050	-1.236551	0.000000
H	7.522050	1.236551	0.000000
H	1.237619	7.532357	0.000000
H	-1.237619	7.532357	0.000000
H	-7.522050	1.236551	0.000000
H	-7.522050	-1.236551	0.000000

Table S5. BP86 Optimized Cartesian Coordinates of P^{2-}

N	0.000000	2.089888	0.000000
N	0.000000	-2.089888	0.000000
N	-2.089888	0.000000	0.000000
N	2.089888	0.000000	0.000000
C	1.093585	2.893545	0.000000
C	-1.093585	2.893545	0.000000
C	1.093585	-2.893545	0.000000
C	-1.093585	-2.893545	0.000000
C	2.893545	1.093585	0.000000
C	-2.893545	1.093585	0.000000
C	2.893545	-1.093585	0.000000
C	-2.893545	-1.093585	0.000000
C	0.686836	4.308820	0.000000
C	-0.686836	4.308820	0.000000
C	0.686836	-4.308820	0.000000
C	-0.686836	-4.308820	0.000000
C	4.308820	0.686836	0.000000
C	-4.308820	0.686836	0.000000
C	4.308820	-0.686836	0.000000
C	-4.308820	-0.686836	0.000000
C	2.432503	2.432503	0.000000
C	-2.432503	2.432503	0.000000
C	2.432503	-2.432503	0.000000
C	-2.432503	-2.432503	0.000000
H	1.352294	5.176780	0.000000
H	-1.352294	5.176780	0.000000
H	1.352294	-5.176780	0.000000
H	-1.352294	-5.176780	0.000000
H	5.176780	1.352294	0.000000
H	-5.176780	1.352294	0.000000
H	5.176780	-1.352294	0.000000
H	-5.176780	-1.352294	0.000000
H	3.207953	3.207953	0.000000
H	-3.207953	3.207953	0.000000
H	3.207953	-3.207953	0.000000
H	-3.207953	-3.207953	0.000000

Table S6. BP86 Optimized Cartesian Coordinates of Pz^{2-}

N	0.000000	1.953902	0.000000
N	0.000000	-1.953902	0.000000
N	-1.953902	0.000000	0.000000
N	1.953902	0.000000	0.000000
C	1.088980	2.758047	0.000000
C	-1.088980	2.758047	0.000000
C	1.088980	-2.758047	0.000000
C	-1.088980	-2.758047	0.000000
C	2.758047	1.088980	0.000000
C	-2.758047	1.088980	0.000000
C	2.758047	-1.088980	0.000000
C	-2.758047	-1.088980	0.000000
C	0.682693	4.185260	0.000000
C	-0.682693	4.185260	0.000000
C	0.682693	-4.185260	0.000000
C	-0.682693	-4.185260	0.000000
C	4.185260	0.682693	0.000000
C	-4.185260	0.682693	0.000000
C	4.185260	-0.682693	0.000000
C	-4.185260	-0.682693	0.000000
N	2.391411	2.391411	0.000000
N	-2.391411	2.391411	0.000000
N	2.391411	-2.391411	0.000000
N	-2.391411	-2.391411	0.000000
H	1.365732	5.036512	0.000000
H	-1.365732	5.036512	0.000000
H	1.365732	-5.036512	0.000000
H	-1.365732	-5.036512	0.000000
H	5.036512	1.365732	0.000000
H	-5.036512	1.365732	0.000000
H	5.036512	-1.365732	0.000000
H	-5.036512	-1.365732	0.000000

Table S7. BP86 Optimized Cartesian Coordinates of TPP^{2-}

N	0.000000	2.080649	0.000000
N	0.000000	-2.080649	0.000000
N	2.080649	0.000000	0.000000
N	-2.080649	0.000000	0.000000
C	1.090905	2.891109	0.000000
C	-1.090905	2.891109	0.000000
C	1.090905	-2.891109	0.000000
C	-1.090905	-2.891109	0.000000
C	2.891109	1.090905	0.000000
C	2.891109	-1.090905	0.000000
C	-2.891109	1.090905	0.000000
C	-2.891109	-1.090905	0.000000
C	2.441014	2.441014	0.000000
C	2.441014	-2.441014	0.000000
C	-2.441014	2.441014	0.000000
C	-2.441014	-2.441014	0.000000
C	0.684476	4.305540	0.000000
C	0.684476	-4.305540	0.000000
C	-0.684476	4.305540	0.000000
C	-0.684476	-4.305540	0.000000
C	4.305540	0.684476	0.000000
C	4.305540	-0.684476	0.000000
C	-4.305540	0.684476	0.000000
C	-4.305540	-0.684476	0.000000
H	1.342795	5.174063	0.000000
H	-1.342795	5.174063	0.000000
H	1.342795	-5.174063	0.000000
H	-1.342795	-5.174063	0.000000
H	5.174063	1.342795	0.000000
H	-5.174063	1.342795	0.000000
H	5.174063	-1.342795	0.000000
H	-5.174063	-1.342795	0.000000
C	3.502594	3.502594	0.000000
C	-3.502594	3.502594	0.000000
C	3.502594	-3.502594	0.000000
C	-3.502594	-3.502594	0.000000
C	4.017584	4.017584	1.203257
C	4.017584	4.017584	-1.203257
C	4.017584	-4.017584	1.203257
C	4.017584	-4.017584	-1.203257
C	-4.017584	4.017584	1.203257
C	-4.017584	4.017584	-1.203257
C	-4.017584	-4.017584	1.203257
C	-4.017584	-4.017584	-1.203257
C	5.006969	5.006969	1.206950
C	5.006969	5.006969	-1.206950
C	5.006969	-5.006969	1.206950
C	5.006969	-5.006969	-1.206950
C	-5.006969	5.006969	1.206950
C	-5.006969	5.006969	-1.206950
C	-5.006969	-5.006969	1.206950
C	-5.006969	-5.006969	-1.206950
C	5.507371	5.507371	0.000000
C	-5.507371	5.507371	0.000000
C	5.507371	-5.507371	0.000000
C	-5.507371	-5.507371	0.000000
H	3.626142	3.626142	2.144109
H	3.626142	3.626142	-2.144109
H	3.626142	-3.626142	2.144109
H	3.626142	-3.626142	-2.144109

H	-3.626142	3.626142	2.144109
H	-3.626142	3.626142	-2.144109
H	-3.626142	-3.626142	2.144109
H	-3.626142	-3.626142	-2.144109
H	5.389349	5.389349	2.157219
H	5.389349	5.389349	-2.157219
H	5.389349	-5.389349	2.157219
H	5.389349	-5.389349	-2.157219
H	-5.389349	5.389349	2.157219
H	-5.389349	5.389349	-2.157219
H	-5.389349	-5.389349	2.157219
H	-5.389349	-5.389349	-2.157219
H	6.280444	6.280444	0.000000
H	-6.280444	6.280444	0.000000
H	6.280444	-6.280444	0.000000
H	-6.280444	-6.280444	0.000000

Table S8. BP86 Optimized Cartesian Coordinates of Pc^{2-}

N	0.000000	1.979508	0.000000
N	1.979508	0.000000	0.000000
N	0.000000	-1.979508	0.000000
N	-1.979508	0.000000	0.000000
N	2.395106	2.395106	0.000000
N	2.395106	-2.395106	0.000000
N	-2.395106	2.395106	0.000000
N	-2.395106	-2.395106	0.000000
C	2.770293	1.101676	0.000000
C	2.770293	-1.101676	0.000000
C	1.101676	-2.770293	0.000000
C	-1.101676	-2.770293	0.000000
C	-2.770293	-1.101676	0.000000
C	-2.770293	1.101676	0.000000
C	-1.101676	2.770293	0.000000
C	1.101676	2.770293	0.000000
C	4.198991	0.709021	0.000000
C	4.198991	-0.709021	0.000000
C	0.709021	-4.198991	0.000000
C	-0.709021	-4.198991	0.000000
C	-4.198991	-0.709021	0.000000
C	-4.198991	0.709021	0.000000
C	-0.709021	4.198991	0.000000
C	0.709021	4.198991	0.000000
C	5.400005	1.421476	0.000000
C	5.400005	-1.421476	0.000000
C	1.421476	-5.400005	0.000000
C	-1.421476	-5.400005	0.000000
C	-5.400005	-1.421476	0.000000
C	-5.400005	1.421476	0.000000
C	-1.421476	5.400005	0.000000
C	1.421476	5.400005	0.000000
C	6.604847	0.704480	0.000000
C	6.604847	-0.704480	0.000000
C	0.704480	-6.604847	0.000000
C	-0.704480	-6.604847	0.000000
C	-6.604847	-0.704480	0.000000
C	-6.604847	0.704480	0.000000
C	-0.704480	6.604847	0.000000
C	0.704480	6.604847	0.000000
H	5.387796	2.513879	0.000000
H	5.387796	-2.513879	0.000000
H	2.513879	-5.387796	0.000000
H	-2.513879	-5.387796	0.000000
H	-5.387796	-2.513879	0.000000
H	-5.387796	2.513879	0.000000
H	-2.513879	5.387796	0.000000
H	2.513879	5.387796	0.000000
H	-1.240969	-7.558300	0.000000
H	1.240969	-7.558300	0.000000
H	7.558300	-1.240969	0.000000
H	7.558300	1.240969	0.000000
H	1.240969	7.558300	0.000000
H	-1.240969	7.558300	0.000000
H	-7.558300	1.240969	0.000000
H	-7.558300	-1.240969	0.000000

Table S9. BP86 Optimized Cartesian Coordinates of Py

N	0.000000	0.000000	2.129848
C	0.000000	-1.128968	2.921036
C	0.000000	1.128968	2.921036
C	0.000000	-0.713095	4.240809
C	0.000000	0.713095	4.240809
H	0.000000	0.000000	1.117181
H	0.000000	-2.121408	2.482901
H	0.000000	2.121408	2.482901
H	0.000000	-1.365334	5.108742
H	0.000000	1.365334	5.108742

Table S10. BP86 Optimized Cartesian Coordinates of *i*-Ind

N	0.000000	0.000000	2.048271
C	0.000000	1.139377	2.814870
C	0.000000	-1.139377	2.814870
C	0.000000	0.728307	4.152271
C	0.000000	-0.728307	4.152271
C	0.000000	1.433127	5.385849
C	0.000000	-1.433127	5.385849
C	0.000000	0.714189	6.561862
C	0.000000	-0.714189	6.561862
H	0.000000	-2.124277	2.361566
H	0.000000	2.124277	2.361566
H	0.000000	0.000000	1.033996
H	0.000000	2.524784	5.399340
H	0.000000	-2.524784	5.399340
H	0.000000	-1.241803	7.517178
H	0.000000	1.241803	7.517178

