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SYNTHESIS AND CHARACTERIZATION OF A NEW METAL-FREE AZAPHTHALOCYANINE CONTAINING FOUR PERIPHERAL ION JACKS

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Abstract–A synthesis of a new 1,10-phenanthroline-appended metal-free azaphthalocyanine(azaPc), which is generated from precursor, 10,12-diimino-11 *H*-pyrrolo[3,4-*b*]dipyrido[3,2-*f*:2',3'-*h*]quinoxaline, is described. This azaPc is purified by absolute methanol in a Soxlet apparatus, then under high vacuum (10^{-4}Pa) and is unequivocally characterized by its elemental analysis and spectrometry.

INTRODUCTION

Phthalocyanines(Pcs) can be use as remarkably functional materials and are finding the applications in a wide range of high tech fields such as nonlinear optics,[1] Langmuir-Blodgett(LB) films,[2] photosensitizers,[3] gas sensors,[4] catalysts,[5] liquid crystals,[6] optical data storage,[7] sensitizers for photodynamic therapy of cancer, [8] electrodes in fuel cell, [9] photoelectric conversion materials in solar cells, [10] laser service substances, [11] single molecular devices, [12] electrochromic devices, [13] among others. A great number of remarkable applications of Pcs arise from their unique 18 π -electron conjugated aromatic cloud, which makes Pcs present high thermal and chemical stability and remarkable photoelectric properties. Material functions of Pcs can be explored in two aspects: the properties determined by molecular structure of Pcs as well as the ones of Pc aggregates formed by molecular interactions. Structural change of Pcs will lead to some new properties. The orderly arrangements of Pc molecule in certain manner can form aggregates possessing particular structures and properties.

The synthesis of Pcs possessing self-assembly function is attracting the interest of many chemists. At present, abundant works focus on the introduction of substituents having self-assembly function into Pc molecules. Direct conversion of some of carbon atoms in Pc rings into heteroatoms, such as nitrogen atoms, is another approach and has been extensively explored. [14]

We report here, synthesis and characterization of the new metal-free azaPc, tetra-2,3-(dipyrido [3,2-*f*:2',3'-*h*]quinoxalino)porphyrazine **1**(azaPc(**1**))（Figure 1）, containing four 1,10-phenanthroline subunits in its molecule. We are involved in the synthesis and characterization of this new family of azaPcs[15] since 2001. AzaPc(**1**) is expected to show exciting coordination function due to the exist of eight nitrogen atoms in its peripheral moieties. Furthermore, it has an expanded π -electron system, which may lead to some new photoelectric properties. The coordination of diimine binding sites (ion jacks) in azaPc(**1**) with some metal ions may self-assemble supramolecular systems containing unique structures. In this way, coordination chemistry of the central cavity in azaPc(**1**), as well as its peripheral ion jacks can be explored for the assembly of new structural topologies with tunable optical, redox and electronic properties.

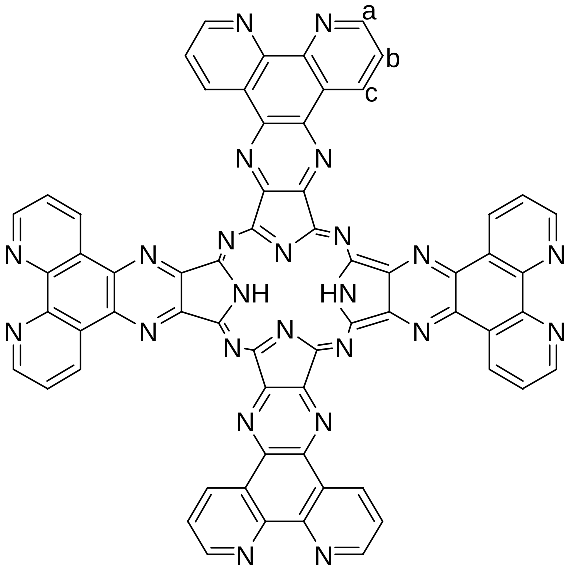


Figure1. Tetra-2,3-(dipyrido[3,2-*f*:2',3'-*h*]quinoxalino)porphyrazine (**1**) (azaPc(**1**)).
Letter a, b, c indicates the protons assigned to ^{1}H NMR spectra of azaPc (**1**)

