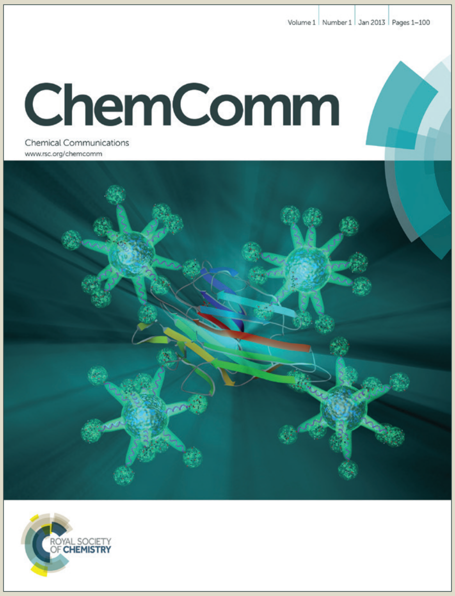
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Chem. Commun.

RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

A Phthalocyanine-Subphthalocyanine Heterodinuclear Dimer: Comparison of Spectroscopic Properties with Those of Homodinuclear Dimers of Constituting Units

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Norio Shibata,[a] Satoru Mori,[a] Masamichi Hayashi,[a] Masashi Umeda,[a] Etsuko Tokunaga[a] Motoo Shiro,[b] Hiroyasu Sato[b] Tomonori Hoshi,[c] and Nagao Kobayashi[d]**

A phthalocyanine-subphthalocyanine heterodinuclear dimer has been disclosed for the first time with its unique flat-bowl-shaped structure revealed by X-ray crystallography. Its spectroscopic properties were compared with those of homodinuclear dimers of constituting units, as well as those of constituting monomeric units.

Phthalocyanines (Pcs) and subphthalocyanines (SubPcs) are some of the most attractive functional dyes and useful as advanced materials due to their unique electronic and optical properties.[1] In addition to sandwich or μ-oxo type cofacial dimers and oligomers,[2] planar dimers and oligomers have been synthesized and characterized in the last three decades.[3] Pcs are disk-like, 18 π-electron aromatic macrocycles consisting of four isoindoline units. On the other hand, SubPcs, which can be regarded as Pc analogues, are non-planar cone-shaped 14 π-electron aromatic macrocycles composed of three isoindoline units.[4] While the flat or nearly flat π-systems of Pcs enhance the molecular aggregations of Pcs, SubPcs generally do not aggregate due to their curved π-structures. One of the current research interests in this field is focused on the polynuclear systems of Pcs and SubPcs to develop novel conjugated π-surfaces. Among various reports, dinuclear Pcs[5] and dinuclear SubPcs[6] fused together having common benzene rings are quite attractive, since their original 18 π- or 14 π-systems interact strongly with each other through a common benzene ring. In contrast to the benzene-fused dinuclear Pcs which have large conjugated planar π-systems, the benzene-fused dinuclear SubPcs exist as geometrical isomers due to a bowl-shaped π-system. In this context, we hypothesized that a combination of Pcs and SubPcs shared a central benzene ring. Although fused Pc dimers and fused SubPc dimers have been reported since 1987 and 1991, respectively, fused heterodinuclear Pc and SubPc dimers have never been reported, despite their potential usefulness in electron transfer processes and so forth. Herein we disclose the structure and spectral data of previously known ZnPc-SubPc fused heterodimer **1**[7] for the first time. X-ray crystallography of **1** revealed an inimitable planar-bowl-shaped π-system for the first time. Comparison of spectroscopic properties of **1** with those of homodinuclear dimers of constituting units, ZnPc-ZnPc **2**[7] and SubPc-SubPc **3**[7], as well as monomeric **8** and **9** are discussed.

