第 28 卷第 9 期
2012 年 9 月

无 机 化 学 学 报
CHINESE JOURNAL OF INORGANIC CHEMISTRY

Vol.28 No.9
1779-1789

一种新型的平面共轭的酞菁卟啉二联体的合成及光谱研究

王 康[1] 齐冬冬[1] Mack John[2] 王海龙[1] 李文军[1] 边永忠[1] 小林长夫[2] 姜建壮*[,1]

([1]北京科技大学化学与生物工程学院,功能分子与晶态材料科学与应用北京市重点实验室,北京 100083)

([2]日本东北大学理学院化学系,仙台 980-8578,日本)

摘要：5,10,15,20-四(4-氯苯基)-2′,3′-二氰基[2,3-β]吡嗪和 4,5-二(丁烷氧基)邻二氰基苯在锂存在的条件下在正戊醇中回流四聚,然后用醋酸处理得到了一种新型的平面共轭酞菁二联体 H_4\{[(DAPc(OC_4H_9)$_6$][TClPP]\} (**1**)(其中 DAPc(OC_4H_9)$_6$ 是 2,3,9,10,16,17-六(丁烷氧基)-22,25-二氮杂酞菁的二价阴离子,TClPP 是 5,10,15,20-四(4-氯苯基)卟啉的二价阴离子)。这种二联体和 $Zn(OAc)_2\cdot 2H_2O$ 在 DMF 和甲苯混合溶剂中反应得到双金属配合物 Zn_2\{[(DAPc(OC_4H_9)$_6$][(TClPP)]\} (**2**)。质谱和核磁共振光谱等一系列的表征方法证明了这种双核的混杂四吡咯结构。电子吸收光谱和磁圆二色谱证明了酞菁发色团和卟啉发色团之间存在有效的分子内电子相互作用。这一结论进一步得到了理论计算的支持。

关键词：四吡咯化合物；酞菁；卟啉；共轭二联体；混杂双核

中图分类号：O614.24+1 **文献标识码**：A **文章编号**：1001-4861(2012)09-1779-11

Fusing Phthalocyanine and Porphyrin together: Unprecedented Co-planar Ring-Fused Diazaphthalocyaninato-porphyrin Dimers

WANG Kang[1] QI Dong-Dong[1] Mack John[2] WANG Hai-Long[1]
LI Wen-Jun[1] BIAN Yong-Zhong[1] KOBAYASHI Nagao[2] JIANG Jian-Zhuang*[,1]

([1]*Beijing Key Laboratory for Science and Application of Functional Molecular and Crystalline Materials, Department of Chemistry, University of Science and Technology Beijing, Beijing* 100083, *China*)

([2]*Department of Chemistry, Graduate School of Science, Tohoku University, Sendai* 980-8578, *Japan*)

Abstract: An unprecedented ring-fused co-planar diazaphthalocyaninato-porphyrin dimer H_4\{[(DAPc(OC_4H_9)$_6$][TClPP]\} (where DAPc (OC_4H_9)$_6$ is the dianion of 2,3,9,10,16,17-hexa (butyloxy)-22,25-diazaphthalocyanine, and TClPP is the dianion of 5,10,15,20-tetra(4-chloro)porphyrin) (**1**) was synthesized by mixed cyclic tetramerization of 5,10,15,20-tetrakis(4-chlorophenyl)-2′,3′-dicyanopyrazino[2,3-β] porphyrin with 4,5-di(butyloxy)phthalonitrile in the presence of lithium in refluxing *n*-pentanol followed by treatment with acetic acid. Reaction of the metal free dimer with $Zn(OAc)_2\cdot 2H_2O$ in DMF and toluene led to the isolation of a bimetallic zinc(Ⅱ) complex Zn_2\{[(DAPc(OC_4H_9)$_6$] [(TClPP)]\} (**2**). The binuclear and mixed tetrapyrrole ring nature of the structure was clearly demonstrated by a series of characterization methods including mass spectrometry and NMR spectroscopy. The Q band region of the electronic absorption and magnetic dichroism (MCD) spectra provide evidence for significant intramolecular interaction between the phthalocyanine and porphyrin chromophores. Theoretical calculations provide further support for this.

Key words: tetrapyrrole; phthalocyanine; porphyrin; conjugated dimer; mixed binuclear

收稿日期：2012-05-09。收修改稿日期：2012-07-16。

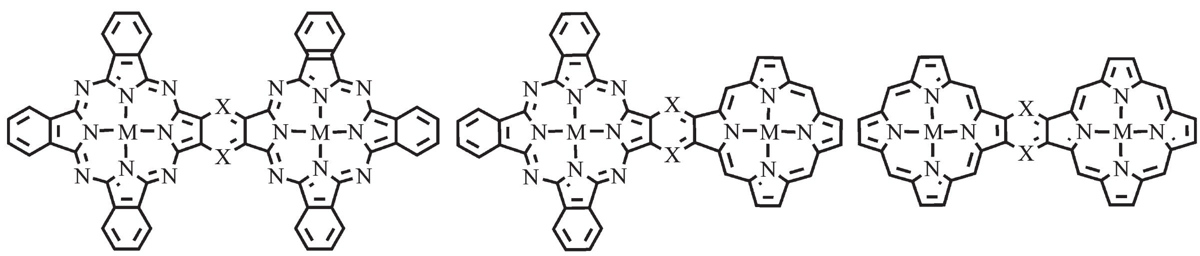
国家自然科学基金(No.2012CB224801),日本教育部科学创新基金(No.20108007)资助项目。

*通讯联系人。E-mail：jianzhuang@ustb.edu.cn

0 Introduction

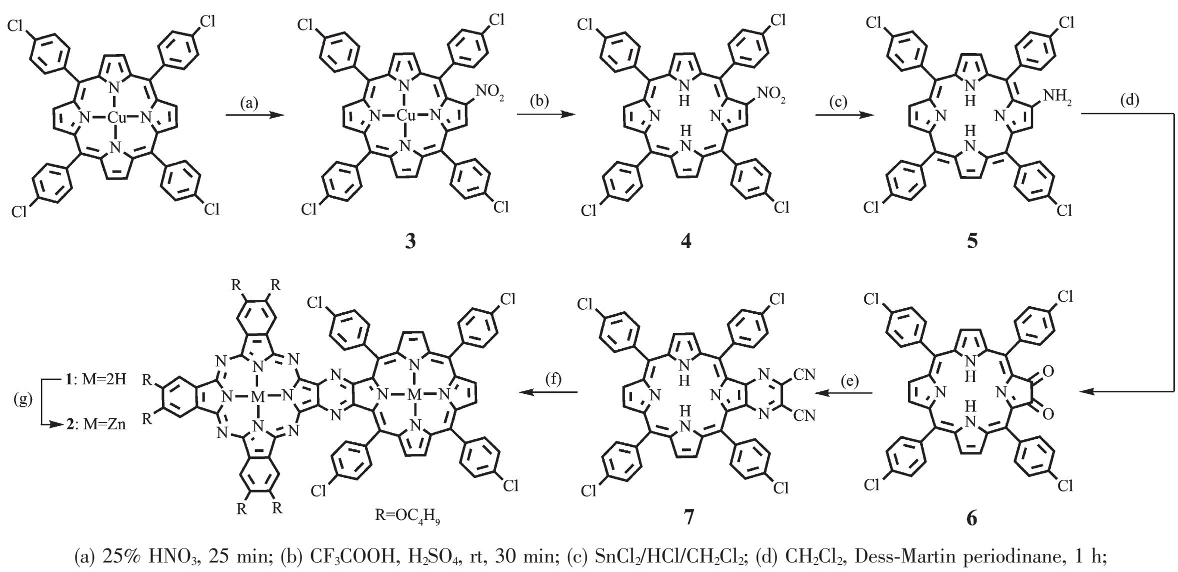
Tetrapyrrole derivatives, including naturally occurring porphyrins and their synthetic structural analogues such as porphyrazines and phthalocyanines, have been studied intensively over the past century due to their biological relevance and wide variety of industrial applications[1]. In the past few decades, conjugated dimers and oligomers of both porphyrins and phthalocyanines with extended π electronic structure have been the focus of significant research interest since their special optical and electrochemical properties make them suitable for applications in molecular devices [2-3]. To the best of our knowledge, no co-planar ring-fused heterodimers or -oligmers have been reported, which contain both porphyrin and phthalocyanine rings. The only heterodimer or -oligmer structures that have been reported are bi- or polymetallic complexes comprised of the same tetrapyrrole ring system (Scheme 1).

