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Tuning J-type dimers of non-peripherally substituted zinc tetra-4-*tert*-butylphenophthalocyanine

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ABSTRACT

It was found, by UV–vis and TOF-MS, that the head-to-tail dimers of non-peripherally substituted zinc tetra-4-*tert*-butylphenophthalocyanine are inclined to form in non-coordinated solvent, e.g. chloroform and especially in dilute solution under 1.25×10^{-6} mol/mL. The aforementioned dimers in solution can be tuned by altering concentration or adding coordinated solvent, e.g. methanol, which might be further improved to a practical strategy for preparation of J-aggregates in the future.

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1. Introduction

Supramolecular aggregations of phthalocyanines (Pcs), dimers and oligomers, have attracted considerable interest for their potential application in optoelectronic technologies such as excitation-energy transfer, charge separation, and hole-transfer reactions, photosynthetic light-harvesting antenna, etc. [1,2]. A number of studies have been carried out on the preparation and property of Pc aggregations [3], especially the structurally various dimers formed via covalent bond linkage [2-5], dialkylammonium cations action [6], intermolecular coordination [1,7,8] and the like. The head-to-tail dimers, J-type aggregates, usually showed strong optical properties, e.g. fluorescence whereas the face-to-face dimers, H-type aggregates, did not [1,2]. The synthesis of I-aggregates, in contrast to Pc monomers, were generally more difficult for the rigorous requirement that Pc substrates must synchronously have unsymmetric structures and special coordination atoms around Pc ring or between Pc molecules [1-8]. The ways to obtain the J-type Pc dimers via straightforwardly intermolecular coordination of tetra-substituted Pc compounds have not ever been found in literatures by us to date. Herein, we present a facile protocol to tune the head-to-tail dimers of non-peripherally substituted zinc tetra-4-*tert*-butylphenophthalocyanine (nsztPc) in chloroform, which might be improved to a practical strategy to prepare the Jaggregates of Pc complexes by intermolecular coordination in the future.

According to a well-established synthetic route to soluble tetra-substituted Pcs via the aromatic nucleophilic substitution reaction between 4-nitrophthalonitrile or 3-nitrophthalonitrile and a suitable oxygen nucleophile followed by cyclotetramerisation of the resultant phthalonitrile derivatives [9–11], we prepared several phenoxy-substituted metal Pcs to study their UV-vis spectral properties. Among them, the non-peripherally substituted zinc Pcs in non-coordinated organic solvents, e.g. chloroform and dichloromethane displayed particular spectra, in which Q bands split to two peaks. The Q band split may be caused by the isomers with C_s , C_2 and C_{2v} symmetry, respectively [12,13] (Fig. 1). But no Q band split was found for them in coordinated organic solvent, e.g. methanol, ethanol and acetone, etc. More importantly, to the best of our knowledge, there are no literatures presently that report the Q band split caused by isomers of peripherally or non-peripherally tetra-substituted metal Pcs. Hence there should be other factors that caused the Q band split. Based on the study on specially coordination-formed J-type Pc dimers [7,8], it was concluded that there were the J-type dimers of the above Pc compounds in chloroform, which lead to Q split. In order to ascertain the split phenomenon, we took nsztPc as an example to study the equilibrium between the J-type dimers

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Fig. 1. Isomers of non-peripherally substituted metal Pc.

and monomers in chloroform by altering concentration and dropping methanol. The imagined structure for J-type dimers of C_4 symmetric nsztPc in chloroform was given in Fig. 2. And the possible structures of J-dimers formed via intermolecular selfcoordination of other isomers were ignored here for their low ratio [14].

2. Experimental

2.1. Materials and methods

Pentan-1-ol was distilled from Na prior to use. DMSO was predried over BaO and distilled under reduced pressure. Column chromatography purifications were preformed on silica gel. All other reagents and solvents are commercial available and used without further purification. Petroleum ether used had b.p. 60-90 °C.