Table S11. $\mathrm{H_2TPP}$ ($\mathrm{H_2Pc}$) TSIEs (eV) of the $10\mathrm{a_u}$ and $13\mathrm{b_{1u}}$ ($7\mathrm{b_{1u}}$ and $4\mathrm{a_u}$) MOs. MTPP and MPc TSIEs of the M ${}^{\sigma}\mathrm{a_{1g}}$, ${}^{\sigma}\mathrm{b_{1g}}$, ${}^{\pi}\mathrm{b_{2g}}$, ${}^{\pi}\mathrm{e_g}$, and pmc-based ${}^{\pi}\mathrm{a_{1u}}$ and ${}^{\pi}\mathrm{a_{2u}}$ SOs. Values of the lowest TSIE are in bold.[a]

	${}^{\sigma}\mathrm{a_{1g}}$	${}^{\sigma}\mathrm{b_{1g}}$	${}^{\pi}\mathrm{b_{2g}}$	${}^{\pi}\mathrm{e_g}$	$\mathrm{a_{1u}}^{\downarrow}$	$\mathrm{a_{2u}}^{\downarrow}$
$\mathrm{H_2TPP}$	–	–	–	–	6.77 ($10\mathrm{a_u}$)	**6.48** ($13\mathrm{b_{1u}}$)
$\mathrm{H_2Pc}$	–	–	–	–	**6.57** ($4\mathrm{a_u}$)	7.74 ($7\mathrm{b_{1u}}$)
VTPP	$6.29^{\uparrow}$	–	$6.37^{\uparrow}$	**5.69**$^{\uparrow}$	6.72	6.50
VPc	$6.74^{\uparrow}$	–	$6.59^{\uparrow}$	**6.17**$^{\uparrow}$	6.49	7.98
CrTPP	$7.28^{\uparrow}$	–	$7.69^{\uparrow}$	$6.63^{\uparrow}$	6.69	**6.54**
CrPc	$7.73^{\uparrow}$	–	$7.44^{\uparrow}$	$7.03^{\uparrow}$	**6.50**	7.99
MnTPP	$9.61^{\uparrow}$	**5.88**$^{\uparrow}$	$9.49^{\uparrow}$	$10.53^{\uparrow}$	6.55	6.36
MnPc	$8.40^{\uparrow}$	–	$9.33^{\uparrow}$	**5.99**$^{\downarrow}$	6.57	8.00
FeTPP	**6.18**$^{\downarrow}$	–	$6.45^{\downarrow}$	$7.08^{\uparrow}$	6.70	6.57
FePc	$6.65^{\downarrow}$	–	$6.77^{\downarrow}$	$8.63^{\uparrow}$	**6.51**	8.01
CoTPP	$8.94^{\uparrow}$	–	$7.60^{\downarrow}$	$6.85^{\downarrow}$	6.69	**6.60**
CoPc	$9.14^{\uparrow}$	–	$7.62^{\downarrow}$	$7.32^{\downarrow}$	**6.54**	8.01
NiTPP	$7.65^{\downarrow}$	–	$8.63^{\downarrow}$	$7.03^{\downarrow}$	6.70	**6.62**
NiPc	$8.36^{\downarrow}$	–	$8.03^{\downarrow}$	$7.47^{\downarrow}$	**6.55**	8.03
CuTPP	$9.72^{\downarrow}$	$6.95^{\uparrow}$	$9.39^{\downarrow}$	$9.64^{\downarrow}$	6.72	**6.55**
CuPc	$9.17^{\downarrow}$	$7.28^{\uparrow}$	$8.08^{\downarrow}$	$7.77^{\downarrow}$	**6.56**	8.01
ZnTPP					6.72	**6.54**
ZnPc					**6.55**	7.98

[a] HS MnTPP TSIE calculations have been run by adopting the B3LYP functional.

Table S12. Comparison of the optimized M–N^{Py} bond length (Å) in MTPP and MPc complexes with experimental evidence, when available.[a]

	MTPP		MPc	
	Theory	Exp.	Theory	Exp.
V	2.046	–	1.996	–
Cr	2.035	2.033[b]	1.982	–
Mn	2.095	2.085[c]	1.952	1.938[d]
Fe	1.990	1.972[e]	1.935	1.927[d]
Co	1.978	1.949[f]	1.928	1.911[g]
Ni	1.967	1.931[h]	1.915	1.913[i]
Cu	2.021	1.981[j]	1.968	1.947[k]
Zn	2.053	2.048[l]	2.004	1.980[m]

[a] HS MnTPP numerical experiments have been carried out by adopting the B3LYP exchange-correlation functional;[57-59] [b] ref. 45-46; [c] ref. 54; [d] ref. 4; [e] ref. 67; [f] ref. 93; [g] ref.103; [h] ref. 113; [i] ref.117; [j] ref. 119; [k] ref. 124; [l] ref.130; [m] ref. 132.

Table S13. BP86 Optimized Cartesian Coordinates of HS ^4E_g VTPP

V	0.000000	0.000000	0.000000
N	0.000000	2.045614	0.000000
N	0.000000	-2.045614	0.000000
N	2.045614	0.000000	0.000000
N	-2.045614	0.000000	0.000000
C	1.114172	2.880130	0.000000
C	-1.114172	2.880130	0.000000
C	1.114172	-2.880130	0.000000
C	-1.114172	-2.880130	0.000000
C	2.880130	1.114172	0.000000
C	2.880130	-1.114172	0.000000
C	-2.880130	1.114172	0.000000
C	-2.880130	-1.114172	0.000000
C	2.456165	2.456165	0.000000
C	2.456165	-2.456165	0.000000
C	-2.456165	2.456165	0.000000
C	-2.456165	-2.456165	0.000000
C	0.685222	4.253414	0.000000
C	0.685222	-4.253414	0.000000
C	-0.685222	4.253414	0.000000
C	-0.685222	-4.253414	0.000000
C	4.253414	0.685222	0.000000
C	4.253414	-0.685222	0.000000
C	-4.253414	0.685222	0.000000
C	-4.253414	-0.685222	0.000000
H	1.348695	5.112917	0.000000
H	-1.348695	5.112917	0.000000
H	1.348695	-5.112917	0.000000
H	-1.348695	-5.112917	0.000000
H	5.112917	1.348695	0.000000
H	-5.112917	1.348695	0.000000
H	5.112917	-1.348695	0.000000
H	-5.112917	-1.348695	0.000000
C	3.517784	3.517784	0.000000
C	-3.517784	3.517784	0.000000
C	3.517784	-3.517784	0.000000
C	-3.517784	-3.517784	0.000000
C	4.023597	4.023597	1.208106
C	4.023597	4.023597	-1.208106
C	4.023597	-4.023597	1.208106
C	4.023597	-4.023597	-1.208106
C	-4.023597	4.023597	1.208106
C	-4.023597	4.023597	-1.208106
C	-4.023597	-4.023597	1.208106
C	-4.023597	-4.023597	-1.208106
C	5.012115	5.012115	1.208223
C	5.012115	5.012115	-1.208223
C	5.012115	-5.012115	1.208223
C	5.012115	-5.012115	-1.208223
C	-5.012115	5.012115	1.208223
C	-5.012115	5.012115	-1.208223
C	-5.012115	-5.012115	1.208223
C	-5.012115	-5.012115	-1.208223
C	5.509042	5.509042	0.000000
C	-5.509042	5.509042	0.000000
C	5.509042	-5.509042	0.000000
C	-5.509042	-5.509042	0.000000

H	3.636128	3.636128	2.152006
H	3.636128	3.636128	-2.152006
H	3.636128	-3.636128	2.152006
H	3.636128	-3.636128	-2.152006
H	-3.636128	3.636128	2.152006
H	-3.636128	3.636128	-2.152006
H	-3.636128	-3.636128	2.152006
H	-3.636128	-3.636128	-2.152006
H	5.394712	5.394712	2.156052
H	5.394712	5.394712	-2.156052
H	5.394712	-5.394712	2.156052
H	5.394712	-5.394712	-2.156052
H	-5.394712	5.394712	2.156052
H	-5.394712	5.394712	-2.156052
H	-5.394712	-5.394712	2.156052
H	-5.394712	-5.394712	-2.156052
H	6.280838	6.280838	0.000000
H	-6.280838	6.280838	0.000000
H	6.280838	-6.280838	0.000000
H	-6.280838	-6.280838	0.000000

Table S14. MTPP and MPc GS terms and low-lying excited state (ExS) terms sharing the same GS spin multiplicity (corresponding electronic configurations are reported with energy ordered SOs); relative energies are in meV.[a,b]