In this paper, we describe the synthesis of unprecedented co-planar binuclear diazaphthalocyaninato-porphyrin dimer compounds, in which the two tetrapyrrole chromophores share a common pyrazine ring, $M_2\{[(DAPc(OC_4H_9)_6][(TClPP)]\}$ (where $DAPc(OC_4H_9)_6$ is the dianion of 2,3,9,10,16,17-hexa(butyloxy)-22,25-diaza-phthalocyanine and TClPP is the dianion of 5,10,15,20-tetra (4-chloro)porphyrin) (M =2H, Zn) (**1**, **2**), Scheme 2. The binuclear and mixed tetrapyrrole ring dimer structures are clearly demonstrated by a series of characterization methods including mass spectrometry and NMR, electronic absorption, and magnetic circular dichroism (MCD)



(A) (B) (C)

Scheme 1 Schematic molecular structures of planar fused homo-binuclear phthalocyaninato-phthalocyanine dimer (A), mixed-binuclear phthalcoyaninato-porphyrin dimer (B), and homo-binuclear porphyrinato-porphyrin dimer (C) with X = CH or N



(a) 25% HNO_3, 25 min; (b) CF_3COOH, H_2SO_4, rt, 30 min; (c) $SnCl_2/HCl/CH_2Cl_2$; (d) CH_2Cl_2, Dess-Martin periodinane, 1 h; (e) Diaminomaleonitrile, THF, reflux, 1 d; (f) Dicyanobenzene, Li, n-$C_5H_{11}OH$, reflux, 1 h; (g) $Zn(OAc)_2\cdot 2H_2O$, DMF and toluene, 80 ℃, 4 h

Scheme 2 Synthesis of planar mixed-binuclear phthalcoyaninato-porphyrin dimer **1** and **2** spectroscopy. In particular, fusion of the individual chromophores with significant different optical, electrochemical, and physiochemical properties into such kind of novel conjugated mixed tetrapyrrole compounds is expected to lead advanced molecular materials with novel property and functionality over individual components.

1 Experimental

1.1 General remarks

n-Pentanol was distilled from sodium. DMF was distilled from anhydrous $MgSO_4$. Column chromatography was carried out on silica gel column (Merck, Kieselgel 60, 70~230 mesh) with the indicated eluents. All other reagents and solvents were used as received. The compounds of 4,5-di (butyloxy) phthalonitrile[4], CuTClPP[5], 2-nitro-*meso*-tetrakis (4-chlorophenyl)porphyrin[6], 2,3-dioxo-5,10,15,20-tetrakis (4-chlorophenyl)porphyrin [7] were prepared according to the published procedure.

^{1}H NMR spectra were recorded on a Bruker DPX 400 spectrometer in $CDCl_3$. Spectra were referenced internally using the residual solvent resonances (δ= 7.26 for ^{1}H NMR) relative to $SiMe_4$. Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. IR spectra were recorded as KBr pellets using a Bruker Tensor 37 spectrometer with 2 cm^{-1} resolution. MALDI-TOF mass spectra were taken on a Bruker BIFLEX Ⅲ ultrahighresolution Fourier transformion cyclotron resonance (FT-ICR) mass spectrometer with alpha-cyano-4-hydroxycinnamic acid as matrix. Elemental analyses were performed on an Elementar Vavio El Ⅲ.

1.2 Computational details

Density functional theory (DFT) and time dependent density functional theory (TD-DFT) methods of hybrid B3LYP functional with Becke exchange[8] and LeeYangParr correlation[9] were used to study the molecular structure, electronic structure, and electronic absorption spectrum. In all the cases, the 6-31G (d) basis set was employed. The Berny algorithm using redundant internal coordinates[10] was utilized in energy minimization, and the default cutoffs were used throughout. The total electron density difference between ground and excited states ($\sum f_{m\rightarrow n}$) is calculated by the molecular orbital electron density difference $f_{m\rightarrow n}=\frac{c^2_{m\rightarrow n}}{\sum c^2_{m\rightarrow n}}(\rho_n-\rho_m)$, where ρ_n and ρ_m are the electron density of the two molecular orbitals relative to the electron transition model of MO (m)→MO (n), $c_{m\rightarrow n}$ is the orthogonal coefficient in the TD-DFT equation, and then $\frac{c^2_{m\rightarrow n}}{\sum c^2_{m\rightarrow n}}$ can be considered as the contribution of this electron transition model to this absorption peak. The electron density difference between ground and excited states is the linear combination of various electron transition models. Also for the reason of time efficiency, only the electron transition models with the configuration larger than 5.0% are taken into account. The electron density difference map is plotted using the isovalue of 2.0×10^{-4} e·au^3. All the calculations were carried out using the Gaussian 03 program[11] on an IBM P690 system housed at Shandong Province High Performance Computing Center.

Preparation of 2-nitro-*meso*-tetrakis (4-chlorophenyl)porphyrin (**4**): Aqueous nitric acid (25%, 25 mL) was added in a dropwise manner via a syringe to a solution of CuTClPP (81 mg, 0.1 mmol) in $CHCl_3$ (140 mL) and stirred at room temperature. The reaction was completed after 30 min as monitored by TLC. Then the resulting reaction mixture was washed with water (4×200 mL) and dried with Na_2SO_4/K_2CO_3. The solvent was removed by evaporation and the residue was chromatographed on a silica gel column using CH_2Cl_2/light petroleum (1∶1) as the eluent. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave pure 2-nitro-meso-tetrakis (4-chlorophenyl)porphyrinato] copper complex (**3**) as purple microcrystals (34 mg, 40%).

To a solution of **3** (68 mg, 0.08 mmol) in concentrated H_2SO_4 (2 mL), CF_3COOH (3 mL) was added slowly in a dropwise manner via a syringe. After stirring at room temperature for 30 min, the reaction mixture was poured into water (100 mL) and extracted with $CHCl_3$ (5×40 mL). The combined organic solution was then washed with water (2×100 mL) and dried with Na_2SO_4/K_2CO_3. After evaporating the solvent, the residue was chromatographed on a silica gel column with CH_2Cl_2/light petroleum (2:3) as eluent. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave pure 2-nitro-meso-tetrakis (4-chlorophenyl)porphyrin (**4**) as purple microcrystals (51 mg, 80%). ^1H NMR ($CDCl_3$, 400 MHz): δ 9.01 (s, 1 H, pyrrole-β-H), 8.92~8.96 (m, 4 H, pyrrole-β-H), 8.86~8.89 (m, 4 H, pyrrole-β-H), 8.69 (m, 2 H, pyrrole-β-H), 8.09~8.14 (m, 8 H, Ar), 7.74~7.77 (m, 6 H, Ar), 7.67~7.79 (d, 2 H, Ar) -2.71 (s 2 H, NH). MALDI-TOF MS: an isotopic cluster peaking at *m/z* 796.0. Calcd. for $C_{44}H_{25}Cl_4N_5O_2$: $[M+2H]^+$ 796.1. Anal. Calcd. for $C_{44}H_{25}Cl_4N_5O_2CH_3OH\cdot2CHCl_3$(%): C, 52.84; H, 2.92; N, 6.56. Found(%): C, 52.90; H, 3.04; N, 6.49.

