Electronic Structure of Metallophthalocyanines, MPc (M = Fe, Co, Ni, Cu, Zn, Mg) and Fluorinated MPc

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Electronic Structure of Metallophthalocyanines, MPc (M = Fe, Co, Ni, Cu, Zn, Mg) and Fluorinated MPc†

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We compute the electronic structure and optical excitation energies of metal-free and transition-metal phthalocyanines (H2Pc and MPc for M = Fe, Co, Ni, Cu, Zn, Mg) using density functional theory with optimally-tuned range-separated hybrid functionals (OT-RSH). We show that the OT-RSH approach provides photoemission spectra in quantitative agreement with experiments as well as optical band gaps within 10% of their experimental values, capturing the interplay of localized d-states and delocalized $\pi - \pi^*$ states for these organometallic compounds. We examine the tunability of MPcs and H2Pc through fluorination, resulting in quasi-rigid shifts of the molecular orbital energies by up to $\simeq 0.7$ eV. Our comprehensive dataset provides a new computational benchmark for gas-phase phthalocyanines, significantly improving upon other density-functional-theory-based approaches.

Phthalocyanines are planar metal-organic complexes that incorporate either two hydrogen atoms (metal-free phthalocyanine H2Pc), or a transition metal atom (metal phthalocyanines MPcs) at the center of their ring structure, as shown in Fig. 1. Their high synthetic tunability, chemical and thermal stability, and large optical cross-sections make them attractive for a wide variety of applications, including textiles, photovoltaics, sensing, thin-film transistors, and spintronics1–4. Many of these applications involve integrating MPcs into mixed-dimensional heterojunctions5–14, with emerging properties depending on the molecular orbital energies at the interface. Despite resulting in minor changes in optical bandgap, substituting the transition metal atom at the center of the molecule results in distinctive photo-responses of MPcs6–8,15,16, suggesting that both localized d and delocalized $\pi - \pi^*$ states contribute at low energy.

The nature and properties of these low-energy states, as well as their role in the photophysics of MPcs have been extensively studied, for example using direct and inverse photoemission spectroscopy17–20, which provide reliable estimates of the molecular orbital energies. Density functional

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† Electronic Supplementary Information (ESI) available: molecular geometries, optimally-tuning of OT-RSH parameters, electronic structure and d-orbitals of MPcs from B3LYP. See DOI: 00.0000/00000000.
theory (DFT) has been the dominant computational approach for understanding the degree of local-
ization of the molecular orbitals of MPcs, yet has shown high variability depending on the choice
of the exchange and correlation functionals \cite{72126}, with different levels of approximation leading to
distinct energy ordering of the molecular levels. Moreover, standard DFT functionals, such as the
local density approximation (LDA), generalized gradient approximations (GGAs), and hybrid func-
tionals like B3LYP, PBEh and HSE, often lead to poor agreement with photoemission experiments. In
contrast, quantitative agreement was obtained for H\textsubscript{2}Pc\textsuperscript{27,28}, CuPc\textsuperscript{29,30}, CoPc\textsuperscript{31}, and ZnPc\textsuperscript{32} using
approaches that incorporate the correct asymptotic behavior of the exchange-correlation potential,
such as range-separated hybrid functionals \cite{33} and the GW method \cite{34}. While promising, and to the
best of our knowledge, these approaches have yet to be applied to, and benchmarked against, a broad
range of metal phthalocyanines.

![Molecular Geometry](image)

**Fig. 1** The molecular geometry of H\textsubscript{2}Pc, MPc, and MPc\textsubscript{16} where M is metal atoms at the center.

