O=C—O—H Torsional Angle

Figure 3. Change in bond angle with O=C—O—H torsional angle for acetic acid (C = conventional bond angle, B = bond path angle).

This is less than half of the difference found for methyl acetate, but the steric interactions in lactones may be less than that in acyclic esters. We are measuring the heats of hydrolysis of lactones

in order to gain a better understanding of the interactions in these types of compounds.

Calculations

The molecular orbital calculations were carried out with GAUSSIAN-82.[35] The analysis of the wave functions in terms of the charge distribution was carried out with PROAIMS.[36] This yields the electron populations (N) and the kinetic energies (T) associated with each of the atoms. In the tables, the quantity L is the integrated value of $-(\hbar^2/4m)\nabla^2\rho$. If the numerical integration for T were exact, it would be zero, and its value represents the possible error in T. In order to use T to obtain the energies of the atoms via the virial theorem, it must be corrected for the virial defect found in the MO calculations. The $-V/T$ values are given in the tables, and K is multiplied by $(-V/T) - 1$ to give T'. The sum of T' will be equal to the total energy found in the MO calculation, within the accuracy of the numerical integration.

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On the Electronic Structure of Substituted Phthalocyanines: A Hartree–Fock–Slater Study of Octacyano- and Octafluoro-Substituted (Phthalocyaninato)silicon Dihydroxide

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Abstract: The effects of peripheral substitution of strongly electron–withdrawing groups (CN and F) on the electronic properties of Si(Pc)(OH)$_2$ (Pc = phthalocyaninato) are studied via the discrete-variational local exchange (DV-Xα) formalism. Comparisons are made to the electronic structure of the parent molecule, Si(Pc)(OH)$_2$, and the results are discussed in terms of changes in the tight-binding band structure of the corresponding cofacially joined phthalocyaninato polymers. Transition-state calculations yield optical and photoemission spectral energy predictions. The former are in good agreement with experimental data. There is a pronounced lowering of all orbital energies and a substantial increase in ionization potential upon CN and F substitution.

I. Introduction

Phthalocyanine macrocycles form the basis for several extensive families of molecular[1,2] and polymeric[1a,c,3,4] low-dimensional molecular metals.[5] In comparison to other classes of molecular

metals, the attractive features of phthalocyanine-based materials include ready availability, chemical stability, low cost, and, in the

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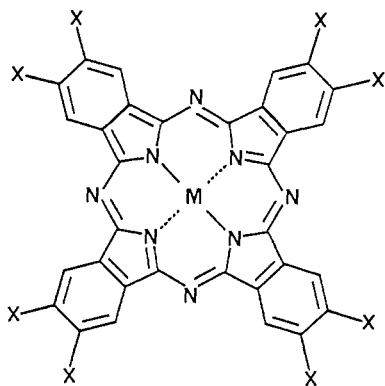
Figure 1. Schematic diagram of the phthalocyanine molecules considered in this work (X = H, C≡N, F).

case of the cofacially joined polymers, structurally enforced molecular stacking.[3] Equally important, however, is the attribute that the basic molecular building block can be subjected to a very wide variety of chemical modifications, including substitution, elaboration, and truncation of the aromatic phthalocyanine macrocycle. These modifications can vary several crucial attributes of the conductive molecular assemblies, including bandwidth, energy of the band center, nature of the carriers, importance of electron correlation, and relative importance of different electron–phonon coupling processes. These materials are also amenable to accurate electronic structure investigations,[6] and such studies have shown, for instance, that above 60 K the stacked Ni(Pc)I compound can be readily understood as a simple narrow-band metal, with dominant resistivity mechanisms due both to twist motions of the Pc ring about the stacking axis and to longitudinal vibrations of the rigid Pc rings along this axis.[7]

One expects that the substitution of electron-withdrawing substituents on the phthalocyanine ring should raise the ionization potential, thus rendering partial oxidation with weak oxidants such as I_2 more difficult to attain. Conversely, however, if enough electron-withdrawing groups are present, they might stabilize an anion, sufficiently that partially reduced stacks or chains, in which electron rather than hole carriers travel along the chain, might be prepared. Indeed, recent electrochemical experiments with $[Si(Pc)O]_n$[2b,3b,8] indicate that partially reduced metallophthalocyanine conductors are synthetically accessible, but at very negative potentials. Hence, these materials are highly air-sensitive.

