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ScienceDirect

Dyes and Pigments 74 (2007) 141–147

DYES and PIGMENTS

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Synthesis and hypochromic effect of phthalocyanines and metal phthalocyanines

Chunyu Ma [a], Kaiqi Ye [c], Shukun Yu [b], Guotong Du [a,b,*], Yunfeng Zhao [c], Fangdi Cong [d], Yuchun Chang [b], Wenhai Jiang [b], Chuanhui Cheng [b], Zhaoqi Fan [b], Haifeng Yu [d], Wancheng Li [b]

[a] *State Key Laboratory of Materials Modification by Laser, Ion and Electron Beams, Department of Physics, Dalian University of Technology, 116024 Dalian, China*

[b] *State Key Laboratory of Integrated Optoelectronics, Jilin University, 130012 Changchun, China*

[c] *Key Laboratory of Supramolecular Structure and Materials of Ministry of Education, College of Chemistry, Jilin University, 130012 Changchun, China*

[d] *Faculty of Chemistry, Northeast Normal University, 130024 Changchun, China*

Received 17 January 2006; accepted 19 January 2006
Available online 3 April 2006

Abstract

Several series of phthalocyanines (Pcs) and metallophthalocyanines (MPcs) were prepared and characterized by MS, ^{1}H NMR, UV–vis and elemental analysis, which were consistent with the proposed structures. These Pcs and their metal complexes are synthesized using 3-(2-isopropyl-5-methylphenoxyl)phthalonitrile or 4-(2-isopropyl-5-methylphenoxyl)phthalonitrile as the starting material in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene(DBU) as the catalyst. An original UV–vis absorption investigation of these compounds is performed. Obvious hypochromic effect of Q-bands was found with the increment of temperature from 293 K to 333 K. B-bands did not show the analogous tendency. The hypochromic effect originates from conversion of Pc framework as a result of thermal vibration, which reduces the localization of π-electron system.

Keywords: Synthesis; Hypochromic effect; Phthalocyanines; Phenoxyl

1. Introduction

Phthalocyanines (Pcs) are macrocyclic complexes whose π systems, localized over an arrangement of alternated carbon and nitrogen atoms, provide their unique chemical and physical properties [1,2], rendering these complexes applicable in different areas, especially in materials science. Due to the significance of π system of Pcs, studying the nature of π system and attempting to modulate π system have been extensively and intensively investigated. Typical examples are the preparation of subphthalocyanines (subPcs) [3] and super-phthalocyanines [4], both of which enrich the number of Pc family and provide the theoretical and applied foreground for Pcs. Mainly owing to the π system, Pcs and metallated Pcs display excellent thermal stability. However, they were found to undergo photooxidative cleavage, particularly in the solution phase, leading to phthalimide derivatives [5].

Pcs' metal complexes generated by the replacement of the hydrogen atoms in central cavity are usually called metallophthalocyanines (MPcs). Central metals play a critical role in tuning the properties of MPcs [6]. What is more, coordination of the Pc ligand with metal and some metalloid will result in the alteration of molecular conformation. In general, since the structural arrangement of metallophthalocyanines (MPcs) is determined by the size and location of the metal center with respect to the mean plane of the aromatic Pc ligand, several conformations are known [7]. Those have been named according to their molecular shape. The most common conformations are planar, ruffled, waved, domed, and skew domed [7]. For

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* Corresponding author. State Key Laboratory of Materials Modification by Laser, Ion and Electron Beams, Department of Physics, Dalian University of Technology, 116024 Dalian, China. Fax: +86 431 516 8270.

E-mail address: yxma76@yahoo.com.cn (G. Du).

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doi:10.1016/j.dyepig.2006.01.044

instance, Pcs metallated with Pb or Sn show the domed conformation [7,8]. The essentially planar conformation of Pcs can also be distorted by substituents alone through conformational stress [9]. In remarkable contrast with the intensive studies of the effect of macrocycle distortion of porphyrins on physicochemical properties, e.g. redox potential and light absorbance [10], few reports [9,11] have mentioned the connections of Pc ring contortion with the properties. In fact, the effect of macrocycle distortion on the properties can be attributed to the alteration in planarity of π-electron system.

Hyperchromic effect or hypochromic effect of Pcs usually accompany the changes in λ_{max} and ϵ values (or absorbance) of Q-band and B-band. Generally, these two effects can be attributed to the alteration in π-electron systems. According to the previous reports [12], formation of dimers, coordination to the central metal with certain ligands and enlargement of π system are the three factors giving rise to hyperchromicity or hypochromicity. In our synthetic laboratory at Dalian University of Technology, we found a hypochromic effect induced by temperature without precedent in the published literatures, which was related to the distortion of π-electron system. In this paper, we describe the synthesis and characterization of series of Pcs and MPcs (M = Cu, Zn, TiO and InCl) (Fig. 1). By using these compounds, we study the hypochromic effect related to temperature.

