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Intermolecular Interaction as the Origin of Red Shifts in Absorption Spectra of Zinc-Phthalocyanine from First-Principles

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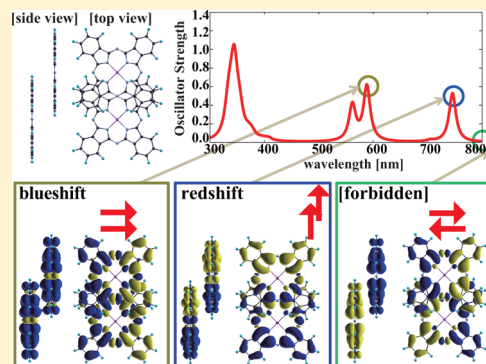
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ABSTRACT: We investigate electronic origins of a redshift in absorption spectra of a dimerized zinc phthalocyanine molecule (ZnPc) by means of hybrid density functional theoretical calculations. In terms of the molecular orbital (MO) picture, the dimerization splits energy levels of frontier MOs such as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the constituent molecules. Consequently, the absorption wavelength seems to become longer than the monomer as the overlap between the monomers becomes larger. However, for a ZnPc dimer configuration with its cofacially stacked monomer arrangement, the calculated absorption spectra within the time-dependent density functional theory indicates no redshift but blueshift in the Q-band absorption spectrum, i.e., a typical H-aggregate. The origin of the apparently contradictory result is elucidated by the conventional description of the interaction between monomer transition dipoles in molecular dimers [Kasha, *M. Radiat. Res.* **1963**, *20*, 55]. The redshift is caused by an interaction between the two head-to-tail transition dipoles of the monomers, while the side-by-side arranged transition dipoles result in a blueshift. By tuning the dipole–dipole interaction based on the electronic natures of the HOMO and the LUMO, we describe a slipped-stacked ZnPc dimer configuration in which the Q-band absorption wavelength increases by as large as 144 nm relative to the monomer Q-band.



INTRODUCTION

Zinc-phthalocyanines (ZnPc) have currently attracted considerable attention as promising photoelectric device materials for energy conversion, such as dye-sensitized solar cells and organic thin-film solar cells. The characteristic absorption bands in the red portion of the sunlight spectrum, which is known as Q-bands often exhibiting high molar extinction coefficients ($\epsilon > 10^4$ [M⁻¹ cm⁻¹]), have been theoretically and experimentally studied in order to extend the excitation window of absorber materials to a near-infrared region.

In tuning the excitation window, modification of the excited states of chromophores induced by molecularly stacked aggregation is of primary interest. Two stack configurations of chromophore molecules, i.e., those with face-to-face cofacial configurations, often referred to as H-type aggregates, and slipped-cofacially stacked configurations, known as J-type aggregates, have been highlighted. It was shown that the slipped-cofacially stacked spatial arrangement fine-tunes the electronic excited states and the electronic energy transfer in the special pair and subunits in photosynthetic light-harvesting antenna consisting of bacteriochlorophyll dimers.^{1,2} For

fluorescence properties, it has been known that in general the J-type aggregates are fluorescent, while the H-aggregates are not,^{3–5} although there are some exceptions.⁶

J-type aggregates of ZnPc have rarely been reported.^{7–10} Based on UV–vis spectroscopy, fluorescence spectroscopy, and MALDI-TOF mass spectrometry measurements of substituted ZnPc's, Huang et al. proposed formation of J-type self-aggregation via Zn–O coordination in noncoordinating solvents at room temperature.⁷ In terms of the molecular orbital (MO), it was shown that the dimerization of ZnPc involved the interaction between the frontier orbitals of the monomers such as the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO), and the redshift resulted from the stabilized LUMO and the destabilized HOMO relative to the monomer.⁸

Given the difficulty in synthesizing the ZnPc J-aggregates, it seems to be difficult to see in experiments what happens

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electronically upon aggregation of the molecules. As reviewed by Kasha, the dipole-allowed redshift in a molecular dimer is realized in case the transition dipoles of the constituent monomers are arranged in a head-to-tail manner.¹¹ In other words, the signs of the wave functions of the initial and final states are opposite with respect to the polarization orientation, so that a matrix element of the transition dipole moment remains.

In the present study, by examination of molecularly stacked dimer configurations of an unsubstituted ZnPc molecule with a density functional theoretical calculation, we simulate dimer configurations and resulting absorption spectra with a red- or blueshift relative to the monomer spectra. We describe a red- or blueshift in terms of the nature of the electronic structure and the resulting transition dipole moment. Although there has been no experimental report of the stable dimer of an unsubstituted ZnPc, simulating an electronic state of the smallest possible ZnPc dimer may enable us to clarify an electronic factor dominating the absorption shifts and may thus lead to the design of ZnPc aggregates with favorable excitation windows.