	GS	ExS1	ExS2	ExS3
VTPP	$^{4}\mathrm{E}_{g}\,[a_{1g}^{\uparrow}b_{2g}^{\uparrow}e_{g}^{\uparrow}]$ (0)	$^{4}\mathrm{B}_{1g}\,[e_{g}^{\uparrow\uparrow}b_{2g}^{\uparrow}]$ (123)	$^{4}\mathrm{A}_{2g}\,[a_{1g}^{\uparrow}e_{g}^{\uparrow\uparrow}]$ (278)	
VPc	$^{4}\mathrm{E}_{g}\,[a_{1g}^{\uparrow}b_{2g}^{\uparrow}e_{g}^{\uparrow}]$ (0)	$^{4}\mathrm{A}_{2g}\,[e_{g}^{\uparrow\uparrow}a_{1g}^{\uparrow}]$ (75)	$^{4}\mathrm{B}_{1g}\,[e_{g}^{\uparrow\uparrow}b_{2g}^{\uparrow}]$ (78)	
CrTPP	$^{5}\mathrm{B}_{1g}\,[b_{2g}^{\uparrow}a_{1g}^{\uparrow}e_{g}^{\uparrow\uparrow}]$ (0)			
CrPc	$^{5}\mathrm{B}_{1g}\,[b_{2g}^{\uparrow}a_{1g}^{\uparrow}e_{g}^{\uparrow\uparrow}]$ (0)			
MnTPP	$^{6}\mathrm{A}_{1g}\,[e_{g}^{\uparrow\uparrow}a_{1g}^{\uparrow}b_{2g}^{\uparrow}b_{1g}^{\uparrow}]$ (0)			
MnPc	$^{4}\mathrm{E}_{g}\,[b_{2g}^{\uparrow}e_{g}^{\uparrow\uparrow}a_{1g}^{\uparrow}e_{g}^{\downarrow}]$ (0)	$^{4}\mathrm{A}_{2g}\,[a_{1g}^{\uparrow}e_{g}^{\uparrow\uparrow}b_{2g}^{\uparrow}b_{2g}^{\downarrow}]$ (314)	$^{4}\mathrm{B}_{1g}$ $[b_{2g}^{\uparrow}e_{g}^{\uparrow\uparrow}a_{1g}^{\uparrow}a_{1g}^{\downarrow}]$ (449)	
FeTPP	$^{3}\mathrm{A}_{2g}\,[e_{g}^{\uparrow\uparrow}b_{2g}^{\uparrow}a_{1g}^{\uparrow}b_{2g}^{\downarrow}a_{1g}^{\downarrow}]$ (0)	$^{3}\mathrm{E}_{g}^{(1)}\,[a_{1g}^{\uparrow}b_{2g}^{\uparrow}e_{g}^{\uparrow\uparrow}b_{2g}^{\downarrow}e_{g}^{\downarrow}]$ (123)	$^{3}\mathrm{B}_{2g}\,[b_{2g}^{\uparrow}a_{1g}^{\uparrow}e_{g}^{\uparrow\uparrow}e_{g}^{\downarrow\downarrow}]$ (253)	$^{3}\mathrm{E}_{g}^{(2)}$ $[b_{2g}^{\uparrow}e_{g}^{\uparrow\uparrow}a_{1g}^{\uparrow}a_{1g}^{\downarrow}e_{g}^{\downarrow}]$ (728)
FePc	$^{3}\mathrm{A}_{2g}\,[e_{g}^{\uparrow\uparrow}b_{2g}^{\uparrow}a_{1g}^{\uparrow}b_{2g}^{\downarrow}a_{1g}^{\downarrow}]$ (0)	$^{3}\mathrm{E}_{g}^{(1)}\,[a_{1g}^{\uparrow}e_{g}^{\uparrow\uparrow}b_{2g}^{\uparrow}b_{2g}^{\downarrow}e_{g}^{\downarrow}]$ (47)	$^{3}\mathrm{B}_{2g}\,[b_{2g}^{\uparrow}a_{1g}^{\uparrow}e_{g}^{\uparrow\uparrow}e_{g}^{\downarrow\downarrow}]$ (62)	$^{3}\mathrm{E}_{g}^{(2)}$ $[b_{2g}^{\uparrow}e_{g}^{\uparrow\uparrow}a_{1g}^{\uparrow}a_{1g}^{\downarrow}e_{g}^{\downarrow}]$ (532)
CoTPP	$^{2}\mathrm{A}_{1g}\,[a_{1g}^{\uparrow}b_{2g}^{\uparrow}b_{2g}^{\downarrow}e_{g}^{\uparrow\uparrow}e_{g}^{\downarrow\downarrow}]$ (0)	$^{2}\mathrm{E}_{g}\,[b_{2g}^{\uparrow}e_{g}^{\uparrow\uparrow}b_{2g}^{\downarrow}a_{1g}^{\uparrow}a_{1g}^{\downarrow}e_{g}^{\downarrow}]$ (172)		
CoPc	$^{2}\mathrm{A}_{1g}\,[a_{1g}^{\uparrow}b_{2g}^{\uparrow}e_{g}^{\uparrow\uparrow}b_{2g}^{\downarrow}e_{g}^{\downarrow\downarrow}]$ (0)	$^{2}\mathrm{E}_{g}\,[b_{2g}^{\uparrow}e_{g}^{\uparrow\uparrow}b_{2g}^{\downarrow}a_{1g}^{\uparrow}a_{1g}^{\downarrow}e_{g}^{\downarrow}]$ (231)		
NiTPP	$^{1}\mathrm{A}_{1g}\,[b_{2g}^{\uparrow\downarrow}e_{g}^{\uparrow\uparrow\downarrow\downarrow}a_{1g}^{\uparrow\downarrow}]$ (0)			
NiPc	$^{1}\mathrm{A}_{1g}\,[b_{2g}^{\uparrow\downarrow}a_{1g}^{\uparrow\downarrow}e_{g}^{\uparrow\uparrow\downarrow\downarrow}]$ (0)			
CuTPP	$^{2}\mathrm{B}_{1g}\,[e_{g}^{\uparrow\uparrow}b_{2g}^{\uparrow}b_{2g}^{\downarrow}e_{g}^{\downarrow\downarrow}a_{1g}^{\uparrow}a_{1g}^{\downarrow}b_{1g}^{\uparrow}]$ (0)			
CuPc	$^{2}\mathrm{B}_{1g}\,[b_{2g}^{\uparrow}b_{2g}^{\downarrow}e_{g}^{\uparrow\uparrow}a_{1g}^{\uparrow}e_{g}^{\downarrow\downarrow}a_{1g}^{\downarrow}b_{1g}^{\uparrow}]$ (0)			
ZnTPP	$^{1}\mathrm{A}_{1g}\,[a_{1g}^{\uparrow\downarrow}b_{1g}^{\uparrow\downarrow}e_{g}^{\uparrow\uparrow\downarrow\downarrow}b_{2g}^{\uparrow\downarrow}]$ (0)			
ZnPc	$^{1}\mathrm{A}_{1g}\,[b_{1g}^{\uparrow\downarrow}e_{g}^{\uparrow\uparrow\downarrow\downarrow}a_{1g}^{\uparrow\downarrow}b_{2g}^{\uparrow\downarrow}]$ (0)			

[a] HS MnTPP calculations have been run by adopting the B3LYP functional. [b] $\parallel$, $\perp$, σ, and π symbols are omitted because no misunderstanding is possible.

Table S15. MTPP (MPc) TSEAs (eV) of low-lying unoccupied SOs. Values of the highest TSEA are in bold.[a,b]

	$^{\sigma}a_{1g}$	$^{\sigma}b_{1g}$	$^{\pi}b_{2g}$	$^{\pi}e_{g}$	$^{pmc}e_{g}$	$^{pmc}b_{1u}$
VTPP	0.66$^{\downarrow}$	0.31$^{\uparrow}$	0.01$^{\downarrow}$	**2.23**$^{\uparrow}$	1.81$^{\downarrow}$	0.43$^{\uparrow}$
VPc	1.18$^{\downarrow}$	-0.95$^{\uparrow}$	0.53$^{\downarrow}$	**2.94**$^{\uparrow}$	2.50$^{\downarrow}$	0.99$^{\uparrow}$
CrTPP	0.39$^{\downarrow}$	0.32$^{\uparrow}$	0.13$^{\downarrow}$	-0.37$^{\downarrow}$	**1.76**$^{\downarrow}$	0.38$^{\uparrow}$
CrPc	1.13$^{\downarrow}$	-0.59$^{\uparrow}$	0.87$^{\downarrow}$	0.96$^{\downarrow}$	**2.47**$^{\downarrow}$	0.97$^{\uparrow}$
MnTPP	-0.20$^{\downarrow}$	-3.59$^{\downarrow}$	-1.17$^{\downarrow}$	-1.57$^{\downarrow}$	**1.33**$^{\downarrow}$	-0.09$^{\uparrow}$
MnPc	2.16$^{\downarrow}$	1.14$^{\uparrow}$	2.25$^{\downarrow}$	1.69$^{\downarrow}$	**2.84**$^{\downarrow}$	0.93$^{\uparrow}$
FeTPP	–	0.41$^{\uparrow}$	–	0.71$^{\downarrow}$	**1.85**$^{\downarrow}$	0.35$^{\uparrow}$
FePc	–	0.30$^{\uparrow}$	–	1.44$^{\downarrow}$	**2.61**$^{\downarrow}$	0.95$^{\uparrow}$
CoTPP	**2.13**$^{\downarrow}$	1.06$^{\uparrow}$	–	–	1.52$^{\uparrow}$	0.26$^{\uparrow}$
CoPc	**3.00**$^{\downarrow}$	1.45$^{\uparrow}$	–	–	2.17$^{\uparrow}$	0.90$^{\uparrow}$
NiTPP	–	1.47$^{\uparrow}$	–	–	**1.53**$^{\uparrow}$	0.27$^{\uparrow}$
NiPc	–	1.88$^{\uparrow}$	–	–	**2.19**$^{\uparrow}$	0.91$^{\uparrow}$
CuTPP	–	1.35$^{\downarrow}$	–	–	**1.61**$^{\uparrow}$	0.33$^{\uparrow}$
CuPc	–	1.78$^{\downarrow}$	–	–	**2.25**$^{\uparrow}$	0.94$^{\uparrow}$
ZnTPP	–	–	–	–	**1.64**$^{\uparrow}$	0.38$^{\uparrow}$
ZnPc	–	–	–	–	**2.26**$^{\uparrow}$	0.96$^{\uparrow}$

[a] HS MnTPP TSEA calculations have been run by adopting the B3LYP functional. [b] TSEA positive values correspond to the IE of the $MTPP^{-}$ (MPc^{-}) species; negative values indicate an unfavorable (costly) electron capture.

Table S16. BP86 Optimized Cartesian Coordinates of HS ^4E_g VPc

V	0.000000	0.000000	0.000000
N	0.000000	1.996056	0.000000
N	1.996056	0.000000	0.000000
N	0.000000	-1.996056	0.000000
N	-1.996056	0.000000	0.000000
N	2.406487	2.406487	0.000000
N	2.406487	-2.406487	0.000000
N	-2.406487	2.406487	0.000000
N	-2.406487	-2.406487	0.000000
C	2.800668	1.133801	0.000000
C	2.800668	-1.133801	0.000000
C	1.133801	-2.800668	0.000000
C	-1.133801	-2.800668	0.000000
C	-2.800668	-1.133801	0.000000
C	-2.800668	1.133801	0.000000
C	-1.133801	2.800668	0.000000
C	1.133801	2.800668	0.000000
C	4.192090	0.708367	0.000000
C	4.192090	-0.708367	0.000000
C	0.708367	-4.192090	0.000000
C	-0.708367	-4.192090	0.000000
C	-4.192090	-0.708367	0.000000
C	-4.192090	0.708367	0.000000
C	-0.708367	4.192090	0.000000
C	0.708367	4.192090	0.000000
C	5.392288	1.426932	0.000000
C	5.392288	-1.426932	0.000000
C	1.426932	-5.392288	0.000000
C	-1.426932	-5.392288	0.000000
C	-5.392288	-1.426932	0.000000
C	-5.392288	1.426932	0.000000
C	-1.426932	5.392288	0.000000
C	1.426932	5.392288	0.000000
C	6.585826	0.705104	0.000000
C	6.585826	-0.705104	0.000000
C	0.705104	-6.585826	0.000000
C	-0.705104	-6.585826	0.000000
C	-6.585826	-0.705104	0.000000
C	-6.585826	0.705104	0.000000
C	-0.705104	6.585826	0.000000
C	0.705104	6.585826	0.000000
H	5.384671	2.516758	0.000000
H	5.384671	-2.516758	0.000000
H	2.516758	-5.384671	0.000000
H	-2.516758	-5.384671	0.000000
H	-5.384671	-2.516758	0.000000
H	-5.384671	2.516758	0.000000
H	-2.516758	5.384671	0.000000
H	2.516758	5.384671	0.000000
H	-1.237018	-7.538070	0.000000
H	1.237018	-7.538070	0.000000
H	7.538070	-1.237018	0.000000
H	7.538070	1.237018	0.000000
H	1.237018	7.538070	0.000000
H	-1.237018	7.538070	0.000000
H	-7.538070	1.237018	0.000000
H	-7.538070	-1.237018	0.000000