In this work, we compute the electronic structure of gas-phase phthalocyanines for an extensive set
of molecules, including H\textsubscript{2}Pc, MgPc, as well as 3\textit{d} transition metals Fe, Co, Ni, Cu, Zn from 3\textit{d}\textsuperscript{6} to 3\textit{d}\textsuperscript{10}
and their fluorinated counterparts H\textsubscript{2}Pc\textsubscript{16}, CoPc\textsubscript{16} and ZnPc\textsubscript{16}, by using the OT-RSH method. We
show that the OT-RSH approach provides quantitative agreement with experiment for both molecular
orbital energies and optical bandgaps for all of these compounds, with the level ordering qualitatively
differing from conventional DFT approaches \cite{24}. We show that fluorination in these compounds can be
used to induce significant energy shifts of the molecular levels, due to the significant change in the
molecular quadrupole upon fluorination. Our results underline the potential of the OT-RSH approach
for understanding the properties of known organo-metallic compounds and predicting the properties
of unknown ones.
The OT-RSH approach is a generalized Kohn-Sham scheme\textsuperscript{35}, in which the non-local exchange potential explicitly depends on the Kohn-Sham orbitals through the Fock operator. In the RSH scheme\textsuperscript{36,37}, the Coulomb operator is divided into short-range (SR) and long-range (LR) components by a range-separation parameter $\gamma$. Noteworthily, by construction, the LR component in the OT-RSH formalism has the asymptotically correct $(\alpha + \beta)/r$ behavior (with $\alpha + \beta = 1$ in the gas-phase)\textsuperscript{33}, with the remaining choices in the construction of the functional being the fraction of Fock exchange applied in the SR component ($\alpha$), and the range separation parameter $\gamma$. While $\alpha$ can generally be chosen to match values of other global hybrid functionals, the values of $\gamma$ tend to be highly system-dependent. $\gamma$ defines the length-scale where the short-range is transitioned into long-range interactions, and is included in both the short-range and long-range exchange expressions\textsuperscript{33}, therefore a key parameter in determining the quantitative accuracy of the final results. A parameter-free approach for finding the system-specific $\gamma$ value has been proposed by Stein, Kronik and Baer\textsuperscript{27,30,38–40}, with $\gamma$ chosen to maximize the compliance with the Koopman’s theorem. Namely, the optimal $\gamma^{\text{opt}}$ is obtained by minimizing:

$$J^2(\gamma) = J_{\text{IE}}^2 + J_{\text{EA}}^2 = (\varepsilon_{\text{HOMO}}^\gamma + \text{IE}^\gamma)^2 + (\varepsilon_{\text{HOMO}}^{\text{anion}} + \text{EA}^\gamma)^2,$$

where $\text{IE}$ and $\text{EA}$ are the ionization energy and electron affinity of the molecule, and $\varepsilon_{\text{HOMO}}^\gamma$ and $\varepsilon_{\text{HOMO}}^{\text{anion}}$ are the highest occupied molecular orbital (HOMO) of neutral and negatively charged system. Minimizing only $J_{\text{IE}}^2$ is also commonly used as the optimal $\gamma$ of $J_{\text{IE}}^2$ and $J^2$ have been empirically found to be in close agreement\textsuperscript{27,31}.

We perform DFT and time-dependent DFT (TDDFT) calculations using the QChem\textsuperscript{41} and NWChem\textsuperscript{42} packages. Molecular geometry and orbitals are generated by IQmol\textsuperscript{43} molecular viewer. cc-PVTZ basis set\textsuperscript{44–46} are used for all atoms in H$_2$Pc, MPcs ($M = \text{Co, Ni, Cu, Zn, Mg}$) and CoPcF$_{16}$, ZnPcF$_{16}$. For FePc, 6-31G(d,p) are used for C, H, N and cc-PVTZ are used for Fe to avoid symmetry breaking\textsuperscript{23}. Effective core pseudopotentials\textsuperscript{45,46} are used for metals in FePc, MgPc, CoPcF$_{16}$, ZnPcF$_{16}$ performed using NWChem while all the others are calculated using QChem. Among them, NiPc, ZnPc, MgPc and H$_2$Pc are closed-shell systems with spin $s=0$, while CoPc and CuPc are open-shell systems with spin $s=1/2$ and FePc has $s=3/2$. 
Table 1  Computed structural parameters for MPc molecules

| MPc          | $R_{M-N}$ (Å) | $R_{N_1-C}$ (Å) | $\theta_{N_1-C-N_2}$ |
|--------------|------------|----------------|----------------------|
|              | this work | exp$^a$         | this work | exp$^a$         | this work | exp$^a$         |
| FePc         | 1.943     | 1.927          | 1.397     | 1.320          | 127.3     | 127.5          |
| CoPc         | 1.936     | 1.908~1.915    | 1.373     | 1.382          | 127.5     | 128.0          |
| CoPcF$_{16}$ | 1.938     | -              | 1.372     | -              | 127.69    |                |
| NiPc         | 1.920     | 1.913          | 1.373     | 1.385          | 127.7     | 128.4          |
| CuPc         | 1.966     | 1.949          | 1.369     | 1.381          | 127.65    | 128.2          |
| ZnPc         | 1.999     | 1.980,1.954    | 1.367     | 1.374,1.369    | 127.43    | 125.7,125.4    |
| ZnPcF$_{16}$ | 2.000     | -              | 1.366     | -              | 127.65    | -              |
| MgPc         | 2.000     | 2.058,1.990    | 1.368     | 1.386,1.366    | 127.35    | 125.9,127.7    |
| H$_2$Pc      | -         | -              | 1.373     | 1.370          | 128.01    | 128.7          |