Preparation of 2,3-dioxo-5,10,15,20-tetrakis (4-chlorophenyl)porphyrin (**6**): Tin(Ⅱ) chloride dihydrate (185 mg, 0.821 mmol) and concentrated hydrochloric acid (0.5 ml) were added to a solution of **4** (64 mg, 0.080 mmol) in dichloromethane (4 mL) and stirred at room temperature under nitrogen atmosphere in the dark. The reaction was completed after 2 h as monitored by TLC. Then dichloromethane (20 mL) and water (20 mL) were added. The organic layer was separated, washed with water and sodium bicarbonate solution (5%, 30 mL), and dried over Na_2SO_4/K_2CO_3. The solvent was removed by evaporation and the residue was purified by recrystallization from $CHCl_3$ and MeOH, yielding a purple solid of **5** (60 mg, 98%).

Dess-Martin periodinane (DMP) (36 mg, 0.08 mmol) was added to a solution of 5 (60 mg, 0.08 mmol) in dichloromethane (10 mL) and stirred at room temperature in the dark. The reaction was completed after 45 min as monitored by TLC. Then hydrochloric acid (1 mol·L^{-1}, 30 mL) was added and the reaction mixture was stirred for further 20 min. The organic layer was separated, washed with water (2×100 mL), and dried over Na_2SO_4/K_2CO_3. The solvent was removed by evaporation and the residue was chromatographed on a silica gel column using a dichloromethane/*n*-hexane mixture (1:1) as eluent. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave **6** as purple microcrystals (16 mg, 25%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.94~9.00 (t, 4 H, pyrrole-β-H), 8.71 (s, 2 H, pyrrole-β-H), 8.09~8.11 (d, 4 H, Ar), 7.93~7.95 (d, 4 H, Ar), 7.32~7.77 (t, 8 H, Ar). MALDI-TOF MS: an isotopic cluster peaking at *m/z* 782.2. Calcd. for $C_{44}H_{24}Cl_4N_4O_2$, $[M+2H]^+$ 782.0. Anal. Calcd. for $C_{44}H_{24}Cl_4N_4O_2\cdot2C_6H_{14}\cdot2CH_3OH\cdot2H_2O$(%): C, 66.03; H, 6.11; N, 5.31. Found (%): C, 66.03; H, 6.05; N, 5.31.

Preparation of 5,10,15,20-tetrakis(4-chlorophenyl)-2′,3′-dicyanopyrazino [2,3-β]porphyrin (**7**): The mixture of 2,3-dioxo-5,10,15,20-tetrakis (4-chlorophenyl)porphyrin (**5**) (32.0 mg, 0.04 mmol) and 2,3-diaminomaleonitrile (4.2 mg 0.04 mmol) in dry THF (5 mL) was stirred at room temperature for 1 d under nitrogen. The solvent was then removed under reduced pressure and the residue was chromatographed on a silica gel column with dichloromethane/light petroleum (3:2) as eluent. Repeated chromatography followed by recrystallization from $CHCl_3$ and *n*-hexane gave **7** as a purple powder (12 mg, 35%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.93~8.94 (d, 2 H, pyrrole-β-H), 8.88~8.92 (d, 2 H, pyrrole-β-H), 8.65 (s, 2 H, pyrrole-β-H), 8.03~8.05 (d, 4 H, Ar), 7.88~7.90 (d, 4 H, Ar), 7.66~7.70 (t, 8 H, Ar), −2.83 (s, 2 H, NH). MALDI-TOF MS: an isotopic cluster peaking at *m/z* 854.0. Calcd. for $C_{48}H_{24}Cl_4N_8$, $[M+2H]^+$ 854.1. Anal. Calcd. for $C_{48}H_{24}Cl_4N_8\cdot2C_6H_{14}$(%): C, 70.17; H, 5.10; N, 1 0.91. Found(%): C, 70.25; H, 5.06; N, 10.70.

Preparation of metal free mixed-binuclear phthalcoyaninato-porphyrin dimer $H_4\{[(DAPc(OC_4H_9)_6][(TClPP)]\}$ (**1**): A mixture of 4,5-di(butyloxy)phthalonitrile (270 mg, 1.0 mmol), 5,10,15,20-tetrakis (4-chlorophenyl)-2′,3′-dicyanopyrazino [2,3-β]porphyrin (30.0 mg, 0.035 mmol), and lithium (7 mg, 1.0 mmol) in *n*-pentanol (5 mL) was heated to reflux under nitrogen for 1.5 h. After being cooled to room temperature, the resulting green solution was poured into methanol (100 mL) containing 2 mL of CH_3COOH. The precipitate was collected by filtration and chromatographed on a silica gel column using CH_2Cl_2 as eluent. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave **1** as a dark-green powder (6.0 mg, 10%). ^1H NMR ($CDCl_3$, 400 MHz): δ 11.43 (s, 2 H, Por-Ph-H), 10.45 (s, 2 H, Por-Ph-H), 9.76 (s, 2 H, pyrrole-β-H), 9.57 (s, 2 H, Por-Ph-H), 8.94 (s, 2 H, pyrrole-β-H), 8.50 (s, 2 H, pyrrole-β-H), 8.38 (s, 2H, Por-Ph-H) 7.71~8.14 (m, 8 H, Pc-α-H, Por-Ph-H), 6.50 (s, 2H, Pc-α-H), 5.78 (s, 2 H, O$\mathbf{CH_2}$$CH_2CH_2CH_3$), 5.34 (s, 2 H, O$\mathbf{CH_2}$$CH_2CH_2CH_3$), 4.44~4.88 (m, 8 H, O$\mathbf{CH_2}$$CH_2CH_2CH_3$), 2.65 (s, 4 H, $OCH_2$$\mathbf{CH_2}$$CH_2CH_3$), 2.05~2.67 (m, 12 H, $OCH_2$$\mathbf{CH_2}$$CH_2CH_3$, $OCH_2CH_2$$\mathbf{CH_2}$$CH_3$), 1.89~2.05 (m, 8 H, $OCH_2CH_2$$\mathbf{CH_2}$$CH_3$), 1.28~1.40 (m, 18 H, $OCH_2CH_2CH_2$$\mathbf{CH_3}$), −4.57 (s, 2 H, NH), −6.40 (s, 2 H, NH). MALDI-TOF MS: an isotopic cluster peaking at *m/z* 1 672.8, Calcd. for $C_{96}H_{86}Cl_4N_{14}O_6$, $[M+2H]^+$ 1 672.6. Anal. Calcd. for $C_{96}H_{86}Cl_4N_{14}O_6\cdot CHCl_3\cdot H_2O$(%): C, 64.33; H, 4.95; N, 10.83. Found(%): C, 64.53; H, 4.96; N, 10.86.