We show that a slipped-stacked dimer configuration gives a large redshift of 144 nm, with the constituent monomer transition dipole moments being stacked in a head-to-tail manner. The calculated formation energy relative to isolated monomers indicates that the dimer is metastable. The large redshift is elucidated in terms of the signs of the frontier molecular orbitals of the monomer such as the HOMO and the LUMO and the resulting transition dipole moments. Such insight may give us a hint to designing dye-molecule aggregates with desirable absorption wavelengths in the optical or near-IR regions.

THEORETICAL METHODS

For the dimer configurations of an unsubstituted ZnPc molecule as we will describe below, we calculate absorption spectra with the time-dependent density functional theory (TDDFT) in the linear-response (-LR) regime,^{12–14} as implemented in the Gaussian 03 program code.¹⁵ The exchange-correlation effect is included with the Becke's three-parameter hybrid functional denoted as B3LYP.¹⁶ We use the 6-31G(d) Gaussian basis set to expand the molecular wave function. The B3LYP/6-31G(d) level of theory was found to describe well the molecular structure and the Q-band of unsubstituted ZnPc or its derivatives, in which no charge-transfer or no d–d excitation was involved because of the closed-shell d¹⁰ configuration of Zn.^{8,17–19}

Within TDDFT-LR, the excitation energy ω_1 is obtained as the square root of an eigenvalue of a matrix eigenvalue problem

$$\Omega \mathbf{F}_1 = \omega_1^2 \mathbf{F}_1 \quad (1)$$

where \mathbf{F}_1 is an eigenvector describing the contributions of occupied-unoccupied orbital pairs to the excitation and qualitatively describes the character of the excited state wave function.^{12–14} The oscillator strength is calculated from \mathbf{F}_1 . For the definition of Ω , see refs 12–14.

We examine dimer configurations of the unsubstituted ZnPc molecule (for the HOMO and the LUMO wave functions of a single ZnPc molecule, see Figure 1). We consider various geometric structures of a ZnPc dimer (see Figure 2), in which two ZnPc molecules are (a) cofacially superposed, (b) planar-arranged side by side, (c and d) partially superposed, with the

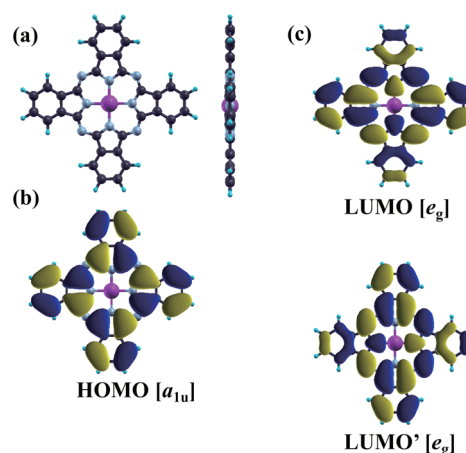


Figure 1. (a) Molecular structure of ZnPc. The H, C, N, and Zn atoms are displayed by a small-sized, middle-sized dark, middle-sized gray, and large sphere, respectively. (b and c) Isosurfaces of the HOMO and the LUMO wave functions of ZnPc monomer as obtained with the B3LYP/6-31G(d) level of theory, along with the irreducible representation. Note that there is a degenerate pair of LUMOs, one of which is obtained by 4-fold rotation of the other, as displayed in (c). They are denoted as LUMO and LUMO'. The difference in brightness of the isosurfaces indicates a difference in sign.

molecules slightly slipped along the superposed molecular axes, or (e and f) partially superposed, with the molecular axes being parallel and a Zn atom in one molecule is placed on the diagonal direction of the other molecule. Notice that in configuration (e), a Zn atom is positioned above one of the four meso-bridging aza N (N_m) atoms surrounding another Zn atom, and in configuration (f), one of the four N_m atoms in a monomer is positioned above another N_m atom in another monomer.

Intuitively, an increase in overlap between monomers causes the energy gap between the HOMO and LUMO to decrease, while the HOMO–LUMO gap is similar to that of an isolated single molecule in the dimer configurations with almost no overlap between the wave functions, for instance, in configuration (b). We did not optimize the dimer geometric structures, so as to clarify the effect of the molecular stacking on the electronic properties. We used the B3LYP-optimized monomer geometry in constructing the dimer configurations.