Two obvious candidates for subunits of such reduced Pc conductors which would be chemically more stable are metallophthalocyanines heavily substituted with cyano or fluoro substituents (e.g., Figure 1). Both general classes of phthalocyanines are known.[9,10] We report here electronic structure studies of octacyano- and octafluoro-substituted Pcs. Calculations have been carried out for two reasons: first to examine the electronic structure properties (energy levels and wave functions) of the substituted Pc ring and to compare them to the parent macrocycle, and second, to use these wave functions in connection with a generalized Wolfsberg–Helmholtz formulation to discuss band structures and electron–phonon coupling in conductive chains of these substituted Pcs. We restrict ourselves here to the first part of this project and discuss the electronic structure of the monomer. The present studies have been carried out by using the first-principles Hartree–Fock–Slater method (local density method), with a discrete variational form for the wave function. All electrons are included and there are no adjustable parameters. This method has been used previously with excellent results on a variety of molecules of various sizes, including aromatics,[11] organometallics[12] and phthalocyanines.[6] The present studies constitute a rigorous test of the method for two reasons: the strongly polar charge distribution expected for these species requires a very accurate self-consistent description of the charge flow, and we require the method to predict the ionization potentials of these Pcs, which have not yet been measured.

The electronic structures calculated for these substituted Pcs are discussed in section III, and comparisons with the unsubstituted parent $Si(Pc)(OH)_2$ are drawn. Section II gives relevant details of the methods used, while concluding remarks are contained in section IV.

II. Calculational Method

Calculations using the discrete-variational local density method (DV–Xα) of Ellis and co-workers[13] were carried out on the Si-$[Pc(CN)_8](OH)_2$ and the $Si(PcF_8)(OH)_2$ molecules for comparison with earlier work on $Si(Pc)(OH)_2$ and $HO[Si(Pc)O]_2H$, which are monomeric and dimeric subunits of the conductive polymer $[Si(Pc)O]_n$. The geometries were taken from the room-temperature X-ray data of Ciliberto et al. on $ROSi(Pc)OSi$-$(Pc)OR$ (R = $Si[C(CH_3)_3](CH_3)_2$[6b]), except that the Pc rings were forced to be rigorously planar (they are approximately planar in the solid state). The C≡N distance was taken to be 1.14 Å and the C–(C≡N) distance as 1.45 Å, based on metrical parameters for phthalonitrile.[14a] For the octafluoro species, a C–F

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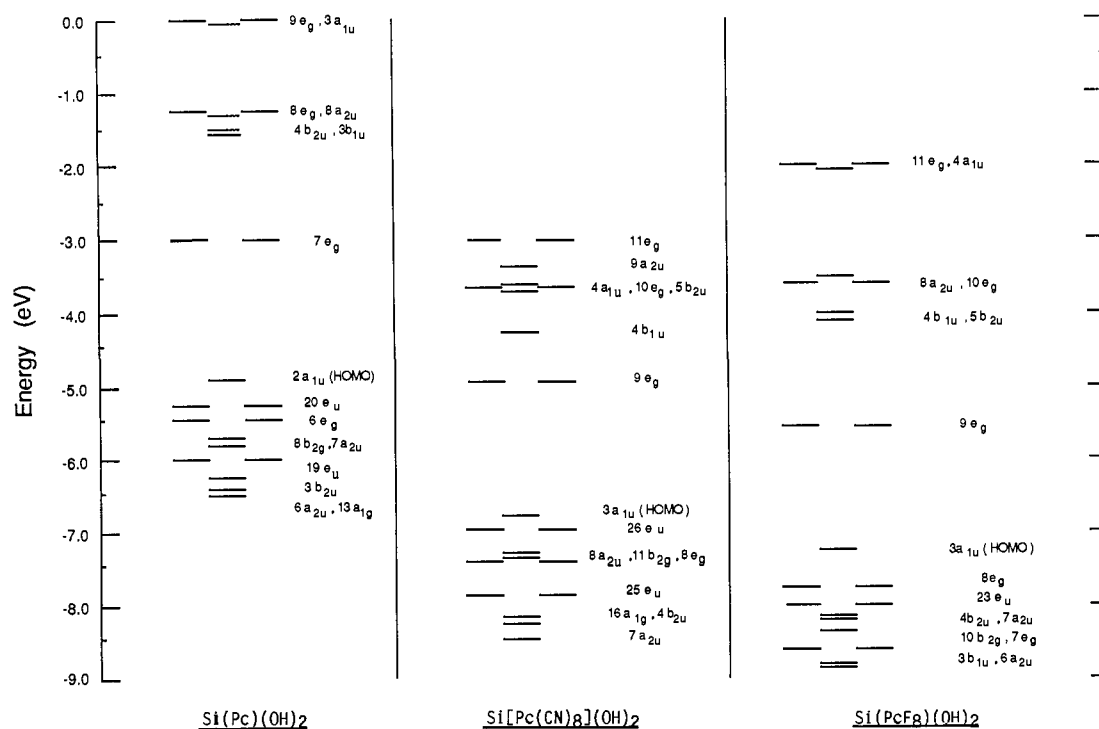
Figure 2. Energy levels for the valence orbitals of parent and substituted $Si(Pc)(OH)_2$ molecules derived from DV-Xα calculations.

