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Research Article

SYNTHESIS, CHARACTERIZATION, AND SPECTROSCOPIC INVESTIGATION OF FULLY CONJUGATED PYRAZINOPORPHYRAZINES

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ABSTRACT

2, 7-Di-tert-butylpyrene was oxidized to 2, 7-di-tert-butylpyrene-4, 5-dione. The latter through condensation reaction with vicinal diamine such asdiaminomaleodinitrile afforded 2, 7-di-tert-butyl pyrene[4,5](2,3-pyrazine-5,6-dinitrile) which on cyclotetramerization produce the corresponding 2H- and metal-pyrazinoporphyrazine (2H-PyzPz and M-PyzPz, M= Co, Ni, Zn or Cu). Elemental Analytical results, Infrared, UV, visible and NMR spectral data of the new prepared molecules were carried out.

Keywords: *Pyrazinoporphyrazine, Fully Conjugated Systems, Cyclotetramerization*

INTRODUCTION

Tetrapyrazinoporphyrazine is one of the phthalocyanine derivatives having two nitrogen atoms at equivalent 1, 4-positions of the phthalocyanine benzene units. Due to the additional nitrogen atoms, tetrapyrazinoporphyrazines are less electron-rich than the corresponding phthalocyanine. There exists a gap in porphyrazine synthesis in the sense that it has not been possible before to ensure the formation of porphyrazines. Therefore, the main effort in this work was directed towards addressing this void. A focus of the research was to investigate introduction of a linker between two monomer dinitrile units, used during the macrocyclisation step, to force the geometry into the porphyrazine. Attention was also given to finding a way to functionalise the macrocycles through complexation with some metals to yield other potentially interesting structures. Phthalocyanines and related tetraazamacrocycles have found wide applications in diverse areas such as biomedical agents for diagnosis and therapy (Motyka *et al.,* 2013), chemical sensors (Tuncer *et al.,* 2011), liquid crystals (Abbasia *et al.,* 2011), nonlinear optics (Donzello *et al.,* 2012; Goslinski *et al.,* 2011) and are precursors to new conducting materials (Stuzhin *et al.,* 2012). Porphyrazines are prepared by magnesium templated cyclization of maleonitrile. Metalloporphyrazines with a 2-methyl-2-pentenyl group fused to each pyrrole unit were synthesized starting with the corresponding unsaturated dicarbonitrile derivative (Tuncer *et al.,* 2011). Porphyrazine complexes of zinc, aluminium and other metals show anticancer properties and uses in photodynamic therapy (Sakamoto *et al.,* 2008).The synthetic route to new fully conjugated systems can be achieved through condensation of diones with diamines. Hexa-1,5-diyne-3,4-diones react smoothly with commercially available diaminomaleodinitrile to give the dicyanodiethynylpyrazines (Sharman and Van-Lier, 2000). In our previous work, dielectric properties of new fully conjugated 2H- and metal-pyrazinoporphyrazine network products were reported (Abdel-Razik *et al.,* 2011). A facile and regioselective synthesis of trans-hetero functionalized porphyrazine derivatives were investigated (Forsyth *et al.,* 1998). The synthesis and X-ray structural characterization of two manganese (III) porphyrazine (tetraazaporphyrin) complexes are reported (Forsyth *et al.,* 1998). Synthesis, characterization of porphyrazinediols and complexation to group IVB metallocenes were investigated (Bellec *et al.,* 2000). Synthesis and photophysical properties of peripherally metallatedbis (dimethylamino) porphyrazines were reported (Sakellariou *et al.,* 2000). Unsymmetrical porphyrazines (tetraazaporphyrins) bearing a single bidentate phenanthroline chelating group M [pz (tbutylphenyl) 6phen] have been prepared by the base-catalyzed cross condensation of 3,4-bis (4-tert-butylphenyl) pyrroline-2,5-diimine (in excess) with 6,7-dicyanodipyridoquinoxaline (Garrido *et al.,* 2001). The synthesis of four novel lanthanide tetraazaporphyrin (porphyrazine) sandwich complexes is reported (Garrido *et al.*, 2001). Base-induced cyclotetramerisation of the aromatic dinitriles with magnesium butoxide in refluxing butanol generates the peripherally peralkynylated phthalocyanine or naphthalocyanine Analyticalogues, namely the tetrapyrazinoporphyrazines and tetra-6, 7-quinoxalinoporphyrazines, respectively (Faust *et al.*, 1999). The pyrazinoporphyrazine system (metal-free, 2H-PyzPz, zinc and copper derivatives) has been synthesized by tetramerization of 2,3-dicyanopyrazine monomer unit (Wang *et al.*, 1997). A new pyrazinoporphyrazinemacrocycle carrying externally appended pyridine rings, tetrakis-2,3- [5,6-di (2-pyridyl) pyrazino] porphyrazine (hydrated) was prepared in high yield by direct cyclotetramerization of the precursor, 2, 3-dicyano-5, 6-di (2-pyridyl)-1, 4-pyrazine, in the presence of 1, 8-diazabicyclo [5.4.0] undec-7-ene (DBU) (Donzello *et al.*, 2004). Condensation of diaminophthalonitrile with 1, 10-phenanthroline-5, 6-dione in EtOH afforded the suitably functionalized phthalonitrile precursor, as a pale yellow solid which was cyclotetramerized in a refluxing solution of lithium metal dissolved in pentanol, followed by demetallation with acetic acid, affording the crude, metal free phthalocyanines,2H-Pc, as a dark green solid (Rusanova *et al.*, 2002). Synthesis of tetra (5-n-nonyl-8-tert-butyl-2, 3-pyrazino [2, 3-b] indolo) porphyrazinato copper (II) was reported (Kim *et al.*, 2008). The present study focuses on the synthesis, characterization and spectral investigations of some novel fully conjugated, pyrazinoporphyrazine.