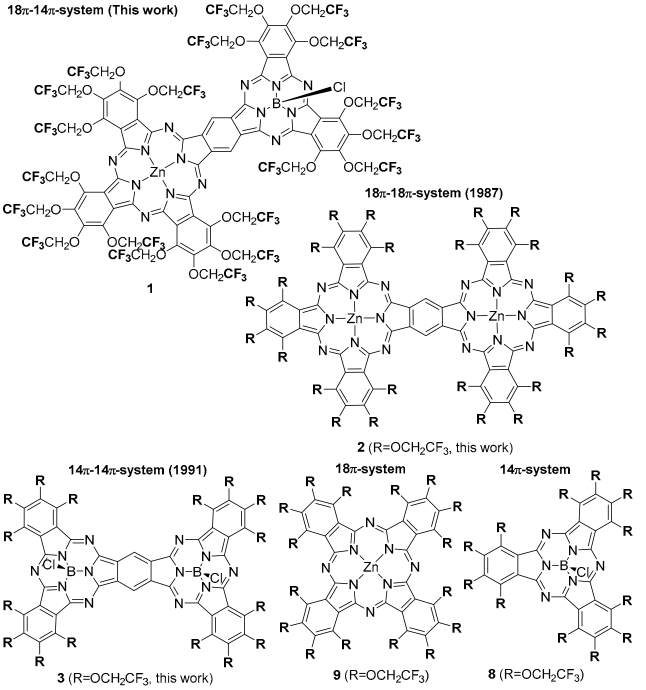


Fig. 1. ZnPc-SubPc heterodimer **1**, homodimers **2**, **3** and monomer **8**, **9**.

Growing crystals of large molecular Pcs is notoriously a difficult task owing to their characteristics to aggregate. However, luckily the molecular structure of **1** was unambiguously revealed by X-ray crystallography. Single crystals of **1** were grown by slow evaporation of the solvent from a solution (ethyl acetate with a small amount of toluene). As shown in Fig. 2, the SubPc unit formed a cone-shaped structure and the Pc moiety has a flat disk-like structure. The zinc center of the Pc unit was coordinated with ethyl acetate, and toluene was confirmed in the crevice of the curve structure of the SubPc unit (Fig. 2).

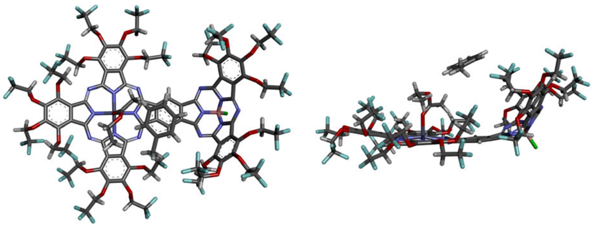


Fig. 2 X-ray crystallography of **1** (CCDC943766).

Figure 3 shows electronic absorption and magnetic circular dichroism (MCD) spectra of **1**, **2**, and **3**. A SubPc **8** prepared from **4** and BCl_3 shows Q band at 604 nm[8] while ZnPc **9** consisting of only four **4** units has Q band peak at 708 nm,[9] so that the absorption spectra shown in this figure are all not expressed as a summation of the spectrum of constituent monomer units, suggesting the presence of interaction between the SubPc and ZnPc units in these dimers.[10] With respect to the electronic absorption data in this figure, the following phenomena can be seen. i) Both the Soret and Q bands generally shift to longer wavelengths with concomitant increase in intensity with increasing molecular size. ii) At least two absorption peaks are observed in the Q band region, and the band at the longest wavelength is stronger. From the MCD spectra, we can extract the following facts. iii) In both the Q and Soret band regions, Faraday *B* terms were observed in accord with the molecular symmetry of **1**-**3**. iv) By comparing MCD and absorption spectra, the Qx (long-axis) and Qy (short axis) bands in absorption spectra can be assigned respectively as follows; 850 and 748 nm for **2** ($D_{Qy\text{-}Qx}$ = 1604 cm^{-1}), 800 and 716 nm for **1** (1466 cm^{-1}), and 728 and 627 nm for **3** (2213 cm^{-1}). v) The minus-to-plus sign change on going from the Qx to Qy bands experimentally suggests that the ΔHOMO (the energy difference between the HOMO and HOMO-1) is larger than ΔLUMO (the energy difference between the LUMO and LUMO+1).[11] Thus, i)-v) suggest that **1** (ZnPc-SubPc) is indeed the intermediary compound situating between ZnPc-ZnPc **2** and SubPc-SubPc **3**.