$^a$ FePc from XRD$^{47}$; CoPc from neutron-diffraction$^{48}$; CuPc from gas-phase electron diffraction (GED)$^{49}$; NiPc from GED$^{50}$; ZnPc from XRD$^{51}$, GED$^{52}$; MgPc from XRD$^{53}$, GED$^{52}$; H$_2$Pc from XRD and neutron-diffraction$^{54}$

The molecular geometries are all optimized using the B3LYP functional$^{55}$, providing structural parameters in agreement with experiments, as shown in Table [1]. The geometry of MPc is shown in Fig. [1]. The bond length between metal and nearest N atom ($R_{M-N}$) is smallest for NiPc while largest for MgPc and ZnPc. Fluorinated CoPc and ZnPc have slightly larger $R_{M-N}$ than non-fluorinated ones.

The range-separation parameter $\gamma$ is determined by minimizing $J^2$ according to Eq [1]. $J^2$ values as a function of $\alpha, \gamma$ are shown in Fig. [S1] and Fig. [S2]. The $\gamma^{opt}$ values for $\alpha$ of 0.1 and 0.2 are summarized in Table [S1] for all Pcs studied in this work. Results discussed in the following are for values of $\alpha$=0.1, following a previous study with OT-RSH for CoPc$^{51}$, while results for $\alpha = 0.2$ are included in the Supporting Information (SI) for comparison. We find that the HOMO/LUMO levels are weakly dependent on the choice of $\alpha$ as shown in Table [S1] with a difference in energy smaller than 0.05 eV for both HOMO and LUMO.

Results on the electronic structure obtained from OT-RSH for all MPs in this work are summarized in Fig. [2] with results from $\alpha$ of 0.2, B3LYP and CAMB3LYP$^{56}$ included in Figs. [S3] - [S5] for comparison. In agreement with experiment, we find that bandgap, ionization energy, and electronic affinity are weakly dependent on the nature of the central atom, varying by less than 0.1 eV for 6 of the 7 molecules, with the exception of FePc for which the higher spin configuration leads to a $\sim 0.2$ eV reduction of the HOMO-LUMO gap. HOMO energies from OT-RSH are within 0.3 eV of experimental ionization potentials$^{17}$, and agree well with GW calculations$^{29}$ for CuPc with HOMO of 6.27 eV. Those results are much improved over B3LYP (Fig. [S4]), HSE$^8$ and CAMB3LYP (Fig. [S5]), as shown in Table [2].
For all MPcs studied in this work, the HOMO is of $a_{1u}$ symmetry with no $d$-character, and LUMO is of $e_g$ symmetry and with $(d_{xz}, d_{yz})$-character for the transition metals. This result is in agreement with HSE\cite{8} and B3LYP results from previous study\cite{21,22} and the current work (see Fig. S4), while disagreeing with a previous study reporting contribution of $e_g(d_{xz,yz})$ to FePc HOMO from Vosko–Wilk–Nusair (VWN)\cite{24}, $b_{1g}(d_{x^2−y^2})$ to NiPc, CuPc LUMO from VWN\cite{24} and PBE\cite{21,22}, $a_{1g}(d_{z^2})$ to FePc HOMO and $b_{1g}(d_{x^2−y^2})$ to CuPc LUMO from DFT+U\cite{7}. We find that the mixing of the $d$-orbitals with the organic ligand states strongly depends on their magnetic quantum number and their empty/occupied character, as shown in Fig. 2.

Fig. 2 Orbital energy levels for $H_2Pc$, MPc (M = Fe, Co, Ni, Cu, Zn, Mg), and CoPcF$_{16}$, ZnPcF$_{16}$ and H$_2$PcF$_{16}$. Ionization energies from experiments for the corresponding phthalocyanine vapors\cite{17} are shown by dashed gray line. The blue dashed line depicts the HOMO level of $H_2Pc$, which lies above that of $H_2PcF_{16}$ by $\Delta HOMO = 0.661$ eV. Energy levels with contributions from the five $d$ orbitals of the metal center are labeled to the right of each energy level.
Table 2  HOMO and LUMO energies for MPcs from B3LYP, OT-RSH and experimental photoelectron spectroscopy results on MPc vapors\textsuperscript{17}. The energy difference between the HOMO and the highest occupied molecular orbital that includes \textit{d}-orbitals from a transition metal with out-of-plane character is denoted as HOMO-\textit{d}\textsubscript{(z)}, where \textit{d}\textsubscript{(z)} is \textit{d}_z for FePc and \textit{d}_xz,yz for all the other MPcs. The spin-polarized values for HOMO-\textit{d}\textsubscript{(z)} are provided, along with \textit{d} contribution in percentage included in parentheses

