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# First observation of excited triplet dimers with strong intramolecular interactions: planar binuclear phthalocyanines

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**Zero field splitting parameters of planar binuclear phthalocyanines in the lowest excited triplet state have been obtained by using a time-resolved EPR method to show a delocalization of excitation over two phthalocyanine units for a homodimer and a contribution from a charge transfer configuration for a heterodimer.**

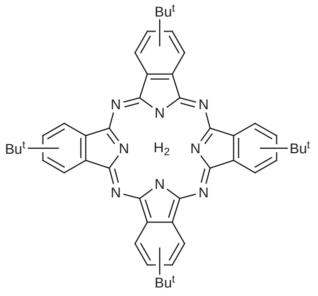
Phthalocyanine (Pc) and porphyrin (Pr) dimers have been intensively investigated as a model of photosynthetic reaction centers.[1] It has been an important objective to evaluate intramolecular interactions of these dimers in the excited state.[2]

Zero field splittings (ZFSs) of dimers in the lowest excited triplet ($T_1$) state, which can be obtained by EPR, are useful parameters for evaluating interactions between constituent units in dimers.[3] Although it is difficult to obtain this kind of information on Pc derivatives due to the lack of phosphorescence in the visible region and the short lifetime,[4] a time-resolved EPR (TREPR) technique has been shown to be useful for analyses of Pc derivatives,[5] and applied to several 'face-to-face' dimers having strong intramolecular interactions.[6] However, 'head-to-tail' dimers with strong interactions have not been observed in the $T_1$ state not only of Pc but also of Pr derivatives, while a charge transfer (CT) contribution in the $T_1$ state is observed for the photosynthetic reaction centers.[7] This originates from the fact that the interaction in the $T_1$ state is much smaller than that in the lowest excited singlet ($S_1$) state.

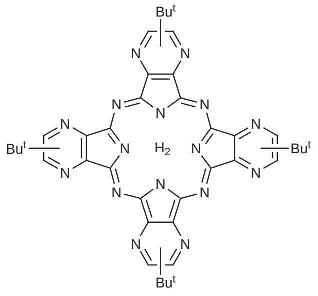
In this study, we have applied the TREPR method to two planar binuclear conjugated Pc derivatives **3** and **4**, in which two Pcs or one Pc and pyrazinoporphyrazine (Pyz) strongly interact with each other through a common benzene ring, and have succeeded in observing TREPR spectra in the $T_1$ state. The ZFSs of these dimers are compared with those of the corresponding monomers, and analyzed in terms of a delocalization of excitation over two units and a contribution of a CT configuration for homo- and hetero-dimers, respectively.

Pc derivatives have been reported by us previously.[8] A 1 : 1 mixture of toluene and $CHCl_3$ of spectral grade was used as solvent for the TREPR measurements. The concentrations of the samples were (0.5–1) $\times 10^{-3}$ M. All samples were deaerated by freeze-pump-thaw cycles. TREPR measurements and simulations of the $T_1$ spectra were carried out following the method already reported.[9,10] Molecular orbital (MO) calculations were performed for the deprotonated species under the Pariser–Parr–Pople (PPP) approximation.[11]

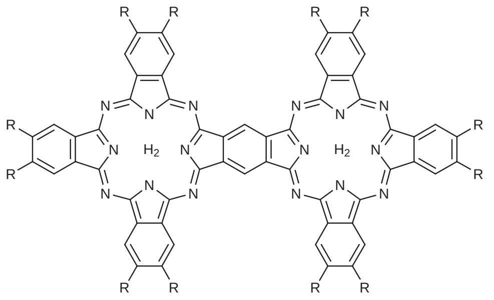
TREPR spectra of **1**, **3** and **4** observed at 20 K and 0.5 μs after laser excitation are shown in Fig. 1. ZFS parameters and intersystem crossing (ISC) ratios evaluated by spectral simulations are summarized in Table 1. The ISC from the $S_1$ state is selective to upper $T_x$ and $T_y$ sublevels for all Pc derivatives, where $T_z$ is the lowest sublevel ($z$ = an out of plane axis). This selectivity is consistent with those of metal-free porphyrins previously reported,[12] and is interpreted by contribution of (n,π*), (σ,π*) and (π, σ*) configurations. These results indicate that the signs of the $D$ ( $= -3E_z/2$) values are positive for all Pc derivatives examined here.



