Significant differences in electronic structure among X-, α- and β-forms of lithium phthalocyanine †

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The X-type dimer of lithium phthalocyanine adopts a significantly different electronic structure from those of the α- and β-type dimers, which leads to a different absorption spectrum and magnetic properties for the X-polymorph compared to those of the α- and β-polymorphs.

Lithium phthalocyanine (LiPc; Pc = phthalocyaninato anion $C_{32}H_{16}N_8^{2-}$) has received recent attention since it forms an unexpectedly stable radical in air and is one of the rare intrinsic semiconductors from which many new applications are expected. In this regard, its electronic structure should be clarified.

Three polymorphs, X-, α- and β-forms, have been reported in powder samples and thin films of LiPc.[1–3] Interestingly, the absorption spectra of the α- and β-forms are quite different from the spectrum of the X-form,[1,3] while all three polymorphs exhibit almost the same ultraviolet photoelectron spectra in the valence region which are similar to those of usual MPcs (M = H_2 or divalent metals) with a closed-shell system.[4] Since both absorption and photoelectron spectra are closely related to the electronic structure, we wondered why the absorption spectra are different but the photoelectron spectra are the same in these three polymorphs. Thus, we need knowledge of the electronic structures of LiPc and its polymorphs. However, a detailed study has not been reported yet. In this communication, we investigated the absorption spectrum of LiPc in solution, in expectation that the spectrum would provide valuable information on an LiPc monomer. Also, we investigated LiPc and its dimers (three polymorphs: α-, β- and X-forms), by the DFT method. Our aims here are to present a clear understanding of the absorption spectra, the valence bands of the ultraviolet photoelectron spectra, and the electronic structures of the α-, β- and X-polymorphs.

As shown in Table 1 (and in the ESI), the absorption spectra of α- and β-polymorphs are almost the same as those observed in solution, while, interestingly, the spectrum of the X-polymorph is quite different from that of the solution. These results clearly show that the X-polymorph adopts a different electronic structure to that of the free LiPc monomer but the α- and β-polymorphs adopt almost the same electronic structure as the monomer.

The unrestricted DFT method with the B3LYP functional was employed for the LiPc monomer and the dimers with the triplet spin state (*vide infra*). For the dimer with the singlet spin state, the usual restricted DFT method was employed. In the X-type dimer, the distance between two LiPc planes and the staggering angle between two LiPc moieties were optimized with the 3-21G basis set, where the geometry of the LiPc moiety was taken to be the same as the optimized one of the free LiPc molecule. In α- and β-type dimers, both the inter-plane distance

between two LiPc moieties and the tilt angle between the LiPc plane and the Li–Li line were optimized. In the singlet state, non-dynamical electron correlation should be taken into consideration, since two electrons occupy two orbitals which are close in energy. Here, we carried out preliminary CAS-SCF calculations in which two orbitals and two electrons were considered. The ionization energies were calculated with the ΔSCF method, where Huzinaga–Dunning (9s5p/3s2p) basis sets[5] were used for all atoms with a d-polarization function added to the N atom. The Gaussian 98 program package was used for these calculations.[6]

The optimized geometry of the LiPc monomer agrees well with the experimental one for the LiPc moiety in the X-polymorph (see ESI). The unpaired electron of LiPc is in the $2a_{1u}$ orbital (SOMO), which is a π-orbital without a contribution from the p_z orbital of N, as shown in Fig. 1.
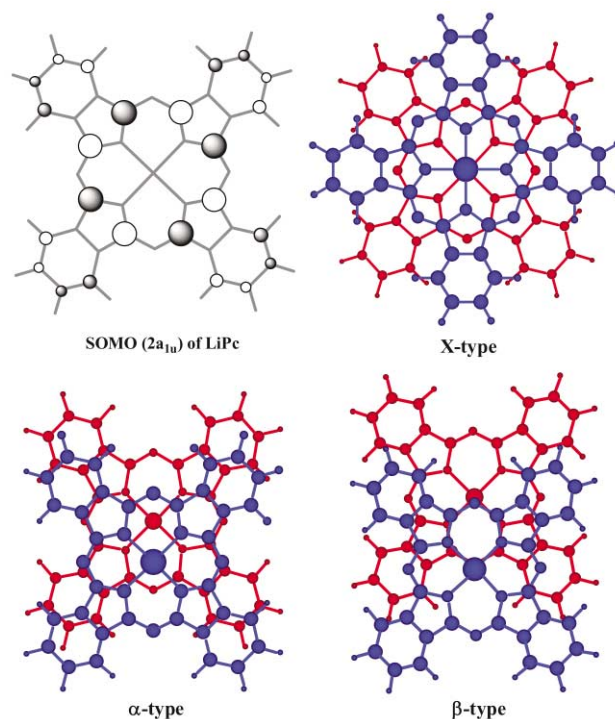