2. Experimental

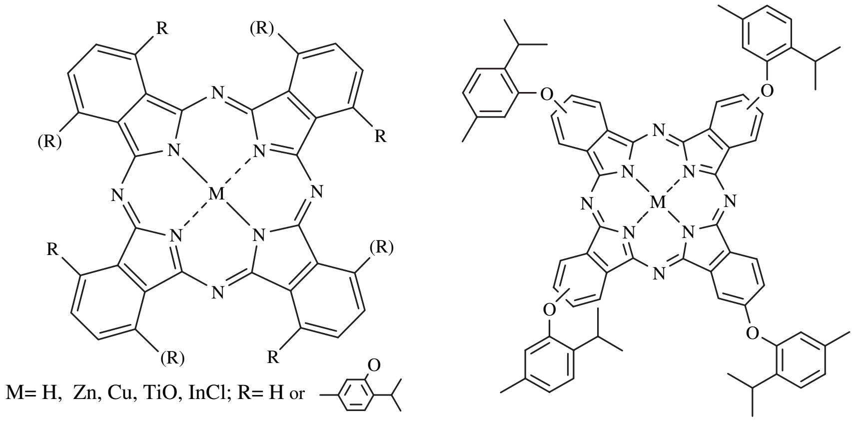
2.1. Materials and instruments

The chloronaphthalene was purchased from J&K Chemical Ltd., which is a mixture of α-chloronaphthalene (90%) and β-chloronaphthalene (10%). Chloronaphthalene was predried by stirring with $CaCl_2$ and then distilled from P_2O_5 prior to use. CuPc was purchased from the market. All other chemicals used were of reagent grade. All other solvents were dried and purified as described by Perrin and Armarego [13]. Syntheses of **1–3b**, **1–3c**, **1d**, and **1e** were carried out according to the relevant literatures [6b,14,15].

High-resolution ^{1}H NMR spectra were recorded on a Bruker AV 500 spectrometer unless otherwise stated. UV–vis spectra were taken on a UV-3100 UV–vis–NIR Recording Spectrophotometer (SHIMADZU, Japan). MS spectra were obtained on an LDI-1700-TOF mass spectrometer (Linear Scientific Inc., USA) or a Kratos MALDI-TOF mass spectrometer (SHIMADZU, Japan). Elemental analyses were performed on a Flash EA1112 Elemental Analyzer (ThermoQuest, Italy).

2.2. UV–vis absorption operation

UV–vis spectra were performed on a UV-3100 Spectrophotometer equipped with a low-constant-temperature bath using water as the heating and cooling media. Cycled water can pass the colormetric stand through the insulating hoses to make the sample solution in quartz flow-cell (10 mm path length) maintain the same temperature as water. Although water temperature is indicated by an electronic meter furnished in this spectrophotometer, a thermometer is still put into water to show correct water temperature. Before measurements, the solutions were saturated for 10 min with dry nitrogen (oxygen-free), which was carried out directly in the quartz flow-cell. The quartz flow-cell was sealed tightly with a quartz cover to prevent volatility of chloronaphthalene causing the increment of sample concentration. Shortly after sometime water was poured into the constant-temperature bath, it was cooled to 293 K by a cooling pump and beginning at this temperature we obtained the UV–vis absorption data for each sample. The highest temperature up to which water in constant-temperature bath can be heated is 333 K, therefore, we cannot get UV–vis absorptions measured at accurate temperatures higher than 333 K. The sample solution in quartz flow-cell can be cooled to 273 K and 283 K, but at those temperatures small water droplet appeared on the surface of flow-cell. Hence, we chose to carry out UV–vis measurements between 293 K and 333 K.



1a M= H, R=H; 2a M= H, R=OC_6H_3(2-iPr)(5-Me)
1b M= Cu, R=H; 2b M= Cu, R=OC_6H_3(2-iPr)(5-Me)
1c M= Zn, R=H; 2c M= Zn, R=OC_6H_3(2-iPr)(5-Me)
1d M= TiO, R=H; 2d M= TiO, R=OC_6H_3(2-iPr)(5-Me)
1e M= InCl, R=H; 2e M= InCl, R=OC_6H_3(2-iPr)(5-Me)

3a M= H
3b M= Cu
3c M= Zn
3d M= TiO
3e M= InCl

Fig. 1. Structures of **1a–e**, **2a–e** and **3a–e**.

