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ARTICLE TYPE

Theoretical study on the stability of double-decker type metal phthalocyanines, M(Pc)$_2$ and M(Pc)$_2^+$ (M = Ti, Sn and Sc): critical assessment on the performance of density functionals

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We report the results of theoretical calculations on the optimized structures and relative energies between the D_{4d} and D_2 symmetries structures for double-decker type phthalocyanine compounds, Ti(Pc)$_2$, Ti(Pc)$_2^+$, Sn(Pc)$_2$, Sn(Pc)$_2^+$, Sc(Pc)$_2$ and Sc(Pc)$_2^+$, using the eighteen types of functionals: B3LYP, B3PW91, B3P86, PBE1PBE, BHandHLYP, BPW91, BP86, M06, M06-2x, M06-HF, M06L, LC-BPW91, LC-ωPBE, CAM-B3LYP, B97D, ωB97, ωB97X and ωB97XD. Two phthalocyanine moieties are stacking at a face-to-face configuration in the D_{4d} structure, but they are stapled by two σ-bonds in the D_2 one. We found that the molecular symmetry of M(Pc)$_2$ and M(Pc)$_2^+$ depends on the balance between stabilization due to electron delocalization and exchange repulsion of π-electrons in the phthalocyanine moieties. We assessed the performance of the well established functionals to select the appropriate functional for calculations on M(Pc)$_2$ and M(Pc)$_2^+$, and several important aspects came out. Generally, the hybrid GGA and hybrid meta GGA functionals with 20-27% of the HF exchange term would give the molecular structures consistent with the experimental expectations for the double-decker type phthalocyanine compounds. Pure GGA and pure meta GGA functionals (BPW91, BP86, M06L and B97D) have the tendency to overestimate the stability of the D_{4d} structure. On the other hand, functionals including HF exchange for 50 % and over or including long-range corrections (BHandHLYP, M06, M06-2x, M06-HF, LC-BPW91, LC-ωPBE, CAM-B3LYP, ωB97, ωB97X and ωB97XD) tend to overestimate the stability of the D_2 structure. It should be emphasized that the B3LYP functional, one of the most commonly used hybrid GGA functional with 20 % HF exchange, cannot estimate the relative stability between the two molecular structures of Ti(Pc)$_2$ appropriately. The calculation for the systems considered in this article required well balanced treatment of the HF exchange with the accompanied exchange-correlation functional. Thus, as pointed rigorously and frequently, the selection of functional is a crucial point to reliability of the calculations.

Introduction

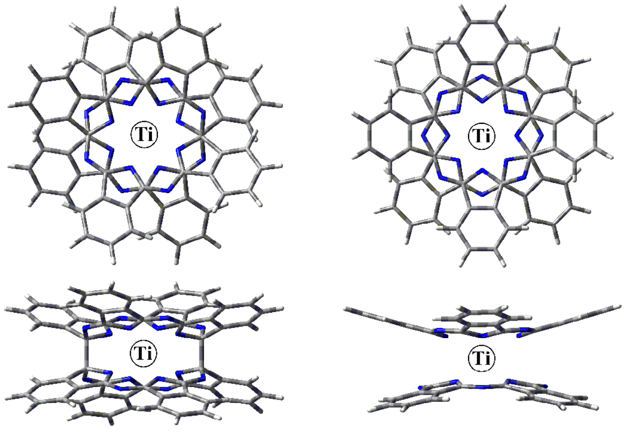
The metal bisphthalocyanine (M(Pc)$_2$; Pc = phthalocyaninato anion $C_{32}H_{16}N_8^{2-}$, M = trivalent or tetravalent metal) is known for its face-to-face stacking molecular structure with D_{4d} symmetry, in which two Pc rings are staggered at 45°.[1-8] Among many bisphthalocyanine compounds, titanium(IV) bisphthalocyanine (Ti(Pc)$_2$) shows a unique molecular structure with “stapled” Pc rings by two interligand C-C σ bonds with a D_2 symmetry as shown in Scheme 1,[9,10] while the usual D_{4d} structure was also suggested from results on the elemental analysis and the electronic absorption spectrum.[11] On the other hand, its oxidized form, Ti(Pc)$_2^+$, has been reported to show the usual sandwich structure with D_{4d} symmetry as shown in Scheme 1, even if starting a reaction with the D_2 neutral materials.[9,10] From our knowledge, the X-ray analysis has been reported only on the D_2 structure for Ti(Pc)$_2$ and on the D_{4d} one for Ti(Pc)$_2^+$ up to now. In the case of tin(IV) bisphthalocyanine (Sn(Pc)$_2$), both neutral and oxidized forms only showed D_{4d} structures.[12-14] Detailed theoretical investigation on the molecular and electronic structures would be indispensable for understanding the physicochemical properties of these double-decker type bisphthalocyanines, especially Ti(Pc)$_2$ and Ti(Pc)$_2^+$.