Fig. 1 SOMO of the LiPc molecule and overlap of two LiPc moieties in the X-, α- and β-type dimers.

The inter-plane distance and the tilt angle of the three dimers agree well with the experimental values,[1–3] as shown in Table 1. The optimized X-type dimer has D_{4d} symmetry, where the staggering angle is 45°. This angle is moderately larger than the reported value of 38.7°.[1] The structure with the angle of 38.7° is slightly less stable than the optimized one by 2.3 kcal mol⁻¹, where only the staggering angle was changed to 38.7° without any other change. The observed staggering angle of 38.7° may be due to the crystal packing. The eclipsed structure is also

† Electronic supplementary information (ESI) available: absorption spectra, optimized geometry of LiPc, and the singlet and triplet energies of the α- and β-type dimers calculated by the DFT method. See http://www.rsc.org/suppdata/dt/b2/b209869e/

Table 1 Optimized structures and total energies of three LiPc dimers, and λ_{max} of solids and solutions

		X-Type	α-Type	β-Type
Plane distance/Å	Calcd.	3.25	3.67	3.53
	Obsd.	3.245[a]	3.41[b]	3.46[c]
Tilt angle/°	Calcd.	—	63.2	42.7
	Obsd.	—	63.5[b]	44.5[c]
ΔE^{d}/kcal mol^{-1}	Singlet	−9.8[e] (−12.3)[f]	−3.3[e]	−5.4[e]
	Triplet	−4.9[g] (−7.1)[f]	−4.0[g]	−6.4[g]
λ_{max}/nm	Solid	1620, 693	821, 717	806, 720
		488, 438	507, 439	510, 430[c]
	Solution		810, 700, 488, 430	

[a] Ref. 1. [b] Ref. 2. [c] Ref. 3. [d] The stabilization energy of dimers relative to two LiPc molecules. [e] CAS-SCF. [f] DFT. [g] ROHF.

calculated to be less stable than the optimized one by 10.5 kcal mol^{-1} with the DFT method. In contrast, the α- and β-type dimers have C_{2h} symmetry.

The DFT and CAS-SCF calculations clearly indicate that the X-type dimer adopts a singlet state, as shown in Table 1. In the X-type dimer, with a staggering angle of 38.7°, the singlet state is more stable than the triplet state by 3.7 kcal mol^{-1} (DFT), too. In the α- and β-type dimers, on the other hand, CAS-SCF calculations indicate little difference in energy between singlet and triplet states. This is the first theoretical support that an anti-ferromagnetic interaction exists in the two LiPc moieties of the X-type dimer but that the unpaired electrons are independent of each other in the α- and β-forms. Actually, an EPR study[7] reported that the spin concentration is about 0.05–0.1 per LiPc molecule in the X-form but 0.8 and 0.7 per LiPc molecule in the α- and β-forms, respectively.

It is of considerable interest to clarify why the X-type dimer takes a different spin state from the α- and β-type dimers. This difference arises from the SOMO–SOMO overlap between two LiPc moieties, as follows: The HOMO of the X-type dimer consists of the bonding overlap between two LiPc moieties. This is because two LiPc moieties rotate by 45° to each other in the X-type dimer and as a result the SOMO of one LiPc overlaps well with that of the other LiPc in a bonding way, as shown in Fig. 1. The overlap between SOMOs decreases by only 6% with the decrease in the staggering angle from 45 to 38.7°. Though the eclipsed structure provides good overlap between SOMOs, the outer phenyl groups give rise to steric repulsion, which disfavors this structure, as discussed above. In the α- and β-type dimers, the SOMOs overlap poorly with each other due to the tilt angle. As a result, the two LiPc planes are very distant and two unpaired electrons exist independently in each LiPc moiety. This difference in the SOMO–SOMO overlap is important in understanding the physicochemical properties of α-, β- and X-polymorphs of LiPc, as will be discussed below.