| MPc     | B3LYP HOMO | B3LYP LUMO | OT-RSH HOMO | OT-RSH LUMO | HOMO-d\textsubscript{(z)} (spin-up, spin-down) |
|---------|------------|------------|------------|------------|-----------------------------------------------|
| FePc    | 4.967      | 6.073      | 6.36       | 3.023      | 2.079 (6.5, 4.6) 0.603 (82.8) 1.372 (83.8) |
| CoPc    | 5.170      | 6.259      | 6.38       | 2.939      | 1.905 (3.6, 2.6) 1.360 (70.4) 1.633 (28.4) |
| NiPc    | 5.197      | 6.259      | 6.38       | 2.966      | 1.932 (2.6, 2.6) 1.605 (30.8) 1.605 (30.8) |
| CuPc    | 5.170      | 6.259      | 6.38       | 2.993      | 1.959 (1.0, 0.8) 2.041 (8.5) 2.122 (6.1) |
| ZnPc    | 5.170      | 6.231      | 6.37       | 2.993      | 1.986 (0.3, 0.3) 2.122 (1.2) 2.122 (1.2) |
| MgPc    | 5.152      | 6.208      | 6.35       | 3.005      | 2.003 - -            |
| H\textsubscript{2}Pc | 5.225 | 6.286 | 6.41 | 3.075 | 2.068 - -            |
| H\textsubscript{2}PcF\textsubscript{16} | 6.001 | 6.947 | - | 3.960 | 2.868 - -            |
| ZnPcF\textsubscript{16} | 5.976 | 6.920 | - | 3.887 | 2.802 (0.3, 0.3) 2.032 (0.38) 2.032 (0.38) |
| CoPcF\textsubscript{16} | 5.958 | 6.934 | - | 3.822 | 2.700 (3.6, 2.7) 1.494 (31.8) 1.705 (23.2) |

Gradual changes in hybridization between \textit{d}-orbitals with out-of-plane character (i.e. \textit{d}\textsubscript{xz},\textsubscript{yz} and \textit{d}\textsubscript{z\textsuperscript{2}}) and underlying substrates have been hypothesized to contribute to the atomic number dependence of the photophysics of substrate-supported MPcs\textsuperscript{8,57}, due to their “flat” adsorbed configurations\textsuperscript{58}. Specifically, resonant Raman enhancement of MPcs of increasing atomic number (for CoPc to ZnPc) have been shown to converge to H\textsubscript{2}Pc upon filling of the \textit{d} shell in phthalocyanine/MoS\textsubscript{2} mixed-dimensional heterojunctions\textsuperscript{8}; The interaction of MPcs with substrate Au(110) is strengthened for FePc and CoPc than NiPc and ZnPc due to \textit{d} orbital energies closer to the Fermi energy\textsuperscript{6}.

As shown in Fig. 2, the LUMOs of all MPcs are doubly degenerate of \textit{e}\textsubscript{g} symmetry, which allows the mixing of \textit{d}\textsubscript{xz}, \textit{d}\textsubscript{yz} states having out-of-plane character. From Fe (3\textit{d}\textsuperscript{6}) to Zn (3\textit{d}\textsuperscript{10}), the fraction of (\textit{d}\textsubscript{xz,\textit{yz}}) decreases from 6.5% to 0.3%, as shown in Table 2, in agreement with the experimental hypothesis.