Table S17. BP86 Optimized Cartesian Coordinates of HS $^5B_{1g}$ CrTPP

Cr	0.000000	0.000000	0.000000
N	0.000000	2.034619	0.000000
N	0.000000	-2.034619	0.000000
N	2.034619	0.000000	0.000000
N	-2.034619	0.000000	0.000000
C	1.109460	2.868807	0.000000
C	-1.109460	2.868807	0.000000
C	1.109460	-2.868807	0.000000
C	-1.109460	-2.868807	0.000000
C	2.868807	1.109460	0.000000
C	2.868807	-1.109460	0.000000
C	-2.868807	1.109460	0.000000
C	-2.868807	-1.109460	0.000000
C	2.450278	2.450278	0.000000
C	2.450278	-2.450278	0.000000
C	-2.450278	2.450278	0.000000
C	-2.450278	-2.450278	0.000000
C	0.683005	4.246273	0.000000
C	0.683005	-4.246273	0.000000
C	-0.683005	4.246273	0.000000
C	-0.683005	-4.246273	0.000000
C	4.246273	0.683005	0.000000
C	4.246273	-0.683005	0.000000
C	-4.246273	0.683005	0.000000
C	-4.246273	-0.683005	0.000000
H	1.350730	5.102289	0.000000
H	-1.350730	5.102289	0.000000
H	1.350730	-5.102289	0.000000
H	-1.350730	-5.102289	0.000000
H	5.102289	1.350730	0.000000
H	-5.102289	1.350730	0.000000
H	5.102289	-1.350730	0.000000
H	-5.102289	-1.350730	0.000000
C	3.511770	3.511770	0.000000
C	-3.511770	3.511770	0.000000
C	3.511770	-3.511770	0.000000
C	-3.511770	-3.511770	0.000000
C	4.017492	4.017492	1.208137
C	4.017492	4.017492	-1.208137
C	4.017492	-4.017492	1.208137
C	4.017492	-4.017492	-1.208137
C	-4.017492	4.017492	1.208137
C	-4.017492	4.017492	-1.208137
C	-4.017492	-4.017492	1.208137
C	-4.017492	-4.017492	-1.208137
C	5.006003	5.006003	1.208251
C	5.006003	5.006003	-1.208251
C	5.006003	-5.006003	1.208251
C	5.006003	-5.006003	-1.208251
C	-5.006003	5.006003	1.208251
C	-5.006003	5.006003	-1.208251
C	-5.006003	-5.006003	1.208251
C	-5.006003	-5.006003	-1.208251
C	5.503033	5.503033	0.000000
C	-5.503033	5.503033	0.000000
C	5.503033	-5.503033	0.000000
C	-5.503033	-5.503033	0.000000

H	3.630077	3.630077	2.152040
H	3.630077	3.630077	-2.152040
H	3.630077	-3.630077	2.152040
H	3.630077	-3.630077	-2.152040
H	-3.630077	3.630077	2.152040
H	-3.630077	3.630077	-2.152040
H	-3.630077	-3.630077	2.152040
H	-3.630077	-3.630077	-2.152040
H	5.388509	5.388509	2.156177
H	5.388509	5.388509	-2.156177
H	5.388509	-5.388509	2.156177
H	5.388509	-5.388509	-2.156177
H	-5.388509	5.388509	2.156177
H	-5.388509	5.388509	-2.156177
H	-5.388509	-5.388509	2.156177
H	-5.388509	-5.388509	-2.156177
H	6.274800	6.274800	0.000000
H	-6.274800	6.274800	0.000000
H	6.274800	-6.274800	0.000000
H	-6.274800	-6.274800	0.000000

Table S18. BP86 Optimized Cartesian Coordinates of HS $^5B_{1g}$ CrPc

Cr	0.000000	0.000000	0.000000
N	0.000000	1.982180	0.000000
N	1.982180	0.000000	0.000000
N	0.000000	-1.982180	0.000000
N	-1.982180	0.000000	0.000000
N	2.400852	2.400852	0.000000
N	2.400852	-2.400852	0.000000
N	-2.400852	2.400852	0.000000
N	-2.400852	-2.400852	0.000000
C	2.789117	1.128550	0.000000
C	2.789117	-1.128550	0.000000
C	1.128550	-2.789117	0.000000
C	-1.128550	-2.789117	0.000000
C	-2.789117	-1.128550	0.000000
C	-2.789117	1.128550	0.000000
C	-1.128550	2.789117	0.000000
C	1.128550	2.789117	0.000000
C	4.184723	0.706646	0.000000
C	4.184723	-0.706646	0.000000
C	0.706646	-4.184723	0.000000
C	-0.706646	-4.184723	0.000000
C	-4.184723	-0.706646	0.000000
C	-4.184723	0.706646	0.000000
C	-0.706646	4.184723	0.000000
C	0.706646	4.184723	0.000000
C	5.382239	1.427343	0.000000
C	5.382239	-1.427343	0.000000
C	1.427343	-5.382239	0.000000
C	-1.427343	-5.382239	0.000000
C	-5.382239	-1.427343	0.000000
C	-5.382239	1.427343	0.000000
C	-1.427343	5.382239	0.000000
C	1.427343	5.382239	0.000000
C	6.576695	0.704571	0.000000
C	6.576695	-0.704571	0.000000
C	0.704571	-6.576695	0.000000
C	-0.704571	-6.576695	0.000000
C	-6.576695	-0.704571	0.000000
C	-6.576695	0.704571	0.000000
C	-0.704571	6.576695	0.000000
C	0.704571	6.576695	0.000000
H	5.374210	2.517645	0.000000
H	5.374210	-2.517645	0.000000
H	2.517645	-5.374210	0.000000
H	-2.517645	-5.374210	0.000000
H	-5.374210	-2.517645	0.000000
H	-5.374210	2.517645	0.000000
H	-2.517645	5.374210	0.000000
H	2.517645	5.374210	0.000000
H	-1.236934	-7.529167	0.000000
H	1.236934	-7.529167	0.000000
H	7.529167	-1.236934	0.000000
H	7.529167	1.236934	0.000000
H	1.236934	7.529167	0.000000
H	-1.236934	7.529167	0.000000
H	-7.529167	1.236934	0.000000
H	-7.529167	-1.236934	0.000000

Table S19. B3LYP Optimized Cartesian Coordinates of HS $^{6}A_{1g}$ MnTPP

Mn	0.000000	0.000000	0.000000
N	0.000000	2.095158	0.000000
N	0.000000	-2.095158	0.000000
N	2.095158	0.000000	0.000000
N	-2.095158	0.000000	0.000000
C	1.114062	2.902190	0.000000
C	-1.114062	2.902190	0.000000
C	1.114062	-2.902190	0.000000
C	-1.114062	-2.902190	0.000000
C	2.902190	1.114062	0.000000
C	2.902190	-1.114062	0.000000
C	-2.902190	1.114062	0.000000
C	-2.902190	-1.114062	0.000000
C	2.459880	2.459880	0.000000
C	2.459880	-2.459880	0.000000
C	-2.459880	2.459880	0.000000
C	-2.459880	-2.459880	0.000000
C	0.683518	4.288720	0.000000
C	0.683518	-4.288720	0.000000
C	-0.683518	4.288720	0.000000
C	-0.683518	-4.288720	0.000000
C	4.288720	0.683518	0.000000
C	4.288720	-0.683518	0.000000
C	-4.288720	0.683518	0.000000
C	-4.288720	-0.683518	0.000000
H	1.339908	5.148161	0.000000
H	-1.339908	5.148161	0.000000
H	1.339908	-5.148161	0.000000
H	-1.339908	-5.148161	0.000000
H	5.148161	1.339908	0.000000
H	-5.148161	1.339908	0.000000
H	5.148161	-1.339908	0.000000
H	-5.148161	-1.339908	0.000000
C	3.527163	3.527163	0.000000
C	-3.527163	3.527163	0.000000
C	3.527163	-3.527163	0.000000
C	-3.527163	-3.527163	0.000000
C	4.033423	4.033423	1.206994
C	4.033423	4.033423	-1.206994
C	4.033423	-4.033423	1.206994
C	4.033423	-4.033423	-1.206994
C	-4.033423	4.033423	1.206994
C	-4.033423	4.033423	-1.206994
C	-4.033423	-4.033423	1.206994
C	-4.033423	-4.033423	-1.206994
C	5.022173	5.022173	1.208138
C	5.022173	5.022173	-1.208138
C	5.022173	-5.022173	1.208138
C	5.022173	-5.022173	-1.208138
C	-5.022173	5.022173	1.208138
C	-5.022173	5.022173	-1.208138
C	-5.022173	-5.022173	1.208138
C	-5.022173	-5.022173	-1.208138
C	5.519434	5.519434	0.000000
C	-5.519434	5.519434	0.000000
C	5.519434	-5.519434	0.000000
C	-5.519434	-5.519434	0.000000

H	3.649375	3.649375	2.148130
H	3.649375	3.649375	-2.148130
H	3.649375	-3.649375	2.148130
H	3.649375	-3.649375	-2.148130
H	-3.649375	3.649375	2.148130
H	-3.649375	3.649375	-2.148130
H	-3.649375	-3.649375	2.148130
H	-3.649375	-3.649375	-2.148130
H	5.402801	5.402801	2.152122
H	5.402801	5.402801	-2.152122
H	5.402801	-5.402801	2.152122
H	5.402801	-5.402801	-2.152122
H	-5.402801	5.402801	2.152122
H	-5.402801	5.402801	-2.152122
H	-5.402801	-5.402801	2.152122
H	-5.402801	-5.402801	-2.152122
H	6.287704	6.287704	0.000000
H	-6.287704	6.287704	0.000000
H	6.287704	-6.287704	0.000000
H	-6.287704	-6.287704	0.000000