In order to enhance the interpretation of the above spectra, molecular orbital (MO) calculations have been performed. The molecular geometries of **2** and **3** were first optimized at the DFT level using the B3LYP/6-31G(d), as implemented in Gaussian 09,[12] while for **1**, we used the X-ray data. The calculated electronic absorption spectra are included in Fig. 3, and partial MO energy diagrams are shown in Fig. 4, while the result of TDDFT calculations are summarized in Table S1 (some frontier MOs of **1** are shown in Fig. S36). As seen in the calculated absorption spectra, experimental tendency is approximately reproduced, although transition energies are slightly overestimated. For example, the above i) and ii) are nicely reproduced. One characteristic point is that a transition of intermediary intensity is predicted between the Q and Soret bands. Although this band is not explicitly seen in the spectra of ZnPc-ZnPc dimer **2**, the 500-550 nm of **1** and 450-500 nm region of **7** may correspond to this band. Fig. 4 suggests the following. vi) MOs in monomer split into two orbitals in dimers, so that one of the two split Q bands are calculated at longer wavelength. Although not shown, dimer orbitals can be expressed as a linear combination of monomer orbitals.[10a,h] For example, a_u (272) and b_{1g} (273) of ZnPc-ZnPc can be expressed as $a_{1u} + a_{1u}$ and $a_{1u} - a_{1u}$, respectively. In the case of LUMOs, e_{gx} component splits more than that of e_{gy}. So, for example, in ZnPc-SubPc, a”(237) and a”(240) originate from e_{gx} components, while a’(238) and a’(239) are from e_{gy}. vii) The energy difference between the HOMO and LUMO decreases with increasing molecular size, in agreement with the experiment-al Q band position (Fig. 3). viii) In heterodinuclear **1**, judging from the orbital energy, the contribution of ZnPc moiety is larger than that from SubPc for both the HOMO and LUMO, and this is indeed shown in Fig. S36. This is unusual in that for both HOMO and LUMO, the contribution of the same moiety is larger than that of another. The configurations in Table S1 suggest the following. ix) The Q band at the longest wavelength (i.e. Qx) is the transition from the HOMO to LUMO, while that Qy is mainly that from the HOMO to LUMO+1. x) For all dimers, the third band from the lower energy corresponds to a transition mainly from HOMO-1 to LUMO+2.

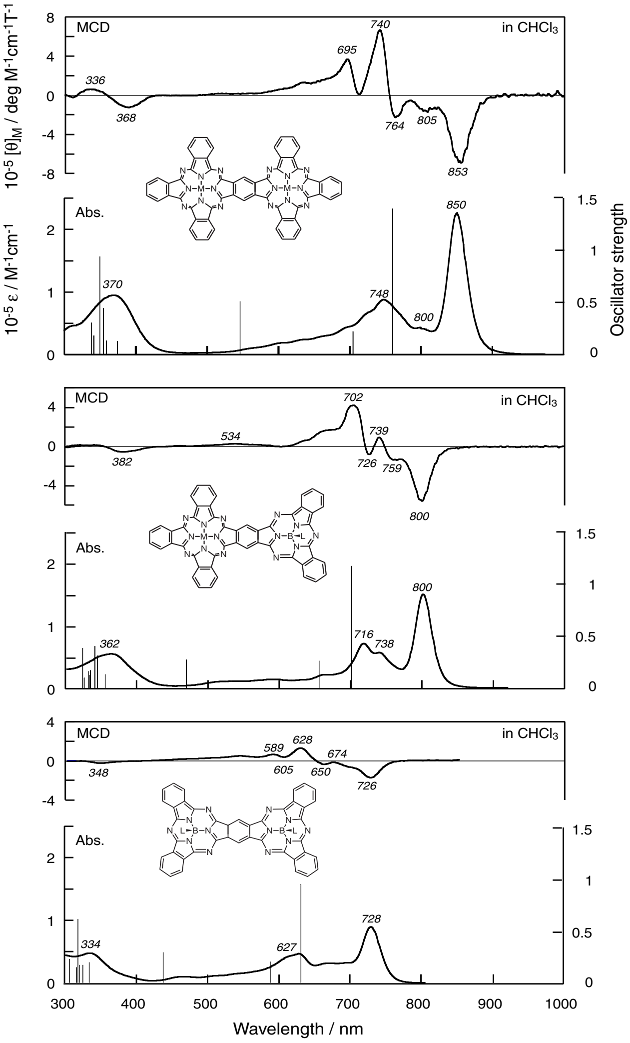


Fig. 3 Electronic absorption and magnetic circular dichroism (MCD) spectra of ZnPc-ZnPc **2** (top), ZnPc-SubPc **1** (middle), and SubPc-SubPc **3** (bottom) in $CHCl_3$. All compounds contain OCH_2CF_3 groups as substituents, but these are omitted in the structure.