Preparation of zinc complex of mixed-binuclear phthalcoyaninato-porphyrin dimer $Zn_2\{[(DAPc(OC_4H_9)_6][(TClPP)]\}$ (**2**): A mixture of $H_4\{[(Pc(OC_4H_9)_6][(TClPP)]\}$ (**1**) (5 mg, 0.003 mmol) and $Zn(OAc)_2\cdot 2H_2O$ (22 mg, 0.01 mmol) in DMF and toluene (1∶1) (4 mL) was heated at 80° for 4 h under nitrogen. After being cooled to room temperature, the mixture was evaporated under reduced pressure and the residue was chromatographed on a silica gel column using $CHCl_3$ as the eluent. The first pale-green band containing the target compound (**2**) was developed. Repeated chromatography followed by recrystallization from $CHCl_3$ and hexane gave green powder (4.3 mg, 85% yield). ^1H NMR ($CDCl_3$/[D_5]Pyridine 10:1, 400 MHz): δ 11.71 (d, 2 H, Por-Ph-H), 10.60 (d, 2 H, Por-Ph-H), 9.70 (d, 2 H, Por-Ph-H), 8.90 (d, 2 H, pyrrole-β-H), 8.52 (s, 2 H, Por-Ph-H), 8.36 (d, 2 H, Por-Ph-H), 8.21 (d, 2 H, pyrrole-β-H), 8.13 (d, 2 H, Por-Ph-H), 8.05 (d, 2 H, Por-Ph-H), 7.65~7.75 (m, 6 H, pyrrole-β-H, Ar, Pc-α-H), 7.02 (d, 2 H, Pc-α-H), 6.11 (d, 2 H, Pc-α-H), 5.69 (m, 2 H, O$\mathbf{CH_2}$$CH_2CH_2CH_3$), 5.29 (m, 2 H, O$\mathbf{CH_2}$$CH_2CH_2CH_3$), 4.06~4.95 (m, 4 H, O$\mathbf{CH_2}$$CH_2CH_2CH_3$), 4.29~4.50 (m, 4 H, O$\mathbf{CH_2}$$CH_2CH_2CH_3$), 2.59 (m, 4 H, $OCH_2$$\mathbf{CH_2}$$CH_2CH_3$), 2.30 (m, 4 H, $OCH_2$$\mathbf{CH_2}$$CH_2CH_3$), 2.20~2.60 (m, 4 H, $OCH_2CH_2$$\mathbf{CH_2}$$CH_3$), 2.15~2.18 (m, 4 H, $OCH_2$$\mathbf{CH_2}$$CH_2CH_3$), 1.97~2.03 (m, 4 H, $OCH_2CH_2$$\mathbf{CH_2}$$CH_3$), 1.83~1.88 (m, 4 H, $OCH_2CH_2CH_2CH_3$), 1.46 (t, 6 H, $OCH_2CH_2CH_2CH_3$), 1.34 (t, 6 H, $OCH_2CH_2$$\mathbf{CH_2}$$CH_3$), 1.24 (t, 6 H, $OCH_2CH_2CH_2$$\mathbf{CH_3}$). MALDI-TOF MS: an isotopic cluster peaking at *m/z* 1 800.2, Calcd. for $Zn_2C_{96}H_{82}Cl_4N_{14}O_6$, $[M+2H]^+$ 1 800.4. Anal. Calcd. for $C_{96}H_{82}Cl_4N_{14}O_6Zn_2$ $2CHCl_3\cdot 2H_2O$ (%): C, 56.72; H, 4.27; N, 9.45. Found (%): C, 56.67; H, 4.33; N, 9.61. MALDI-TOF MS: an isotopic cluster peaking at *m/z* 1 800.2, Calcd. for $Zn_2C_{96}H_{82}Cl_4N_{14}O_6$, $[M+2H]^+$ 1 800.4. Anal. Calcd. for $C_{96}H_{82}Cl_4N_{14}O_6Zn_2\cdot 2CHCl_3\cdot 2H_2O$ (%): C, 56.72; H, 4.27; N, 9.45. Found(%): C, 56.67; H, 4.33; N, 9.61.

2 Results and discussion

2.1 Synthesis

The key precursor for the synthesis of 1,5,10,15,20-tetrakis(4-chlorophenyl)-2′,3′-di-cyanopyrazino[2,3-β]porphyrin (**7**), was prepared in five steps from CuTClPP in approximately 2.7% overall yield[4-7]. 4,5-Di (butyloxy)phthalonitrile was chosen as the second precursor to enhance the solubility of the target diazaphthalocyaninato-porphyrin dimer. Mixed cyclic tetramerization of **7** and 4,5-di(butyloxy)phthalonitrile in the presence of lithium pentanolate in refluxing *n*-pentanol followed by treatment with acetic acid led to the isolation of target metal free mixed-binuclear diazaphthalocyaninato-porphyrin dimer compound **1** in addition to a large quantity of 2,3,9,10,16,17,23,24-octakis (butyloxy) phthalocyanine $H_2Pc(OC_4H_9)_8$, Scheme 2. It is worth noting that MS measurements have demonstrated that if DBU is used instead as the basic catalyst, $H_2Pc(OC_4H_9)_8$ is the main product and only a trace amount of **1** is formed. The metal template provided by the Li(Ⅰ) ions clearly plays a pivotal role during the formation of binuclear and mixed tetrapyrrole ring dimer structure. Reaction of the metal free dimer **1** with $Zn(OAc)_2\cdot 2H_2O$ in a mixture of DMF and toluene (1∶1) at 80 ℃ led to the isolation of a zinc complex **2**, Scheme 2.

2.2 Spectroscopic characterization

Satisfactory elemental analysis result were obtained for both **1** and **2** after repeatedly column chromatographic purification and recrystallization. The MALDI-TOF mass spectrum of **1** showed an intense cluster corresponding to the molecular ion (M^+) and closely resembled the simulated one given in Fig.1. These two new mixed-binuclear phthalcoyaninato-porphyrin dimers were also characterized with a range of spectroscopic methods.

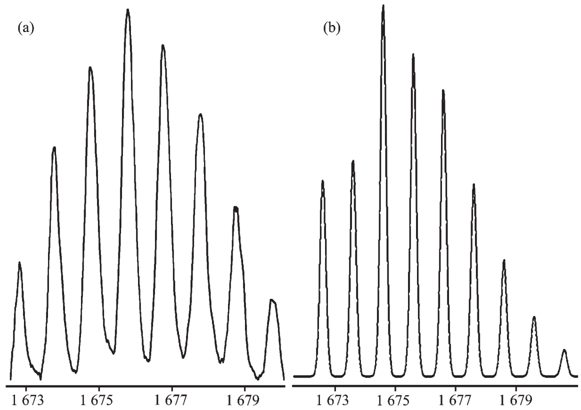
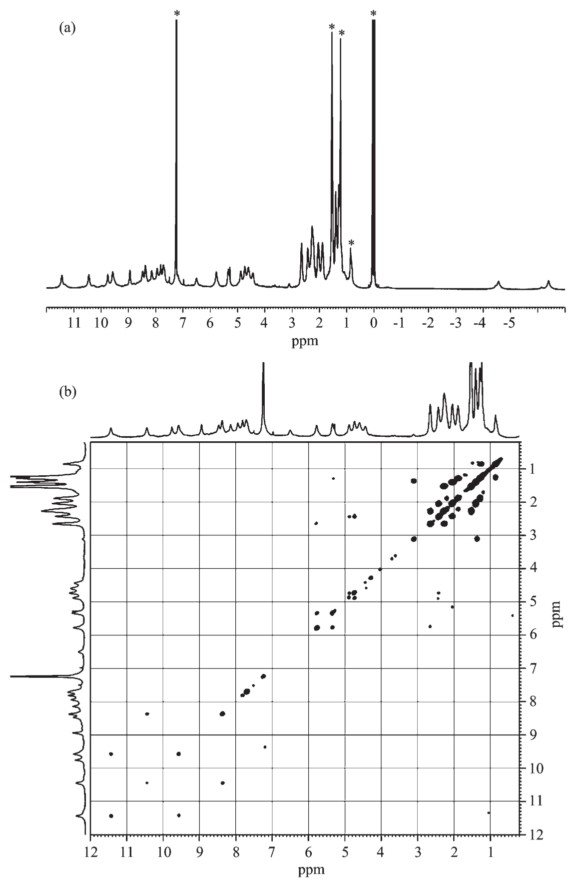


