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COMMUNICATION

A zinc gable phthalocyanine and a derived planar bis-phthalocyanine containing a shared anthracene unit†

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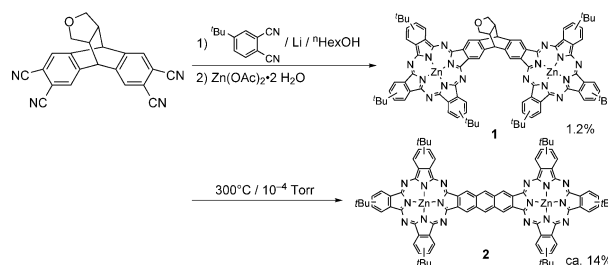
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A gable-type zinc phthalocyanine and a derived planar bis-phthalocyanine containing a shared anthracene unit have been synthesized and their spectroscopic properties examined. The former showed a split Q band, while the latter exhibited a red-shifted but unsplit Q band, as explained by exciton coupling theory and molecular orbital calculations.

Various types of phthalocyanine (Pc) dimers have been reported to date. The most representative of these include rare-earth sandwich-, μ -oxo-dimers of silicon, iron, and some metal–metal directly-linked dimers. A gable-type metal-free homo-Pc dimer linked with a bicyclo[2.2.2]octadiene ring is also known.¹ As planar dimers,² Leznoff was the first to report Pcs sharing a common benzene ring.^{1–5} Since then, more than 20 papers describing planar Pc dimers and oligomers have been published. However, the effect of increasing Pc–Pc distance has not yet been examined. In this report, we describe the synthesis and spectroscopic (electronic absorption, fluorescence, and magnetic circular dichroism (MCD)) properties of the dizinc derivative of the gable-type metal-free Pc (ZnGPc (**1**)) and the derived planar Pc dimer (bis-ZnPc (**2**)) containing a shared anthracene ring which was obtained by heat treatment of ZnGPc (**1**). These two compounds are spectroscopically interesting, in that the Pc–Pc distance in (**2**) is much longer than those reported to date, and that the line connecting the two Pc units of (**2**) is folded while two lines normal to it through the Pcs of (**1**) are parallel to each other. As will be shown here, the Q band of the planar Pc in the present study appears different from that of the control monomeric Pc, and these characteristics are clearly interpreted with the help of molecular orbital (MO) calculations.⁶

At first, metal-free GPc was obtained by cross condensation using 2,3,6,7-tetracyano-9,10,11,12,13,14-hexahydrofuranthracene and *tert*-butylphthalonitrile in the presence of lithium alkoxide.¹ Since the interpretation of spectra is easier for metalated species from the standpoint of molecular symmetry, we changed metal-free GPc to its Zn complex by reacting with $\text{Zn}(\text{OAc})_2$ in dichloroethane–ethanol (3 : 2 v/v) under reflux for 12 hours in the dark. ZnGPc (**1**), thus obtained was then transformed



Scheme 1 Synthesis of the gable bis-Zn(II)Pc (**1**) and the conjugate planar bis-Zn(II)Pc (**2**).

into a planar Pc dimer by heat treatment, as reported for the formation of planar porphyrin dimers by Ono *et al.*^{3b} Here, ¹H NMR signals originating from the gable moiety disappeared to produce an anthracene molecule, so that in the resulting dimer, two Pc units are connected by this anthracene molecule. The details of the synthesis are described in Scheme 1.⁷

Fig. 1 shows the electronic and MCD spectra of **1**, **2** and *tert*-*tert*-butylated ZnPc **3**.⁸ The Q band of a typical monomeric Pc (D_{4h}), such as **3**, mainly consists of an $1E_u \leftarrow 1A_{1g}$ transition,⁹ and comprises an unsplit Q absorption band, while the corresponding Faraday *A* MCD term (a derivative-shaped signal) at the center of the absorption band identifies a degenerate excited state ($1E_u$).⁹ The Q band of C_{2v} symmetry **1** is split at 677 nm and 694 nm, and the MCD spectrum shows coupled pairs of oppositely-signed

