

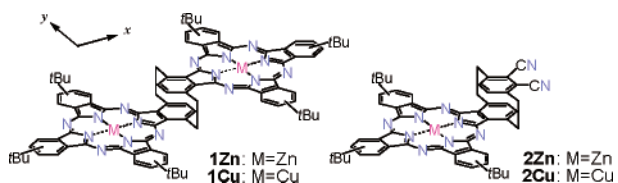
## *anti*-[2.2](1,4)Phthalocyaninophane: Spectroscopic Evidence for Transannular Interaction in the Excited States

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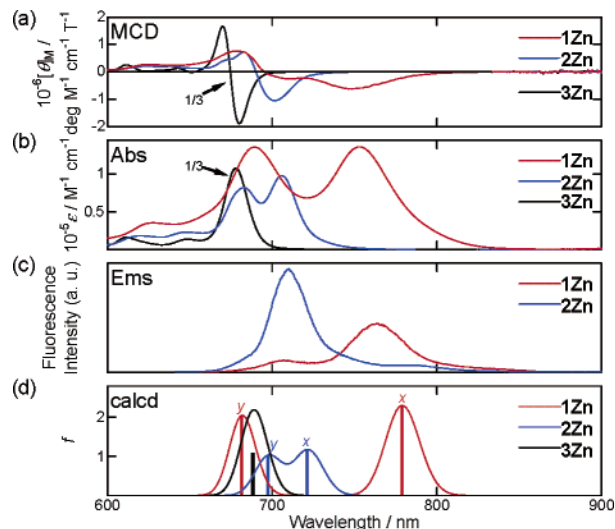
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An enhanced understanding of the electronic communication between chromophores is of great importance in designing organic materials for applications in optoelectronic technologies. In this respect, bis- and multiphthalocyanines have attracted considerable interest because of their high stability, the presence of intense  $\pi$ - $\pi^*$  transitions in the visible region (Q-band), and their redox ability.<sup>1</sup> Since the relative orientation and distance between phthalocyanine (Pc) chromophores are essential to their electronic excited states, a number of Pc dimers and oligomers have been explored.<sup>2</sup> Herein we report a novel type of bisphthalocyanines, *anti*-[2.2]-phthalocyaninophanes (**1Zn** and **1Cu**), in which two Pc units are linked by ethano bridges at the para positions, to create a [2.2]-paracyclophane moiety. The cyclophane framework could allow for a well-defined slipped-stack arrangement of the two Pc units. Construction of this kind of a slipped-stack dimer has been stimulated by the fact that the special pair and antenna subunits in photosynthetic light-harvesting antenna consisting of bacteriochlorophyll dimers have a similar spatial arrangement to fine-tune the electronic excited states,<sup>3</sup> and that the fluorescence properties of a Pc chromophore preserve, which is in contrast to nonfluorescent Pc oligomers with face-to-face geometry.<sup>2,4</sup>



The *anti*-[2.2](1,4)-zinc(II)-9(10),16(17),23(24)-tri-*tert*-butylphthalocyaninophane (**1Zn**) was synthesized from [2.2]paracyclophane in three steps (see Supporting Information). The *anti*-[2.2](3,6)-phthalonitrilo(1,4)zinc(II)-9(10),16(17),23(24)-tri-*tert*-butylphthalocyaninophane (**2Zn**) was also obtained in the synthetic procedure. The Cu complexes (**1Cu** and **2Cu**) were synthesized similarly to the Zn complexes. Figure 1 shows experimental and calculated spectra of **1Zn**, **2Zn**, and reference zinc(II) tetra-*tert*-butylated Pc (**3Zn**). The 678 nm absorption band of **3Zn** splits into two well-resolved bands (683 and 706 nm) in the case of **2Zn**. The splitting of the Q-band appears to be similar to that of conventional low-symmetrical Pc derivatives reported previously.<sup>5</sup> In contrast, **1Zn** exhibited significantly split and red-shifted absorption bands, observed at 753 and 690 nm. It should be noted that, when compared to the dimeric Pcs with a similar geometrical arrangement, the lowest-energy Q-band position of the dimer lies midway