As far as the Q-band of the dimers is concerned, we find that inclusion of the long-range correction (LC) into the TDDFT-LR^{20,21} does not affect the calculated excitation energies.²² We thus confirm the effectiveness of the present approach without LC in the excitations of the dimers and that the charge-transfer excitation between the monomers seems to play a minor role.

Formation energies of the dimers relative to the isolated monomers are calculated by using DFT-D2 as proposed by Grimme²³ describing the dispersion forces between the monomers, as implemented in the STATE program code.²⁴ Electron–ion interactions are described by pseudopotentials,^{25,26} and wave functions and augmented charge density are expanded using a plane-wave basis set with the cutoff energies of 25 and 400 Ry, respectively. To avoid artificial interactions between the periodic replicas, we use a large unit cell in which the distances between the periodic images are more than 15 Å.

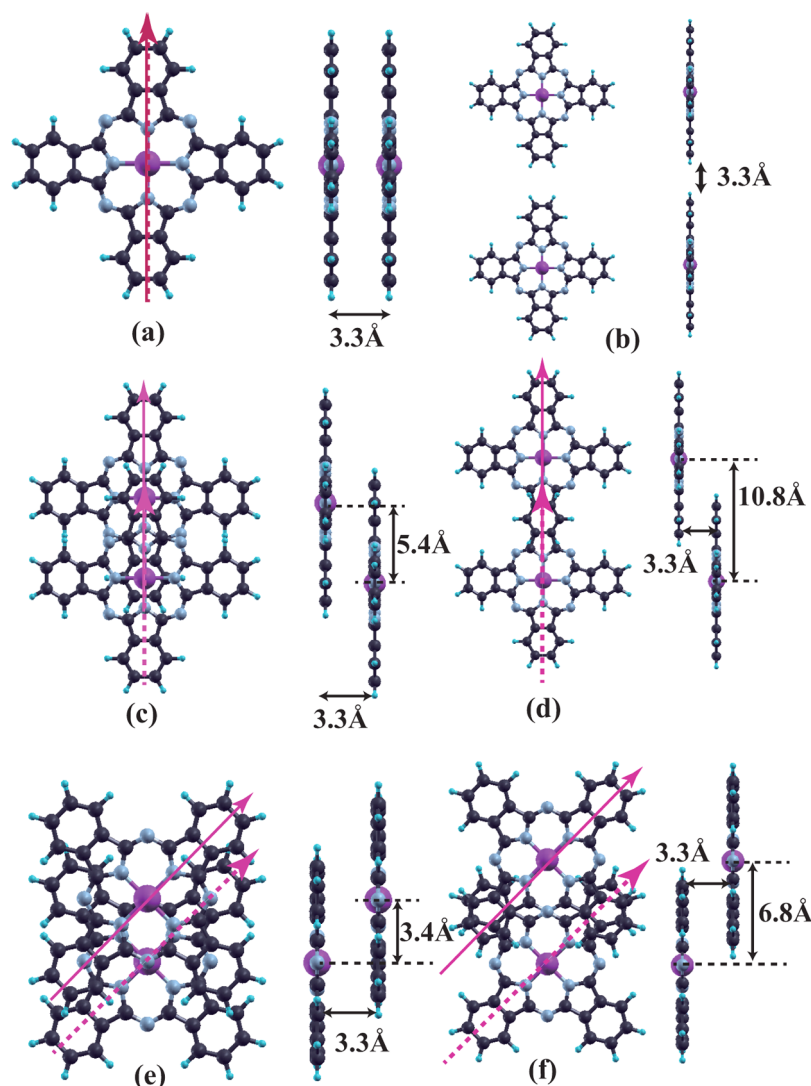


Figure 2. Dimer configurations investigated in the present study (left: top view; right: side view). Note that the distance between the monomer planes is fixed to 3.3 Å, and the intramolecular structure is fixed to that of the optimized isolated molecule. The H, C, N, and Zn atoms are displayed by a small-sized, middle-sized dark, middle-sized gray, and large sphere, respectively. The molecular axis of each of the monomers is displayed as a solid arrow or a dashed arrow. For the detail of the structures, see the Theoretical Methods section.

RESULTS AND DISCUSSIONS

HOMO and LUMO Levels of ZnPc Monomers and Dimers. Molecular orbital (MO) character of the HOMO and the LUMO of the monomer obtained with B3LYP/6-31G(d) is displayed in Figure 1. The calculated HOMO–LUMO energy gap is shown in Table 1. The calculated gap is 2.19 eV, in good agreement with a previous study using the same methodology,²⁸ and is in reasonable agreement with the energy gap observed with photoemission technique of 1.94 eV.²⁷ The HOMO extends along the orthogonal molecular axes, while the degenerate LUMOs extend along one of the molecular axes, implying that in-plane transition dipole moment along the molecular plane is involved in the electronic transitions between the HOMO and the LUMO.