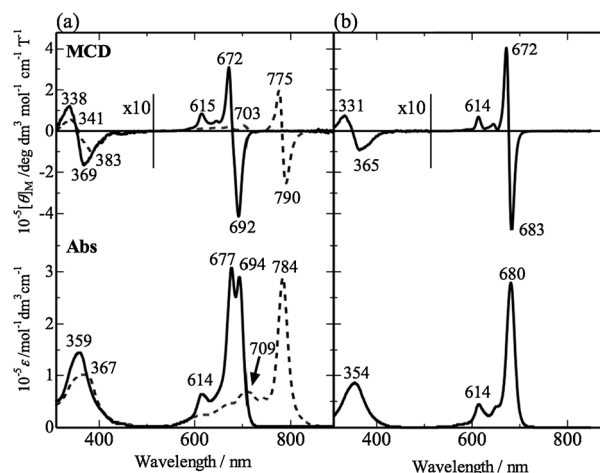


Fig. 1 Electronic absorption (bottom) and MCD (top) spectra recorded in pyridine: (a) **1** (solid lines), **2** (broken lines), (b) **3**.

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Faraday *B*-term signals at 672 nm and 692 nm. For **2**, an apparently unsplit Q band appears at 784 nm in the near IR region, although **2** has approximate D_{2h} symmetry. The associated MCD spectrum is a pseudo Faraday *A*-term, since its trough and peak approximately correspond to the positions of the two absorption peaks.

The splitting of the Q band of compound **1** is quite easily explained by exciton coupling in an oblique two-chromophore system.¹⁰ If we set the *x*-axis along the line connecting the two ZnPc units and the *y*-axis normal to the *x*-axis in the Pc plane, a transition along the *x*-axis shifts to longer wavelength, while that along the *y*-axis does not, so that the single Q band in D_{4h} symmetry **3** splits into two in C_{2v} symmetry **1**. However, the apparently unsplit Q band of **2** with D_{2h} symmetry was quite unexpected, particularly since it is known that the interaction of the two Pc units in this kind of planar system can be expressed as a linear combination of two almost independent Pc chromophores, by exciton coupling.^{4c,d}

The calculated absorption spectra and molecular orbitals are shown in Fig. 2 and 3, respectively, with obtained data summarized in Table 1. From TD-DFT calculations at the B3LYP/631SVPs level, mutually perpendicularly polarized transitions of **1'** are calculated at 638, 607, 590 and 588 nm.⁶ From two e_g LUMOs and an a_{1u} HOMO of monomeric **3'**, four unoccupied orbitals and two occupied orbitals are produced as a linear combination of the LUMOs and HOMO, respectively. These results indicate that $318 \rightarrow 319$, $318 \rightarrow 322$, $317 \rightarrow 319$ and $317 \rightarrow 322$ are assigned to $a_{1u} \rightarrow e_{gy}$ -type transitions, while $317 \rightarrow 320$ and $318 \rightarrow 321$ are assigned to $a_{1u} \rightarrow e_{gx}$ -type transitions. Therefore, these calculated transitions at 638 and 607 nm can be assigned to the experimental Q bands at 694 nm, while those calculated at 590 nm can be associated to the observed band at 677 nm, respectively. The oppositely-signed MCD signals (692 and 672 nm) also support this assignment, since perpendicularly-polarized transitions give

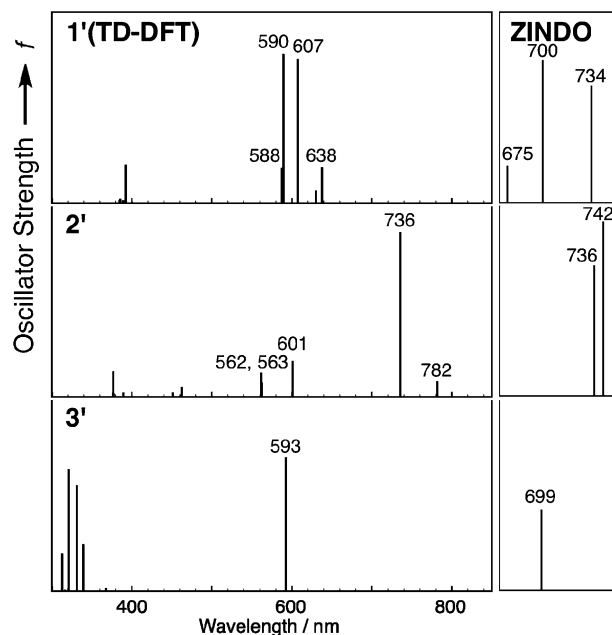


Fig. 2 Calculated absorption spectra of **1'** (top), **2'** (middle) and **3'** (bottom).⁶ Calculated at B3LYP/6-31G*, SVP for Zn (left) or ZINDO/S (right).