This trend is magnified for occupied states, with atomic number decreasing both the out-of-plane \textit{d} character of the HOMO-1 and its proximity with the frontier orbitals (the HOMO’s \textit{a}\textsubscript{1\textit{u}} character preventing mixing with the \textit{d} states), as shown in Table 2. Unlike the frontier orbitals, the energy of the HOMO-1 varies with atomic number: the energy differences between HOMO and HOMO-1 increase gradually from 0.603 eV[82.8% \textit{a}\textsubscript{1\textit{g}}(\textit{d}_z)] in the case of FePc to 1.360 eV[70.4% \textit{e}\textsubscript{g}(\textit{d}\textsubscript{xz,\textit{yz}})], 1.605 eV[30.8% \textit{e}\textsubscript{g}(\textit{d}\textsubscript{xz,\textit{yz}})], 1.388 eV[42.7% \textit{b}\textsubscript{1\textit{g}}(\textit{d}\textsubscript{\textit{x}^2–\textit{y}^2})+0.4% \textit{b}\textsubscript{2\textit{g}}(\textit{d}\textsubscript{\textit{xy}})], 1.878 eV[\textit{b}\textsubscript{1\textit{g}}(\textit{d}\textsubscript{\textit{x}^2–\textit{y}^2}) 30.5%+0.1%
for CoPc, NiPc, CuPc, and ZnPc, respectively (for MgPc and H$_2$Pc, HOMO-1 is also $a_{1u}$).

We find that frontier orbital energies can be significantly tuned through fluorination of the outer Pc ring, with HOMO (LUMO) energy shifts of 0.661 (0.800), 0.676 (0.795) eV and 0.688 (0.815) eV, respectively for H$_2$Pc, CoPc and ZnPc, which is comparable to the experimentally reported increase of 1.05 ± 0.2 eV in ionization potential for CuPc organic films after perfluorination$^{59}$. Interestingly, fluorination impacts occupied and unoccupied states uniformly, as shown in Fig. 2. We attribute this energy level shift to a near-uniform shift in the electrostatic potential upon replacement of the peripheral hydrogens by more electronegative fluorine atoms$^{60}$. The electrostatic potential in the molecular plane are shown in Fig. 3 for CoPc and CoPcF$_{16}$. With F atoms, the electrostatic potential of the molecules are reduced and the change, $\Delta V$ is shown in Fig. 3(c). The value of this change can be approximated by averaging the electrostatic potential at the center of the molecule, as shown by the dashed lines in Fig. S11. The electrostatic potential is shifted down by about 0.7–0.8 V, which is consistent with the HOMO/LUMO energy shifts. Same results are found for H$_2$Pc and ZnPc, see Fig. S8 and Fig. S10 which has similar electrostatic potential shift as for CoPc, consistent with similar shift of HOMO/LUMO energies for H$_2$Pc, CoPc and ZnPc, which indicates that the orbital energy shifts induced by fluorine atoms are electrostatic in origin. This effect can be captured through a multi-
pole expansion of the molecular charge density—specifically its quadrupole moment, as the dipole moments are zero due to the $D_{4h}$ symmetry. The change in quadrupole between the hydrogenated and fluorinated $H_2Pc$ and $ZnPc$ are similar, (138.5, 138.5, 54.6) DebyeÅ and (139.2, 139.2, 54.5) DebyeÅ, respectively, for the (XX, YY, ZZ) components, and is captured by OT-RSH and B3LYP with energy shifts within 0.1 eV of OT-RSH.

Interestingly, despite the significant change in orbital energy due to fluorination, qualitative symmetry and composition features are maintained for the molecular orbitals, as shown in Fig. 2 and Table 2. This may allow for additional tunability of photocatalytic reactivity, and band alignment in MPc-containing heterojunctions, which are critical in controlling the rate of charge transfer that governs the performance of such heterojunctions\textsuperscript{60–62}.

### Table 3

Optical gaps for MPcs from B3LYP, OT-RSH and experimental photoabsorption results. The fraction of HOMO $\rightarrow$ LUMO to the excitation in percentage are included in parentheses

| MPcs      | $E_{\text{opt}}^g$ B3LYP | $E_{\text{opt}}^g$ OT-RSH | exp.$^a$ |
|-----------|--------------------------|----------------------------|---------|
| FePc      | 1.987(100)               | 1.923 (100)                | 1.83    |
| CoPc      | 2.116 (100)              | 2.124 (100)                | 1.89    |
| NiPc      | 2.095(100)               | 2.098(100)                 | 1.90    |
| CuPc      | 2.083 (100)              | 2.065(94.9)                | 1.89    |
| ZnPc      | 2.077 (95.4)             | 2.058 (100)                | 1.88    |
| ZnPcF$_{16}$ | 1.987(94.2)         | 1.967(93.1)                | -       |
| CoPcF$_{16}$ | 2.017(100)            | 2.020 (94.9)               | -       |
| MgPc      | 2.046(93.1)              | 2.026(91.4)                | 1.86    |
| $H_2Pc$   | 2.054(94.6)              | 2.022(94.6)                | 1.81,1.99 |
| $H_2PcF_{16}$ | 1.970(91.6)        | 1.937(90.2)                | -       |