Several aspects could be supposed for the molecular structure of Ti(Pc)$_2$ in order to explain the experimental observations as follows: 1) the M(Pc)$_2$ compounds would have some possibilities to take two stable molecular structures with D_2 and D_{4d} symmetries, 2) the relative stability between these two structures would vary with the central metal, 3) there would be a small energy difference between these two molecular structures in the case of Ti(Pc)$_2$, 4) the stable structure highly depends on the ionic radius of M, and 5) the D_2 and D_{4d} structures would be preferable in Ti(Pc)$_2$ and Ti(Pc)$_2^+$, respectively. This work was conducted to investigate thoroughly these hypotheses on the molecular structures of M(Pc)$_2$ by the theoretical calculations.

Theoretical calculation has become a very powerful tool to investigate the chemical and physical properties not only by theoreticians but also experimentalists, and has been applied to relatively large systems such as phthalocyanine compounds.[4-8,15-35] The density functional theory (DFT) method is one of the successful methods in order to investigate on both the geometric and electronic structures, and many functionals are proposed for the calculations by several theoretical chemists. The choice of an appropriate functional among them is critical, however, the appropriate one is nontrivial for most cases. For the sake of quantitative discussion on the stability of the molecular structures, the theoretical calculations must be performed with great care, especially in selecting the appropriate functionals.

In previous works on stacking-type metal phthalocyanine systems, we experienced difficulty in choosing the appropriate functionals for these studies.[19-22] The difficulty arises mainly from accurate treatments for electrons of a transition metal atom and the large π conjugated system and for weak interaction in the stacking system simultaneously. Moreover, systems such as $Ti(Pc)_2$ and $Ti(Pc)_2^+$ are expected to have isomers with small energy difference. The systems considered in the article also require quantitative calculations, and would be a good candidate as an excellent system for critical assessment on the functional systems of the DFT method. The assessment will provide great deal of insight for wide variety of further application of DFT calculations.

In this paper, we will present theoretical investigation on the stability of the double-decker structure for $Ti(Pc)_2$, $Ti(Pc)_2^+$, $Sn(Pc)_2$, $Sn(Pc)_2^+$, scandium(III) bisphthalocyanine ($Sc(Pc)_2$), and $Sc(Pc)_2^+$. In order to make critical assessment on the performance of typically used density functionals, we selected eighteen different types of functionals: B3LYP, B3PW91, B3P86, PBE1PBE, BHandHLYP, BPW91, BP86, M06, M06-2x, M06-HF, M06L, LC-BPW91, LC-ωPBE, CAM-B3LYP, B97D, ωB97, ωB97X, and ωB97XD. These functionals are well established and applied to many different systems. We will discuss how the functional affects the geometric structures and the relative energies of the $M(Pc)_2$ and $M(Pc)_2^+$ (M = Ti, Sn, and Sc).



Ti(Pc)$_2$ **Ti(Pc)$_2^+$**

Scheme 1 X-ray crystallographic structures of $Ti(Pc)_2$ and $Ti(Pc)_2^+$.