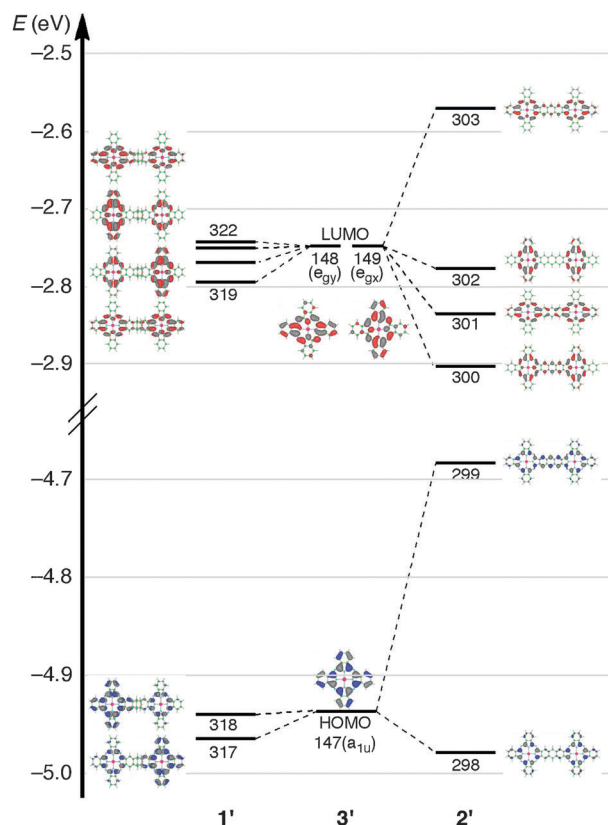


Fig. 3 Partial molecular energy diagram/orbitals of **1'**, **2'** and **3'**.⁶

Table 1 The calculated excitation wavelength (λ), oscillator strength (*f*) for the components of Q bands of **1'**, **2'** and **3'** calculated by B3LYP/631SVPs (a) or the ZINDO/S Hamiltonian (b)⁶

Compd	λ /nm	<i>f</i>	Composition (%)
(a)			
1'	638	0.19	$318 \rightarrow 319$ (84%)
	607	0.76	$317 \rightarrow 322$ (83%), $318 \rightarrow 319$ (9%)
	590	0.78	$317 \rightarrow 320$ (49%), $318 \rightarrow 321$ (45%)
	588	0.18	$317 \rightarrow 319$ (39%), $318 \rightarrow 322$ (54%)
2'	782	0.16	$299 \rightarrow 300$ (97%)
	736	1.73	$299 \rightarrow 301$ (99%)
	601	0.38	$298 \rightarrow 302$ (91%), $299 \rightarrow 304$ (6%)
	563	0.15	$299 \rightarrow 304$ (90%), $298 \rightarrow 302$ (5%)
3'	562	0.25	$298 \rightarrow 303$ (96%)
	593	0.42	$147 \rightarrow 148$ (77%), $147 \rightarrow 149$ (17%)
3'	593	0.42	$147 \rightarrow 149$ (77%), $147 \rightarrow 148$ (17%)
(b)			
1'	734	1.53	$195 \rightarrow 196$ (54%), $194 \rightarrow 197$ (43%)
	700	1.87	$195 \rightarrow 199$ (48%), $194 \rightarrow 198$ (46%)
	675	0.48	$195 \rightarrow 197$ (48%), $194 \rightarrow 196$ (46%)
2'	742	2.28	$189 \rightarrow 190$ (65%), $188 \rightarrow 193$ (31%)
	736	1.71	$189 \rightarrow 191$ (56%), $188 \rightarrow 192$ (38%)
3'	699	1.06	$93 \rightarrow 94$ (93%)
	699	1.06	$93 \rightarrow 95$ (93%)