$^a$ absorption spectroscopy results for vapor phase $H_2Pc$ and MPcs\textsuperscript{63}

Optical band gaps $E_{g}^{\text{opt}}$ for MPcs from B3LYP and OT-RSH as well as experimental absorption spectroscopy results are included in Table 3, with similar values from B3LYP and OT-RSH, which are $\sim$0.2eV to the blue of the experimental values. OT-RSH functionals applied to TDDFT calculations can also reproduce quantitatively accurate optical absorption for organic systems, with or without transition metal incorporation\textsuperscript{64}. Experimental absorptions were measured at temperatures over 500$^\circ$C\textsuperscript{63}, which may be the reason for smaller values of $E_{g}^{\text{opt}}$ than those calculated. $E_{g}^{\text{opt}}$ values for different MPcs vary only slightly, and are almost all from HOMO to LUMO, as shown in Table 3. For those
involving other molecular orbitals, the excitations are also from occupied states with no $d$ fraction to LUMO. Therefore the excitations are mainly from ligand to LUMO states which include small fraction of $d$-orbitals.

In summary, we computed the electronic structures of $\text{H}_2\text{Pc}$, MgPc and 3d transition metallophthalocyanines ($M = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$), as well as perfluorinated $\text{H}_2\text{PcF}_{16}$, CoPcF$_{16}$, ZnPcF$_{16}$ using an optimally-tuned range-separated hybrid functionals. The HOMOs of all molecules are found to be of $a_{1u}$ symmetry with no $d$-orbital contribution. The LUMOs are all $e_g$ with $d_{xz}, d_{yz}$ participation decreasing with increasing atomic number. Both the energy and out-of-plane $d$-orbital character of the HOMO-1 decrease with increasing atomic number. Fluorination was found to result in near-uniform shifts in the HOMO/LUMO energies, on the scale of 0.7-0.8eV, while maintaining other features of the electronic structure, including level ordering.

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Conflicts of interest

There are no conflicts to declare.

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Electronic Structure of Metallophthalocyanines, MPc (M = Fe, Co, Ni, Cu, Zn, Mg) and Fluorinated MPc†

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Fig. S1 2D map of $J^2$ as a function of $(\alpha, \gamma)$ for H$_2$Pc and MPc (M=Co,Ni,Cu,Zn). For each $\alpha$, the optimal $\gamma$ value is selected at minimum of $J^2$.

Table S1 Optimally-tuned range-separation parameter $\gamma$, HOMO, and LUMO energies in eV for each MPcs at $\alpha$ of 0.1 and 0.2. $\gamma$ values are slightly different for different MPcs. And HOMO or LUMO differs by less than 0.05 eV for $\alpha$ of 0.1 and 0.2.

|         | $\alpha = 0.1$ |         | $\alpha = 0.2$ |
|---------|----------------|---------|----------------|
| $\gamma^{opt}$ (Bohr$^{-1}$) | HOMO | LUMO | $\gamma^{opt}$ (Bohr$^{-1}$) | HOMO | LUMO |
| H$_2$Pc | 0.141          | 6.286   | 2.068          | 0.121          | 6.231   | 2.068 |
| H$_2$PcF$_{16}$ | 0.142          | 6.947   | 2.869          | 0.124          | 6.994   | 2.931 |
| MgPc   | 0.138          | 6.208   | 2.003          | 0.120          | 6.177   | 2.010 |
| FePc   | 0.143          | 6.073   | 2.079          | 0.124          | 6.056   | 2.073 |
| CoPc   | 0.140          | 6.259   | 1.905          | 0.123          | 6.204   | 1.905 |
| CoPcF$_{16}$ | 0.144          | 6.934   | 2.700          | 0.125          | 6.970   | 2.771 |
| NiPc   | 0.138          | 6.259   | 1.932          | 0.120          | 6.231   | 1.959 |
| CuPc   | 0.144          | 6.259   | 1.959          | 0.124          | 6.231   | 1.986 |
| ZnPc   | 0.139          | 6.231   | 1.986          | 0.122          | 6.204   | 1.986 |
| ZnPcF$_{16}$ | 0.140          | 6.920   | 2.802          | 0.122          | 6.964   | 2.864 |