RESULTS AND DISCUSSION

We prepare successfully the fully conjugated metal-free azaPc(**1**), containing four ion jacks, which is fully characterized by its elemental analysis, ^{1}H NMR, ^{13}C NMR, MS, UV-VIS and IR spectra.

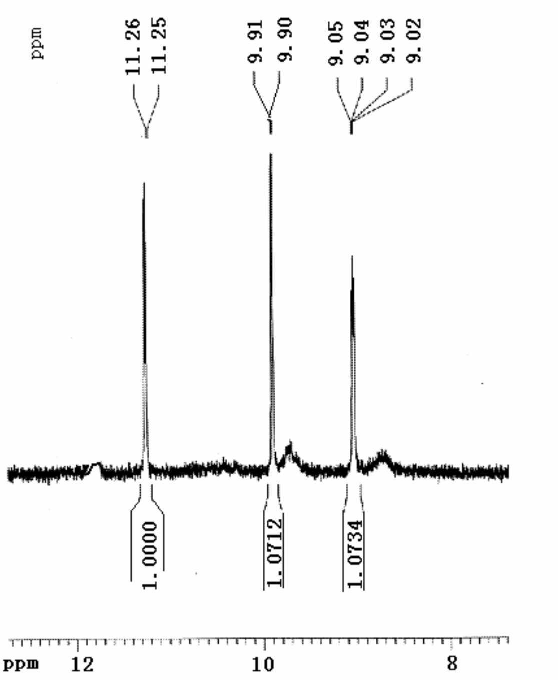


Figure 2. ^{1}H NMR (400 MHz，CF_3COOD) spectra of azaPc(**1**)

The ^{1}H NMR spectra (Figure 2) of azaPc(**1**) clearly exhibits signals of three kinds of aromatic protons, whose peak area shows the quantity ratio of them is 1:1:1. Due to the close adjacence of Ha to N atom (Figure 1), value of Ha (appears at δ = 11.25, 11.26) is the largest compared to that of Hb and Hc. As a result of the coupling between Ha and Hb, the signal of Ha is a doublet (^{3}J(H,H)=5 Hz). Owning to conjugative effect, the NMR resonance value of Hc is under the influence of N atom adjacent to Ha and shifts to downfield (observed at δ =9.90, 9.91). Quartet (^{3}J(H,H)=5 Hz) for Hb is found at δ =9.02-9.05. Electro-pulling inductive effect and electro-pushing conjugative effect lead to the electronic density around Hb is the largest among Ha, Hb and Hc, so the resonance value of Hb is the smallest compared to that of Ha and Hc. Since the spectrum was run in CF_3COOD, the inner NH protons are not visible.[17]

The ^{13}C NMR spectra (run in CF_3COOH) of azaPc(**1**) shows the sort of carbon atoms. The signal at 142.211(δ [ppm]) (Figure 3) (C-8) is the characteristic chemical shift of carbon atoms in porphyrazine ring.[16] Some of other signals are assigned as the following: 149.639, 148.640 (C-2', C-2), 121.243, 119.630(C-3', C-3), 143.256,136.629 (C-4', C-4). The coordination of azaPc(**1**) with H^{+} in CF_3COOH leads to the larger value of C-2', C-3', C-4' than the one of C-2, C-3, C-4. They exhibit tertiary carbon characteristic and are found in the DEPT-135 spectroscopy. The signals found at 128.853 (C-1), 130.081, 129.737(C-6, C-5) and 140.073(C-7) show quaternary carbon characteristic and are unobserved in DEPT -135 spectroscopy of azaPc(**1**). All ^{1}H NMR and ^{13}C NMR data are in agreement with the proposed structure of azaPc(**1**).