distance of 1.328 Å[14b] was used. In both cases, the HO–Si–OH chain was taken as linear, with O–H and O–Si distances of 0.957[15] and 1.636 Å,[6b] respectively.

The DV–Xα method consists of a self-consistent solution of the Hartree–Fock–Slater one-electron equations

$$\{P_i^2/2m + V_{xc}(x_i) + V_{Coul} - \epsilon_i\}\psi_i(x_i) = 0 \qquad (1)$$

where the one-electron wave function ψ_i for the ith electron at position x_i has an energy eigenvalue ϵ_i. The first term in braces in eq 1 is the usual kinetic energy operator, and the next two are exchange-correlation and Coulomb potential terms, respectively. In Hartree–Fock–Slater studies, both of these potentials are local functionals of the electron density. In particular, the Slater form[16] of the exchange-correlation potential is given by

$$V_{xc}(x_i) = V_{xc}[\rho(x_i)] = -\frac{8\alpha}{3\pi}\left[\frac{\rho(x_i)}{2}\right]^{1/3} \qquad (2)$$

where $\rho(x_i)$ is the total computed electron density at point x_i and α is taken as 0.70. These calculations are not spin-polarized, so eq 2 is independent of spin and $\rho(x_i)$ is the total density. In the calculations reported here, the Hedin–Lundqvist form[17] of the exchange-correlation potential was used rather than the Slater choice of eq 2; this involves a more accurate and elaborate form based on results for the electron gas.

The HFS eq 1 must be solved self-consistently, since $\rho(x_i)$ is determined by the $\{\psi_i\}$, which are in turn determined by V_{xc} (which is a functional of $\rho(x_i)$). To implement this, the wave functions ψ_i are expanded in a discrete basis of atomic functions, analogous to usual LCAO–MO methods. The atomic basis functions are taken as products of a spherical harmonic (for the angular part) and a numerical function describing the r dependence. The basis sets were determined by atomic HFS calculations on neutral atoms placed in trapezoidal wells. Large basis sets were used, including

double-ζ p functions on C, N, F, and Si, plus a single set of d functions on Si. The core orbitals (1s on C, N, O, and F; 1s and 2s on Si) were frozen throughout the SCF cycles.

The corrected-potential representation of Delley and Ellis[13b] was used to compute $V_{xc}(x_i)$. The potential included $l = 0,1,2$ waves (centered on Si) and $l = 0,1$ waves (on C, N, O, and F). Calculations were run until convergence (to approximately 0.002 eV) was achieved for the HOMO and LUMO energy levels; this normally required roughly 30 iterations.