In order to examine change in the HOMO–LUMO gap induced by intermolecular interactions, we investigated ZnPc dimers with several configurations (see Figure 2a–f). It is found that the HOMO–LUMO gap decreases in all of the dimer configurations. Specifically, the HOMO–LUMO gap of the cofacial dimer (a), with the largest geometrical overlap between

Table 1. HOMO–LUMO Energy Gap of ZnPc Monomer and Dimers Calculated at the B3LYP/6-31G(d) Level^a

	B3LYP	ref
monomer	2.19	1.94 ^b
dimer (a)	1.35	
dimer (b)	2.15	
dimer (c)	2.06	
dimer (d)	2.08	
dimer (e)	2.05	
dimer (f)	1.87	

^aUnits are in eV. For notations and the geometric configurations of the dimers, see Figures 1 and 2. ^bReference 27. Photoemission experiment.

the monomers, is 1.35 eV. The shrinking of the HOMO–LUMO energy gap of aggregates originates from the HOMO–HOMO and the LUMO–LUMO interactions between the monomers.⁸

Absorption Spectra of Unsubstituted ZnPc Monomer: Absorption Strengths and Absorption Peak Shifts.

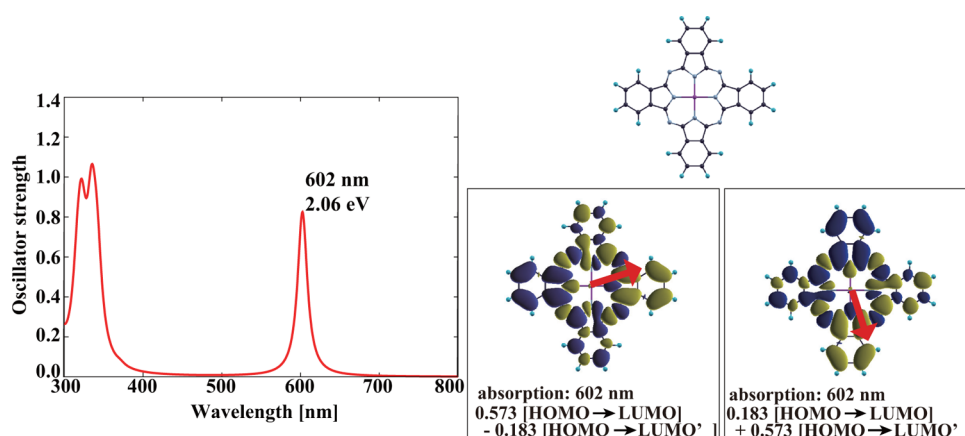


Figure 3. Q-band absorption spectra of the unsubstituted ZnPc molecule. The spectrum simulated at the B3LYP/TDDFT level is described by the calculated oscillator strengths and the excitation energies broadened with Lorentzian functions. The resulting transition dipole moments are shown by the arrows, whose directions are tilted from the molecular axes because of the mixing transitions to the degenerate LUMO's. The first-order density responses of the two degenerate excitations constituting the Q-band peak are displayed as isosurfaces, describing the characters of the excitations (see eq 4). The dominant transitions and the corresponding eigenvector components of the TDDFT-LR equation (eq 1) are also shown. The difference in brightness of the isosurfaces indicate a difference in sign.

Figure 3 shows the simulated absorption spectrum of the ZnPc molecule. The calculated HOMO–LUMO excitation energy of 2.06 eV (602 nm), corresponding to the Q-band ($a_{1u} \rightarrow e_g$), is in reasonable agreement with the experimental values of 1.85–1.89 eV (671–656 nm) observed in gas phase²⁹ or Ar matrix.³⁰ The calculated absorption peak largely consists of the two excitations from the HOMO to the degenerate LUMO's (denoted as LUMO and LUMO'). Because of the fractional proportions of the HOMO–LUMO and the HOMO–LUMO' excitations with their polarizations along the different orthogonal molecular axes, the resulting transition dipole moments are tilted from the molecular axes. The shorter absorption wavelength or higher excitation energy, obtained with the B3LYP/TDDFT methodology, than experiments is consistent with the previous theoretical study of ZnPc molecule or Zn-based porphyrin derivatives employing the same methodology, in which the calculated excitation energies were larger than experiments by 0.1–0.4 eV.^{18,19}