2.3. Synthesis

2.3.1. Unsubstituted metal-free Pc **1a**

Phthalonitrile (1.024 g, 8 mmol) was added under stirring to 1-pentanol (10 mL) in a 25 mL one-neck round-bottomed flask equipped with an air condenser. Then, a catalytic amount of DBU was added, and the mixture was heated at 135 °C under N_2 for over 12 h. After cooling under N_2, anhydrous methanol was added into the reaction mixture to precipitate the solid and 1-pentanol was removed under reduced pressure. The collected solid was extracted with anhydrous methanol and acetone, respectively, in a soxhlet extractor. Further purification was performed at 150 °C under high vacuum ($<2.0 \times 10^{-3}$ Pa). Yield: 0.615 g (60%). UV–vis (chloronaphthalene, λ_{max}/nm) 341, 601, 635, 663, 699. Anal.: Calc. for $C_{32}H_{18}N_8$: C, 74.70; H, 3.53; N, 21.78%. Found: C, 74.51; H, 3.43; N, 21.90.

2.3.2. 2-Isopropyl-5-methylphenoxyl substituted metal-free Pcs **2a** and **3a**

3-(2-Isopropyl-5-methylphenoxyl)phthalonitrile (0.276 g, 1 mmol) or 4-(2-isopropyl-5-methylphenoxyl)phthalonitrile (0.276 g, 1 mmol) was added under stirring to 1-pentanol (6 mL) in a 25 mL one-neck round-bottomed flask equipped with an air condenser. Then, a catalytic amount of DBU was added, and the mixture was heated at 135 °C under N_2 for over 12 h. After cooling under N_2, anhydrous methanol was added into the reaction mixture to precipitate the solid and 1-pentanol was removed under reduced pressure. The collected solid was extracted with anhydrous methanol in a soxhlet extractor for 24 h and further purified twice by chromatography with Et_2O–petroleum ether (2:9) to afford green powder **2a**. Yield: 0.13 g (46%). UV–vis (chloronaphthalene, λ_{max}/nm) 344, 631, 665, 699, 729; ^1H NMR (500 MHz, $CDCl_3$) δ: −2.016(s, 2H, NH), 1.449–1.498(m, 24H, CH_3), 2.395(t, 12H, CH_3), 3.665–3.757(m, 4H, CH), 6.994–7.076(m, 4H, ArH), 7.138–7.230(m, 4H, ArH), 7.420–7.509(m, 4H, ArH), 7.965–8.036(m, 4H, ArH), 8.888–8.990(m, 4H, ArH), 9.156–9.236(m, 4H, ArH). MS(LDI-TOF): *m/z* 1107.6 ($M + H^+$). Anal.: Calc. for $C_{72}H_{66}N_8O_4$: C, 78.09; H, 6.01; N, 10.12%. Found: C, 78.31; H, 6.00; N, 9.90 or purified twice by chromatography with CH_2Cl_2 to afford green powder **3a**. Yield: 0.17 g (61%). UV–vis (chloronaphthalene, λ_{max}/nm) 343, 612, 646, 676, 710; ^1H NMR (500 MHz, $CDCl_3$) δ: −2.037(s, 2H, NH), 1.428–1.479(m, 24H, CH_3), 2.379–2.462(t, 12H, CH_3), 3.586–3.599(m, 4H, CH), 7.182(t, 8H, ArH), 7.479–7.502(m, 4H, ArH), 7.681(s, 4H, ArH), 8.636(s, 4H, ArH), 9.019(s, 4H, ArH). MS(LDI-TOF): *m/z* 1107.7 ($M + H^+$). Anal.: Calc. for $C_{72}H_{66}N_8O_4$: C, 78.09; H, 6.01; N, 10.12%. Found: C, 78.01; H, 6.30; N, 10.24.