Fig.1 (a) Experimental and (b) simulated isotopic distribution patterns for the molecular ion of **1**

Fig.2 shows the ^1H NMR spectrum of the mixed-binuclear phthalocyaninato-porphyrin dimer **1** in $CDCl_3$. As can be seen, signals at δ=11.44, 10.45, 9.57, and 8.38 ppm can be assigned to the four different types of proton in the two C_6H_4Cl rings which lie next to the Pc chromophore, since they lie markedly down-field in comparison to those of H_2TClPP in $CDCl_3$ as would be anticipated based on the deshielding effect of the Pc and Por rings. The signals observed at δ=9.76, 8.94, and 6.50 ppm are attributed, respectively, to the two types of β protons on the Por moiety and the α protons of the Pc moiety. The signals for four protons in the two C_6H_4Cl rings which do not lie next to the Pc chromophore, the third type of β protons in the Por moiety, and two types of α protons in the Pc moiety overlap in δ=7.71~8.47 ppm region. The signal for a second group of protons associated with the C_6H_4Cl rings lies at 7.24 ppm and overlaps with the $CDCl_3$ solvent signal. The aliphatic proton signals can be assigned unambiguously based on a ^1H-^1H COSY analysis, Fig.2. The multiplets at δ 5.34~5.78 and 4.34~4.88 ppm are associated with the O**CH₂** methylene protons, while those which lie between δ 1.89~2.65 ppm can be ascribed to the OCH_2**CH_2CH_2** methylene protons. The remaining signals for the **$-CH_3$** methyl protons which are correlated with the signals of OCH_2CH_2**CH_2** methylene protons are overlaped by the solvent signals at δ 1.54 and 1.23. The ^1H NMR spectrum of **2** was assigned in a similar manner, Table 1. It should be noted that while the ^1H NMR spectrum of **2** recorded in pure $CDCl_3$ has broad and indistinguishable signals due to aggregation[12], this problem was resolved by addition of a drop of [D_5]pyridine. The disappearance of the signal associated with the inner pyrrole/isoindole protons that is observed in the NMR spectrum of **1**, provides strong evidence that **2** is a metal complex.



(a) $CDCl_3$, * indicates solvent impurities

Fig.2 (a) ^1H NMR and (b) ^1H-^1H COSY spectra of **1**

The IR spectra of **1** and **2** are shown in Fig.3. In addition to the bands associated with the aromatic Pc

Table 1 ^{1}H NMR data (δ) for 1 and 2 in $CDCl_3$

Compound	**1**	**2**[b]
Por-Ph-H	11.43(s, 2H)	11.71(d, 2H)
	10.45(s, 2H)	10.60(d, 2H)
	9.57(s, 2H)	9.70(d, 2H)
	8.38(s, 2H)	8.52(s, 2H)[c]
	7.71~8.14(m, 8H)[a]	8.36(d, 2H)
		8.13(d, 2H)
		8.05(d, 2H)
pyrrole-β-H	9.76(s, 2H)	8.90(d, 2H)[c]
	8.94(s, 2H)	8.21(d, 2H)
	8.50(s, 2H)	7.65~7.75(m, 6H)[a,c]
Pc-α-H	7.71~8.14(m, 8H)[a]	7.65~7.75(m, 6H)[a,c]
	6.50(s, 2H)	7.02(d, 2H)
		6.11(d, 2H)
O**CH_2**	5.78(s, 2H)	5.69(m, 2H)
	5.34(s, 2H)	5.29(m, 2H)
	4.44~4.88(m, 8H)	4.06~4.95(m, 4H)
		4.29~4.50(m, 4H)
CH_2**CH_2**CH_2	2.65(s, 4H)	2.59(m, 4H)
	2.05~2.67(m, 12H)[a]	2.30(m, 4H)
		2.15~2.18(m, 4H)
CH_2CH_2**CH_2**	2.05~2.67(m, 12H)[a]	2.20~2.60(m, 4H)
	1.89~2.05(m, 8H)	1.97~2.03(m, 4H)
		1.83~1.88(m, 4H)
CH_3	1.28~1.40(m, 18H)	1.46(t, 6H)
		1.34(t, 6H)
		1.24(t, 6H)
metal-free H	−4.57(s, 2H)	—
	−6.40(s, 2H)	

[a] These signals overlap with each other; [b] Recorded in $CDCl_3$/[D_5]Pyridine (10:1); [c] These signals are overlapped by the bands of pyridine.

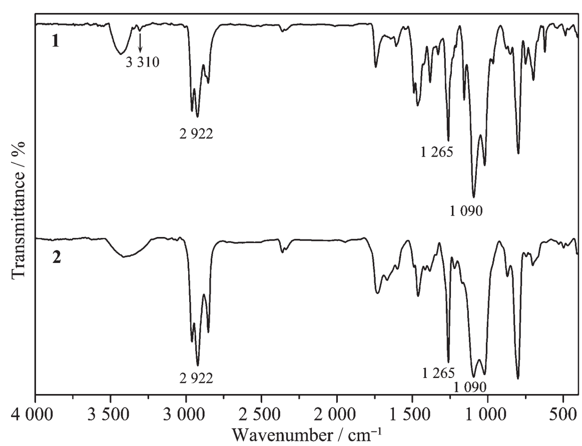


Fig.3 IR spectra of **1** and **2** in the region of 400~4 000 cm^{-1} with 2 cm^{-1} resolution

and Por moieties, such as the C-H wagging and torsion vibrations, and the isoindole ring and the C=N aza group stretching vibrations,[13] the bands observed at 2 958~2 960, 2 922~2 925, and 2 850~2 852 cm^{-1} are assigned to the asymmetric and symmetric C-H stretching vibrations of the butyloxy side chains, while those at 1 260 and 1 090 cm^{-1} are ascribed to the asymmetric and symmetric C-O-C stretching vibrations. In the IR spectrum of **1**, a weak band at *ca.* 3 310 cm^{-1} can be assigned to the asymmetrical N-H stretching vibration of the isoindole and pyrrole moieties[14-15], which disappears in the IR spectrum of zinc complex **2**.