Experimental

Characterization and Sample Preparation

Fourier-transform infrared spectrometer (8101 M-Shimadzu) was used in spectral measurements. UV-Vis spectra were obtained using Unicam UV-Vis spectrometer. NMR spectra were recorded in deuteriochloroform, on a Varian VXR 400S NMR spectrometer operating at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) with tetramethylsilane as internal standards. Elemental analysis for metal content was carried out by an Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP-AES), using a Varian Liberty-100 Sequential Spectrometer. Elemental analysis was determined with Perkin-Elmer 2400 CHN.

Preparation of 2, 7-Di-tert-butylpyrene-4, 5-Diones 2

Pyrene was purchased from Acros and used as received. Other materials were obtained from Aldrich and used as received. 2, 7-Di-tert-butylpyrene 1 was synthesized by using the reported procedure (Yamato *et al.*, 1997) in greater than 90 % yield. Compound 2 was prepared as previously reported (Hu *et al.*, 2005). To a solution of 2, 7-Di-tert-butylpyrene 1 (10 mmol) in CH_2Cl_2 (40 ml) and CH_3CN (40 ml) were added $NaIO_4$ (10.0 g, 46.8 mmol), H_2O (50 ml) and $RuCl_3.xH_2O$ (0.20 g, 0.96 mmol). The dark brown suspension was stirred at room temperature overnight. The reaction mixture was poured into 500 ml of water and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 50 ml). The CH2Cl2 extracts were combined with the organic phase and washed with water to give a dark orange solution. The solvent was removed under reduced pressure to afford a dark orange solid. Column chromatography (CH_2Cl_2) gave pure product of compound **2** as bright orange crystals, mp 302-304 °C (Hu *et al.*, 2005).

Preparation of 2, 7-Di-tert-butylpyrene [4, 5] (2, 3-pyrazine-5, 6-dinitrile) **3**

A solution of dione**2** (10 mg, 0.027 mmol) in acetic acid (50 ml) was treated with diaminomaleonitrile (2.915 mg, 0.027mmol). The mixture was refluxed with stirring at room temperature for 2 h. The precipitate was filtered off and washed with acetic acid to give yellowish brown solid. 10.04 mg, 94 %; mp = 194 °C. IR (KBr): ν cm^{-1}, 2228 (CN), 1515 (C=N), 1613 (C=C). ^{1}H NMR (CDCl3): δ = 7.78 (d, aromatic-H), 7.62(s, aromatic-H), 1.67 (s, aliphatic-H); ^{13}C NMR (CDCl3): 151.5 (C), 146.3 (C), 144.8 (C), 143.2(C), 142.5 (C), 141.6 (C), 136.4 (C), 135.4 (C), 132.7 (C), 131.8 (C), 84.6 (C), 119.7 (CN) , 37.4 (CH3), 34.6 (CH3). Analytical calculated for C28H26N4; FW: 418.53; C, 80.35; H, 6.26; N, 13.39. Found: C, 80.46; H, 6.29; N, 13.44.