III. Results: Electronic Structure of Parent and Substituted $Si(Pc)(OH)_2$

The results of the closed-shell ground-state calculations for octacyanophthalocyanine, octafluorophthalocyanine, and the parent silicon phthalocyanine monomer are shown schematically in Figure 2. The energy ordering for the parent species agrees well with the results of other calculations.[6,18,19] As we found previously[6] the ordering of the π levels and their separations also agree well with semiempirical (PPP) calculations.[18] The energy ordering for the substituted phthalocyanines is similar, but the electron-withdrawing groups cause both the occupied and unoccupied levels to shift lower in energy (the shift is approximately 2 eV for the octacyano species and 2.5 eV for the octafluoro molecule). While there are a few differences in the order of the energy levels between the parent and substituted molecules, it is clear from Figure 2 that the symmetries of the highest occupied and lowest unoccupied orbitals remain the same upon ring substitution (a_{1u} and e_g symmetry, respectively). In a simple tight-binding band picture, the phthalocyanine a_{1u} HOMOs interact to form the conduction band in the corresponding polymers and molecular stacks.[7] After partial oxidation, this band is no longer completely full, and conductivity may therefore occur via the overlapping monomer a_{1u} orbitals.

In Figure 3 are shown contour diagrams for the a_{1u} HOMO of the parent and substituted phthalocyanine molecules. For the parent species, this orbital is composed entirely of out-of-plane

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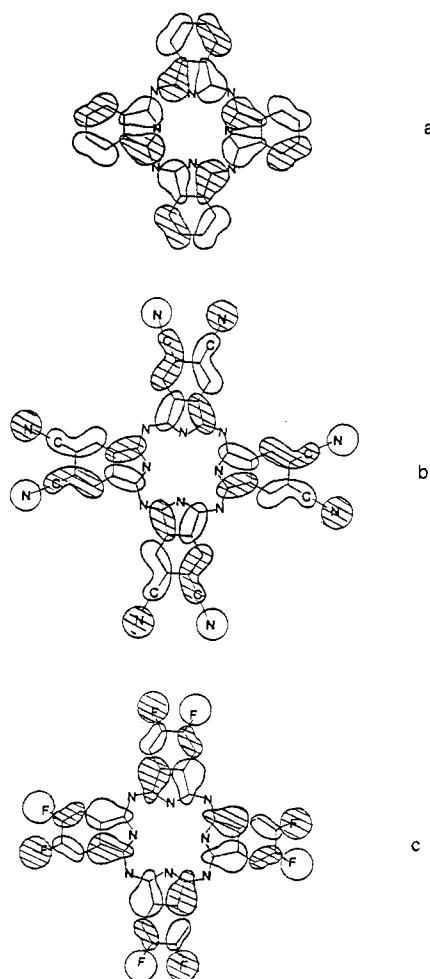
Figure 3. Graphic representation of the highest occupied molecular orbital of parent and substituted Si(Pc)(OH)$_2$ molecules: (a) 2a$_{1u}$ orbital of Si(Pc)(OH)$_2$; (b) 3a$_{1u}$ orbital of Si[Pc(CN)$_8$](OH)$_2$; (c) 3a$_{1u}$ orbital of Si(PcF$_8$)(OH)$_2$ viewed perpendicular to the ring plane.

Table I. 2p$_z$ Coefficients of the a$_{1u}$ HOMO for Parent and Substituted Si(Pc)(OH)$_2$

atom[a]	Si(Pc)(OH)$_2$	Si[Pc(CN)$_8$](OH)$_2$	Si(PcF$_8$)(OH)$_2$
C1	0.515	0.431	0.169
C2	0.434	0.499	0.703
C3	−0.337	−0.233	−0.581
C4	−0.485	−0.376	−0.424
C$_{CN}$		−0.116	
N$_{CN}$		0.260	
F			0.275

[a] The numbering for the nonequivalent carbon centers is as follows:
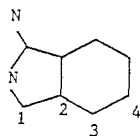
p$_z$ functions localized on the carbon atoms. For the other two molecules, the a$_{1u}$ HOMOs are also made up of p$_z$ atomic functions, but both have considerable amplitude on the outer ring substituents in addition to the carbon atoms. For all three molecules, this orbital has no amplitude on silicon or oxygen; this implies, as was found previously[6] for the parent species, that the siloxane backbone should not play a significant role in the conduction process in the corresponding polymer systems. Table I shows how the 2p$_x$ coefficients of this molecular orbital change upon substitution of C≡N and F on the periphery of the Pc. The most striking feature is the decrease in amplitude on the innermost carbon atoms, accompanied by an increase in amplitude on carbon C2 (see the diagram accompanying Table I) and, of course, by