2.3 Electronic absorption and MCD spectra

The electronic absorption spectrum of **1** was recorded in $CHCl_3$ and the data are compiled in Table 2. Fig.4 compares the electronic absorption spectrum of **1** with those of $H_2Pc(OC_4H_9)_8$ and H_2TClPP. In the $H_2Pc(OC_4H_9)_8$ spectrum, there are an intense B (or Soret) band at 348 nm and two intense Q bands at 664 and 702 nm, while in the H_2TClPP spectrum there are a strong B band at 418 nm and four weak Q bands at 514, 548, 588, and 646 nm. Two strong

Table 2 Electronic absorption data for dimers 1 and 2 in $CHCl_3$

	λ_{max} / nm (lg[ε / ($L\cdot mol^{-1}\cdot cm^{-1}$)])			
1	352(5.15)	414(5.27)	475(4.86)	722(5.16)
2	313(4.89)	371(5.06)	427(5.27)	774(4.90)

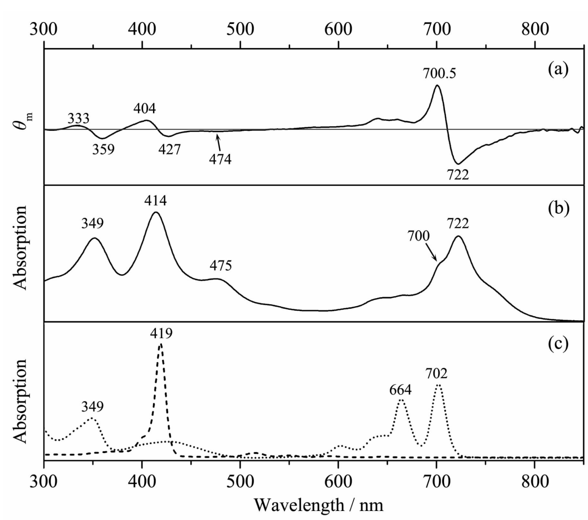


Fig.4 (a) MCD and (b) electronic absorption spectra of **1** together with (c) the electronic absorption spectra of $H_2Pc(OC_4H_9)_8$ (···) and H_2TClPP (---) in $CHCl_3$

bands are observed at 352 and 414 nm in the spectrum of **1** along with a broad envelope of bands with medium to strong intensity in the 450~820 nm region. On the basis of previous studies of alkoxy-substituted phthalocyanines, a broad envelope with a maximum at 475 nm can be assigned to a relatively weak n-π^* bands associated the lone pairs on the oxygen atoms[16]. The electronic absorption spectrum of **2**, Fig.5, is broadly similar to that of the metal free compound since the co-planar ring-fused lacks a four-fold symmetry axis unlike the Zn(Ⅱ) complexes of radially symmetric porphyrin and phthalocyanines derivatives.

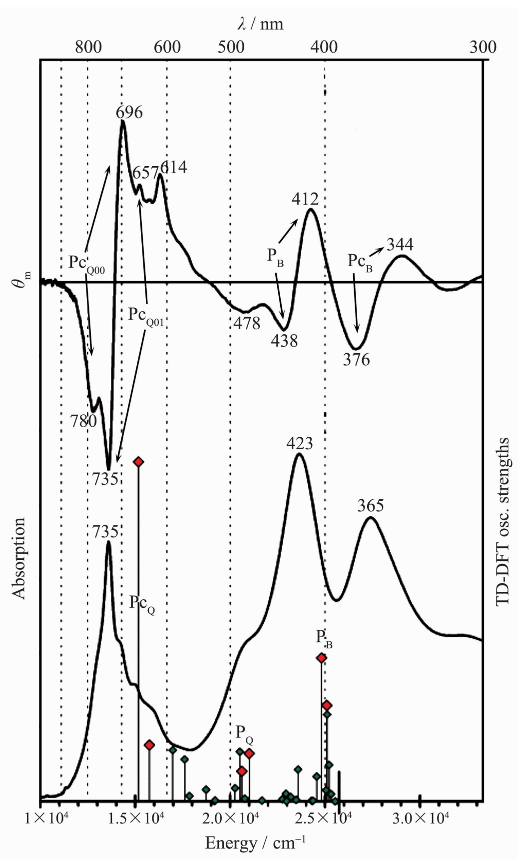


Fig.5 MCD and electronic absorption spectra of **2** in $CHCl_3$ plotted against wavenumber and wavelength scales together with the simulated electronic absorption spectrum of $Zn_2\{[DAPc(OCH_3)_6][(TClPP)]\}$, TD-DFT spectra calculated using the B3LYP optimized structure is plotted against the right-hand axis using green diamonds

In order to gain insights into the relationship between the electronic structure and electronic absorption spectrum, quantum chemistry investigation was carried out for $H_4\{[DAPc(OCH_3)_6][(TClPP)]\}$. Calculation result using density functional theory (DFT) methods at the B3LYP/6-31G(d)[11] suggests that the metal free phthalcoyaninato-porphyrin dimer dominantly employs the conformation as shown in Conformation A in Fig.6 due to the lowest energy of

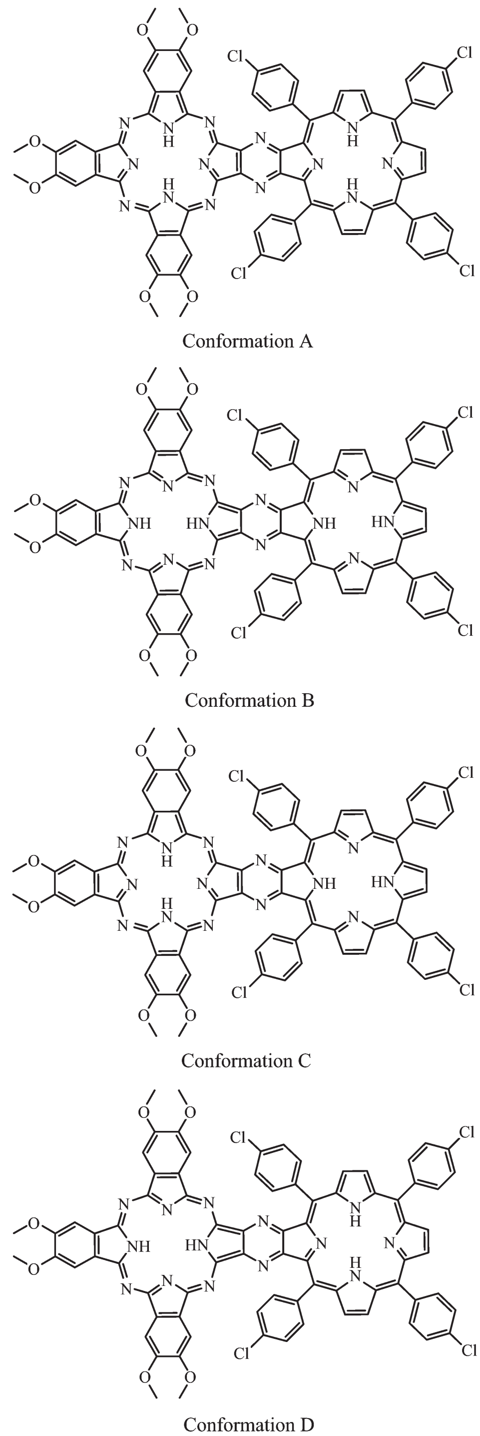


Fig.6 N-H tautomers for $H_4\{[DAPc(OCH_3)_6][(TClPP)]\}$

this species among all the four tautomeric isomers of **1**. On the basis of calculation result, when DAPc and Por are fused into conjugated dimer, the HOMO of DAPc forms the HOMO of H_4 {[DAPc(OCH_3)$_6$][(TClPP)]} (named as HOMO (π_{Pc})), while the HOMO of Por becomes the HOMO-1 of H_4 {[DAPc(OCH_3)$_6$][(TClPP)]} (named as HOMO-1 (π_{Por})), Fig.7. There exists almost no coupling between the HOMOs of DAPc and Por in the conjugated dimer H_4{[DAPc(OCH_3)$_6$][(TClPP)]}. However, the LUMOs (π_x, π_y) of the isolated Pc couple with those of Por, forming the molecular orbitals from LUMO to LUMO+3 for H_4{[DAPc(OCH_3)$_6$][(TClPP)]}, Fig.7. Actually, according to the simulated electronic absorption spectrum of