Lastly, we examined ZnPc-SubPc **1** and its homodinuclear dimers **2**, **3** using steady-state fluorescence spectroscopy in solvents of different polarities (CH_2Cl_2, trifluorotoluene and dioxane) (Figs. S13-S17). When ZnPc-SubPc **1** was excited at vibrational region of the Q band (i.e. 650 nm), two emission peaks appeared at 720 nm and 809 nm. Since Qy and Qx bands of **1** are at 716 and 800 nm (Fig. 3), this indicates that emission occurs from both the Qy and Qx states. However, since the emission band at the lowest energy is the strongest, it is considered that emission occurs mostly from the Qx excited state. Table 1 summarizes the data.

In conclusion, we disclosed a novel hetero-dinuclear ZnPc-SubPc **1** for the first time. An inimitable planar-bowl-shaped π-surface was revealed by X-ray crystallographic analysis. Photo-physical studies indicate that **1** is free from aggregation and that there is good intramolecular communication between the Pc and SubPc moieties. The spectroscopic properties of heterodinuclear **1** are indeed intermediary between those of the homodimers of the constituent unit, i.e. ZnPc-ZnPc **2** and SubPc-SubPc **3**.

This study was financially supported in part by the Platform for Drug Discovery, Informatics, and Structural Life Science, Grant-in-Aids for Scientific Research on Innovative Areas (“Advanced Molecular Transformations by Organocatalysts”; “Stimuli-responsive Chemical Species”) and Scientific Research (B) from MEXT Japan, ACT-C from JST, Exploratory Research, Encouragement of Scientists (to ET, 24915016) from JSPS.

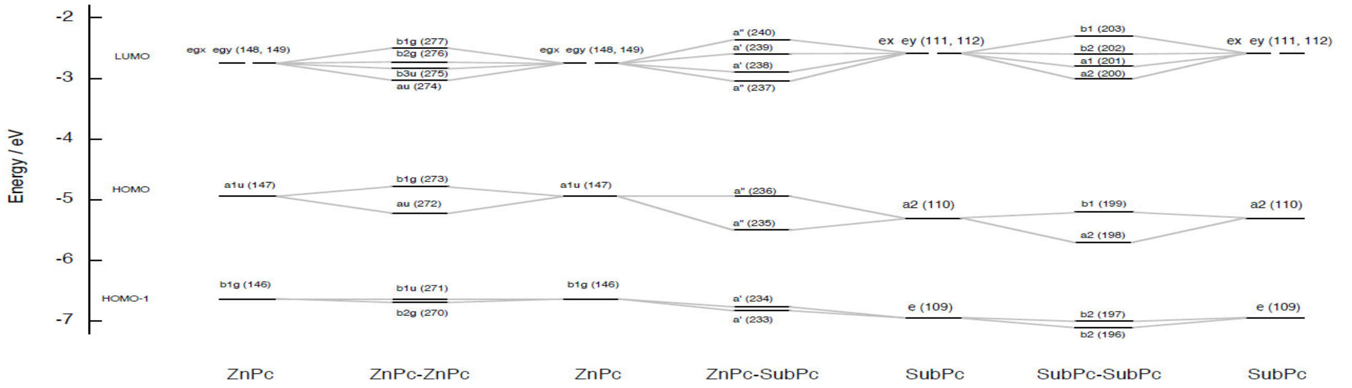


Fig. 4 Partial molecular orbital energy diagram for ZnPc-ZnPc, ZnPc-SubPc, and SubPc-SubPc, and for ZnPc and SubPc, and their mutual relationship. The numbers in the parentheses indicate orbital number.

Table 1 Fluorescence quantum yields[a] (Φ_F) and emission maxima (λ_{em}[nm]) of **1**, **8** and **9** upon excitation at (a) 650 nm and (b) 530 nm.

	dioxane	$PhCF_3$	$PhCF_3$[b]	CH_2Cl_2
(a)				
ZnPc-SubPc **1**	0.095 (722,810)	0.014 (725,812)	0.053 (723,810)	0.0065 (763)
ZnPc **9**	0.28 (720)	0.29 (716)		
(b)				
ZnPc-SubPc **1**	0.068 (619,810)	0.0065 (615,817)	0.027 (618,808)	0.010 (623,795)
SubPc **8**	0.85 (621)	0.95 (618)		

[a] Determined by using ZnPc in 1-chloronaphthalene as reference (Φ_F = 0.30). [b] Addition of 1% volume of pyridine

Notes and references

[a] Department of Nanopharmaceutical Science and Department of Frontier Materials Nagoya Institute of Technology. Gokiso, Showa-ku, Nagoya 466-8555, Japan.
[b] Rigaku Corporation, 3-9-12 Mastubara-cho, Akishima, Tokyo 196-8666, Japan.
[c] Pharmaceutical Institute, Tohoku University, Sendai 980-8578, Japan.
[d] Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan.