Table S20. BP86 Optimized Cartesian Coordinates of IS ^4E_g MnPc

Mn	0.000000	0.000000	0.000000
N	0.000000	1.951773	0.000000
N	1.951773	0.000000	0.000000
N	0.000000	-1.951773	0.000000
N	-1.951773	0.000000	0.000000
N	2.396997	2.396997	0.000000
N	2.396997	-2.396997	0.000000
N	-2.396997	2.396997	0.000000
N	-2.396997	-2.396997	0.000000
C	2.773696	1.127805	0.000000
C	2.773696	-1.127805	0.000000
C	1.127805	-2.773696	0.000000
C	-1.127805	-2.773696	0.000000
C	-2.773696	-1.127805	0.000000
C	-2.773696	1.127805	0.000000
C	-1.127805	2.773696	0.000000
C	1.127805	2.773696	0.000000
C	4.163375	0.705262	0.000000
C	4.163375	-0.705262	0.000000
C	0.705262	-4.163375	0.000000
C	-0.705262	-4.163375	0.000000
C	-4.163375	-0.705262	0.000000
C	-4.163375	0.705262	0.000000
C	-0.705262	4.163375	0.000000
C	0.705262	4.163375	0.000000
C	5.361079	1.427873	0.000000
C	5.361079	-1.427873	0.000000
C	1.427873	-5.361079	0.000000
C	-1.427873	-5.361079	0.000000
C	-5.361079	-1.427873	0.000000
C	-5.361079	1.427873	0.000000
C	-1.427873	5.361079	0.000000
C	1.427873	5.361079	0.000000
C	6.554490	0.705235	0.000000
C	6.554490	-0.705235	0.000000
C	0.705235	-6.554490	0.000000
C	-0.705235	-6.554490	0.000000
C	-6.554490	-0.705235	0.000000
C	-6.554490	0.705235	0.000000
C	-0.705235	6.554490	0.000000
C	0.705235	6.554490	0.000000
H	5.352581	2.518106	0.000000
H	5.352581	-2.518106	0.000000
H	2.518106	-5.352581	0.000000
H	-2.518106	-5.352581	0.000000
H	-5.352581	-2.518106	0.000000
H	-5.352581	2.518106	0.000000
H	-2.518106	5.352581	0.000000
H	2.518106	5.352581	0.000000
H	-1.237543	-7.506985	0.000000
H	1.237543	-7.506985	0.000000
H	7.506985	-1.237543	0.000000
H	7.506985	1.237543	0.000000
H	1.237543	7.506985	0.000000
H	-1.237543	7.506985	0.000000
H	-7.506985	1.237543	0.000000
H	-7.506985	-1.237543	0.000000

Table S21. BP86 Optimized Cartesian Coordinates of IS $^3A_{2g}$ FeTPP

Fe	0.000000	0.000000	0.000000
N	0.000000	1.990545	0.000000
N	0.000000	-1.990545	0.000000
N	1.990545	0.000000	0.000000
N	-1.990545	0.000000	0.000000
C	1.100991	2.837587	0.000000
C	-1.100991	2.837587	0.000000
C	1.100991	-2.837587	0.000000
C	-1.100991	-2.837587	0.000000
C	2.837587	1.100991	0.000000
C	2.837587	-1.100991	0.000000
C	-2.837587	1.100991	0.000000
C	-2.837587	-1.100991	0.000000
C	2.440626	2.440626	0.000000
C	2.440626	-2.440626	0.000000
C	-2.440626	2.440626	0.000000
C	-2.440626	-2.440626	0.000000
C	0.681888	4.214274	0.000000
C	0.681888	-4.214274	0.000000
C	-0.681888	4.214274	0.000000
C	-0.681888	-4.214274	0.000000
C	4.214274	0.681888	0.000000
C	4.214274	-0.681888	0.000000
C	-4.214274	0.681888	0.000000
C	-4.214274	-0.681888	0.000000
H	1.354259	5.066448	0.000000
H	-1.354259	5.066448	0.000000
H	1.354259	-5.066448	0.000000
H	-1.354259	-5.066448	0.000000
H	5.066448	1.354259	0.000000
H	-5.066448	1.354259	0.000000
H	5.066448	-1.354259	0.000000
H	-5.066448	-1.354259	0.000000
C	3.501404	3.501404	0.000000
C	-3.501404	3.501404	0.000000
C	3.501404	-3.501404	0.000000
C	-3.501404	-3.501404	0.000000
C	4.006838	4.006838	1.208336
C	4.006838	4.006838	-1.208336
C	4.006838	-4.006838	1.208336
C	4.006838	-4.006838	-1.208336
C	-4.006838	4.006838	1.208336
C	-4.006838	4.006838	-1.208336
C	-4.006838	-4.006838	1.208336
C	-4.006838	-4.006838	-1.208336
C	4.995330	4.995330	1.208319
C	4.995330	4.995330	-1.208319
C	4.995330	-4.995330	1.208319
C	4.995330	-4.995330	-1.208319
C	-4.995330	4.995330	1.208319
C	-4.995330	4.995330	-1.208319
C	-4.995330	-4.995330	1.208319
C	-4.995330	-4.995330	-1.208319
C	5.492300	5.492300	0.000000
C	-5.492300	5.492300	0.000000
C	5.492300	-5.492300	0.000000
C	-5.492300	-5.492300	0.000000

H	3.619366	3.619366	2.152184
H	3.619366	3.619366	-2.152184
H	3.619366	-3.619366	2.152184
H	3.619366	-3.619366	-2.152184
H	-3.619366	3.619366	2.152184
H	-3.619366	3.619366	-2.152184
H	-3.619366	-3.619366	2.152184
H	-3.619366	-3.619366	-2.152184
H	5.377848	5.377848	2.156159
H	5.377848	5.377848	-2.156159
H	5.377848	-5.377848	2.156159
H	5.377848	-5.377848	-2.156159
H	-5.377848	5.377848	2.156159
H	-5.377848	5.377848	-2.156159
H	-5.377848	-5.377848	2.156159
H	-5.377848	-5.377848	-2.156159
H	6.264055	6.264055	0.000000
H	-6.264055	6.264055	0.000000
H	6.264055	-6.264055	0.000000
H	-6.264055	-6.264055	0.000000

Table S22. BP86 Optimized Cartesian Coordinates of IS $^3A_{2g}$ FePc

Fe	0.000000	0.000000	0.000000
N	0.000000	1.938380	0.000000
N	1.938380	0.000000	0.000000
N	0.000000	-1.938380	0.000000
N	-1.938380	0.000000	0.000000
N	2.392934	2.392934	0.000000
N	2.392934	-2.392934	0.000000
N	-2.392934	2.392934	0.000000
N	-2.392934	-2.392934	0.000000
C	2.758900	1.118667	0.000000
C	2.758900	-1.118667	0.000000
C	1.118667	-2.758900	0.000000
C	-1.118667	-2.758900	0.000000
C	-2.758900	-1.118667	0.000000
C	-2.758900	1.118667	0.000000
C	-1.118667	2.758900	0.000000
C	1.118667	2.758900	0.000000
C	4.153278	0.704499	0.000000
C	4.153278	-0.704499	0.000000
C	0.704499	-4.153278	0.000000
C	-0.704499	-4.153278	0.000000
C	-4.153278	-0.704499	0.000000
C	-4.153278	0.704499	0.000000
C	-0.704499	4.153278	0.000000
C	0.704499	4.153278	0.000000
C	5.349405	1.428580	0.000000
C	5.349405	-1.428580	0.000000
C	1.428580	-5.349405	0.000000
C	-1.428580	-5.349405	0.000000
C	-5.349405	-1.428580	0.000000
C	-5.349405	1.428580	0.000000
C	-1.428580	5.349405	0.000000
C	1.428580	5.349405	0.000000
C	6.542603	0.705244	0.000000
C	6.542603	-0.705244	0.000000
C	0.705244	-6.542603	0.000000
C	-0.705244	-6.542603	0.000000
C	-6.542603	-0.705244	0.000000
C	-6.542603	0.705244	0.000000
C	-0.705244	6.542603	0.000000
C	0.705244	6.542603	0.000000
H	5.340426	2.518759	0.000000
H	5.340426	-2.518759	0.000000
H	2.518759	-5.340426	0.000000
H	-2.518759	-5.340426	0.000000
H	-5.340426	-2.518759	0.000000
H	-5.340426	2.518759	0.000000
H	-2.518759	5.340426	0.000000
H	2.518759	5.340426	0.000000
H	-1.236959	-7.495414	0.000000
H	1.236959	-7.495414	0.000000
H	7.495414	-1.236959	0.000000
H	7.495414	1.236959	0.000000
H	1.236959	7.495414	0.000000
H	-1.236959	7.495414	0.000000
H	-7.495414	1.236959	0.000000
H	-7.495414	-1.236959	0.000000

Table S23. BP86 Optimized Cartesian Coordinates of LS $^2A_{1g}$ CoTPP

Co	0.000000	0.000000	0.000000
N	0.000000	1.978291	0.000000
N	0.000000	-1.978291	0.000000
N	1.978291	0.000000	0.000000
N	-1.978291	0.000000	0.000000
C	1.099643	2.828005	0.000000
C	-1.099643	2.828005	0.000000
C	1.099643	-2.828005	0.000000
C	-1.099643	-2.828005	0.000000
C	2.828005	1.099643	0.000000
C	2.828005	-1.099643	0.000000
C	-2.828005	1.099643	0.000000
C	-2.828005	-1.099643	0.000000
C	2.436695	2.436695	0.000000
C	2.436695	-2.436695	0.000000
C	-2.436695	2.436695	0.000000
C	-2.436695	-2.436695	0.000000
C	0.680023	4.206140	0.000000
C	0.680023	-4.206140	0.000000
C	-0.680023	4.206140	0.000000
C	-0.680023	-4.206140	0.000000
C	4.206140	0.680023	0.000000
C	4.206140	-0.680023	0.000000
C	-4.206140	0.680023	0.000000
C	-4.206140	-0.680023	0.000000
H	1.354321	5.056663	0.000000
H	-1.354321	5.056663	0.000000
H	1.354321	-5.056663	0.000000
H	-1.354321	-5.056663	0.000000
H	5.056663	1.354321	0.000000
H	-5.056663	1.354321	0.000000
H	5.056663	-1.354321	0.000000
H	-5.056663	-1.354321	0.000000
C	3.497426	3.497426	0.000000
C	-3.497426	3.497426	0.000000
C	3.497426	-3.497426	0.000000
C	-3.497426	-3.497426	0.000000
C	4.002894	4.002894	1.208297
C	4.002894	4.002894	-1.208297
C	4.002894	-4.002894	1.208297
C	4.002894	-4.002894	-1.208297
C	-4.002894	4.002894	1.208297
C	-4.002894	4.002894	-1.208297
C	-4.002894	-4.002894	1.208297
C	-4.002894	-4.002894	-1.208297
C	4.991388	4.991388	1.208125
C	4.991388	4.991388	-1.208125
C	4.991388	-4.991388	1.208125
C	4.991388	-4.991388	-1.208125
C	-4.991388	4.991388	1.208125
C	-4.991388	4.991388	-1.208125
C	-4.991388	-4.991388	1.208125
C	-4.991388	-4.991388	-1.208125
C	5.488262	5.488262	0.000000
C	-5.488262	5.488262	0.000000
C	5.488262	-5.488262	0.000000
C	-5.488262	-5.488262	0.000000

H	3.615702	3.615702	2.152242
H	3.615702	3.615702	-2.152242
H	3.615702	-3.615702	2.152242
H	3.615702	-3.615702	-2.152242
H	-3.615702	3.615702	2.152242
H	-3.615702	3.615702	-2.152242
H	-3.615702	-3.615702	2.152242
H	-3.615702	-3.615702	-2.152242
H	5.374196	5.374196	2.155955
H	5.374196	5.374196	-2.155955
H	5.374196	-5.374196	2.155955
H	5.374196	-5.374196	-2.155955
H	-5.374196	5.374196	2.155955
H	-5.374196	5.374196	-2.155955
H	-5.374196	-5.374196	2.155955
H	-5.374196	-5.374196	-2.155955
H	6.260163	6.260163	0.000000
H	-6.260163	6.260163	0.000000
H	6.260163	-6.260163	0.000000
H	-6.260163	-6.260163	0.000000