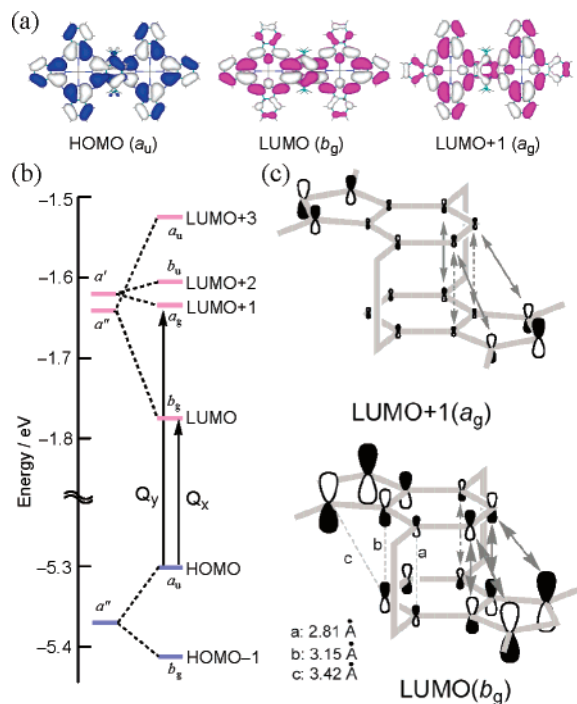


**Figure 1.** MCD (a), absorption (b), and fluorescence (c) spectra of **1Zn** (red), **2Zn** (blue), and **3Zn** (black) in benzene. ZINDO/S calculations (d). Gaussian bands with half-bandwidth of 400  $\text{cm}^{-1}$  were used; *x* and *y* indicate transition polarizations.

between those of the Pc dimer without  $\pi$ -conjugation (*J*-type Pc dimer, 700 nm)<sup>6</sup> and  $\pi$ -conjugated planar Pc dimer (852 nm).<sup>7</sup> The magnetic circular dichroism (MCD) signals of **1Zn** and **2Zn** associated with the two lowest-energy transitions have negative  $\{[\theta]_M = -6.23 \times 10^5$  (**1Zn**),  $-1.05 \times 10^6$  (**2Zn**) $\}$  and positive signs  $\{[\theta]_M = 7.52 \times 10^5$  (**1Zn**),  $7.21 \times 10^5$  (**2Zn**) $\}$ , respectively. The Q absorption peak positions are almost the same as the observed Faraday *B* terms, which arise from magnetically induced mixing of nondegenerate excited states.<sup>8</sup> Since the spectral pattern of **1Zn** was unchanged upon addition of pyridine and a linear relationship between absorbance and concentration was confirmed in Beer's law experiments, aggregation behavior should be negligible under the experimental conditions. The spectroscopic properties of the Cu complexes (**1Cu** and **2Cu**) were almost identical to those of the Zn complexes. From these spectroscopic data, it is evident that significant through-space  $\pi$ - $\pi$  interactions are involved in the excited singlet states of the present system. This is quite different from the bisphthalocyanine system consisting of a [2.2]paracyclophane bridge reported by Torres et al.<sup>9</sup>

**1Zn** exhibited a fluorescence peak at 764 nm longer than those of **2Zn** (710 nm) and **3Zn** (684 nm), which is consistent with the formation of *J*-type aggregate of organic dyes.<sup>10</sup> The fluorescence quantum yields in benzene were determined to be 0.12 (**1Zn**) and 0.19 (**2Zn**) using **3Zn** as a standard.<sup>11</sup> The value of **1Zn** is smaller than that of a *J*-type Pc dimer,<sup>6</sup> but 1 order higher than those of