The result does not describe the two smaller absorption peaks close to the main Q-band peak which have been labeled as Q(1,0) and Q(2,0) vibronic contribution, ranging between 590 and 620 nm, with the main peak being at 656 nm, observed in Ar matrix.³⁰ Based on the TDDFT calculation employing a pure exchange-correlation functional, Nemykin et al. proposed the origin of the Q(2,0) envelope to be coupling of the electronically forbidden 1^1E_g symmetry HOMO–1 \rightarrow LUMO transition with an e_u symmetry vibrational normal mode, although they did not actually take into account the vibronic effect in the calculation.¹⁸ The present calculation included no vibronic effect, and we found the corresponding excitation to be 413 nm (3.00 eV), quite higher than the Q-band. The theoretical excitation energy of the 1^1E_g state seems to be more sensitive to the portion of the Hartree–Fock exchange incorporated into the exchange functional than the main Q(0,0) peak.¹⁸ In the present study, we will focus on the main Q(0,0) peak modified by the dimerization of ZnPc.

The solvent effect on absorption spectra of ZnPc solute was investigated both theoretically and experimentally in ref 18. Both the experimental UV–vis spectra and the simulated excitation energies within TDDFT employing hybrid functionals indicated that the shift in the absorption spectra was

0.01–0.03 eV with respect to the solvent such as hexane, toluene, dichloromethane, and dimethylsulfoxide. Compared to the small shift with respect to the solvents, the appreciable redshift in absorption and fluorescence spectra of ZnPc, which was ascribed to the J-aggregate formed by slipped-stacked dimerization, indicates modification of the electronic structure through the π – π interaction between the monomers.^{7–10} Next, as a possible source of the large redshift, we examine the effect of the stacking of ZnPc molecules.

Absorption Spectra of the ZnPc Dimer: Absorption Strengths and Absorption Peak Shifts.

As we mentioned above, we investigate the electronic excitation in the ZnPc dimer configurations, specifically the Q-band absorption modified by the intermolecular interaction. The distance between the two ZnPc molecular planes is fixed to 3.3 Å, based on the similar optimized interplane distances of MgPc and NiPc obtained with the van der Waals (vdW) correction to the DFT calculation.³¹

Figure 4 displays the Q-band absorption spectra of the ZnPc monomer, cofacially stacked (for the geometrical configuration,

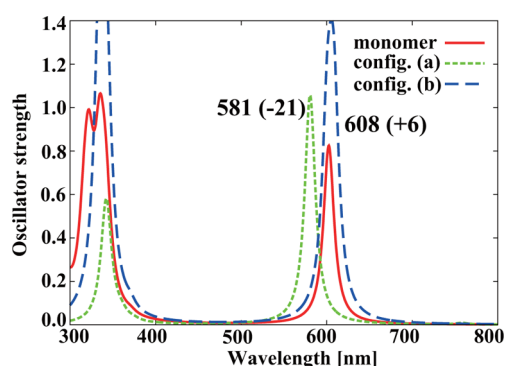


Figure 4. Absorption spectra of ZnPc dimers with configurations (a) and (b). The computed absorption wavelength is displayed in units of nm, along with the difference from the Q-band peak of the monomer in parentheses. The spectra simulated at the B3LYP/TDDFT level are described using the calculated oscillator strengths and the excitation energies broadened with Lorentzian functions. The simulated spectrum of the monomer is displayed for comparison.

see Figure 2a), and side-by-side arranged (Figure 2b) ZnPc dimers, corresponding to largest and zero geometrical overlap between the monomers, respectively. It is found that the cofacial stacking results in blueshift by 21 nm relative to the monomer Q-band. On the other hand, depositing the monomers side-by-side, without any geometrical overlap, causes the absorption wavelength to slightly increase by 6 nm. The results indicate that increasing the geometrical overlap between the monomers does not always redshift the absorption peak, even with the significant decrease in the HOMO–LUMO gap by 1.84 eV. On the contrary, the absorption peak is further blueshifted, indicative of a typical H-aggregate. Figure 5 displays

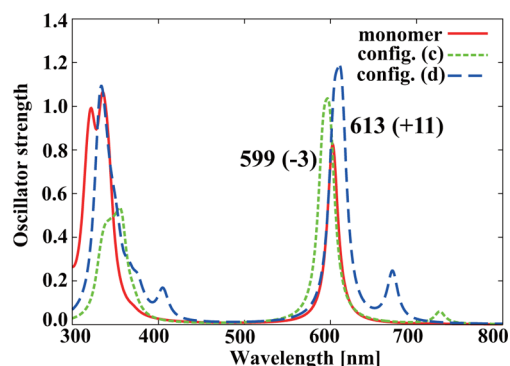


Figure 5. Absorption spectra of ZnPc dimers with configurations (c) and (d). The computed absorption wavelength is displayed in units of nm, along with the difference from the Q-band peak of the monomer in parentheses. The spectra simulated at the B3LYP/TDDFT level are described using the calculated oscillator strengths and the excitation energies broadened with Lorentzian functions.