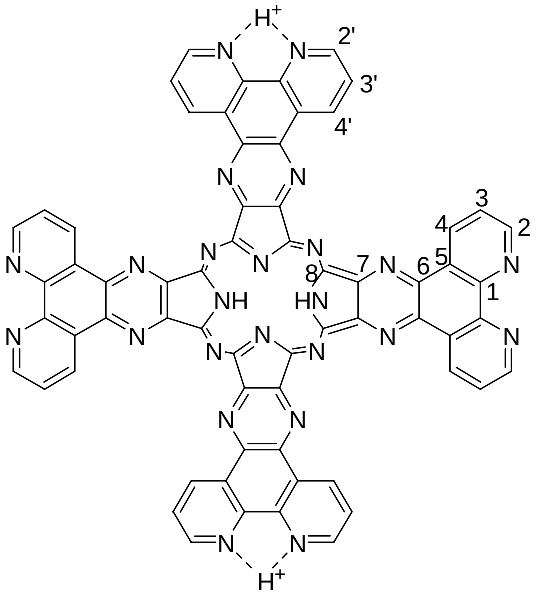


Figure 3. The assignment indication of ^{13}C NMR of azaPc(**1**)

The data in IR spectra of azaPc(**1**) indicate the formation of a Pc ring. The peak centered at 3382 cm^{-1} corresponds to an N-H stretching vibration and the one lying at 1557.97 cm^{-1} is attributable to Pc framework. The bending vibration of N-H in Pc ring locates at 1091 cm^{-1}. These assignments are consistent with the report of reference 17. Furthermore, comparison of IR data for azaPc(**1**) and compound(**4**) clearly reveals the presence of azaPc(**1**) by the absence of the imino N-H vibration (3201.33 cm^{-1}) and the secondary amino N-H vibration (1630.97 cm^{-1}), which are observed in the IR spectra of compound(**4**).