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**Figure 2.** (a) Frontier MOs of the B3LYP-optimized **1Zn**. (b) Energy correlation diagram of zinc dimethyl Pc (left) and **1Zn** (right). (c) Schematic representation of the origin of the  $\pi$ - $\pi$  interaction. The relative  $\pi$  orbital size is based on the CI calculations. Bonding and antibonding interactions are indicated by solid and dotted arrows, respectively.

coplanar Pc dimers.<sup>12</sup> The Stokes shift of **1Zn** was fairly small (ca. 190  $\text{cm}^{-1}$ ), thus indicative of a rigid structure of the molecule.

According to the B3LYP/6-31G\* optimized structures, the average distance between the facing benzene planes is 2.98 Å. The geometrical parameters of the cyclophane moiety of **1Zn** and **2Zn** are close to those of [2.2]paracyclophane calculated using the B3LYP functional,<sup>13</sup> suggesting that a considerable electron exchange within the  $\pi$  units should be taken into account.<sup>14</sup> The calculated spectral features (ZINDO/S) are in good agreement with the experimental spectra. It is clearly seen from Figure 2a that the MOs of **1Zn** consist of linear combinations of the monomeric MOs. The lowest and second lowest energy absorption bands of both **1Zn** and **2Zn** can be attributed to long- and short-axis polarized Q transitions, respectively, since these transitions were formed predominantly through combinations of MOs derived from Gouterman's orbitals.<sup>15</sup> These results agree with the observed coupled Faraday *B* terms since transitions of different polarizations generally have differently signed MCD signals.<sup>8</sup> In view of the assignment of the polarization of the Q-bands, the MO calculation is consistent with Kasha's exciton coupling theory.<sup>16</sup>

The origin of the spectral features of **1Zn** was rationalized as shown in Figure 2b. The HOMO and LUMO are destabilized and stabilized, respectively, compared with a corresponding Pc monomer due to the significant orbital interactions, which leads to the spectral red shift ( $Q_x$ ). Since the stabilization of the LUMO+1 is modest, the energy difference between the LUMO and LUMO+1 becomes large, which results in the marked  $Q_x$ - $Q_y$  splitting. The orbital interaction energies of **1Zn** are calculated to lie midway between those of the corresponding Pc dimer with and without  $\pi$ -conjugation (see Supporting Information). Figure 2c illustrates a schematic representation of the  $\pi$  orbitals of the cyclophane moiety in the LUMO and LUMO+1. In the case of the LUMO, bonding interactions between the benzene  $\pi$  orbitals on one Pc unit and the

pyrrole  $\pi$  orbitals on the other Pc unit contribute to the stabilization of the LUMO energy, although the interaction between the  $\pi$  orbitals on the nearest carbons is slightly antibonding. In contrast, since the relative size of the  $\pi$  orbitals on the cyclophane moiety of the LUMO+1 is considerably small, the through-space  $\pi$ - $\pi$  interactions between the benzene and pyrrole units are weak, which results in moderate stabilization of the LUMO+1.<sup>17</sup> The small Q-band splitting observed for **2Zn** can also be rationalized by considering the relative size of the  $\pi$  orbitals in the cyclophane moiety (see Supporting Information).

In summary, we have demonstrated the design and synthesis of a novel bisphthalocyanine system (**1Zn** and **1Cu**) that exhibited significantly split and red-shifted absorption in the near-IR region. It was found that **1Zn** maintained the fluorescence properties of Pcs. The MO model analysis provides a clear-cut picture for the nature of the electronic communication between the two Pc chromophores, which could offer a new approach for understanding transannular interactions of cyclophanes. In addition, since the phthalocyaninophanes can mimic the slipped-stack arrangement with significant interchromophore coupling, the present system has potential application as a novel model of the special pair and subunits in photosynthetic systems.

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**Supporting Information Available:** Experimental and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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