2.3.3. Tetra-(2-isopropyl-5-methylphenoxylphthalocyaninato)-titanium(IV) oxide **2d** and **3d**

3-(2-Isopropyl-5-methylphenoxyl)phthalonitrile (0.4934 g, 1.78 mmol) or 4-(2-isopropyl-5-methylphenoxyl)phthalonitrile (0.4934 g, 1.78 mmol), urea (0.2 g, 3.3 mmol), $Ti(OBu)_4$ (0.5 mL, 1.5 mmol) and six drops of DBU were dissolved in 6 mL of 1-pentanol and heated at 155 °C for 24 h. After cooling to room temperature the reaction mixture was poured into 100 mL mixture of methanol and de-ionized water (4:1), precipitate was collected and adequately extracted with anhydrous methanol in a soxhlet extractor. The obtained mixture of metallated and metal-free phthalocyanines was purified by column chromatography on silica gel. Elution with a mixture of petroleum/CH_2Cl_2 (1:1) gave the metal-free Pc **2a**. The target product **2d** was eluted twice with methanol/CH_2Cl_2 (1:30). Yield: 0.182 g (35%). UV–vis (chloronaphthalene, λ_{max}/nm) 350, 428, 661, 738; ^1H NMR (500 MHz, $CDCl_3$) δ: 1.499–1.546(m, 24H, CH_3), 2.372–2.418(m, 12H, CH_3), 3.725–3.787(m, 4H, CH), 7.026–7.079(m, 4H, ArH), 7.182–7.244(m, 4H, ArH), 7.521–7.599(m, 4H, ArH), 8.037–8.113(m, 4H, ArH), 9.057–9.167 (m, 4H, ArH), 9.310–9.391(m, 4H, ArH). MS(MALDI-TOF): *m/z* 1168.2 (M, isotopic cluster). Anal.: Calc. for $C_{72}H_{64}N_8O_5Ti$: C, 73.96; H, 5.52; N, 9.58%. Found: C, 74.01; H, 5.40; N, 9.67.

Metal-free Pc **3a** was obtained by the elution with a mixture of petroleum/CH_2Cl_2 (1.5:1). Pc **3d** was purified twice with methanol/CH_2Cl_2 (1:40) as the mobile phase. Yield: 0.234 g (45%). UV–vis (chloronaphthalene, λ_{max}/nm) 349, 397, 639, 712; ^1H NMR (500 MHz, $CDCl_3$) δ: 1.36–1.444(m, 24H, CH_3), 2.421–2.442(m, 12H, CH_3), 3.538–3.586(m, 4H, CH), 7.177–7.223(m, 8H, ArH), 7.453–7.483(m, 4H, ArH), 7.778–7.815(t, 4H, ArH), 8.731(s, 4H, ArH), 9.065–9.170(m, 4H, ArH). MS(LDI-TOF): *m/z* 1168.6 ($M + H^+$). Anal.: Calc. for $C_{72}H_{64}N_8O_5Ti$: C, 73.96; H, 5.52; N, 9.58%. Found: C, 73.83; H, 5.40; N, 9.86.

2.3.4. Chloroindium(III)tetra-(2-isopropyl-5-methylphenoxyl)phthalocyanine **2e**

A mixture of $InCl_3 \cdot 2H_2O$ (0.3084 g, 1.05 mmol), 3-(2-isopropyl-5-methylphenoxyl)phthalonitrile (1.16 g, 4.2 mmol) and six drops of DBU were stirred and dissolved in quinoline (8 mL). The reaction mixture was heated at 180 °C for 24 h under N_2. After cooling to room temperature, anhydrous methanol was added into the mixture to precipitate the blue-green solid. The solvent was removed by distillation under reduced pressure. The collected solid was extracted with anhydrous methanol in a soxhlet extractor for 24 h and then eluted by column chromatography on silica gel using petroleum/ether(3:2) as the eluent. Yield: 0.579 g (44%). UV–vis (chloronaphthalene, λ_{max}/nm) 359, 661, 738; ^1H NMR (500 MHz, $CDCl_3$) δ: 1.478–1.560(m, 24H, CH_3), 2.357–2.393(m, 12H, CH_3), 3.708–3.782(m, 4H, CH), 6.992–7.054(m, 4H, ArH), 7.162–7.240(m, 4H, ArH), 7.476–7.551(m, 4H, ArH), 7.989–8.068(m, 4H, ArH), 8.965–9.065(m, 4H, ArH), 9.220–9.312(m, 4H, ArH). MS(MALDI-TOF): *m/z* 1256.2 (M, isotopic cluster). Anal.: Calc. for $C_{72}H_{64}N_8O_4ClIn$: C, 68.87; H, 5.14; N, 8.92%. Found: C, 68.63; H, 5.26; N, 8.81.

2.3.5. Chloroindium(III)tetra-(2-isopropyl-5-methylphenoxyl)phthalocyanine **3e**

$InCl_3 \cdot 2H_2O$ (0.1825 g, 0.62 mmol), 4-(2-isopropyl-5-methylphenoxyl)phthalonitrile (0.685 g, 2.48 mmol) and six drops of DBU were dissolved in dry quinoline (6 mL). The reaction mixture was stirred and heated at 180 °C for 24 h under N_2.