The optimal $\gamma^{opt}$ values vary slightly for MPcs with different transition metals. $\gamma^{opt}$ can also be slightly affected by the basis set, which can be the reason for slightly different $\gamma^{opt}$ values obtained here from previous studies, i.e. for CoPc$^{[1]}$ $\gamma^{opt}(\alpha = 0.1) = 0.146$ and $\gamma^{opt}(\alpha = 0.2) = 0.127$, for CuPc$^{[2]}$ $\gamma^{opt}(\alpha = 0.1) = 0.137$ and $\gamma^{opt}(\alpha = 0.2) = 0.120$. 
**Fig. S2** \( J^2 \) as a function of \( \gamma \) at (a)-(d) \( \alpha = 0.1 \) and (e)-(h) \( \alpha = 0.2 \) for ZnPcF\(_{16} \), MgPc, FePc, CoPcF\(_{16} \). The optimal \( \gamma \) values are same from both \( J_{IE}^2 \) and \( J_{EA}^2 \) as shown in (a) and (b). The dashed lines of parabolas are fitted from calculated data.

**Fig. S3** Orbital energy levels for gas-phase \( H_2Pc \), MPc (M=Fe, Co, Ni, Cu, Zn, Mg), as well as CoPcF\(_{16} \), ZnPcF\(_{16} \) and \( H_2PcF \) from OTRSH (\( \alpha = 0.2 \)). HOMO levels are indicated by blue triangles. Dashed gray line shows the ionization energies from experiments\(^{3} \). The blue dashed line depicts the HOMO level of \( H_2Pc \), which is larger than that of \( H_2PcF \) by \( \Delta \text{HOMO} = 0.763 \) eV. Energy levels with contributions from the five \( d \) orbitals of metal center are labeled to the right of each energy level.
Table S2 HOMO, LUMO for MPcs from B3LYP, OT-RSH (α=0.2) and experimental photoelectron spectroscopy results of MPc vapors. The energy difference between HOMO and the highest occupied molecular orbital that includes d-orbitals from transition metal with out-of-plane character, HOMO-d_z^2 in eV, where d_z^2 for FePc and d_xz,dyz for all the other MPcs. The spin-up and spin-down values for HOMO-d_z^2 are provided, along with d contribution in percentage included in parentheses.

| MPc       | HOMO | LUMO(fraction of d_xz, %) | HOMO-d_z^2 (fraction of d_z^2, %) |
|-----------|------|----------------------------|----------------------------------|
|           | B3LYP | OT-RSH | exp | B3LYP | OT-RSH | spin-up | spin-down |
| FePc      | 4.967 | 6.056  | 6.36 | 3.023 | 2.073  | (4.4,3.6) | 0.955(82.9) | 1.784(83.4) |
| CoPc      | 5.170 | 6.204  | 6.38 | 2.939 | 1.905  | (2.8,2.1) | 1.660(30.7) | 1.878(22.8) |
| NiPc      | 5.197 | 6.231  | 6.38 | 2.966 | 1.959  | (2.0,2.0) | 1.850(24.0) | 1.850(24.0) |
| CuPc      | 5.170 | 6.231  | 6.38 | 2.993 | 1.986  | (0.8,0.6) | 2.150(5.7)  | 2.204(4.0)  |
| ZnPc      | 5.170 | 6.204  | 6.37 | 2.993 | 1.986  | (0.3,0.3) | 2.231(1.0)  | 2.231(1.0)  |
| ZnPcF_{16}| 5.976 | 6.964  | -   | 3.887 | 2.864  | (0.3,0.3) | 2.032(0.2)  | 2.032(0.2)  |
| CoPcF_{16}| 5.958 | 6.970  | -   | 3.822 | 2.771  | (2.8,2.2) | 1.72(26.3)   | 1.8762(17.3) |
| MgPc      | 5.152 | 6.177  | 6.35 | 3.005 | 2.010  | -        | -             | -             |
| H_2Pc     | 5.225 | 6.231  | 6.41 | 3.075 | 2.068  | -        | -             | -             |
| H_2PcF_{16}| 6.001 | 6.994  | -   | 3.960 | 2.931  | -        | -             | -             |