MCD signals of opposite sign.¹¹ The band calculated at 588 nm also corresponds to $a_{1u} \rightarrow e_{gy}$ -type transitions. But this band is considerably weaker than the calculated 590 nm band so that the corresponding band cannot be found in the experimental spectrum. By using ZINDO/S Hamiltonian, the Q_y and Q_x -polarized transitions of comparative intensity were calculated at 734 and 700 nm (Fig. 2, right). The band calculated at 675 nm corresponds to *z*-polarized transitions, but its position cannot be

assigned in the experimental spectrum since vibronic bands are considered to be superimposed in the same region.

The analysis of **2** was conducted similarly. Based on the TD-DFT method at the B3LYP/631SVPs level, several mutually-perpendicularly polarized, and closely-lying allowed transitions were calculated at 782 and 736 nm in the near infrared region. These calculated transitions are assigned to the Q_y and Q_x bands, respectively, since these are also $a_{1u} \rightarrow e_g$ -type transitions ($1E_u \leftarrow 1A_{1g}$ transition under D_{4h} symmetry). In the case of the ZINDO/S calculation, these bands were estimated at 742 and 736 nm as bands of comparative intensity (Fig. 2, right). The calculated small energy difference between the Q_x and Q_y bands supports the experimentally-observed single Q band of **2** (Fig. 1). From the data in Fig. 3 and Fig. S1 (ESI[†]), the small energy difference between the Q_x and Q_y bands may be attributable to the small energy difference between the LUMO and LUMO + 1 of this molecule.¹² Thus, this feature is close to those of metalloPcs of D_{4h} symmetry. Other allowed transitions were calculated at 601, 563, and 562 nm. These may be associated with an absorption peak at 709 nm and a MCD peak at 703 nm. The longer wavelength shift of the Q band of **2** compared to that of monomeric **3** can be ascribed to the smaller energy difference between the HOMO and LUMO in **2**.

In order to further strengthen the above assignments, we have attempted simultaneous band deconvolution analyses for the experimental electronic absorption and MCD spectra (Fig. S2, ESI[†]).¹³ Band deconvolution analysis is carried out using the same number of components, same or very close energy, and same bandwidth for the absorption and MCD spectra, by fitting each band with a Gaussian line shape. As seen in the figure, the Q bands of both **1** and **2** were fitted with two Gaussian lines whose relative intensities are close to those estimated by calculation (f values in Table 1). In particular, the single Q band of **2** can be decomposed by two closely-lying (8 nm difference) components, supporting the reliability of the calculated data. Several types of conjugated, planar bis-Pcs sharing one benzene unit⁴ or two benzene units (naphthalene unit)^{4b,g} have been reported to date. Our bis-ZnPc (**2**) shares three benzene units (anthracene unit) between the Pcs, where the only structural difference is the number of common benzene units. MO calculations on the basis of the PPP approximation of conjugated, planar bis-Pcs connected by different numbers of benzene rings have been attempted previously.^{4c,13} According to these reports, it is anticipated that the larger the distance between the two Pc centers, the smaller will be the splitting of the Q band. In accordance with this prediction, in the case of a conjugated, planar bis-Pc sharing one benzene ring, the splitting of the Q band is about 100 nm^{4c} and the MCD spectrum shows coupled pairs due to opposite Faraday B terms, while in the present **2**, it is considered that the splitting is so small (8 nm) that the Q band is observed as a single band. This in turn indicates that the interaction between the two Pc units can be explained by exciton type coupling. Thus, the conjugation between the two ZnPc units in **2** appears smaller than for a bis-Pc sharing a benzene unit.^{4,5,14}

In this communication, we have prepared two types of bis-ZnPc, and conducted their spectroscopic analyses in terms of electronic

absorption and MCD spectroscopy. The spectroscopic properties of both gable-type **1** and the planar **2** containing a shared anthracene ring have been reasonably explained through the concept of exciton coupling. The unsplit Q band of **2** appears to be the result of weak exciton coupling between the constituting ZnPc units. This is, however, an unexpected result, considering that bis-ZnPc **2** is a molecule with D_{2h} symmetry and that the ratio between the long- and short axes is clearly fairly different.

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