Table II. Calculated Optical and Ionization Energies for Parent and Substituted Si(Pc)(OH)$_2$ Molecules

molecule	ionization energy, eV (a$_{1u}$ HOMO)	calcd optical transition, nm a$_{1u}$ → e$_g$(exptl)
Si(Pc)(OH)$_2$	6.8[a]	673 (671)[b]
Si[Pc(CN)$_8$](OH)$_2$	8.1	685 (690)[c]
Si(PcF$_8$)(OH)$_2$	8.8	756 (730)[d]

[a] Experimental ionization energy = 6.46 eV.[6b] [b] Reference 6b. [c] For Zn[Pc(CN)$_8$].[9a] [d] For Ni(PcF$_{16}$).[10b]

the additional amplitude on the outer substituents.

The nature of the monomer a$_{1u}$ HOMO should play a key role in the conductivity behavior of the corresponding polymer. Previous work[7] showed that bandwidth-modulating lattice motions (that is, lattice motions that affect the interaction between monomer a$_{1u}$ HOMOs on adjacent sites) are dominant sources of resistivity along the Pc chain. For the nonpolymeric Pc stack Ni(Pc)I, the temperature dependence of the resistivity was described in terms of scattering by a longitudinal stretch and an interplanar twist (libron).[7b] The scattering due to the stretch phonon is primarily a first-order process (resistivity ρ porportional to temperature T), while that due to the librational motion is mainly second order ($\rho \propto T^2$). In the present case, where the electron-withdrawing substituents have, in effect, pulled the amplitude of the a$_{1u}$ HOMO away from the inner carbon atoms, one might expect the bandwidths to be more sensitive to the libron. It should be realized, however, that without an actual calculation of the relevant electron–phonon coupling constants,[7b] it is impossible to say if this would remain a second-order scattering mechanism, of if a substantial first-order contribution would also arise from this motion. Studies are presently under way to clarify this point and to study the importance of other lattice motions in changing the interaction between adjacent a$_{1u}$ monomer HOMOs (and hence the bandwith) in the substituted phthalocyanine systems.

In addition to changes in the electron–phonon coupling constants arising from the effect of the electron-withdrawing groups on the monomer a$_{1u}$ HOMO, the magnitude of the bandwidth should also change considerably. Since this orbital is localized to a greater extent on the outer atoms of the macrocycle in the substituted Pc complexes, because the molecules usually stack in a staggered conformation,[1,2] the bandwidth for the octacyano- and octafluoro-Pc stacks should be less than that for the unsubstituted Pc chain. This point is a minor one because the resistivity in these systems does not depend on the magnitude of the bandwith itself, but is instead proportional to the quantity $[(1/W)(\partial W/\partial u)]^2$ for first-order scattering processes.[20] Here W is the bandwith and u refers to some lattice motion which scatters the conduction electrons; $\partial W/\partial u$ is then the electron–phonon coupling constant mentioned above. For second-order scattering, the relationship is similar, with $\rho \propto [(1/W)(\partial^2 W/\partial u^2)]^2$.

The discussion above has been confined to the case where the phthalocyanine molecules of the cofacial polymer or stack have been partially oxidized. The substitution of electron-withdrawing groups on the Pc macrocycle should, however, make partial oxidation with weak oxidants[1c] more difficult to achieve. This point is borne out in the results of calculations of ionization potentials for the parent and substituted Pc molecules (see Table II). Recall that Koopmans' theorem is not valid for Xα calculations, so these ionization energies, as well as the optical transition (HOMO → LUMO, $\pi \to \pi^*$) energies, were calculated by using Slater's transition-state procedure,[16] which corrects the calculated orbital energies for relaxation effects. The results predict that the ionization potential of Si[Pc(CN)$_8$](OH)$_2$ species should be 1.6 eV higher than that of the unsubstituted molecule, while the IP of Si(PcF$_8$)(OH)$_2$ species should be 2.3 eV higher. Clearly, it would be much more difficult to attain partial oxidation of these substituted molecues. It can also be seen in Table II that there is