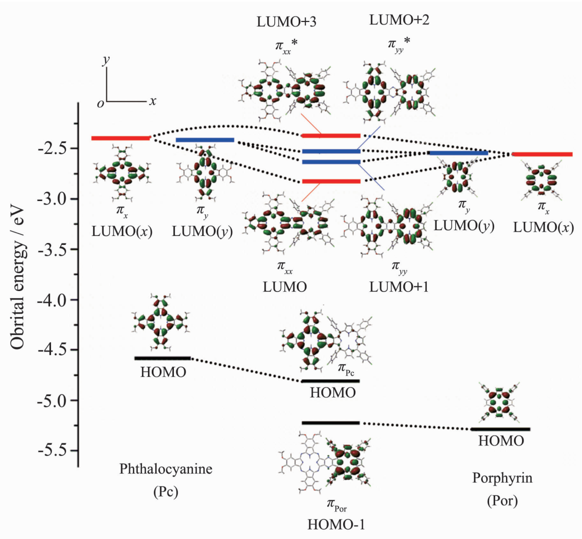


Fig.7　Frontier orbital coupling of H_4{[DAPc(OCH_3)$_6$][(TClPP)]} (isovalue=0.02)

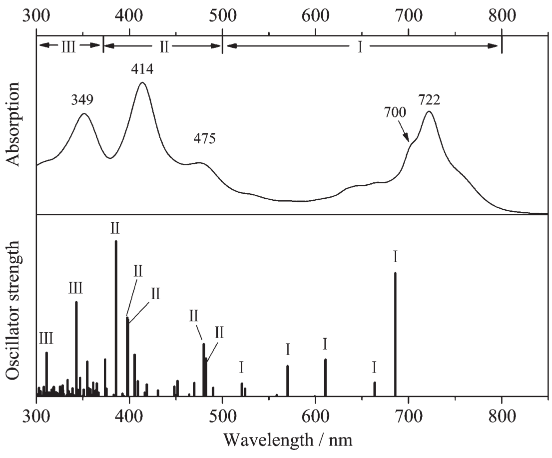


Fig.8　Experimental and simulated electronic absorption spectra for **1** and H_4{[DAPc(OCH_3)$_6$][(TClPP)]}, respectively

H_4{[DAPc(OCH_3)$_6$][(TClPP)]}, Fig.8, the electronic absorption spectrum of **1** can be divided into three regions due to the different electron transition models. As shown in Fig.9, a broad absorption band from 500 to 750 nm (Region Ⅰ) due to the electron transitions between HOMO (π_{Pc})/HOMO-1 (π_{Por}) and LUMO(π_{xx})/LUMO+1(π_{yy})/LUMO+2(π_{yy*})/LUMO+3(π_{xx*}) is assigned to the Q band of dimer **1** because of their complicated transition nature[1c,17]. The bands from 375 to 500 nm (Region Ⅱ) attributed mainly to the electron transitions of HOMO-3 → LUMO/LUMO+1/LUMO+2/LUMO+3 coupled with HOMO-4/HOMO-6/HOMO-7 → LUMO/LUMO+1/LUMO+2/LUMO+3, Fig.9, also with complicated transition nature, are assigned to the Soret bands of the conjugated dimer **1**. This is also true for the bands from 300 to 375 nm (Region Ⅲ) contributed mainly due to the electron transitions of HOMO-12→LUMO/LUMO+1/LUMO+2/LUMO+3, Fig. 9. These results clearly reveal the significant interaction between the Pc and Por chromophores in dimer **1** due to the direct fusing between the Pc-18-electron-π-conjugated and Por-18-electron-π-conjugated chromophores. However, it is worth noting that the interaction should be relatively smaller than that in similar homodinuclear coplanar systems[2h,18] because of the difference in the energy of molecular orbitals of

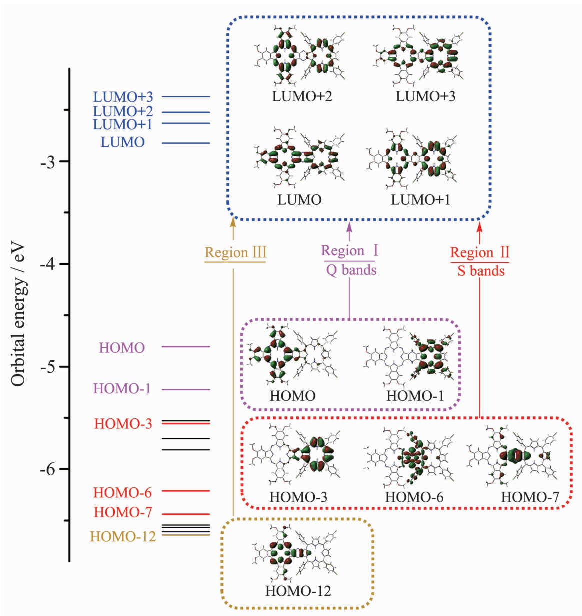


Fig.9　Main electron transitions for Region Ⅰ, Ⅱ, and Ⅲ of H_4{[DAPc(OCH_3)$_6$][(TClPP)]} (isovalue=0.02)

constituting chromophores in the present case. This should be also true for the zinc analogue **2**, Fig.5 and 10.

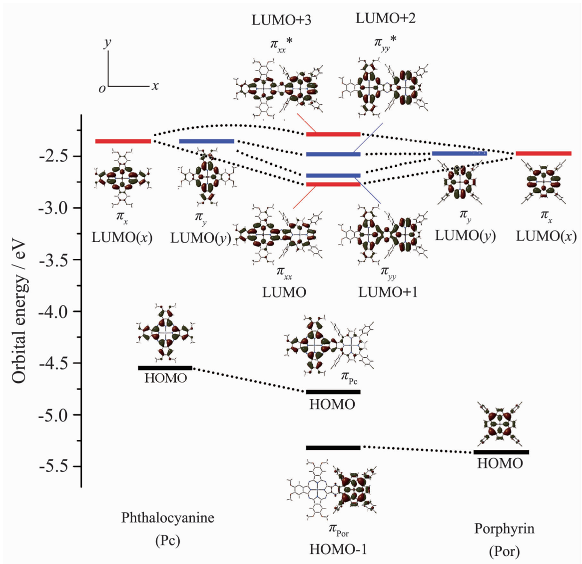


Fig.10 Frontier orbital coupling of $Zn_2\{[DAPc(OCH_3)_6][(TClPP)]\}$ (isovalue=0.02)