After cooling to room temperature, anhydrous methanol was added into the mixture to precipitate the blue-green solid. The solvent was removed by distillation under reduced pressure. The collected solid was extracted with methanol and purified by column chromatography on silica gel using petroleum/ether (2:1) as the eluent. Yield: 0.466 g (61%). UV−vis (chloronaphthalene, λ_{max}/nm) 359, 638, 710; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.352−1.420(m, 24H, CH_3), 2.420(t, 12H, CH_3), 3.489−3.528(m, 4H, CH), 7.107−7.192(m, 8H, ArH), 7.442−7.476(m, 4H, ArH), 7.789−7.843(m, 4H, ArH), 8.789−8.860(m, 4H, ArH), 9.262−9.317(m, 4H, ArH). MS(LDI-TOF): *m/z* 1255.5 ($M+H^+$). Anal.: Calc. for $C_{72}H_{64}N_8O_4ClIn$: C, 68.87; H, 5.14; N, 8.92%. Found: C, 68.94; H, 5.21; N, 8.78.

3. Results and discussion

3.1. Synthesis and characterization

Pc **1a** was prepared through a route, which is little different from the frequently used strategy [16], the direct cyclotetramerisation of phthalonitrile at 135 °C in the presence of DBU in 1-pentanol under N_2 atmosphere. Pcs **2a** and **3a** were also synthesized by using the same approach with the corresponding phthalonitrile derivatives, namely 3-(2-isopropyl-5-methylphenoxyl)phthalonitrile or 4-(2-isopropyl-5-methylphenoxyl)phthalonitrile [14]. In our opinion, this method is more convenient than the previous one reported [16] and the yields are satisfactory as well. But the shortcoming of this strategy is that not all the dinitrile derivatives can form the homologous Pcs. For example, 4-nitrophthalonitrile could be transferred to tetranitrophthalocyanine in 1-pentanol using this approach, while 3-nitrophthalonitrile could not generate the Pc even if the reaction temperature raised to 220 °C. Analogous case can be found in one of our reports [17].

From Fig. 2, we can see the characteristic Q-band split of Pcs, indicating the formation of the Pc ring. For **2a**, an additional peak centered at 789 nm was observed, which was solvent-dependent and similar to the one formerly reported [14,18]. We prepared **1−3d** and **1−3e** on guidelines of literatures of Hanack [6b,15]. We failed to synthesize **1−3e** in 1-pentanol and the possible reason was that the atomic radius of indium was relatively large. So its cyclotetramerisation reaction occurred at around 180 °C in quinoline.

3.2. Hypochromic effect

The choice of a suitable solvent plays a crucial role in investigating light absorbance properties of these Pcs of the present work. We select chloronaphthalene as the solvent to dissolve the samples. The advantages are as follows: (i) the good solubility of **1a−e**, **2a−e**, **3a−e** in chloronaphthalene. The large π-electron conjugate system similar to, to some extent, Pcs and strong polarity related to electron-withdrawing chlorine atom render chloronaphthalene to even dissolve unsubstituted Pcs as well; (ii) high boiling point allows at farthest to avoid the alteration in sample concentration during the measurement of light absorption performed from 293 K to 333 K; (iii) no chemical reaction such as coordination to the central metal will occur between chloronaphthalene and the sample molecules. In solution, Pcs often tend to bind axial ligands [19]. It has been shown that in such cases the distribution of electronic density within the macrocycle may be noticeably affected [20]. What is more, chloronaphthalene shows excellent stability to light and thermal. We also attempted to use DMSO, DMF or chlorobenzene as the sample solvent, but they were not adopted due to one or two drawbacks of them. For example, chlorobenzene is decomposed under light and CuPc **1b** is undissolved even in boiling DMF.

The UV−vis spectra of **1a−e**, **2a−e** and **3a−e** measured at 293 K, 303 K, 313 K, 323 K and 333 K, respectively, display the hypochromic effect. We take UV−vis spectra of **1d** and **2a** (Fig. 3) as the typical examples to present and discuss these hypochromicities. As we all know aggregation of Pcs or MPcs in solution may result in hypochromic effect. The characteristic of aggregation is the blue-shift of Q-band and the reduction in Q-band's intensity. The nature of Pc aggregation in solution has been well discussed and widely granted [1]. In Fig. 3, the intensity of bands of dimers does not increase with the raising temperature. In these cases, it seems that only the increase in Pc solution concentration could enhance the degree of