Important orbital energies of dimers are shown in Fig. 2, where notations are given with the D_{4d} representation for the X-type dimer and with the C_{2h} representation for the α- and β-type dimers. The orbitals of the X-type dimer are generated from two orbitals of the LiPc moiety through in-phase or out-of-phase combination, where plus and minus signs in parentheses represent the in-phase and out-of-phase combinations, respectively. The molecular orbitals, which mainly consist of the SOMO of the LiPc monomer, are remarkably different between the X-type dimer and the others; the energy difference between the in-phase and out-of-phase combinations was estimated to be 1.2 eV in the X-type dimer (DFT), whereas these two orbitals of the other dimers are nearly degenerate. As a result, the X-type dimer takes a singlet state but the α- and β-type dimers take a triplet state.

The orbital energy diagram also provides clear understanding of the different absorption spectra of these polymorphs, as follows: (1) The α- and β-polymorphs should show almost the same spectrum as that of the free LiPc molecule, since each LiPc molecule is independent in these polymorphs. (2) The
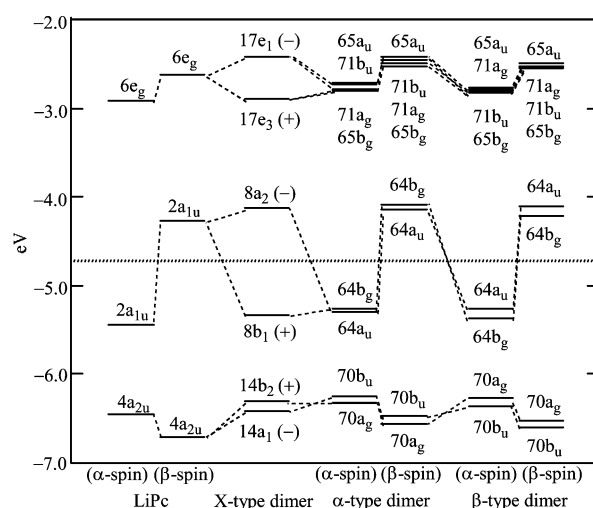

Fig. 2 Several frontier orbitals near the HOMO and LUMO of LiPc and its dimers. The orbital symmetries are labelled under the D_{4h}, D_{4d}, C_{2h} and C_{2h} symmetries for the LiPc molecule, X-, α- and β-type dimers, respectively. The orbitals below the dotted line are occupied.

X-polymorph exhibits a completely different spectrum from those of the other two polymorphs and LiPc in solution since the $8b_1$ MO is doubly occupied. (3) In the X-polymorph, three excitations occur; one is the excitation from $8b_1$ to $8a_2$ which would be observed in the near-IR region, and the second and the third ones arise from excitations from $8b_1$ to $17e_3$ and from $14b_2$ to $17e_3$ which would be observed in the UV-VIS region. And, (4) the former excitation has a transition dipole moment perpendicular to the molecular plane, while the latter two excitations possess a transition dipole moment parallel to the molecular plane. All these results agree with the experimental data.[8] In other words, the differences in absorption spectra are reasonably interpreted in terms of the energy diagram of Fig. 2.

The ionization potential was evaluated to be 6.26, 6.14, and 6.15 eV for the X-, α- and β-type dimers, respectively. The difference in these values is less than the resolution of photoelectron spectroscopy of the solid state sample. Thus, the computational results clearly show that three polymorphs possess different electronic structure and spin state but exhibit almost the same ionization potential in the photoelectron spectrum.

In summary, we have presented in this study the first clear understanding of electronic structures, absorption and photoelectron spectra and magnetic properties of LiPc polymorphs.

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