High-resolution ¹H NMR spectra were recorded on a Varian Unity 500 spectrometer. IR spectra were measured on a Magna 560 FT-IR spectrometer. UV–vis spectra were taken on a Cary 500 UV–VIS–NIR spectrophotometer. MS spectra were obtained on a Voyager-De STR MALDI-TOF-MS spectrometer. Elemental analyses were performed on a PerkinElmer 2400 Elemental Analyzer.

2.2. The synthesis of 3-tert-butylphenophthalonitrile

3-Nitrophthalonitrile (6.92 g, 40 mmol) and 4-*tert*-butylphenol (6.08 g, 40 mmol) were added to 100 mL anhydrous DMSO at RT. The reaction mixture was stirred and 4.2 g LiOH·H₂O (100 mmol) was interfused over a 2-h period and the mixture was then stirred for 1 day. The reaction was monitored by TLC. The mixture was

then poured into 10% NaCl solution (400 mL) and stirred till precipitate appeared. The product was collected and future purified by flash column (petroleum ether–ethyl ether 1:1) to afford 3-*tert*-butylphenophthalonitrile (9.52 g, 86%). m.p. 104–106 °C; ¹H NMR (500 MHz, CDCl₃): (7.55 (dd, 1H, *J*=8 Hz, ArH), 7.45 (d, 2H, *J*=9 Hz, ArH), 7.43 (d, 1H, *J*=8 Hz, ArH), 7.09 (d, 1H, *J*=8 Hz, ArH), 7.02 (d, 2H, *J*=9 Hz, ArH), 1.34 (s, 9H, *t*-C₄H₉); TOF-MS–*m*/*z*: 299.1 [M+Na⁺], 314.9 [M+K⁺]; IR (KBr): 2231 (CN), 1276 $\nu_{\rm s}$ cm⁻¹ (COC). Anal. Calcd for C₁₈H₁₆N₂O: C 78.2, H 5.8, N 10.1; found: C 78.5, H 5.9, N 9.8.

2.3. The synthesis of nsztPc

3-*tert*-Butylphenophthalonitrile (1.04 g, 4.0 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (0.22 g, 1.0 mmol) were added under stirring to pentan-1-ol (10 mL) with a catalytic amount of 1,8diazabicyclo[5.4.0]undec-7-ene (DBU) in a 25-mL one-neck round-bottomed flask equipped with an air condenser. The mixture was stirred and heated at $135 \degree C$ under N₂ for 24 h. After cooling under N₂, the black cyan solution was poured into methanol, stirred and collected by vacuum filtration to afford the crude product after dried. It was washed with methanol by Soxhlet extraction to remove 3-tert-butylphenophthalonitrile and other remnants. In the end, the collected solid was purified by column chromatography with chloroform-methanol (10:1) as the mobile phase to give pure blue-green solid nsztPc (0.64 g, 50%). m.p. >320 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.31-7.39 (m, 12H, ArH), 6.86-7.03 (m, 16H, ArH), 1.29-1.35 (m, 36H, 4t-C₄H₉), LDI-1700-TOF-MS-m/z: 1168.6 [M]⁺; IR (KBr): 1251 ν_{s} cm⁻¹ (COC); Anal. Calcd for C₇₂H₆₄N₈O₄Zn: C 73.9, H 5.5, N 9.6; found: C 73.6, H 5.8, N 9.4.



Parallel J-dimer

Gradient J-dimer



Fig. 3. The UV-vis spectra of nsztPc in chloroform.