Computational details

The geometry optimizations of $Ti(Pc)_2$, $Ti(Pc)_2^+$, $Sn(Pc)_2$, $Sn(Pc)_2^+$, $Sc(Pc)_2$, and $Sc(Pc)_2^+$ were carried out under D_{4d} and D_2 molecular symmetries by the DFT method using eighteen functionals listed in Table 1: B3LYP[36-40] (hybrid generalized gradient approximation (GGA) with 20% of the Hartree-Fork (HF) exchange term), B3PW91[36,37,41-44] (hybrid GGA with 20% of the HF exchange term), B3P86[36,37,45] (hybrid GGA with 20% of the HF exchange term with the correlation functional of Perdew), PBE1PBE[46-48] (hybrid GGA with 25% of the HF exchange term), BHandHLYP[36,38,40,49] (hybrid GGA with 50% of the HF exchange term), BPW91[36,41-44] (pure GGA), BP86[36,45] (pure GGA), M06[50] (hybrid meta GGA functional with 27% of HF exchange term), M06-2x[50] (hybrid meta GGA functional with 54% of HF exchange term), M06-HF[51,52] (hybrid meta GGA functional with 100% of HF exchange term), M06L[53] (pure meta GGA functional), LC-BPW91[36,41-44,54] (pure GGA functional with the long-range correction), LC-ωPBE[55-58] (long-range corrected version of ωPBE), CAM-B3LYP[59] (Coulomb attenuated version of B3LYP including 19% HF exchange at short-range and 65% HF exchange at long-range), B97D[60] (semiempirical xc functional additionally including C_6/R^6-type dispersive term), ωB97[61,62] (range-separated version of Becke's 97 functional with range separation parameter $\mu = 0.4$), ωB97X[61] (same as ωB97 but containing 16% short-range HF exchange term and $\mu = 0.3$), and ωB97XD[63] (same as ωB97 with additional dispersion correction, containing 22% short-range HF exchange term and $\mu = 0.2$). Analytical vibrational frequency computations at the optimized structure were then performed to confirm that the optimized structure was at an energy minimum. The LANL2DZ basis set has been generally employed for calculations of molecules with metal atoms, and the same level of calculations can be achieved for Ti, Sn, and Sc; therefore we used this basis set to represent the valence electrons of Ti, Sn, and Sc, where the effective core potentials (ECPs) were employed to replace core electrons. For C, N, and H atoms, the usual 6-311G(d) basis sets were employed. All these calculations were performed with the Gaussian09 program package.[64] All molecular structures were drawn with the GaussView5.0.[65]

Results and discussion

We would like to summarize briefly the experimental results on the molecular structures of these compounds up to now in our knowledge. The "stapled" D_2 molecular structure of $Ti(Pc)_2$ has been rigorously investigated and reported in its crystal structure.[9,10] The usual D_{4d} structure was also suggested from results on the elemental analysis and the electronic absorption spectrum;[11] however, its structural parameters have not been reported up to now. On the other hand, $Ti(Pc)_2^+$ has been reported to show the usual sandwich structure with D_{4d} symmetry even if starting a reaction with the D_2 neutral materials.[9,10] In the case of $Sn(Pc)_2$, both neutral and oxidized forms only showed D_{4d} structures.[12-14] The stable D_{4d} structure is also suggested for $Sc(Pc)_2$ as comparison with a X-ray diffraction pattern of lanthanide bisphthalocyanine.[66] This would imply that $Ti(Pc)_2$ probably takes both molecular structures depending on circumstances, but $Ti(Pc)_2^+$, $Sn(Pc)_2$, $Sn(Pc)_2^+$, and $Sc(Pc)_2$ prefer the D_{4d} geometry.

In order to investigate the molecular structures of $M(Pc)_2$ theoretically, we started with a selection of the appropriate

Table 1 The stability of the D_{4d} and D_2 structures for $Ti(Pc)_2$, $Ti(Pc)_2^+$, $Sn(Pc)_2$, $Sn(Pc)_2^+$, $Sc(Pc)_2$, and $Sc(Pc)_2^+$ in DFT calculation.