b Photoelectron spectroscopy results

Fig. S4 Orbital energy levels for gas-phase H_2Pc, MPc (M=Fe, Co, Ni, Cu, Zn, Mg), as well as CoPcF_{16}, ZnPcF_{16} and H_2PcF_{16} from B3LYP. HOMO levels are indicated by blue triangles. Dashed gray line shows the ionization energies from experiments. The blue dashed line depicts the HOMO level of H_2Pc, which is larger than that of H_2PcF_{16} by ΔHOMO=0.776 eV. Energy levels with contributions from the five d orbitals of metal center are labeled to the right of each energy level.
Fig. S5 Orbital energy levels for gas-phase $H_2Pc$, $MPc$ ($M=Fe$, Co, Ni, Cu, Zn, Mg) from CAMB3LYP, a range-separated hybrid functional with range-separated parameters of $\alpha=0.19$, $\beta=0.46$, $\gamma=0.33$. HOMO levels are indicated by blue triangles. Dashed gray line shows the ionization energies from experiments\cite{1}. Comparing with results from B3LYP as shown in Fig. S4, the ionization energies from CAMB3LYP are largely improved but are still about 0.7 eV away from the experimental results for FePc and $\sim$0.5 eV for other MPcs. While ionization energies from OT-RSH have best agreement with experimental results, with $<0.3$ eV difference for FePc and $<0.15$ eV difference for other MPcs (Fig. 2). Meanwhile, the HOMO and HOMO-1 energy differences are much larger from CAMB3LYP than that from OT-RSH.

Table S3 Eigenvalues of the spin-squared operator $\langle S^2 \rangle$ for open-shell systems, CoPc, CuPc, CoPcF$_{16}$ and FePc, from unrestricted calculations using B3LYP and OT-RSH methods ($\alpha =0.1, 0.2$), $\langle S^2 \rangle_{UDFT}$, as well as the exact values $\langle S^2 \rangle_{exact}$. The differences between $\langle S^2 \rangle_{UDFT}$ and $\langle S^2 \rangle_{exact}$ are small, implying that the spin contamination effects are small for those systems from both B3LYP and OT-RSH methods.

| MPc     | method | $\langle S^2 \rangle_{exact}$ | $\langle S^2 \rangle_{UDFT}$ |
|---------|--------|-----------------------------|-----------------------------|
| CoPc    | B3LYP  | 0.75                        | 0.756                       |
|         | $\alpha=0.1$ | 0.75                        | 0.758                       |
|         | $\alpha=0.2$ | 0.75                        | 0.757                       |
| CuPc    | B3LYP  | 0.75                        | 0.753                       |
|         | $\alpha=0.1$ | 0.75                        | 0.753                       |
|         | $\alpha=0.2$ | 0.75                        | 0.753                       |
| CoPcF$_{16}$ | B3LYP | 0.75                        | 0.757                       |
|         | $\alpha=0.1$ | 0.75                        | 0.759                       |
|         | $\alpha=0.2$ | 0.75                        | 0.758                       |
| FePc    | B3LYP  | 2.00                        | 2.018                       |
|         | $\alpha=0.1$ | 2.00                        | 2.020                       |
|         | $\alpha=0.2$ | 2.00                        | 2.020                       |

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Fig. S6 Orbital energy levels for closed shell NiPc and ZnPc from restricted (black) and unrestricted broken symmetry (blue) calculations using OT-RSH with $\alpha = 0.1$. HOMO levels are indicated by blue triangles. Energy levels with contributions from the five $d$ orbitals of metal center are labeled to the right of each energy level.

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Fig. S7 Orbital energy levels for closed shell NiPc and ZnPc from restricted (black) and unrestricted broken symmetry (blue) calculations using B3LYP. HOMO levels are indicated by blue triangles. Energy levels with contributions from the five $d$ orbitals of metal center are labeled to the right of each energy level.

Fig. S8 Electrostatic potential $V_{pot}$ for (a) H$_2$Pc, (b) H$_2$PcF$_{16}$, and (c) change of potential $\Delta V_{pot} = V_{pot}[H_2PcF_{16}] - V_{pot}[H_2Pc]$ in the plane of molecule.
Fig. S9 Electrostatic potential $V_{pot}$ for (a) CoPc, (b) CoPcF$_{16}$, and (c) change of potential $\Delta V_{pot} = V_{pot}[\text{CoPcF}_{16}] - V_{pot}[\text{CoPc}]$ in the plane of the molecule.

Fig. S10 Electrostatic potential $V_{pot}$ for (a) ZnPc, (b) ZnPcF$_{16}$, and (c) change of potential $\Delta V_{pot} = V_{pot}[\text{ZnPcF}_{16}] - V_{pot}[\text{ZnPc}]$ in the plane of molecule.
**Fig. S11** Electrostatic potential averaged along x direction for H$_2$PcF$_{16}$ (blue) and H$_2$Pc (orange) along the lines as shown in Fig. S8(a) and (b). The dashed horizontal lines indicates approximate averaged electrostatic potential in the middle of the molecules. The change of electrostatic potential ΔV is around 0.7~0.8 eV, which is consistent with the orbital energy level shifts.