3. Results and discussion

3.1. Tuning J-type nsztPc dimers by altering concentration

As a non-peripherally phenoxy-substituted metal Pc, the nsztPc could dissolved in some non-coordinated organic solvents such as chloroform, dichloromethane and chlorobenzene, etc., as well as some coordinated organic solvents, e.g. methanol, ethanol, acetone, DMF and DMSO, etc. In non-coordinated solvents, it showed Q-band split phenomenon (Fig. 3), which differed from that with the other metals and the peripherally phenoxy-substituted metal Pcs. Based on the analysis in Section 1 the Q split might be for the existence of I-type nsztPc dimers in non-coordinated solvent, e.g. chloroform, which usually displayed two peaks in the region of Oband absorbance. In our research, it was found that the two split peaks can be tuned by altering the concentration of znstPc in chloroform (Fig. 3 and Table 1). After the concentration decreases under a critical value 1.25×10^{-6} mol/mL (c_c), the Q absorbance shows the characters of J-type Pc dimers, which has two immobilized split peaks Q_1 (712 nm) and Q_2 (744 nm), and always is the one right higher than that left for the former from the energy-lower π - π * transition [1–8]. According to the interpretation on exciton interaction of Q_x and Q_y transition dipoles [1,12], here Q_2 and Q_1 correspond to Q_x and Q_y transition absorbance, respectively (Fig. 2). Another interesting phenomenon was that the B band and shoulder absorbance also split two peaks B_1 (325 nm) and B_2 (416 nm), and S_1 (645 nm) and S_2 (667 nm), respectively. Moreover, the log ε of all

Parameters on UV-vis spectra of nsztPc in chloroform under different concentration



Fig. 4. Mass spectra of nsztPc in chloroform.

peaks increased with concentration diluted. But above the c_c , only the Q_2 , B_2 and S_2 were immobile, whereas the Q_1 702 nm, B_1 334 nm and S_1 633 nm with the absorbance of monomers and J-dimers, gradually shifted to the Q_1 712 nm, B_1 324 nm and S_1 645 nm with the absorbance of J-dimers along with the concentration diluted till c_c . From Fig. 3, it was obviously seen that the absorbance of Q_1 relative to Q_2 decreased with concentration diluted. Namely, the monomers gradually transform to J-dimers with concentration diluted till c_c .

3.2. Understanding the forming of J-type nsztPc dimers

The dimer peak could also be directly detected by TOF-MS even if the dimers were prone to decompose to monomers under detecting condition (Fig. 4). And also it is found that the peak height of charged dimer ions obviously increased with concentration diluted. The phenomenon disobeyed the routine that aggregates formed at high concentration and molecular monomers existed at low concentration. The possible reasons that caused J-type nsztPc dimers to be incline to form at low concentration might be ascribed to two intermolecular actions: the non-polar action from Pc rings with $18-\pi$ electron conjugated systems and the polar action from coordination between phenoxy-oxygen atom around one Pc ring and zinc atom in the center of another Pc ring. As we all knew that the former was so strong as to cause Pc compounds being insoluble in common organic solvents if no suitable substituents around Pc ring [9–11]. And the latter was so weak as to be hard found

$\lambda^a (nm)/\log \varepsilon$	C ^b								
	a	b	С	d	е	f	g	h	i
Q ₁	702, 5.45	704, 5.31	711, 5.17	712, 5.17	712, 5.20	712, 5.25	712, 5.36	712, 5.51	712, 5.69
Q ₂	744, 4.79	744, 5.16	744, 5.33	744, 5.36	744, 5.39	744, 5.44	744, 5.50	744, 5.61	744, 5.77
B ₁	334, 4.93	332, 4.90	327, 4.86	325, 4.88	325, 4.93	325, 5.04	325, 5.20	325, 5.36	325, 5.55
B ₂	416, 4.57	416, 4.62	416, 4.70	416, 4.75	416, 4.81	416, 4.95	416, 5.13	416, 5.31	416, 5.52
S ₁	633, 4.72	638, 4.64	644, 4.69	645, 4.75	645, 4.82	645, 4.98	645, 5.15	645, 5.39	645, 5.64
S ₂	667, 4.74	667, 4.75	667, 4.77	667, 4.81	667, 4.88	667, 5.01	667, 5.17	-, - ^c	-, -

^a Taken on a Cary-500 UV-vis spectrophotometer.

^b (*a-i*) represent 1.0 × 10⁻⁵, 5.0 × 10⁻⁶, 2.5 × 10⁻⁶, 1.25 × 10⁻⁶, 6.25 × 10⁻⁷, 3.13 × 10⁻⁷, 1.56 × 10⁻⁷, 7.81 × 10⁻⁸ and 3.91 × 10⁻⁸ mol/L, respectively.