	$Ti(Pc)_2$		$Ti(Pc)_2^+$		$Sn(Pc)_2$		$Sn(Pc)_2^+$		$Sc(Pc)_2$		$Sc(Pc)_2^+$	
Functional	D_{4d}	D_2	D_{4d}	D_2	D_{4d}	D_2	D_{4d}	D_2	D_{4d}	D_2	D_{4d}	D_2
B3LYP	○	○	○	×	○	○	○	○	○	×	○	○
B3PW91	○	○	○	×	○	○	○	○	○	×	○	○
PBE1PBE	○	○	○	×	○	○	○	○	○	×	○	○
B3P86	○	○	○	×	○	○	○	○	○	×	○	○
BHandHLYP	○	○	×	×	○	○	×	×	○	×	○	○
BPW91	○	○	○	×	○	○	○	○	○	○	○	○
BP86	○	○	○	○	○	○	○	○	○	○	○	○
M06	○	○	○	○	○	○	○	○	○	○	○	○
M06-2x	○	○	×	○	○	○	×	○	○	×	○	○
M06-HF	×	○	×	×	×	○	×	×	×	×	○	○
M06L	○	○	○	○	○	○	○	○	○	○	○	○
LC-BPW91	×	○	○	×	×	○	○	×	○	×	×	×
LC-ωPBE	×	○	○	×	×	○	○	×	○	×	×	×
CAM-B3LYP	○	○	×	×	○	○	×	×	○	×	○	○
B97D	○	○	○	○	○	○	○	○	○	○	○	○
ωB97	×	○	○	×	×	○	○	×	○	×	○	○
ωB97X	×	○	×	×	×	○	×	×	×	×	○	○
ωB97XD	○	○	×	×	○	○	×	×	×	×	○	○

Table 2 The energetics of the D_{4d} and D_2 structures for $Ti(Pc)_2$, $Ti(Pc)_2^+$, $Sn(Pc)_2$, $Sn(Pc)_2^+$, $Sc(Pc)_2$, and $Sc(Pc)_2^+$ in DFT calculation.

	$Ti(Pc)_2$	$Ti(Pc)_2^+$	$Sn(Pc)_2$	$Sn(Pc)_2^+$	$Sc(Pc)_2$	$Sc(Pc)_2^+$
Functional	ΔE_{D2}	ΔE_{D2}	ΔE_{D2}	ΔE_{D2}	ΔE_{D2}	ΔE_{D2}
B3LYP	4.0	–	14.1	17.2	–	0.2
B3PW91	−2.0	–	9.0	15.8	–	0.3
PBE1PBE	−8.0	–	3.5	14.3	–	0.3
B3P86	−3.0	–	7.9	14.8	–	0.3
BHandHLYP	−27.3	–	−16.5	–	–	0.1
BPW91	14.1	–	24.6	0.3	0.3	0.3
BP86	13.4	0.3	23.7	0.3	0.3	0.3
M06	−6.5	−0.2	3.6	10.8	−0.5	−0.5
M06-2x	−16.1	–	−4.4	–	–	0.4
M06-HF	–	–	–	–	–	0.1
M06L	23.7	0.2	34.1	0.4	0.6	0.6
LC-BPW91	–	–	–	2.0	–	–
LC-ωPBE	–	–	–	6.1	–	–
CAM-B3LYP	−28.5	–	−17.6	–	–	0.1
B97D	23.2	0.0	33.8	0.1	0.0	0.0
ωB97	–	–	–	13.5	–	0.5
ωB97X	–	–	–	–	–	0.6
ωB97XD	−28.6	–	−16.7	–	–	0.6

functional, which could reproduce the experimental results for these systems. We performed the geometry optimizations of $Ti(Pc)_2$, $Ti(Pc)_2^+$, $Sn(Pc)_2$, $Sn(Pc)_2^+$, $Sc(Pc)_2$, and $Sc(Pc)_2^+$ under D_{4d} and D_2 symmetries with the DFT method using eighteen types of functionals. The imaginary vibration in analytical vibrational frequency calculations was an index of completeness for the geometry optimizations. The results are summarized in Table 1, where the optimized geometry with or without imaginary vibrations is indicated by a cross or a circle, respectively. The total energy of the D_2 structure was compared to that of the D_{4d} one for the functionals which gave the optimized structures under both D_2 and D_{4d} symmetries. The relative energies of the D_2 structure to the D_{4d} one are also compiled in the table as ΔE_{D2}.