† Experimental and spectral data, and Electronic Supplementary Information (ESI) available: See DOI: 10.1039/c000000x/

---

1 a) Handbook of Porphyrin Science, (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), World Scientific, Singapore, Vols. 1-25, 2010-2012; b) The Porphyrin Handbook, (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, Vols. 1-20, 1999, 2003C; c) Phthalocyanines - Properties and Applications, (Eds.: C. C. Leznoff, A. B. P. Lever), VCH, XXX, Vols. 1-4, 1989, 1992, 1993, 1996; d) Advances in Functional Phthalocyanine Materials, Structure and Bonding, Vol. 135 (Ed.: J. Jiang; Series Ed.: D. M. P. Mingos), Springer, Heidelberg, 2010.

2 a) J. Jiang, D. K. P. Ng, *Acc. Chem. Res.* **2009**, *42*, 79; b) J. Jiang, W. Liu, D. P. Arnold, *J. Porphyrins Phthalocyanines* **2003**, *7*, 459; c) D. K. P. Ng, J. Jiang, *Chem. Soc. Rev.* **1997**, *26*, 433.

3 a) N. Kobayashi, *Coord. Chem. Rev.* **2002,** *227*, 129; b) G. de la Torre, G. Bottari, M. Sekita, A. Hausmann, D. M. Guldi, T. Torres, *Chem. Soc. Rev.* **2013**, *42*, 8049.

4 a) T. Torres, *Angew. Chem., Int. Ed.* 2006, **45**, 2834. b) C. G. Claessens, D. Gonzlez-Rodrguez, T. Torres, *Chem. Rev.* **2002**, *102*, 835.

5 C. C. Leznoff, H. Lam, S. M. Marcuccio, W. A. Nevin, P. Janda, N. Kobayashi, A. B. P. Lever, *J. Chem. Soc., Chem. Commun.* **1987**, 699.

6 N. Kobayashi, *J. Chem. Soc., Chem. Commun.*, **1991**, 1203.

7 The experimental procedure for the synthesis of all the novel compounds **1**, **2** and **3** with their spectral data are available in ESI. The detailed discussion for their synthesis will be reported elsewhere.

8 N. Shibata, B. Das, E. Tokunaga, M. Shiro, N. Kobayashi, *Chem. Eur. J.* 2010, **16**, 7554.

9 N. Kobayashi, N. Sasaki, Y.Higashi, T. Osa, *Inorg. Chem.* 1995, **34**, 1636.

10 The presence of electronic interaction between the two constituent units in planar homodimers and heterodimers were reported, for example, in the following (a)-(g) and (h), respectively. a) N. Kobayashi, H. Lam, W. A. Nevin, P. Janda, C. C. Leznoff, T. Koyama, A. Monden, H. Shirai, *J. Am. Chem. Soc.* 1994, **116**, 879. b) N. Kobayashi, T. Fukuda, D. Lelievre, *Inorg. Chem.* 2000, **39**, 3632. c) C. G. Claessens, T. Torres, *Angew. Chem. Int. Ed.* 2002, **47**, 2561. d) T. Fukuda, R. J. Stork, R. J. Potucek, M. M. Olmstead, B. C. Noll, N. Kobayashi, W. S. Durfee, *Angew. Chem. Int. Ed.* 2002, **47**, 2565. e) S. Makarov, C. Litwinski, E. A. Ermilov, O. Suvorova, B. Roder, D. Wöhrle, *Chem. Eur. J.* 2006, **12**, 1468. f) T. V. Dubinina, N. E. Borisova, K. V. Paramonova, L. G. Tomilova, *Mendeleev Commun.* 2011, **21**, 165. g) Y. Asano, J. Sato, T. Furuyama, N. Kobayashi. *Chem. Commun.* 2012, **48**, 4365.h) N. Kobayashi, H. Ogata, *Eur. J. Inorg. Chem.* **2004**, 906.

11 a) J. Michel, *J. Am. Chem. Soc.* 1978, **100**, 6801, 6812. b) J. Michl, *Tetrahedron* 1984, **40**, 3845. c) N. Kobayashi, A. Muranaka, J. Mack, in *Circular Dichroism and Magnetic Circular Dichroism for Organic Chemists*, Royal Society of Chemistry, London, 2011.

12 M. J. Frisch et al., Gaussian 09, Revision C. 01, Gaussian Inc., Wallingford, CT, 2009. See the ESI for the full list of authors.