the simulated Q-band of configurations (c) and (d). In configuration (c), the cofacially stacked monomers (configuration (a)) slip on the molecular axis of the other monomer by 5.4 Å. In configuration (d), the monomers shift by twice the distance of that in configuration (c). Similarly to configurations (a) and (b), the large overlap between the monomers in configuration (c) causes the blueshift by 3 nm, while the further slipped configuration (d) results in the redshift by 11 nm.

We investigate other types of slipped stacked configurations (e) and (f), in which the molecular axes of the monomers are parallel and a central Zn atom in one molecule is located on the diagonal direction of the other molecule. The resulting Q-band peak is displayed in Figure 6. As was found in the other configurations, the largely overlapped monomers (see Figure 2e) cause the blueshift relative to the monomer Q-band peak by 5 nm. However, the further slipped configuration (f) induces remarkably large redshift of 144 nm, characteristic of a J-aggregate.

The result may be elucidated in terms of the interaction between the transition dipole moments of the constituent monomers. As reviewed by Kasha,¹¹ an electronic excitation in side-by-side and head-to-tail configurations of the monomer transition dipole moments may be classified as follows. In a side-by-side configuration, the oppositely directed transition dipoles of the monomers become more stable than the parallel dipoles because of the electrostatic interaction. However, only the parallel dipoles result in an allowed transition, and thus blueshift occurs. A head-to-tail configuration, in which the tail of one of the monomer transition dipoles is followed by the

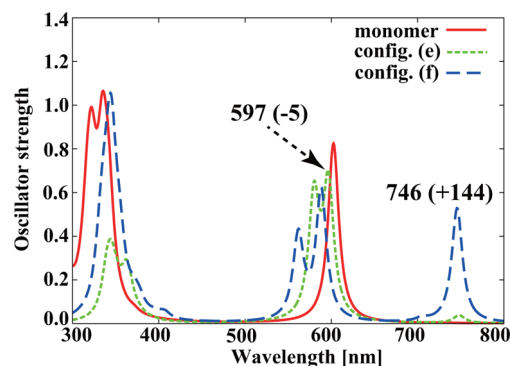


Figure 6. Absorption spectra of ZnPc dimers with configurations (e) and (f). The computed absorption wavelength is displayed in units of nm, along with the difference from the Q-band peak of the monomer in parentheses. The spectra simulated at the B3LYP/TDDFT level are described using the calculated oscillator strengths and the excitation energies broadened with Lorentzian functions.

head of the other transition dipole, orienting to the same direction, becomes more stable, resulting in an allowed redshift.

Whether an electronic excitation of interest is allowed or not is dominated by the matrix element of the transition dipole moment within the long-wavelength approximation

$$\mu_{FI} = \langle \Psi_F^{(0)} | e \mathbf{r} | \Psi_I^{(0)} \rangle \quad (2)$$

where $\Psi_F^{(0)}$ and $\Psi_I^{(0)}$ are the final and initial states in an electronic excitation of interest, respectively, and the absorption strength is proportional to the square of the norm of the matrix element. The matrix element gives us insight on the electronic excitation in terms of the character of the wave functions of the initial and final states: the matrix element of the odd function \mathbf{r} in space becomes zero (nonzero) in case the product of $\Psi_F^{(0)}$ and $\Psi_I^{(0)}$ is even (odd). In other words, the wave functions must have opposite symmetry along the direction of the transition dipole moment. On the basis of the unperturbed Kohn–Sham orbitals, the transition dipole moment may be qualitatively described as^{12–14}

$$\mu_{FI} = \sum_{i,a} \langle \phi_i | e \mathbf{r} | \phi_a \rangle F_{ia} \quad (3)$$

where i and a indicate occupied and unoccupied Kohn–Sham orbitals, respectively, and F_{ia} denotes the eigenvector component in eq 1 of the transition between ϕ_i and ϕ_a . In elucidating the transition dipole moments in terms of the constituent monomers and the resulting dimer electronic structures, the first-order density response is useful

$$\rho_{FI}(\mathbf{r}) = \sum_{i,a} \phi_i(\mathbf{r}) \phi_a^*(\mathbf{r}) F_{ia} \quad (4)$$