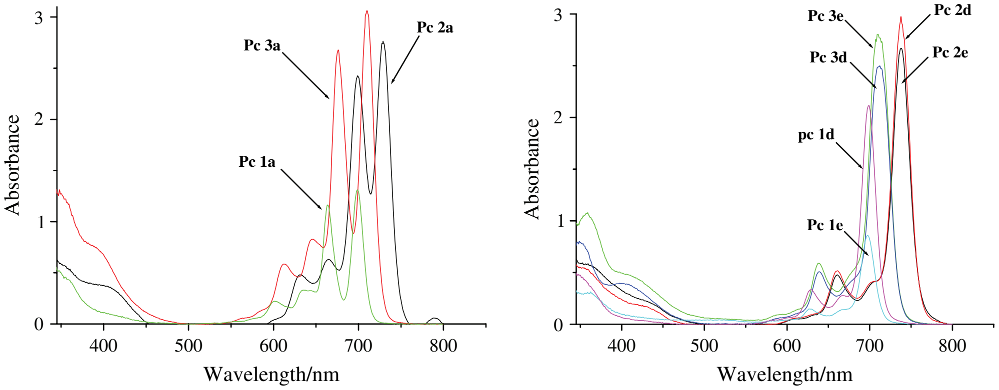


Fig. 2. UV−vis spectra of **1a−3a**, **1d−3d** and **1e−3e** in chloronaphthalene at 293 K.

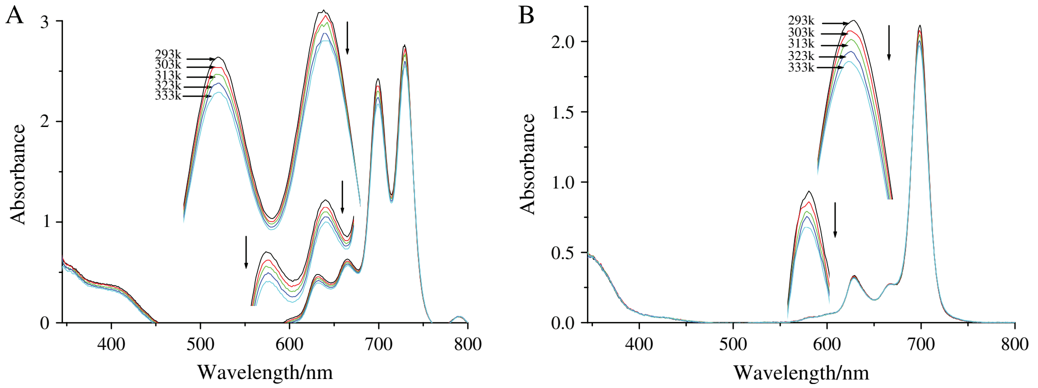


Fig. 3. UV–vis spectra of **2a** (A) and **1d** (B). Arrows indicate changes in absorbance in the direction from 293 K to 333 K.

molecular aggregation, but such conditions cannot be achieved by raising temperature. Therefore, molecular face-to-face stacks should be excluded among the factors that cause the hypochromic effect.

The intensity of both band of dimers and Q-band of 2a and 1d show the decreasing tendency with the enhancement of temperature. These are similar to UV–vis spectra of Pcs whose concentrations are lessened gradually or molecules are being broken down little by little. We repeated the UV–vis adsorption measurement of each sample shortly after it was measured from 293 K to 333 K and the UV–vis spectra did not show any alteration. It appears that these freshly prepared sample solutions could not be decomposed under this measurement condition, which is possibly attributable to the stable nature of samples investigated or measures preventing the decomposition of Pcs, e.g. deaeration of sample solution by a 10-min blowing off oxygen-free nitrogen and adequate purification of chloronaphthalene.

Based on the discussion above, we attribute the hypochromic effect to the distortion of Pc ring. In our opinion, macrocycle contortion actually is the distortion of 18 π-electron system, reducing conjugation degree of π system. The hypochromic effect is related to the molecular thermal vibration, we call it temperature-induced hypochromic effect. This is not hard to be understood: the π conjugated system is rigid by itself, which is derived with the distinct space tropism of sp^3 hybrid orbital of nitrogen atoms and p orbital of carbon atoms around Pc's central cavity (Fig. 4). As we all know bonding of both kinds of orbitals partly constitute the π system. Thermal vibration will easily cause the contortion of π system, which results lowering of absorbance of Q-bands and wavelength shift of the hypochromic effect. For metallated Pcs derivatives, the essential planarity of π system is further distorted due to the complex metals and conformational stress of substituents. In these cases, thermal vibration is more readily to distort the Pc ring, vide infra.

The hypochromic effect is obviously different from the report [9] of Cook and co-workers. Firstly, the hypochromic effect in literature [9] was the result of conformational distortion caused solely by the stress of the substituents. In our cases, the hypochromicity was a result of Pc ring contortion induced by temperature. Secondly, the conclusion of Prof. M.J. Cook was based on the UV–vis study of several analogous Pc derivatives in structure, while, in our contribution, the conclusion of a wavelength shift and fall of absorbance was drawn from UV–vis spectrum and data of the same Pc. We think that it is hard to determine the conformation when thermal vibration is distorting Pc framework. Probably, the Pc ring would experience the wave-shape, dome-shape, ruffle-shape and saddle-shape [10a] or other conformations. However, we observe evident fall of absorbance of Q-bands and slight wavelength shift, which is in general agreement with the results reported by M.J. Cook.