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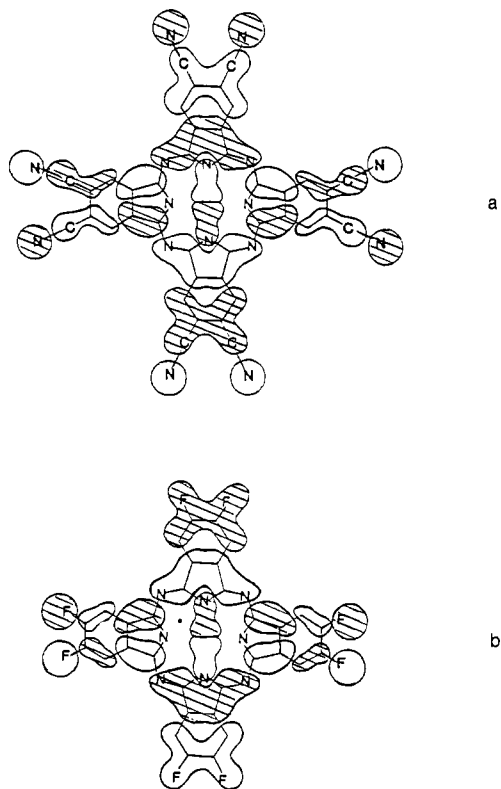
Figure 4. Graphic representation of the lower unoccupied molecular orbital ($9e_g$) of (a) $Si[Pc(CN)_8](OH)_2$ and (b) $Si(PcF_8)(OH)_2$ viewed perpendicular to the ring planes.

good agreement between calculated and experimental HOMO → LUMO optical transition energies.

On the other hand, it is highly possible that the electron-withdrawing substituents will stabilize the anion sufficiently that facile partial reduction of the Pc polymer or stack may be possible. In such a case, the conduction band would no longer consist of the overlapping monomer a_{1u} HOMOs, since this band would remain completely filled. Instead, a partially filled band made up of e_g (monomer LUMO) molecular orbitals would serve as the conduction band in the tight-binding picture. Because this conduction band would be partially filled rather than partially depleted, the charge carriers would be electrons instead of holes. Apart from the difference in the charge carriers, the conductivity behavior in the partially reduced Pc system should be considerably different from that in the partially oxidized system simply because of the nature of the e_g monomer LUMO. As the contour diagrams in Figure 4 show, this orbital has a substantial amount of silicon–oxygen π-bonding character, as well as extensive π-bonding

within the phthalocyanine ring. The large amplitude at the center of the molecule indicates that the siloxane backbone might play a significant role in the charge-transport process in the partially reduced Si(Pc) polymer. This is quite unlike the partially oxidized Pc system, where this backbone plays no role in the conduction process.

While it is difficult to say how the various lattice motions will affect the interaction between adjacent e_g monomer LUMOs (and thus affect the bandwidth), it is clear that several motions should be important. As in the system studied previously,[7] the longitudinal stretch phonon should be an important source of resistivity along the chain. Also, because of the inversion symmetry of the e_g LUMO, the twist libron should remain an important bandwidth-modulating motion. Again, an actual calculation of the electron–phonon coupling constants (as performed in ref 7b) is necessary in order to determine if these motions are dominant sources of conduction electron scattering and if other lattice motions are also important (e.g., interplanar tilt and slip modes). Such calculations are also required to determine the nature of each of the scattering modes, that is, to determine which motions scatter in first order and which scatter in second order. Nevertheless, one might expect these partially reduced phthalocyanine systems to have a cnductivity behavior (e.g., temperature dependence) that differs substantially from that of the systems previously examined,[7] with this difference arising primarily from the nature of the monomer e_g LUMO.

IV. Conclusions

This work further demonstrates that first-principles local exchange DV–Xα calculations on monomeric phthalocyanine stack fragments can provide valuable predictive information about the conduction pathway in "molecular metals". The previous success of this method in providing quantitative descriptions of π–π interactions and tight-binding bandwidths in low-dimensional metallomacrocyclic conductors certainly warrants its use as a predictive tool. Such information permits discussion of the changes one might expect to see in the nature of the conduction band when the macrocyle is modified. These changes can be described in terms of how the individual monomer molecular orbitals (which interact to form the band structure) are affected by ring modification, thus clarifying those parameters critical to the design of new molecular metals. Finally, the prediction of ionization potentials and optical transition energies for the substituted phthalocyanines considered in this work should serve as a valuable test of the DV–Xα techndique.