Figure 7 displays the schematics of the transition dipoles of the constituent monomers in the calculated optical absorptions in configuration (f), along with the density response (eq 4) obtained with the eigenvectors \mathbf{F} calculated within TDDFT. Notice that each of the constituent monomers has nonzero transition dipole because of the different signs of the HOMO and the LUMO (see Figure 1b,c). This is the characteristic common to HOMO and LUMO wave functions of a π -conjugated molecule in general. The directions of the monomer transition dipoles are oriented to the diagonal directions of the molecules, as a result of the modified orientations of the original monomer transition dipole moments (Figure 3) by the

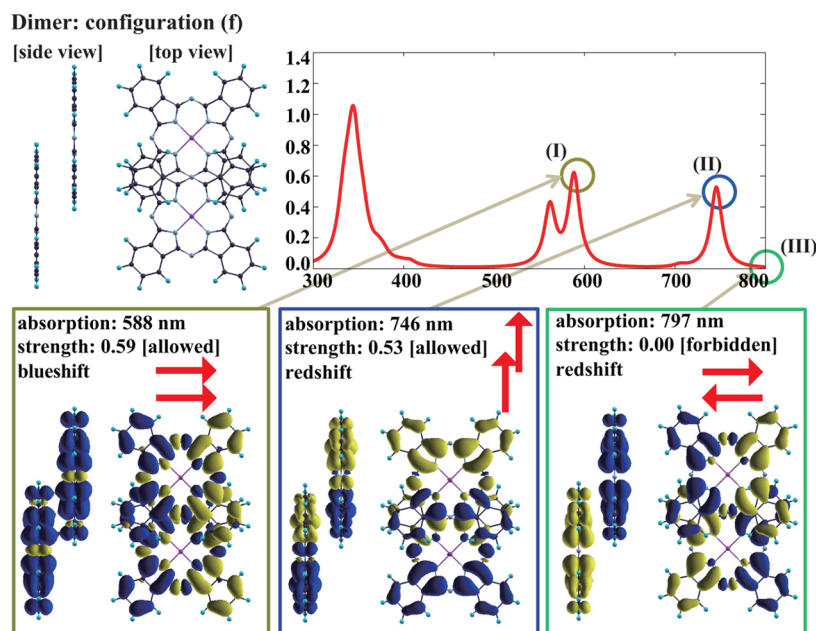


Figure 7. Absorption spectra of ZnPc dimer in configuration (f) and the constituent transition dipoles of the monomers in each of the excitations. The isosurfaces display the first-order density response on the basis of the Kohn–Sham orbitals (eq 4), and the difference in brightness corresponds to signs of the isosurfaces. The transition dipole of each of the constituent monomers is qualitatively described by the arrows. For the characters of the excitations in the monomer, see Figure 3

interaction between the LUMO and the LUMO' of the different monomers. The electronic transitions in the dimer are elucidated in terms of the configurations of monomer transition dipoles. In the allowed transitions, for instance, in (I) and (II) of Figure 7, the parallel transition dipoles are oriented to the same direction and thus result in the nonzero net transition dipole moment. For the transition (III), the dipoles are antiparallel, and thus the transition is forbidden. Because of the electrostatic interaction between the monomer dipoles, the parallel configuration of the side-by-side positioned dipoles in transition (I) results in the blueshift. On the other hand, the parallel configuration of the head-to-tail positioned dipoles in (II) results in the redshift relative to the monomer excitation energy.¹¹

In addition to the geometrical configurations and the resulting transition dipoles, the effect of the stack distance between the monomer planes is investigated. Figure 8 shows the absorption spectra of configurations (a), (e), and (f) when the interplane distance is decreased. It is found that in configuration (a) there is almost no change in absorption wavelength with respect to the change in interplane distance from 3.1 to 3.5 Å. For the configurations with the redshift, specifically in configuration (f), further redshift is induced by the decrease in the interplane distance. The sensitivity of the redshift upon the intermolecular distance, which is not found in the H-aggregate, may be utilized in tuning the excitation window by varying the intermolecular distance once a J-aggregate is formed.