Table S24. BP86 Optimized Cartesian Coordinates of LS $^{2}A_{1g}$ CoPc

Co	0.000000	0.000000	0.000000
N	0.000000	1.928001	0.000000
N	1.928001	0.000000	0.000000
N	0.000000	-1.928001	0.000000
N	-1.928001	0.000000	0.000000
N	2.389166	2.389166	0.000000
N	2.389166	-2.389166	0.000000
N	-2.389166	2.389166	0.000000
N	-2.389166	-2.389166	0.000000
C	2.751081	1.116929	0.000000
C	2.751081	-1.116929	0.000000
C	1.116929	-2.751081	0.000000
C	-1.116929	-2.751081	0.000000
C	-2.751081	-1.116929	0.000000
C	-2.751081	1.116929	0.000000
C	-1.116929	2.751081	0.000000
C	1.116929	2.751081	0.000000
C	4.146790	0.702899	0.000000
C	4.146790	-0.702899	0.000000
C	0.702899	-4.146790	0.000000
C	-0.702899	-4.146790	0.000000
C	-4.146790	-0.702899	0.000000
C	-4.146790	0.702899	0.000000
C	-0.702899	4.146790	0.000000
C	0.702899	4.146790	0.000000
C	5.341225	1.428156	0.000000
C	5.341225	-1.428156	0.000000
C	1.428156	-5.341225	0.000000
C	-1.428156	-5.341225	0.000000
C	-5.341225	-1.428156	0.000000
C	-5.341225	1.428156	0.000000
C	-1.428156	5.341225	0.000000
C	1.428156	5.341225	0.000000
C	6.535460	0.704733	0.000000
C	6.535460	-0.704733	0.000000
C	0.704733	-6.535460	0.000000
C	-0.704733	-6.535460	0.000000
C	-6.535460	-0.704733	0.000000
C	-6.535460	0.704733	0.000000
C	-0.704733	6.535460	0.000000
C	0.704733	6.535460	0.000000
H	5.331871	2.518402	0.000000
H	5.331871	-2.518402	0.000000
H	2.518402	-5.331871	0.000000
H	-2.518402	-5.331871	0.000000
H	-5.331871	-2.518402	0.000000
H	-5.331871	2.518402	0.000000
H	-2.518402	5.331871	0.000000
H	2.518402	5.331871	0.000000
H	-1.237096	-7.487980	0.000000
H	1.237096	-7.487980	0.000000
H	7.487980	-1.237096	0.000000
H	7.487980	1.237096	0.000000
H	1.237096	7.487980	0.000000
H	-1.237096	7.487980	0.000000
H	-7.487980	1.237096	0.000000
H	-7.487980	-1.237096	0.000000

Table S25. BP86 Optimized Cartesian Coordinates of LS $^3A_{1u}$ CoPc$^+$

Co	0.000000	0.000000	0.000000
N	0.000000	1.922634	0.000000
N	1.922634	0.000000	0.000000
N	0.000000	-1.922634	0.000000
N	-1.922634	0.000000	0.000000
N	2.388044	2.388044	0.000000
N	2.388044	-2.388044	0.000000
N	-2.388044	2.388044	0.000000
N	-2.388044	-2.388044	0.000000
C	2.748293	1.115139	0.000000
C	2.748293	-1.115139	0.000000
C	1.115139	-2.748293	0.000000
C	-1.115139	-2.748293	0.000000
C	-2.748293	-1.115139	0.000000
C	-2.748293	1.115139	0.000000
C	-1.115139	2.748293	0.000000
C	1.115139	2.748293	0.000000
C	4.147717	0.701701	0.000000
C	4.147717	-0.701701	0.000000
C	0.701701	-4.147717	0.000000
C	-0.701701	-4.147717	0.000000
C	-4.147717	-0.701701	0.000000
C	-4.147717	0.701701	0.000000
C	-0.701701	4.147717	0.000000
C	0.701701	4.147717	0.000000
C	5.335757	1.429279	0.000000
C	5.335757	-1.429279	0.000000
C	1.429279	-5.335757	0.000000
C	-1.429279	-5.335757	0.000000
C	-5.335757	-1.429279	0.000000
C	-5.335757	1.429279	0.000000
C	-1.429279	5.335757	0.000000
C	1.429279	5.335757	0.000000
C	6.534923	0.701634	0.000000
C	6.534923	-0.701634	0.000000
C	0.701634	-6.534923	0.000000
C	-0.701634	-6.534923	0.000000
C	-6.534923	-0.701634	0.000000
C	-6.534923	0.701634	0.000000
C	-0.701634	6.534923	0.000000
C	0.701634	6.534923	0.000000
H	5.329422	2.519109	0.000000
H	5.329422	-2.519109	0.000000
H	2.519109	-5.329422	0.000000
H	-2.519109	-5.329422	0.000000
H	-5.329422	-2.519109	0.000000
H	-5.329422	2.519109	0.000000
H	-2.519109	5.329422	0.000000
H	2.519109	5.329422	0.000000
H	-1.234819	-7.486202	0.000000
H	1.234819	-7.486202	0.000000
H	7.486202	-1.234819	0.000000
H	7.486202	1.234819	0.000000
H	1.234819	7.486202	0.000000
H	-1.234819	7.486202	0.000000
H	-7.486202	1.234819	0.000000
H	-7.486202	-1.234819	0.000000

Table S26. Theoretical and experimental[110-111] values (cm^{-1}) of the MPc and MPc^+ (M = Co, Ni, Cu, and Zn) IR-active $22e_u$ vibrational mode (MPc^+ carries a vacancy in the $2a_{1u}^{\downarrow}$ $^{pmc}\pi$ SO.

	MPc		MPc^+	
	Theory	Exp.	Theory	Exp.
Co	1517	1505	1513	1532
Ni	1524	1520	1520	1412
Cu	1491	1505	1491	-
Zn	1470	1480	1471	~1049

Table S27. BP86 Optimized Cartesian Coordinates of LS $^1A_{1g}$ NiTPP

Ni	0.000000	0.000000	0.000000
N	0.000000	1.967191	0.000000
N	0.000000	-1.967191	0.000000
N	1.967191	0.000000	0.000000
N	-1.967191	0.000000	0.000000
C	1.097534	2.817943	0.000000
C	-1.097534	2.817943	0.000000
C	1.097534	-2.817943	0.000000
C	-1.097534	-2.817943	0.000000
C	2.817943	1.097534	0.000000
C	2.817943	-1.097534	0.000000
C	-2.817943	1.097534	0.000000
C	-2.817943	-1.097534	0.000000
C	2.434283	2.434283	0.000000
C	2.434283	-2.434283	0.000000
C	-2.434283	2.434283	0.000000
C	-2.434283	-2.434283	0.000000
C	0.679814	4.195779	0.000000
C	0.679814	-4.195779	0.000000
C	-0.679814	4.195779	0.000000
C	-0.679814	-4.195779	0.000000
C	4.195779	0.679814	0.000000
C	4.195779	-0.679814	0.000000
C	-4.195779	0.679814	0.000000
C	-4.195779	-0.679814	0.000000
H	1.356819	5.043944	0.000000
H	-1.356819	5.043944	0.000000
H	1.356819	-5.043944	0.000000
H	-1.356819	-5.043944	0.000000
H	5.043944	1.356819	0.000000
H	-5.043944	1.356819	0.000000
H	5.043944	-1.356819	0.000000
H	-5.043944	-1.356819	0.000000
C	3.494583	3.494583	0.000000
C	-3.494583	3.494583	0.000000
C	3.494583	-3.494583	0.000000
C	-3.494583	-3.494583	0.000000
C	3.999689	3.999689	1.208453
C	3.999689	3.999689	-1.208453
C	3.999689	-3.999689	1.208453
C	3.999689	-3.999689	-1.208453
C	-3.999689	3.999689	1.208453
C	-3.999689	3.999689	-1.208453
C	-3.999689	-3.999689	1.208453
C	-3.999689	-3.999689	-1.208453
C	4.988155	4.988155	1.208308
C	4.988155	4.988155	-1.208308
C	4.988155	-4.988155	1.208308
C	4.988155	-4.988155	-1.208308
C	-4.988155	4.988155	1.208308
C	-4.988155	4.988155	-1.208308
C	-4.988155	-4.988155	1.208308
C	-4.988155	-4.988155	-1.208308
C	5.484941	5.484941	0.000000
C	-5.484941	5.484941	0.000000
C	5.484941	-5.484941	0.000000
C	-5.484941	-5.484941	0.000000

H	3.612149	3.612149	2.152167
H	3.612149	3.612149	-2.152167
H	3.612149	-3.612149	2.152167
H	3.612149	-3.612149	-2.152167
H	-3.612149	3.612149	2.152167
H	-3.612149	3.612149	-2.152167
H	-3.612149	-3.612149	2.152167
H	-3.612149	-3.612149	-2.152167
H	5.370890	5.370890	2.156028
H	5.370890	5.370890	-2.156028
H	5.370890	-5.370890	2.156028
H	5.370890	-5.370890	-2.156028
H	-5.370890	5.370890	2.156028
H	-5.370890	5.370890	-2.156028
H	-5.370890	-5.370890	2.156028
H	-5.370890	-5.370890	-2.156028
H	6.256757	6.256757	0.000000
H	-6.256757	6.256757	0.000000
H	6.256757	-6.256757	0.000000
H	-6.256757	-6.256757	0.000000