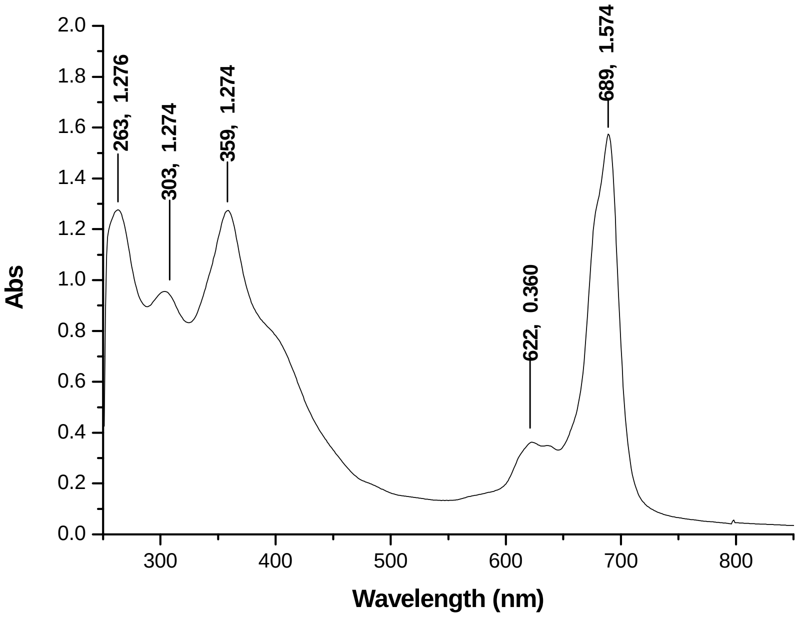


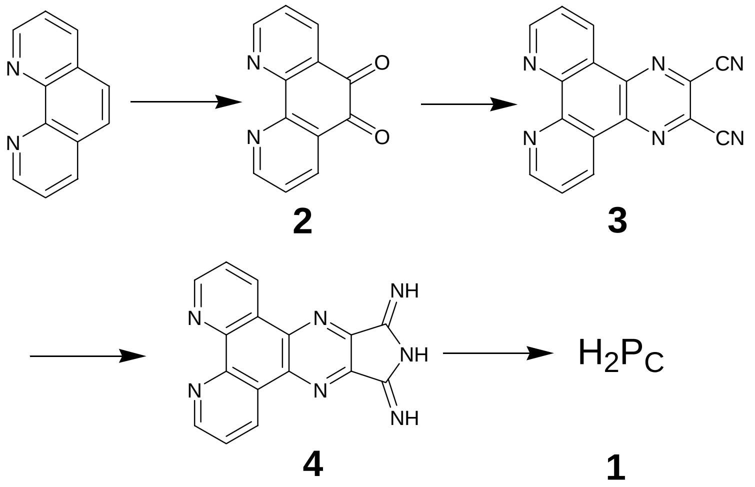
Figure 4. UV-VIS spectra of azaPc(**1**)

A reproducible peak at m/z= 566.0385 is observed in the MS spectra, corresponding to **1** plus two hydrogen ions. Full conjugation structure of azaPc(**1**) accounts for this double-proton phenomenon. The protonation of one 1,10-phenanthroline subunits will lead to the electronic density around nitrogens in other three 1,10-phenanthroline subunits decreased. The decrease of electronic density around nitrogens reduces their coordination abilities with hydrogen protons. The coordination of 1,10-phenanthorline subunits in azaPc(**1**) with two protons will cause other two 1,10-phenanthroline moieties unable to combine with protons any more. The system energy of azaPc(**1**) is the lowest as two protons coordinate with the opposite diimine binding sites in this molecule. The elemental analysis data for azaPc(**1**) are consistent with an azaPc containing two water molecules and two carbon dioxide molecules. As already reported in the chemical literature, azaPcs are often isolated as hydrates.[14] The strong peak centered at 2362.1 cm^{-1}(CO_2 absorption) is found in IR spectra of azaPc(**1**). The UV-VIS spectra (Figure 4) exhibits characteristic absorption peak of Pcs, Q band, at 689 nm and also shows a relatively weaker absorption peak (centered at 623nm), which can be assigned either to vibrational overtones of Q band[18] or to molecular dimerisation of azaPc(**1**) in CF_3COOH. In addition, three absorption peaks observed at 263 nm, 303 nm and 359 nm, respectively, may contain the B-band and absorption of peripheral bidentate ligand in azaPc(**1**). Comparison of UV-VIS spectra data for compounds (**1～4)** reveals that the absorption at 263 nm may be assigned to the bidentate ligand in azaPc(**1**) and those at 303 and 359 nm may be attributed to the superposition of B band and absorption of bidentate ligand.

To summarize, elemental analysis, ^{1}H NMR, ^{13}C NMR, MS, IR and UV-VIS spectra indicate the presence of azaPc(**1**), which is expected to show ion jack function. The central cavity of azaPc(**1**) together with its peripheral ion jacks present new exciting prospects for the preparation of molecular solid materials of azaPc(**1**), which can be further explored in magnetic, electronic, redox and photo-active aspects.

EXPERIMENTAL

The following compounds were prepared as described in the literature: 1,10-phenanthroline-5,6-dione (**2**),[19] 2,3-dicyanodipyrido[3,2-*f*:2',3'-*h*]quinoxaline(**3**).[20] Commercial available 1,10-phenanthroline, dicyanomaleonitril, quinoline, H_2SO_4, HNO_3, CH_3OH, CH_3CH_2OH and KBr were used without further purification. NMR: Bruker AV 500，Bruker AV 600, Bruker AV 400 (^{1}H: 500 MHz，600 MHz, ^{13}C: 100 MHz). IR: Magna 560 FT-IR (American Nicolet Company). UV-VIS: Cary 500 UV-VIS-NIR Spectrophotometer. MS: LDI1700-TOF-MS (Linear Scientific Inc.,USA), QUSTAR-TOF-MS. Elemental analysis: Flash EA1112 (ThermoQuest, Italy).