All functionals tested in this study gave the optimized geometry with D_2 symmetry without imaginary vibration for $Ti(Pc)_2$, and many functionals revealed that the D_{4d} structures are at an energy minima for both $Ti(Pc)_2$ and $Ti(Pc)_2^+$. On the contrary, most of the functionals suggested that the optimized D_2 geometry of $Ti(Pc)_2^+$ has imaginary frequencies, and showed that the D_2 structure is more stable compared to the D_{4d} one for $Ti(Pc)_2$ and vice versa for $Ti(Pc)_2^+$ with respect to the total energy. This would imply that $Ti(Pc)_2$ has two stable structures and the geometry would depend on the environment, but $Ti(Pc)_2^+$ prefers the D_{4d} geometry, which is consistent with the expectations from the experimental results.[9,10] The relative energy difference between these two structures ranged from −28.6 to 23.7 kcal/mol for $Ti(Pc)_2$ and from −0.2 to 0.3 for $Ti(Pc)_2^+$. This shows that there exist some difficulties to reproduce the experimental results for these systems using the DFT method. Selection of an appropriate functional for these systems is crucial even for qualitative calculations.

For $Ti(Pc)_2$, thirteen types of functional (B3PW91, B3P86, PBE1PBE, BHandHLYP, M06, M06-2x, M06-HF, LC-BPW91, LC-ωPBE, CAM-B3LYP, ωB97, ωB97X, and ωB97XD) estimated the D_2 molecular structure to be more stable than the D_{4d} one agreeing with experimental observation. It should be noted that B3LYP, which is a generally used functional, shows different result from an experimental expectation. In addition, pure GGA (BPW91 and BP86) and standalone functionals (M06L and B97D) without the HF exchange term tended to show the D_2 structure to be less stable than the D_{4d} one for this compound.

On the other hand, the optimized structures under D_{4d} symmetry for $Ti(Pc)_2^+$ were more stable than those under D_2 symmetry in eight types of functionals (B3LYP, B3PW91, PBE1PBE, B3P86, BPW91, BP86, M06L, and ωB97) without imaginary frequencies. Additionally, the optimized geometries under D_2 symmetry were extremely similar to the D_{4d} structures in the case of four functionals (BP86, M06, M06L, and B97D), and a stable D_2 structure could not be obtained. The calculation results of LC-BPW91 and LC-ωPBE functionals showed that the D_2 structure was optimized to be more stable than the D_{4d} one but with imaginary frequencies, while the D_{4d} geometry had no imaginary frequency.

The relative energy difference between these two structures ranged from −17.6 to 34.1 kcal/mol for $Sn(Pc)_2$, while most of the functionals found the D_{4d} structure to be stable for $Sn(Pc)_2^+$, $Sc(Pc)_2$, and $Sc(Pc)_2^+$. This shows that an accurate description on the electronic structure of $Sn(Pc)_2$ requires a careful selection of the appropriate calculation method and an profound insight into the obtained results. Nine functionals (B3LYP, B3PW91, PBE1PBE, B3P86, BPW91, BP86, M06, M06L, and B97D) showed the optimized geometries with the appropriate symmetry agreeing with experimental observations, which suggested the D_{4d} molecular structures for these compounds.[12-14,66] It should be mentioned that the optimized structure of $Sc(Pc)_2$ with D_2 symmetry using M06 functional is close to that obtained with D_{4d} symmetry, and a stable D_2 structure could not be obtained. Moreover, the optimized geometries of $Sc(Pc)_2^+$ under D_2 symmetry using eighteen functionals were also close to those obtained under D_{4d} symmetry, which indicates that D_2 structure is not a minimum.

The calculation results suggest that two stable molecular structures with small energy difference exists for the double-decker type phthalocyanines, and the D_{4d} structure is usually stable as compared to the D_2 one except for $Ti(Pc)_2$, which prefers the latter. The reason why the molecule tends to take one of these two structures will be discussed later.

From the viewpoint of the calculation methods, several important aspects come out. Generally, the hybrid GGA and hybrid meta GGA functionals with 20-27% of the HF exchange term would give the molecular structures consistent with the experimental expectations for the double-decker type phthalocyanine compounds. Pure GGA and pure meta GGA functionals (BPW91, BP86, M06L, and B97D) have the tendency to overestimate the stability of the D_{4d} structure. On the other hand, functionals including 50 % or more HF exchange or the long-range corrections (BHandHLYP, M06, M06-2x, M06-HF, LC-BPW91, LC-ωPBE, CAM-B3LYP, ωB97, ωB97X, and ωB97XD) tend to overestimate the stability of the D_2 structure. It should be emphasized that the B3LYP functional, one of the most commonly used hybrid GGA functionals with 20 % of the HF exchange, cannot estimate the relative stability between the two molecular structures of $Ti(Pc)_2$ appropriately. The calculation for the systems considered in this article required well balanced treatment of the HF exchange with the accompanied exchange-correlation functional. In passing, even if using the 6-311G(d) basis set for all atoms instead of the LANL2DZ one, the B3LYP and PBE1PBE methods gave the same results for $Ti(Pc)_2$. The D_2 structure of $Ti(Pc)_2$ was still unstable about 5.6 kcal/mol by the B3LYP functional, and was stable about 6.2 kcal/mol by the PBE1PBE method as compared to the D_{4d} structure. Thus, as pointed rigorously and frequently, the selection of functional is a crucial point for reliability of the calculations.