Table S28. BP86 Optimized Cartesian Coordinates of LS $^{1}A_{1g}$ NiPc

Ni	0.000000	0.000000	0.000000
N	0.000000	1.915197	0.000000
N	1.915197	0.000000	0.000000
N	0.000000	-1.915197	0.000000
N	-1.915197	0.000000	0.000000
N	2.386627	2.386627	0.000000
N	2.386627	-2.386627	0.000000
N	-2.386627	2.386627	0.000000
N	-2.386627	-2.386627	0.000000
C	2.740794	1.114288	0.000000
C	2.740794	-1.114288	0.000000
C	1.114288	-2.740794	0.000000
C	-1.114288	-2.740794	0.000000
C	-2.740794	-1.114288	0.000000
C	-2.740794	1.114288	0.000000
C	-1.114288	2.740794	0.000000
C	1.114288	2.740794	0.000000
C	4.136381	0.701987	0.000000
C	4.136381	-0.701987	0.000000
C	0.701987	-4.136381	0.000000
C	-0.701987	-4.136381	0.000000
C	-4.136381	-0.701987	0.000000
C	-4.136381	0.701987	0.000000
C	-0.701987	4.136381	0.000000
C	0.701987	4.136381	0.000000
C	5.330023	1.428707	0.000000
C	5.330023	-1.428707	0.000000
C	1.428707	-5.330023	0.000000
C	-1.428707	-5.330023	0.000000
C	-5.330023	-1.428707	0.000000
C	-5.330023	1.428707	0.000000
C	-1.428707	5.330023	0.000000
C	1.428707	5.330023	0.000000
C	6.523838	0.704890	0.000000
C	6.523838	-0.704890	0.000000
C	0.704890	-6.523838	0.000000
C	-0.704890	-6.523838	0.000000
C	-6.523838	-0.704890	0.000000
C	-6.523838	0.704890	0.000000
C	-0.704890	6.523838	0.000000
C	0.704890	6.523838	0.000000
H	5.320468	2.518887	0.000000
H	5.320468	-2.518887	0.000000
H	2.518887	-5.320468	0.000000
H	-2.518887	-5.320468	0.000000
H	-5.320468	-2.518887	0.000000
H	-5.320468	2.518887	0.000000
H	-2.518887	5.320468	0.000000
H	2.518887	5.320468	0.000000
H	-1.237122	-7.476417	0.000000
H	1.237122	-7.476417	0.000000
H	7.476417	-1.237122	0.000000
H	7.476417	1.237122	0.000000
H	1.237122	7.476417	0.000000
H	-1.237122	7.476417	0.000000
H	-7.476417	1.237122	0.000000
H	-7.476417	-1.237122	0.000000

Table S29. BP86 Optimized Cartesian Coordinates of LS $^{2}A_{1u}$ NiPc^{+}

Ni	0.000000	0.000000	0.000000
N	0.000000	1.909054	0.000000
N	1.909054	0.000000	0.000000
N	0.000000	-1.909054	0.000000
N	-1.909054	0.000000	0.000000
N	2.385471	2.385471	0.000000
N	2.385471	-2.385471	0.000000
N	-2.385471	2.385471	0.000000
N	-2.385471	-2.385471	0.000000
C	2.737860	1.112412	0.000000
C	2.737860	-1.112412	0.000000
C	1.112412	-2.737860	0.000000
C	-1.112412	-2.737860	0.000000
C	-2.737860	-1.112412	0.000000
C	-2.737860	1.112412	0.000000
C	-1.112412	2.737860	0.000000
C	1.112412	2.737860	0.000000
C	4.136759	0.700799	0.000000
C	4.136759	-0.700799	0.000000
C	0.700799	-4.136759	0.000000
C	-0.700799	-4.136759	0.000000
C	-4.136759	-0.700799	0.000000
C	-4.136759	0.700799	0.000000
C	-0.700799	4.136759	0.000000
C	0.700799	4.136759	0.000000
C	5.324212	1.429748	0.000000
C	5.324212	-1.429748	0.000000
C	1.429748	-5.324212	0.000000
C	-1.429748	-5.324212	0.000000
C	-5.324212	-1.429748	0.000000
C	-5.324212	1.429748	0.000000
C	-1.429748	5.324212	0.000000
C	1.429748	5.324212	0.000000
C	6.522780	0.701846	0.000000
C	6.522780	-0.701846	0.000000
C	0.701846	-6.522780	0.000000
C	-0.701846	-6.522780	0.000000
C	-6.522780	-0.701846	0.000000
C	-6.522780	0.701846	0.000000
C	-0.701846	6.522780	0.000000
C	0.701846	6.522780	0.000000
H	5.317929	2.519497	0.000000
H	5.317929	-2.519497	0.000000
H	2.519497	-5.317929	0.000000
H	-2.519497	-5.317929	0.000000
H	-5.317929	-2.519497	0.000000
H	-5.317929	2.519497	0.000000
H	-2.519497	5.317929	0.000000
H	2.519497	5.317929	0.000000
H	-1.234865	-7.474150	0.000000
H	1.234865	-7.474150	0.000000
H	7.474150	-1.234865	0.000000
H	7.474150	1.234865	0.000000
H	1.234865	7.474150	0.000000
H	-1.234865	7.474150	0.000000
H	-7.474150	1.234865	0.000000
H	-7.474150	-1.234865	0.000000

Table S30. BP86 Optimized Cartesian Coordinates of $^2B_{1g}$ CuTPP from ref. 32

Cu	0.000000	0.000000	0.000000
N	0.000000	2.018890	0.000000
N	0.000000	-2.018890	0.000000
N	-2.018890	0.000000	0.000000
N	2.018890	0.000000	0.000000
C	1.102640	2.849765	0.000000
C	-1.102640	2.849765	0.000000
C	1.102640	-2.849765	0.000000
C	-1.102640	-2.849765	0.000000
C	2.849765	1.102640	0.000000
C	2.849765	-1.102640	0.000000
C	-2.849765	1.102640	0.000000
C	-2.849765	-1.102640	0.000000
C	0.681271	4.231323	0.000000
C	-0.681271	4.231323	0.000000
C	0.681271	-4.231323	0.000000
C	-0.681271	-4.231323	0.000000
C	4.231323	0.681271	0.000000
C	4.231323	-0.681271	0.000000
C	-4.231323	0.681271	0.000000
C	-4.231323	-0.681271	0.000000
C	2.441741	2.441741	0.000000
C	-2.441741	2.441741	0.000000
C	2.441741	-2.441741	0.000000
C	-2.441741	-2.441741	0.000000
H	1.351245	5.084940	0.000000
H	-1.351245	5.084940	0.000000
H	1.351245	-5.084940	0.000000
H	-1.351245	-5.084940	0.000000
H	5.084940	1.351245	0.000000
H	5.084940	-1.351245	0.000000
H	-5.084940	1.351245	0.000000
H	-5.084940	-1.351245	0.000000
C	3.503113	3.503113	0.000000
C	-3.503113	3.503113	0.000000
C	3.503113	-3.503113	0.000000
C	-3.503113	-3.503113	0.000000
C	4.008566	4.008566	1.207580
C	-4.008566	4.008566	1.207580
C	4.008566	-4.008566	1.207580
C	-4.008566	-4.008566	1.207580
C	4.008566	4.008566	-1.207580
C	-4.008566	4.008566	-1.207580
C	4.008566	-4.008566	-1.207580
C	-4.008566	-4.008566	-1.207580
C	4.997364	4.997364	1.208380
C	-4.997364	4.997364	1.208380
C	4.997364	-4.997364	1.208380
C	-4.997364	-4.997364	1.208380
C	4.997364	4.997364	-1.208380
C	-4.997364	4.997364	-1.208380
C	4.997364	-4.997364	-1.208380
C	-4.997364	-4.997364	-1.208380
C	5.494535	5.494535	0.000000
C	-5.494535	5.494535	0.000000
C	5.494535	-5.494535	0.000000
C	-5.494535	-5.494535	0.000000
H	3.620145	3.620145	2.150933
H	-3.620145	3.620145	2.150933
H	3.620145	-3.620145	2.150933

H	-3.620145	-3.620145	2.150933
H	3.620145	3.620145	-2.150933
H	-3.620145	3.620145	-2.150933
H	3.620145	-3.620145	-2.150933
H	-3.620145	-3.620145	-2.150933
H	5.379179	5.379179	2.156140
H	-5.379179	5.379179	2.156140
H	5.379179	-5.379179	2.156140
H	-5.379179	-5.379179	2.156140
H	5.379179	5.379179	-2.156140
H	-5.379179	5.379179	-2.156140
H	5.379179	-5.379179	-2.156140
H	-5.379179	-5.379179	-2.156140
H	6.266138	6.266138	0.000000
H	-6.266138	6.266138	0.000000
H	6.266138	-6.266138	0.000000
H	-6.266138	-6.266138	0.000000

Table S31. BP86 Optimized Cartesian Coordinates of $^2B_{1g}$ CuPc from ref. 24

Cu	0.000000	0.000000	0.000000
N	0.000000	1.968115	0.000000
N	1.968115	0.000000	0.000000
N	0.000000	-1.968115	0.000000
N	-1.968115	0.000000	0.000000
N	2.395396	2.395396	0.000000
N	2.395396	-2.395396	0.000000
N	-2.395396	2.395396	0.000000
N	-2.395396	-2.395396	0.000000
C	2.772347	1.121142	0.000000
C	2.772347	-1.121142	0.000000
C	1.121142	-2.772347	0.000000
C	-1.121142	-2.772347	0.000000
C	-2.772347	-1.121142	0.000000
C	-2.772347	1.121142	0.000000
C	-1.121142	2.772347	0.000000
C	1.121142	2.772347	0.000000
C	4.172097	0.705018	0.000000
C	4.172097	-0.705018	0.000000
C	0.705018	-4.172097	0.000000
C	-0.705018	-4.172097	0.000000
C	-4.172097	-0.705018	0.000000
C	-4.172097	0.705018	0.000000
C	-0.705018	4.172097	0.000000
C	0.705018	4.172097	0.000000
C	5.367736	1.427764	0.000000
C	5.367736	-1.427764	0.000000
C	1.427764	-5.367736	0.000000
C	-1.427764	-5.367736	0.000000
C	-5.367736	-1.427764	0.000000
C	-5.367736	1.427764	0.000000
C	-1.427764	5.367736	0.000000
C	1.427764	5.367736	0.000000
C	6.562369	0.704564	0.000000
C	6.562369	-0.704564	0.000000
C	0.704564	-6.562369	0.000000
C	-0.704564	-6.562369	0.000000
C	-6.562369	-0.704564	0.000000
C	-6.562369	0.704564	0.000000
C	-0.704564	6.562369	0.000000
C	0.704564	6.562369	0.000000
H	5.359430	2.517992	0.000000
H	5.359430	-2.517992	0.000000
H	2.517992	-5.359430	0.000000
H	-2.517992	-5.359430	0.000000
H	-5.359430	-2.517992	0.000000
H	-5.359430	2.517992	0.000000
H	-2.517992	5.359430	0.000000
H	2.517992	5.359430	0.000000
H	-1.236974	-7.514740	0.000000
H	1.236974	-7.514740	0.000000
H	7.514740	-1.236974	0.000000
H	7.514740	1.236974	0.000000
H	1.236974	7.514740	0.000000
H	-1.236974	7.514740	0.000000
H	-7.514740	1.236974	0.000000
H	-7.514740	-1.236974	0.000000