Scheme 1. Synthetic route of azaPc(**1**)

10,12-Diimino-11*H*-pyrrolo[3,4-*b*]dipyrido[3,2-*f*:2’,3’-*h*]quinoxaline(4): Compound(**3**) (0.28 g, 1 mmol) was added to stirring anhydrous methanol(30 mL) in a 50-mL three-necked round-bottomed flask equipped with a reflux condenser. Then, a catalytic amount of sodium methoxide in anhydrous methanol was added to the reaction mixture, which was stirred over 1 h at rt while bubbling a rapid steam of anhydrous ammonia into the reaction system. After that, temperature of the mixture was raised up to 50℃ with a continuous passage of ammonia. A yellow-grey solid was formed during the reaction. Stopped the reaction and filtered resulting solution. The collected solid was recrystallized from DMSO to afford a grey solid (0.15 g, 49.8%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 9.61-9.62(d, 2H, J=7.8 Hz), 9.28-9.29(d, 2H, J=4.2 Hz), 8.02-8.04 (dd, 2H, J=7.8 Hz, 4.2 Hz); UV/VIS(DMSO) λmax: 689 nm, 623, 359, 303, 263; IR(KBr) $\tilde{v}$: 3201 cm^{-1}(=N-H), 1631 cm^{-1}(C=NH), 1585 cm^{-1} (C=N in heterocycles), 1557.9 cm^{-1} (C=C); TOF-MS (DMSO) m/z: 300.0708 [M+H$^+$] (calcd 299.09 [M$^+$])

Tetra-2,3-(dipyrido[3,2-*f*:2’,3’-*h*]quinoxalino)porphyrazine(1): Compound(**4**) (0.30 g, 1 mmol) was added to quinoline(15 mL) in a 25-mL three-necked round-bottomed flask, then the solution was heated and refluxed at 232-236℃ under a nitrogen atmosphere. A deep green solid was formed soon. After cooling under the nitrogen atmosphere, quinoline was removed under reduced pressure. Then, the product was washed with hot DMSO, extracted in a soxlet apparatus with anhydrous methanol (12 h) and dried at 80℃ in air. The collected product was further purified at 300℃ under 10^{-4}Pa to afford 0.81g (63%) of dark-green solid.

^{1}H NMR (500 MHz,CF_3COOD): δ 11.25-11.26 (d, 2H, J=5 Hz), 9.90-9.91 (d, 2H, J=5 Hz), 9.02-9.05(q, 2H, J=5 Hz); ^{13}C NMR(100 MHz,CF_3COOD): δ 149.64, 148.64(C-2’,C-2), 121.24, 119.63(C-3’,C-3), 143.26, 136.63(C-4’,C-4), 142.21(C-8), 128.85(C-1), 130.08, 129.74(C-6,C-5), 140.07(C-7); ^{13}C NMR, DEPT-135(CF_3COOD) δ 142.21, 136.63, 130.08, 129.74, 128.85; UV/VIS (CF_3COOD) λmax: 689 nm, 623, 359, 303, 263; IR(KBr) $\tilde{v}$: 3382 cm^{-1}(N-H), 1558 cm^{-1} (porphyrazine ring), 1091 cm^{-1}(N-H);

TOF-MS(HCOOH) m/z: 566.0385 [M+2H$^+$](calcd 566.1464[M+2H$^+$]); Anal. Calcd for $C_{66}H_{30}N_{24}O_6$: C, 63.16; H, 2.41; N, 26.78; O, 7.65. Found: C, 62.90; H, 2.44; N, 26.08; O, 7.45.

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