The MCD spectra shown in Fig.4 and 5 gives more information on the electronic structure of **1** and **2** by providing band polarization information that is unavailable from the electronic absorption spectrum alone. It has characteristics of normal porphyrins and phthalocyanines. That is, the MCD intensity of the Q band is much stronger than that in the Soret band region, reflecting large angular momentum change in the former. Judging from the symmetry of the molecule, all curves are Faraday B terms (or pseudo Faraday A terms). Indeed, MCD troughs and peaks are corresponding to absorption peaks or shoulders. For example, in the MCD spectrum of **1**, trough at 722 nm and peak at 700 nm are corresponding to an absorption peak at 722 and a shoulder at 700 nm. Similar sets of coupled B terms are observed at 333/359 and 404/427 nm corresponding to the broader absorption bands in the UV region at 349 and 414 nm. Three sets of coupled oppositely-signed Faraday B terms are also observed in the MCD spectrum of **2** at 735/696, 438/412, and 376/344 nm, Fig.5, with the -ve/+ve sign sequence in ascending energy normally observed in the MCD spectra of porphyrins and phthalocyanines. As suggested by MO calculations of **1**, the shape and intensity in the region of *ca.* 500~800 nm are those of phthalocyanines. The pseudo Faraday A term in *ca.* 380~440 nm is also consistent with the results of MO calculation in that this band is mainly from the porphyrin chromophore. Although transitions from the porphyrin and phthalocyanine moiety to whole molecule of **1** were suggested for the 300~375 nm region, the pseudo Faraday A term MCD in *ca.* 300~380 nm which has a similar anisotropy factor to the band in the 380~440 nm suggests that this is a transition attributable mainly to the phthalocyanine moiety. Based on MO calculations, the MCD of **2** provides similar information, Fig.5. The shoulder of absorbance at 780 nm in the spectrum of **2** is tentatively assigned as the Q_{00} bands with the more intense bands immediately to the blue assigned as Q_{01} vibrational bands, Fig.5, due to a totally symmetric overtone. The bands at 423 and 365 nm are tentatively assigned as porphyrin B and phthalocyanine B1 bands[19], respectively, based on the presence of coupled Faraday B terms in each case and the close alignment with the B and B1 band of H_2TClPP and $H_2Pc(OC_4H_9)_8$, respectively.

3 Conclusions

In summary, we have carried out the rational design and synthesis of two novel co-planar ring-fused diazaphthalocyaninato-porphyrin dimer compounds $M_2\{[(DAPc(OC_4H_9)_6][(TClPP)]\}$ (M=2H, Zn), which represent the first examples of a co-planar fused porphyrinoid dimer containing two different tetrapyrrole moieties. A detailed analysis of electronic absorption and MCD spectral data and theoretical calculations demonstrates that there is significant interaction between the phthalocyanine and porphryin chromphores in the Q band region. These results suggest that a far wider range of mixed co-planar ring-fused tetrapyrrole oligomer structures can be prepared, which could be used in a wide range of applications such as dye-sensitized solar cells and molecular devices.

Acknowledgements: Financial support from the Natural Science Foundation of China, National Ministry of Science and

Technology of China (Grant No.2012CB224801), Beijing Municipal Commission of Education, and University of Science and Technology Beijing and a Grant-in-Aid for Scientific Research on Innovative Areas (No.20108007, "pi-Space") from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan is gratefully acknowledged. We are also grateful to the Shandong Province High Performance Computing Center for a grant of computer time and Prof. Dr. Feiwu Chen in University of Science and Technology Beijing for kind discussion and help.

References:

[1] (a)Lever A B P, Leznoff C C. *Phthalocyanine: Properties and Applications: Vol.*1~4. New York: VCH, **1989-1996**.
(b)McKeown N B. *Phthalocyanines Materials: Synthesis, Structure and Function*. New York: Cambridge University Press, **1998**.
(c)Kadish K M, Smith K M, Guilard R. *The Porphyrin Handbook: Vol.*1~20. San Diego: Academic Press, **2000** and **2003**.
(d)Jiang J. *Advances in Functional Phthalocyanine Materials, Structure and Bonding*. Heidelberg: Springer-Verlag, **2010**.

[2] (a)Leznoff C, Kobayashi N, Lever A B P, et al. *Chem. Commun.*, **1987**:699-701
(b)Kobayashi N, Lam H, Nevin W A, et al. *J. Am. Chem. Soc.*, **1994**,**116**:879-890
(c)Ishii K, Kobayashi N, Higashi Y, et al. *Chem. Commun.*, **1999**:969-970
(d)Makarov S, Litwinski C, Ermilov E A, et al. *Chem. Eur. J.*, **2006**,**12**:1468-1474
(e)Makarov S G, Piskunov A V, Suvorova O N, et al. *Chem. Eur. J.*, **2007**,**13**:3227-3233
(f)Zhang Q M, Li H, Poh M, et al. *Nature*, **2002**,**419**:284-287

[3] (a)Tsuda A, Osuka A. *Science*, **2001**,**293**:79-82
(b)Ikeue T, Furukawa K, Hata H, et al. *Angew. Chem. Int. Ed.*, **2005**,**44**:6899-6901
(c)Nakamura Y, Aratani N, Shinokubo H, et al. *J. Am. Chem. Soc.*, **2006**,**128**:4119-4127
(d)Uoyama H, Kim K, Kuroki K, et al. *Chem. Eur. J.*, **2010**, **16**:4063-4074
(e)Crossley M J, Thordarson P. *Angew. Chem. Int. Ed.*, **2002**, **41**:1709-1712

[4] Nishi H, Azuma N, Kitahara K. *J. Heterocycl. Chem.*, **1992**, **29**:475-477

[5] Barnett G H, Hudson M F, Smith K M. *J. Chem. Soc. Perkin Trans.* 1, **1975**:1401-1403

[6] Wyrbek P, Ostrowski S. *J. Porphyrins Phthalocyanines*, **2007**, **11**:822-828

[7] (a)Promarak V, Burn P L. *J. Chem. Soc., Perkin Trans.* 1, **2001**: 14-20
(b)Khoury T, Crossley M J. *Chem. Commun.*, **2007**:4851-4853

[8] Lee C, Yang W, Parr R G. *Phys. Rev. B*, **1988**,**37**:785-789

[9] Dunning J T H, Hay P J. *Modern Theoretical Chemistry: Vol.*3. New York: Plenum, **1976**:1-28

[10]Peng C, Ayala P Y, Schlegel H B, et al. *J. Comput. Chem.*, **1996**,**17**:49-56

[11]Frisch M J, Trucks G W, Schlegel H B, et al. *Gaussian* 03, *Revision B*.05; Gaussian, Inc.: Pittsburgh, PA, **2003**.

[12]Shimizu S, Zhu H, Kobayashi N. *Chem. Eur. J.*, **2010**,**16**: 11151-11159

[13](a)Jiang J, Bao M, Rintoul L, et al. *Coord. Chem. Rev.*, **2006**, **250**:424-448 and references therein
(b)Dong S, Qi D, Zhang Y, et al. *Vib. Spectrosc.*, **2011**,**56**: 245-249

[14]Zhang X, Zhang Y, Jiang J. *Vib. Spectrosc.*, **2003**,**33**:153-161

[15]Zhang Y, Ma P, Zhu P, et al. *J. Mater. Chem.*, **2011**,**21**: 6515-6524

[16]Kobayashi N, Ogata H, Nonaka N, et al. *Chem. Eur. J.*, **2003**,**9**:5123-5134

[17]Qi D, Zhang L, Zhang Y, et al. *J. Phys. Chem. A*, **2010**,**114**: 13411-13417

[18](a)Kobayashi N, Numao M, Kondo R, et al. *Inorg. Chem.*, **1991**,**30**:2241-2244
(b)Litwinski C, Corral I, Ermilov E A, et al. *J. Phys. Chem. B*, **2008**,**112**:8466-8476

[19]Mack J, Stillman M J, Kobayashi N. *Coord. Chem. Rev.*, **2007**,**251**:429-453