Table S32. BP86 Optimized Cartesian Coordinates of $^3B_{1u}$ CuPc$^+$

Cu	0.000000	0.000000	0.000000
N	0.000000	1.962521	0.000000
N	1.962521	0.000000	0.000000
N	0.000000	-1.962521	0.000000
N	-1.962521	0.000000	0.000000
N	2.394036	2.394036	0.000000
N	2.394036	-2.394036	0.000000
N	-2.394036	2.394036	0.000000
N	-2.394036	-2.394036	0.000000
C	2.769622	1.119699	0.000000
C	2.769622	-1.119699	0.000000
C	1.119699	-2.769622	0.000000
C	-1.119699	-2.769622	0.000000
C	-2.769622	-1.119699	0.000000
C	-2.769622	1.119699	0.000000
C	-1.119699	2.769622	0.000000
C	1.119699	2.769622	0.000000
C	4.172900	0.703759	0.000000
C	4.172900	-0.703759	0.000000
C	0.703759	-4.172900	0.000000
C	-0.703759	-4.172900	0.000000
C	-4.172900	-0.703759	0.000000
C	-4.172900	0.703759	0.000000
C	-0.703759	4.172900	0.000000
C	0.703759	4.172900	0.000000
C	5.361981	1.428890	0.000000
C	5.361981	-1.428890	0.000000
C	1.428890	-5.361981	0.000000
C	-1.428890	-5.361981	0.000000
C	-5.361981	-1.428890	0.000000
C	-5.361981	1.428890	0.000000
C	-1.428890	5.361981	0.000000
C	1.428890	5.361981	0.000000
C	6.561454	0.701513	0.000000
C	6.561454	-0.701513	0.000000
C	0.701513	-6.561454	0.000000
C	-0.701513	-6.561454	0.000000
C	-6.561454	-0.701513	0.000000
C	-6.561454	0.701513	0.000000
C	-0.701513	6.561454	0.000000
C	0.701513	6.561454	0.000000
H	5.355031	2.518908	0.000000
H	5.355031	-2.518908	0.000000
H	2.518908	-5.355031	0.000000
H	-2.518908	-5.355031	0.000000
H	-5.355031	-2.518908	0.000000
H	-5.355031	2.518908	0.000000
H	-2.518908	5.355031	0.000000
H	2.518908	5.355031	0.000000
H	-1.233939	-7.513138	0.000000
H	1.233939	-7.513138	0.000000
H	7.513138	-1.233939	0.000000
H	7.513138	1.233939	0.000000
H	1.233939	7.513138	0.000000
H	-1.233939	7.513138	0.000000
H	-7.513138	1.233939	0.000000
H	-7.513138	-1.233939	0.000000

Table S33. BP86 Optimized Cartesian Coordinates of $^1A_{1g}$ ZnTPP

Zn	0.000000	0.000000	0.000000
N	0.000000	2.053458	0.000000
N	0.000000	-2.053458	0.000000
N	2.053458	0.000000	0.000000
N	-2.053458	0.000000	0.000000
C	1.108132	2.877817	0.000000
C	-1.108132	2.877817	0.000000
C	1.108132	-2.877817	0.000000
C	-1.108132	-2.877817	0.000000
C	2.877817	1.108132	0.000000
C	2.877817	-1.108132	0.000000
C	-2.877817	1.108132	0.000000
C	-2.877817	-1.108132	0.000000
C	2.450672	2.450672	0.000000
C	2.450672	-2.450672	0.000000
C	-2.450672	2.450672	0.000000
C	-2.450672	-2.450672	0.000000
C	0.683118	4.259910	0.000000
C	0.683118	-4.259910	0.000000
C	-0.683118	4.259910	0.000000
C	-0.683118	-4.259910	0.000000
C	4.259910	0.683118	0.000000
C	4.259910	-0.683118	0.000000
C	-4.259910	0.683118	0.000000
C	-4.259910	-0.683118	0.000000
H	1.349323	5.117260	0.000000
H	-1.349323	5.117260	0.000000
H	1.349323	-5.117260	0.000000
H	-1.349323	-5.117260	0.000000
H	5.117260	1.349323	0.000000
H	-5.117260	1.349323	0.000000
H	5.117260	-1.349323	0.000000
H	-5.117260	-1.349323	0.000000
C	3.512605	3.512605	0.000000
C	-3.512605	3.512605	0.000000
C	3.512605	-3.512605	0.000000
C	-3.512605	-3.512605	0.000000
C	4.018507	4.018507	1.208034
C	4.018507	4.018507	-1.208034
C	4.018507	-4.018507	1.208034
C	4.018507	-4.018507	-1.208034
C	-4.018507	4.018507	1.208034
C	-4.018507	4.018507	-1.208034
C	-4.018507	-4.018507	1.208034
C	-4.018507	-4.018507	-1.208034
C	5.006984	5.006984	1.208106
C	5.006984	5.006984	-1.208106
C	5.006984	-5.006984	1.208106
C	5.006984	-5.006984	-1.208106
C	-5.006984	5.006984	1.208106
C	-5.006984	5.006984	-1.208106
C	-5.006984	-5.006984	1.208106
C	-5.006984	-5.006984	-1.208106
C	5.503934	5.503934	0.000000
C	-5.503934	5.503934	0.000000
C	5.503934	-5.503934	0.000000
C	-5.503934	-5.503934	0.000000

H	3.631325	3.631325	2.152080
H	3.631325	3.631325	-2.152080
H	3.631325	-3.631325	2.152080
H	3.631325	-3.631325	-2.152080
H	-3.631325	3.631325	2.152080
H	-3.631325	3.631325	-2.152080
H	-3.631325	-3.631325	2.152080
H	-3.631325	-3.631325	-2.152080
H	5.389581	5.389581	2.155976
H	5.389581	5.389581	-2.155976
H	5.389581	-5.389581	2.155976
H	5.389581	-5.389581	-2.155976
H	-5.389581	5.389581	2.155976
H	-5.389581	5.389581	-2.155976
H	-5.389581	-5.389581	2.155976
H	-5.389581	-5.389581	-2.155976
H	6.275750	6.275750	0.000000
H	-6.275750	6.275750	0.000000
H	6.275750	-6.275750	0.000000
H	-6.275750	-6.275750	0.000000

Table S34. BP86 Optimized Cartesian Coordinates of $^1A_{1g}$ ZnPc

Zn	0.000000	0.000000	0.000000
N	0.000000	2.004022	0.000000
N	2.004022	0.000000	0.000000
N	0.000000	-2.004022	0.000000
N	-2.004022	0.000000	0.000000
N	2.402191	2.402191	0.000000
N	2.402191	-2.402191	0.000000
N	-2.402191	2.402191	0.000000
N	-2.402191	-2.402191	0.000000
C	2.797886	1.127434	0.000000
C	2.797886	-1.127434	0.000000
C	1.127434	-2.797886	0.000000
C	-1.127434	-2.797886	0.000000
C	-2.797886	-1.127434	0.000000
C	-2.797886	1.127434	0.000000
C	-1.127434	2.797886	0.000000
C	1.127434	2.797886	0.000000
C	4.199224	0.707544	0.000000
C	4.199224	-0.707544	0.000000
C	0.707544	-4.199224	0.000000
C	-0.707544	-4.199224	0.000000
C	-4.199224	-0.707544	0.000000
C	-4.199224	0.707544	0.000000
C	-0.707544	4.199224	0.000000
C	0.707544	4.199224	0.000000
C	5.396676	1.426979	0.000000
C	5.396676	-1.426979	0.000000
C	1.426979	-5.396676	0.000000
C	-1.426979	-5.396676	0.000000
C	-5.396676	-1.426979	0.000000
C	-5.396676	1.426979	0.000000
C	-1.426979	5.396676	0.000000
C	1.426979	5.396676	0.000000
C	6.591796	0.704229	0.000000
C	6.591796	-0.704229	0.000000
C	0.704229	-6.591796	0.000000
C	-0.704229	-6.591796	0.000000
C	-6.591796	-0.704229	0.000000
C	-6.591796	0.704229	0.000000
C	-0.704229	6.591796	0.000000
C	0.704229	6.591796	0.000000
H	5.388914	2.517373	0.000000
H	5.388914	-2.517373	0.000000
H	2.517373	-5.388914	0.000000
H	-2.517373	-5.388914	0.000000
H	-5.388914	-2.517373	0.000000
H	-5.388914	2.517373	0.000000
H	-2.517373	5.388914	0.000000
H	2.517373	5.388914	0.000000
H	-1.236630	-7.544321	0.000000
H	1.236630	-7.544321	0.000000
H	7.544321	-1.236630	0.000000
H	7.544321	1.236630	0.000000
H	1.236630	7.544321	0.000000
H	-1.236630	7.544321	0.000000
H	-7.544321	1.236630	0.000000
H	-7.544321	-1.236630	0.000000

Table S35. BP86 Optimized Cartesian Coordinates of $^{2}A_{1u}$ ZnPc^{+}

Zn	0.000000	0.000000	0.000000
N	0.000000	1.998289	0.000000
N	1.998289	0.000000	0.000000
N	0.000000	-1.998289	0.000000
N	-1.998289	0.000000	0.000000
N	2.401013	2.401013	0.000000
N	2.401013	-2.401013	0.000000
N	-2.401013	2.401013	0.000000
N	-2.401013	-2.401013	0.000000
C	2.795131	1.125759	0.000000
C	2.795131	-1.125759	0.000000
C	1.125759	-2.795131	0.000000
C	-1.125759	-2.795131	0.000000
C	-2.795131	-1.125759	0.000000
C	-2.795131	1.125759	0.000000
C	-1.125759	2.795131	0.000000
C	1.125759	2.795131	0.000000
C	4.199945	0.706332	0.000000
C	4.199945	-0.706332	0.000000
C	0.706332	-4.199945	0.000000
C	-0.706332	-4.199945	0.000000
C	-4.199945	-0.706332	0.000000
C	-4.199945	0.706332	0.000000
C	-0.706332	4.199945	0.000000
C	0.706332	4.199945	0.000000
C	5.390806	1.428177	0.000000
C	5.390806	-1.428177	0.000000
C	1.428177	-5.390806	0.000000
C	-1.428177	-5.390806	0.000000
C	-5.390806	-1.428177	0.000000
C	-5.390806	1.428177	0.000000
C	-1.428177	5.390806	0.000000
C	1.428177	5.390806	0.000000
C	6.591054	0.701081	0.000000
C	6.591054	-0.701081	0.000000
C	0.701081	-6.591054	0.000000
C	-0.701081	-6.591054	0.000000
C	-6.591054	-0.701081	0.000000
C	-6.591054	0.701081	0.000000
C	-0.701081	6.591054	0.000000
C	0.701081	6.591054	0.000000
H	5.385762	2.518187	0.000000
H	5.385762	-2.518187	0.000000
H	2.518187	-5.385762	0.000000
H	-2.518187	-5.385762	0.000000
H	-5.385762	-2.518187	0.000000
H	-5.385762	2.518187	0.000000
H	-2.518187	5.385762	0.000000
H	2.518187	5.385762	0.000000
H	-1.234254	-7.542354	0.000000
H	1.234254	-7.542354	0.000000
H	7.542354	-1.234254	0.000000
H	7.542354	1.234254	0.000000
H	1.234254	7.542354	0.000000
H	-1.234254	7.542354	0.000000
H	-7.542354	1.234254	0.000000
H	-7.542354	-1.234254	0.000000