Stability of the Dimers: Formation Energy Relative to Isolated Monomers. Finally, we investigate the stability of the dimer configurations relative to the isolated ZnPc monomer. Table 2 displays the calculated formation energies of the dimers (a), (e), and (f). The intermolecular interaction seems to be dominated by the vdW interaction, and DFT-D2 describes well the attractive interaction between the monomers. The interaction energy is sensitive to the intermolecular distance

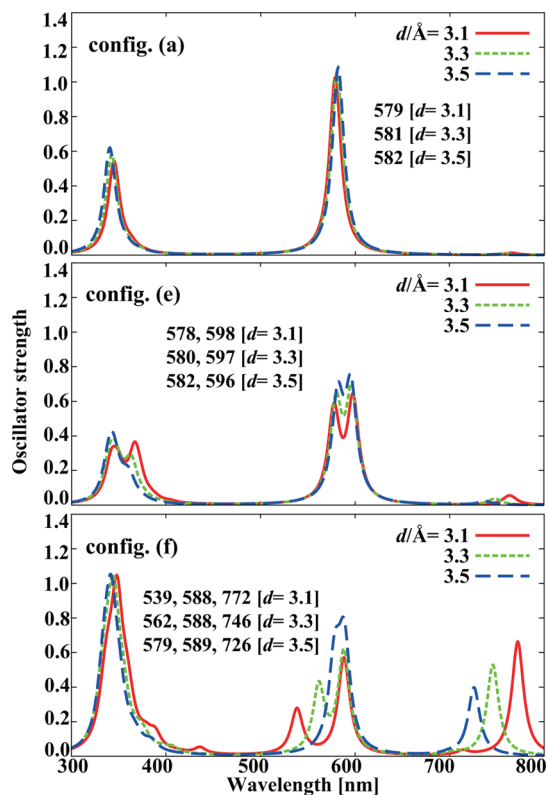


Figure 8. Absorption spectra of ZnPc dimer in configurations (a), (e), and (f), for different interplane distances $d = 3.1, 3.3$, and 3.5 Å. The computed absorption wavelength is displayed in units of nm, with the corresponding distances in parentheses.

and the overlap between the molecular planes. For configurations (e) and (f), where the molecular planes are partially superimposed, the predicted equilibrium distance lies close to 3.3 Å, in agreement with the previous theoretical study,³¹ and

Table 2. Formation Energies of the Dimer Configurations (a), (e), and (f) for Different Intermolecular Distances d = 3.1, 3.3, and 3.5 Å Calculated with DFT+D2^a

$d/\text{Å}$	3.1	3.3	3.5
dimer (a)	+32.7	−55.4	−85.4
dimer (e)	−120.2	−123.9	−112.9
dimer (f)	−51.2	−64.2	−63.5

^aThe units are in kJ/mol.

Notes

The authors declare no competing financial interest.

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they are similar to twice the vdW radius of carbon atom (170 pm). For the cofacial configuration (a), the formation energy is more sensitive to the interplane distance, and the equilibrium distance seems to be longer than (e) and (f).

The dimer configuration (f), in which the redshift is largest, is found to be metastable, with a formation energy of −64.2 kJ/mol. The formation energies of the other dimer configurations are larger (see Table 2). Therefore, a J-type aggregate of unsubstituted ZnPc as simulated in this study seems unlikely to be observed experimentally. Nevertheless, a similar J-type aggregate with more attractive intermolecular interaction might be realized by introducing substituents into the monomers, for instance, alkoxy groups, so that the binding between the central Zn atom and the O atom can be induced.

CONCLUSIONS

We investigated origins of the redshift in absorption spectra of dimerized ZnPc by means of density functional theoretical calculations. Interactions between HOMOs or between LUMOs in general decrease the HOMO–LUMO gap of an unsubstituted ZnPc dimer specifically when the molecules are arranged cofacially. The calculated absorption spectra with the time-dependent density functional theory, however, show no redshift but appreciable blueshift, indicative of a H-aggregate. As elucidated by a conventional model of transition dipole–dipole interaction proposed by Kasha, the absence of the redshift but the presence of the blueshift in absorption bands of the HOMO–LUMO excitations comes from the monomer transition dipoles being arranged side-by-side, and thus the allowed transition becomes relatively unstable as a result of the electrostatic repulsion. The appreciable redshift of 144 nm in the slipped-cofacial stacked configuration relative to the monomer Q-band, indicative of a J-aggregate, is caused by an interaction between the monomer transition dipole moments arranged in a head-to-tail manner. These selection rules are elucidated in terms of the nature of the constituent monomer’s HOMO and the LUMO, the signs of which along the polarization direction determine the transition dipole moments. Sensitivity of the redshift to the stack distance between the monomers is also investigated. The slipped-cofacial dimer configuration is found to be metastable. By introducing substituents or ligands, a stable ZnPc dimer or a larger aggregate with a similar monomer configuration or orientation might be realized. These findings may give us a hint to designing a J-aggregate of a ZnPc derivative with favorable near-infrared absorption, and our investigation of a stable ZnPc J-aggregate with favorable excitation windows is in progress.

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