^c The peak is not clear.

Table 1



Fig. 5. The UV–vis spectrum of solid nsztPc film on a piece of quartz glass (10 mm × 10 mm × 0.2 mm), prepared by immerging the glass into 30 mL solution (1.3×10^{-6} mol/L, nsztPc in CHCl₃) in a 50-mL beaker, and enveloping mouth with filter paper and setting for 3 days.

in coordinated solvents. In terms of nsztPc in chloroform, at high concentration, the strongly non-polar action covered the weakly polar action, and easily caused nsztPc molecules to form H-dimers, instead of J-dimers, after chloroform volatilizing (Fig. 5). Whereas, at low concentration, the abundant chloroform molecules caused the intermolecular distances of nsztPcs to increase and weaken the non-polar action. In the circumstance, the zinc atom in the center of Pc ring and the phenoxy-oxygen atom around Pc ring just liked the positive charge and the negative charge to attract each other. Namely, the coordinated action unfolded and caused the J-dimers to form. However, the aforementioned understanding to the unconventional phenomenon was not perfect and needed further studied by us.

As for as the peripherally phenoxy-substituted metal Pcs, it was considered by us that the substituents of them could rotate freely and then disturbed the coordination between phenoxy-oxygen atom and metal in Pc ring. So no Q-band split phenomenon were found for them. In another way, the zinc in Pc ring relative to the other metals was prone to coordinate with oxygen or nitrogen [1–8]. In our research, the non-peripherally phenoxy-substituted Pcs with other metals also did not show the Q-band split. The result was that only the non-peripherally phenoxy-substituted zinc Pcs, e.g. nsztPc displayed Q-band split phenomenon because their substituents could not rotate freely due to the steric hindrance from Pc ring.

3.3. Tuning J-type nsztPc dimers by coordinated solvent

The movement of equilibrium between the J-dimers and monomers of nsztPc can further be confirmed with the effect of some coordinated solvents, methanol or ethanol, on the UV–vis spectra of nsztPc in chloroform. With methanol continuously dropped into the solution, all peaks changes except for S_2 . The Q_2 as well as B_2 decreases obviously and disappears finally, and contrarily the Q_1 and B_1 not only increase but also shift blue to 700 nm and shift red to 334 nm, respectively, and again the S_1 increases and shifts blue to 630 nm. In the end, the UV–vis spectrum of J-dimers is converted to that of monomers with one Q band and one B band (Fig. 6). In other words, the methanol as a coordination reagent has an oxygen atom to replace the *tert*-butylpheno-oxygen atom to



Fig. 6. The UV–vis spectra of solution (1.3×10^{-6} mol/L, nsztPc in CHCl₃) with 0, 5, 10, 15, 20 and 25 drops of CH₃OH, respectively).

coordinate with zinc in the center of Pc ring and then decompound the J-dimers to monomers. The S_1 of monomers, like the shoulder peaks of many other Pc complexes, is ascribed to the absorbance of $n-\pi^*$ transition associated with the aza nitrogen lone pairs [15–18], which has been testified by the disappearance of the S_1 after protonation of aza nitrogen [19]. However, the S_2 does not give obvious difference during the course of methanol being dropped in solution, which needs further investigation. In addition, it seems that no absorbance of H-type dimers in the above liquid-phase UV-vis spectra because it should appears between the said S_1 (630 nm) and S_2 (667 nm) of monomers according to the previous reports [20–25], which is proved by the UV-vis spectrum of nsztPc in solid. H-type dimer and monomer absorbance of nsztPc were at 650 nm and 700 nm, respectively (Fig. 5).

4. Conclusion

In summary, J-dimers of nsztPc have a dynamic equilibrium with its monomers in chloroform and are almost unique bellow 1.25×10^{-6} mol/mL, which can be verified by altering concentration or dropping methanol. Namely, the preparation of J-type dimers of Pc like nsztPc must be carried out in dilute solution with non-coordinated organic liquid as solvent, for example by the way treating the dilute solution with lyophilization.

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