As shown in Fig. 3, absorbance values of Q-band and bands of dimers decrease with the raise of temperature from 293 K to 333 K. The absorbance differences, Δ_a, are apparent and comparable. For metal-free Pc **2a**, Δ_a values of peaks at about 699 nm and 729 nm are relatively large in comparison with those of bands between 703 nm and 723 nm. The Δ_a values of dimer bands of **2a** from 631 nm to 665 nm are clear diagnostic of hypochromic effect, but absorbance differences at around 699 nm and 729 nm are more obvious. Specific absorbance data are summarized in Table 1. Fine structures of Q-bands and dimer bands were enlarged to place besides the original ones (Fig. 3). Specific absorbance data of **2a** reveal

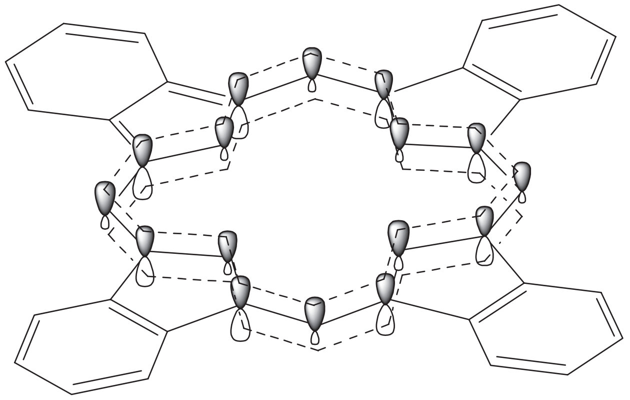


Fig. 4. Representation of Pc π-electron conjugated system. Central atoms and substituents are removed for clarity.

Table 1
Spectroscopic data of **2a** and **1d**

Temperature	**2a**			**1d**		
293 K	729.0 nm (2.763)	699.0 nm (2.426)	665.0 nm (0.618)	631.0 nm (0.481)	699.0 nm (2.117)	629.0 nm (0.336)
303 K	729.5 nm (2.724)	698.0 nm (2.352)	665.0 nm (0.611)	633.0 nm (0.457)	698.5 nm (2.078)	629.0 nm (0.329)
313 K	729.5 nm (2.659)	698.5 nm (2.303)	664.5 nm (0.598)	631.0 nm (0.439)	698.5 nm (2.049)	628.5 nm (0.324)
323 K	729.5 nm (2.598)	699.5 nm (2.239)	665.0 nm (0.583)	632.5 nm (0.421)	698.5 nm (2.006)	628.5 nm (0.321)
333 K	730.5 nm (2.542)	699.5 nm (2.174)	665.0 nm (0.568)	633.0 nm (0.396)	698.0 nm (1.971)	628.0 nm (0.315)

Note: data in the bracket represents the absorbance.

that its absorbance differences of Q-bands are larger than those of dimer bands, which suggest that face-to-face stacks are, to some extent, immune to the distortion of molecular conformation induced by temperature. As for wavelength shift of the hypochromicity, we cannot find the regular red-shift or blue-shift with the raise in temperature. The red-shift or blue-shift is about 1 or 2 nm. So we are just convinced that distortion of Pc skeleton can result in a wavelength shift and not in a bathochromic shift. In the cases of phenoxyl substituted **2a–e** and **3a–e**, the wavelength maybe a combined result. We think that the p–π conjugation of oxygen bridge atoms with Pc rings and phenyls also plays a role in the wavelength of Q-bands. On account of thermal vibration, carbon–oxygen σ bonds may rotate, which could give rise to alternation in Pc π conjugation system. For **1d**, its hypochromic effect is similar to those of **2a**.

Among Pcs investigated in the present work, we found that non-peripherally substituted Pcs have relatively obvious hypochromic effect in comparison with peripherally substituted Pcs and unsubstituted Pcs. Taking **1–3a** as the examples, non-peripherally substituted Pc **2a** has relatively large absorbance differences compared with **1a** and **3a**, which are mainly due to the relatively large steric hindrance of non-peripheral phenoxyl substituents of **2a**. Other series of MPcs also display the same regularity as that of **1–3a**. We expect that the dome-shaped InClPcs **1–3e** and TiOPcs **1–3d** should have relatively large absorbance differences, Δ_a, than nearly planar **1–3a**, **1–3b** and **1–3c**, but we did not observe such a rule from the specific data of Δ_a. This may suggest that, for these compounds, conformational stress of phenoxyl substituents was more effective on the distortion of Pc ring in comparison with complex metals.