Here, we would like to discuss the molecular structures of $Ti(Pc)_2$ and $Ti(Pc)_2^+$ with the results obtained from PBE1PBE, which gave the consistent results with the experimental data and showed good performance in these systems. $Ti(Pc)_2$ has a unique structure like a sandwich-type molecule "stapled" by two interligand C-C σ bonds with D_2 symmetry. The optimized distances between Ti and isoindole N (N_{iso}) atoms in $Ti(Pc)_2$ were calculated to be 2.176 and 2.260 Å and were almost the same as the observed values (2.170 and 2.260 Å).[9] The optimized lengths of interligand C-C σ bond were calculated to be 1.580 Å and were slightly longer than the observed values (1.556 and 1.575 Å). On the other hand, $Ti(Pc)_2^+$ has the usual sandwich structure with D_{4d} symmetry. The optimized distances between Ti and isoindole N (N_{iso}) atoms in $Ti(Pc)_2^+$ were calculated to be 2.250 Å and were almost the same as the observed value (2.246 Å).[10]

These results provide a clear understanding on the stable molecular structures of the double-decker type phthalocyanine compounds, $M(Pc)_2$ and $M(Pc)_2^+$. Firstly, the compounds with the open-shell π-electron system preferred strongly to take the D_{4d} molecular geometry even in the case of the central metal atom with the relatively small ionic radius. The stability of the D_{4d} molecular structure arises from reduction in the exchange repulsion between electrons of two Pc moieties due to a deficiency of an electron and from stabilization by delocalization of an unpaired electron over the whole molecule. Secondly, the compounds with the closed-shell electron system would take one of two stable structures with D_{4d} or D_2 symmetry. We propose that the molecular symmetry depends on the balance between stabilization due to electron delocalization and exchange repulsion of π-electrons; therefore, the ionic radius of the central metal atom would be a crucial parameter.

Compared to Sn and Sc, Ti has a small ionic radius which plays an important role in the stability of the two structures for $M(Pc)_2$. The ionic radius of Ti^{4+}, Sn^{4+}, and Sc^{3+} are 0.74, 0.81, and 0.87 Å,[67] respectively. The interligand C-C σ bond of the D_2 geometry is shorter than the diameters of Sn^{4+} and Sc^{3+} estimated from twice their ionic radii, but longer than that of Ti^{4+}. Therefore, it can be predicted that the D_2 structure will become rather unstable for Sn and Sc, while both D_2 and D_{4d} structures are stable for Ti. Our calculation using appropriate functionals confirms this as well.

We finally discuss the origin of the different behavior found in calculations for the double-decker type phthalocyanine compounds, $M(Pc)_2$ and $M(Pc)_2^+$ employing the well established eighteen functionals. Pure GGA and pure meta GGA functionals showed the tendency to overestimate the stability of the D_{4d} structure through an underestimate of the exchange repulsion of

π-electrons in the phthalocyanine moieties. On the other hand, functionals including 50 % or more HF exchange tended to overestimate the stability of the D_2 structure, because the exchange repulsion of π-electrons would be overestimated. Long-range corrected functionals employed in our calculations showed the same tendency and also overestimated the exchange repulsion. Long-range corrected functionals usually divide the exchange term into long-range and short range parts, and the two electron operator, $1/r_{12}$, is described by using the standard error functions, erf(μr) and erfc(μr) for the long-range and short-range parts, respectively, as $1/r_{12}$ = erf(μr)/r + erfc(μr)/r,[54,68] where r is relative coordinate between two electrons and μ is an adjustable parameter. The amount of HF exchange in long-range corrected functionals depends on the parameter μ. It should be noted about the recent development in this field of the range-separated functionals, especially on non-empirically tuned range-separated functionals,[69,70] in which the HF exchange is determined non-empirically. Actually, a remarkable success has been achieved in describing the electronic structure of CuPc monomer,[34] where the amount of μ was appropriately optimized. This method should remedy our results employing long-range corrected functionals through adjusting the exact amount of HF exchange.