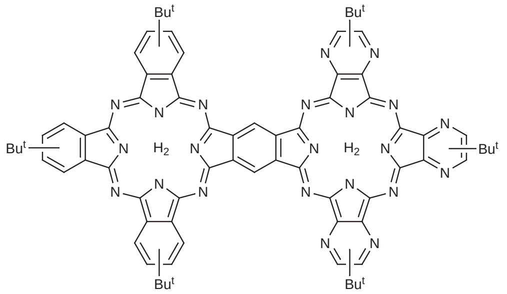
**1**



**2**



**3** R = $OCH_2CHEt(CH_2)_3CH_3$



**4**

It is found that the $D$ value of **3** is much smaller than that of **1**. This decrease can be explained by a delocalization of excitation over two Pc units in the $T_1$ state. This is supported by a MO analysis of **3**, where the π-electrons of the HOMO and LUMO delocalize over two Pc units.[8,11] To allow a quantitative discussion, $D$ values were calculated under a half-point charge approximation.[11,13,14] The results are summarized in Table 1, where the calculated $D$ value (0.426 GHz) of **3** is smaller than that (0.605 GHz) of **1** in analogy with the experimental results.

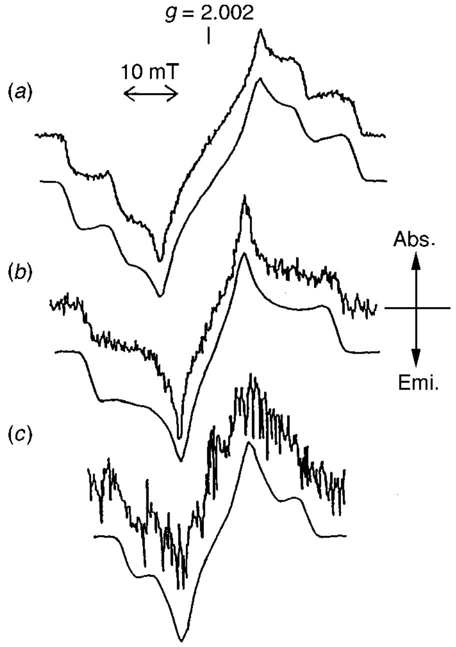


**Fig. 1** TREPR spectra of (*a*) **1**, (*b*) **3** and (*c*) **4** with their simulations (lower line). These spectra were observed at 20 K and 0.5 μs after laser excitation.

**Table 1** ZFS parameters and ISC ratio[a]

| | $D^b$/GHz | $E$/GHz | $P_x:P_y:P_z$ | $D_{\text{calc}}$/GHz |
|---|---|---|---|---|
| **1** | 0.758 | 0.070 | 0.46 : 0.54 : 0 | 0.605 |
| **2** | 0.900 | 0.080 | 0.47 : 0.53 : 0 | 0.673 |
| **3** | 0.645 | 0.105 | 0.35 : 0.65 : 0 | 0.426 |
| **4** | 0.480 | 0.040 | 0.4 : 0.6 : 0 | 0.422 |

[a] $D = -3E_z/2$, $E = |E_x - E_y|/2$ and $P_i$ ($i = x, y$ and $z$) denotes anisotropic ISC. [b] Errors of $D$ values are within 0.016 and 0.008 GHz for **4** and the other Pcs, respectively.

The *D* value (0.480 GHz) of **4** is the smallest in our Pc derivatives, and cannot be interpreted simply by the expansion of π delocalization in the $T_1$ state. Since the *D* value of **2** is larger than that of **1**, localization of excitation on the Pyz ring can be ruled out. The MO analyses of the monomers suggest that the HOMO (−7.49 eV) and LUMO (−3.74 eV) of **1** are higher than the HOMO (−7.98 eV) and LUMO (−4.02 eV) of **2**, respectively. In fact, the electron density on the Pc ring is larger than that on the Pyz ring for the HOMO of **4**, while it is smaller for the LUMO. Therefore, the small *D* of **4** originates from a contribution of a CT configuration between the Pc and Pyz systems. The calculated *D* value of **4** is smaller than that of **3** in accordance with the experimental trend.

In summary, planar and conjugated Pc dimers have been studied in terms of *D* values. The *D* value of **3** is smaller than that of **1** and can be explained by a delocalization of excitation over two Pc units in the $T_1$ state. The *D* value of **4** is further lowered and can be interpreted as the contribution of the CT configuration between the Pc and Pyz systems. The CT contribution to the *D* value is strikingly similar to the photosynthetic reaction center. To the best of our knowledge, 'head-to-tail' dimers with such strong $T_1$ interactions have not been reported in Pr and Pc derivatives to date. Therefore, these results are not only important as a model of the photosynthetic reaction center but also attractive in relation to the mechanism of electron and energy transfer in photonic devices.

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14 The *D* values were evaluated using HOMO and LUMO calculated under the PPP approximation (ref. 11)

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