An additional band can be found at 789 nm for Pc **2a**, which we think is solvent-dependent and not related to the Pc π system. In UV–vis spectra of **2b** and **2c**, such solvent-dependent bands can be seen as well. The UV–vis spectra of **2c** measured in chloronaphthalene, $CHCl_3$, CH_2Cl_2, CH_3OCH_3, CH_3CN and THF, respectively, (Fig. 5) clearly indicate the phenomenon of solvent-dependent bands. Owing to the solvent effect of chloronaphthalene, absorption spectrum of **2c** performed in chloronaphthalene presents apparent bathochromic shift of Q-band in comparison with those measured in $CHCl_3$, CH_2Cl_2, CH_3OCH_3, CH_3CN and THF. Besides, the absorbance of chloronaphthalene-dependent band at 759 nm of **2c** is higher than that of Q-band (725 nm), which makes UV–vis spectrum of **2c** look like that of a metal-free Pc. The solvent-dependent bands of **2a** and **2b** centered at 789 nm and 776 nm, respectively, do not show the hypochromic effect, which contrasts with the good hypochromicity of solvent-dependent band of **2c** at 759 nm (Fig. 6). Due to the nature of solvent-dependent bands needs to be explored further, so we cannot discuss this topic deeply and present reasonable answer to the phenomenon. Pc **3c** did not show the hypochromic effect due to a strong solvent effect of chloronaphthalene on its UV–vis spectrum.

The hypochromic effect is not applied for the B-bands. It appears that thermal vibration had negligible effect on B-bands, the similarity of influence of π system on B-bands have been

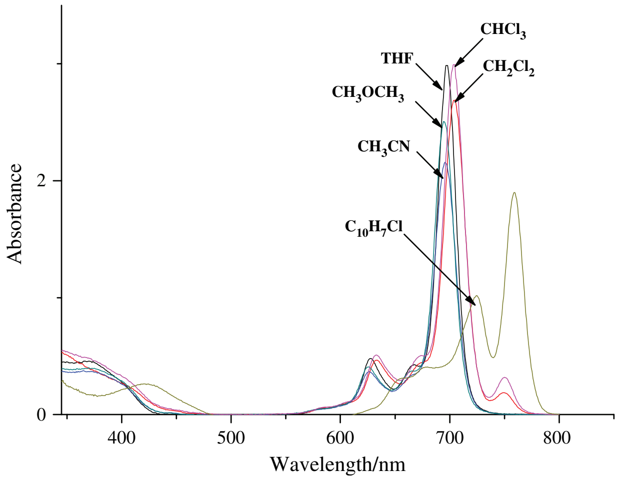


Fig. 5. UV–vis spectra of **2c** in different solvents.

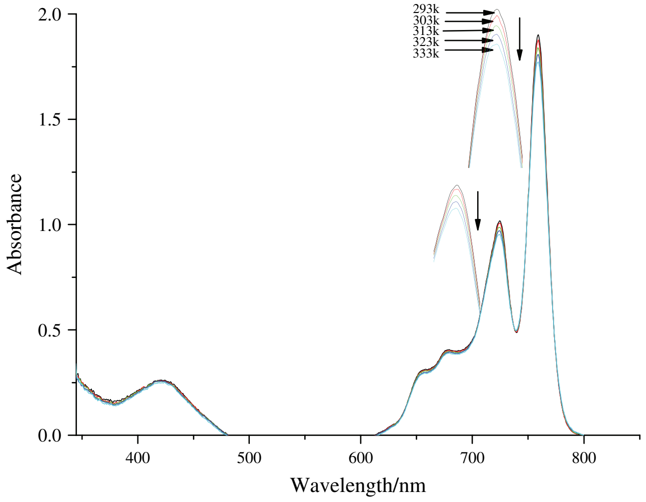


Fig. 6. Hypochromic effect of **2c** in chloronaphthalene.

reported [21]. Other Pcs investigated in this work present the same or analogous hypochromic effect to those of **1d** or **2a**.

4. Conclusion

In summary, we for the first time demonstrate the hypochromic effect of Pcs and MPcs induced by temperature, which is attributable to the distortion of nearly planar Pc ring due to a result of thermal vibration. The discovery enables us to finely and readily tune the spectroscopic properties or other properties and presents us an exciting foreground for Pcs' potential applications.

Acknowledgements

Financial support by the NSFC(60307002) and Innovation Foundation of Jilin University are gratefully acknowledged.

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