The appropriate functionals for the present systems treated the stabilization due to electron delocalization and the destabilization due to exchange repulsion of π-electrons well-balanced. This can be confirmed by comparing the calculation results of BPW91, B3PW91, and LC-BPW91 for $Ti(Pc)_2$ and $Sn(Pc)_2$. The difference among these functionals is the amount of HF exchange included. BPW91, which is a pure functional without HF exchange, underestimated the exchange repulsion and estimated the D_{4d} structure to be stable for both $Ti(Pc)_2$ and $Sn(Pc)_2$. LC-BPW91, which contains long-range correction using HF exchange, on the other hand, gave the opposite results. By contrast with these calculations, B3PW91 predicted the D_2 and D_{4d} structures for $Ti(Pc)_2$ and $Sn(Pc)_2$, respectively, which agreed with experimental results. The amount of HF exchange in balance with the accompanied correlation-exchange functional may be a key for quantitative calculation of these challenging systems such as those considered in this article.

Conclusion

We reported the results of theoretical calculations on the optimized structures and relative energies between the D_{4d} and D_2 structures for $Ti(Pc)_2$, $Ti(Pc)_2^+$, $Sn(Pc)_2$, $Sn(Pc)_2^+$, $Sc(Pc)_2$, and $Sc(Pc)_2^+$ using the eighteen types of functionals: B3LYP, B3PW91, B3P86, PBE1PBE, BHandHLYP, BPW91, BP86, M06, M06-2x, M06-HF, M06L, LC-BPW91, LC-ωPBE, CAM-B3LYP, B97D, ωB97, ωB97X, and ωB97XD.

We conclude from the present calculation results that $Ti(Pc)_2$ tends to take a D_2 molecular structure with two C-C σ bonds in the neutral state but a D_{4d} structure similar to usual double-decker type compounds in the oxidized state. On the other hand, $Sn(Pc)_2$ and $Sc(Pc)_2$ would be revealed to prefer the D_{4d} structure in both the neutral and oxidized states. These results were consistent with the expected molecular geometries of these compounds from the experimental observations.

The compounds with the open-shell π-electron system preferred strongly to take the D_{4d} molecular symmetry, and compounds with the closed-shell electron system would take one of two stable structures with the D_{4d} or D_2 symmetry. The stability of the D_{4d} molecular structure arises from delocalization of an unpaired electron over the whole molecule, while the D_2 structure is stabilized from exchange repulsion of π-electrons. We suggest that the molecular symmetry depends on the balance between stabilization due to electron delocalization and exchange repulsion of π-electrons for the double-decker type phthalocyanine compounds, $M(Pc)_2$ and $M(Pc)_2^+$.

We assessed the performance of the well established functionals to select the appropriate one, and several important aspects came out. Generally, the hybrid GGA and hybrid meta GGA functionals with 20-27 % of the HF exchange term would give the molecular structures consistent with the experimental expectations for the double-decker type phthalocyanine compounds. Pure GGA and pure meta GGA functionals have the tendency to overestimate the stability of the D_{4d} structure, because the exchange repulsion of π-electrons in the phthalocyanine moieties are underestimated. On the other hand, functionals including HF exchange 50 % and over or including long-range corrections tend to overestimate the stability of the D_2 structure, because the exchange repulsion of π-electrons are overestimated. It should be noted that the B3LYP functional cannot estimate the relative stability between the two molecular structures of $Ti(Pc)_2$ appropriately. The calculation for the systems considered in this article required well balanced treatment of the HF exchange. Thus, the selection of functional is a crucial point to reliability of the calculations.

Notes and references

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† Electronic Supplementary Information (ESI) available: Cartesian coordinates for $M(Pc)_2$ and $M(Pc)_2^+$ with the PBE1PBE functional. See DOI: 10.1039/b000000x/

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