Preparation of tetra [2, 3-(1, 4-diazaphenanthreno) porphyrazine] **4**

Lithium metal (20 mg, 2.8 mmol) was added to a refluxing solution of **3** (259.28 mg, 0.5 mmol) in pentanol (2 ml). The solution was heated at reflux for 18 h. On cooling, acetic acid (0.2 ml) was added to the reaction mixture and the crude product was collected by centrifugation. The green material was purified by column chromatography (eluent: dichloromethane) and by precipitation from toluene. IR (KBr): ν cm^{-1}, 1521 (C=N), 3356 (NH), 1614 (C=C). UV-Vis λmax (CH_2Cl_2)/nm): 344, 438, 637, 692. ^1H NMR (CDCl3) δ = 9.73 (s, H, NH), 7.68 (s, aromatic-H), 7.62 (d, aromatic-H), 1.41 (s, aliphatic-H). Analytical calculated for C112H98N16 requires C, 80.64; H, 5.92; N, 13.44. Found: C, 80.72; H, 5.96; N, 13.47.

Preparation of tetra [2, 3- (1, 4-diazaphenanthreno) porphyrazinato]-metal II **5a-d**

The compound**3** (259.28 mg, 0.5 mmol) was subjected to tetramerization on heating with 0.75 mmol of metal salt (cobalt II chloride, nickel II chloride, zinc acetate or copper nitrate) in quinoline (2 ml) at 200 ºC for 18 h. The material was dissolved in acetone, and the un-trapped metal was precipitated and removed from the solution. To the resulting acetone solution, an excess of cold methanol was added, precipitating blue (**5a, b**) or dark green (**5c, d**) solids. The solubility of these products was examined in various solvents, showing that they are soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, THF and acetone at room temperature and are easily purified by chromatography on silica gel. The product was vacuum dried overnight.

5a: IR (KBr): ν cm^{-1}, 1515 (C=N), 1610 (C=C). UV-Vis λmax(CH_2Cl_2)/nm): 364, 449 (shoulder), 663, 721. ^1H NMR (CDCl3) δ = 8.37 (s, aromatic-H), 1.38 (s, aliphatic-H), 7.61 (d, aromatic-H). Analytical calculated for the product, C112H104N16Co requires C, 77.62; H, 6.05; N, 12.93; Co, 3.40. Found: C, 77.69; H, 6.03; N, 12.98; Co, 3.43.

5b: IR (KBr): ν cm^{-1}, 1509 (C=N), 1611 (C=C). UV-Vis λmax (CH_2Cl_2)/nm): 366, 447 (shoulder), 660, 723. ^1H NMR (CDCl3) δ = 8.34 (s, aromatic-H), 1.36 (s, aliphatic-H), 7.57 (d, aromatic-H). Analytical calculated for the product, C112H104N16Ni requires C, 77.63; H, 6.05; N, 12.93, Ni, 3.39. Found: C, 77.68; H, 6.07; N, 12.97; Ni, 3.42.

5c: IR (KBr): ν cm^{-1}, 1512 (C=N), 1594 (C=C). UV-Vis λmax (CH_2Cl_2)/nm): 359, 451 (shoulder), 659, 704. ^1H NMR (CDCl3) δ = 8.38 (s, aromatic-H), 1.43 (s, aliphatic-H), 7.56 (d, aromatic-H). Analytical calculated for the product, C112H104N16Zn requires C, 77.33; H, 6.03; N, 12.88; Zn, 3.76. Found: C, 77.38; H, 6.06; N, 12.91; Zn, 3.77.

5d: IR (KBr): ν cm^{-1}, 1511 (C=N), 1600 (C=C). UV-Vis λmax (CH_2Cl_2)/nm): 364, 443 (shoulder), 655, 702. ^1H NMR (CDCl3) δ = 8.33 (s, aromatic-H), 1.45 (s, aliphatic-H), 7.59 (d, aromatic-H). Analytical calculated for the product, C112H104N16Cu requires C, 77.41; H, 6.03; N, 12.90; Cu, 3.66. Found: C, 77.46; H, 6.06; N, 12.96; Cu, 3.69.

RESULTS AND DISCUSSION

Synthesis, characterisation and spectral properties of the novel fully conjugated, products of tetramerized metal free pyrazinoporphyrazine, 2H-PyzPz, and metal-pyrazinoporphyrazine, M-PyzPz, containing four peripheral diimine binding sites. The key intermediate in the synthesis is the precursor 2, 7-di-tert-butylpyrene [4,5] [9,10] bis (2, 3-pyrazine-5, 6-dinitrile) **3**. The starting material is 2, 7-di-tert-butylpyrene **1** which was synthesized by using the reported procedure. Compound **1** was converted in the first step to 2, 7-di-tert-butylpyrene-4, 5-dione **2** by treatment with NaIO4 and RuCl3.xH2O. Condensation of 2 with commercially available diaminomaleodinitrile in acetic acid afforded the suitably functionalized pyrene [4,5] [9,10] bis (2, 3-pyrazine-5, 6-dinitrile) **3**, as a pale yellow solid. Cyclotetramerisation of the aromatic dinitrile **3** with lithium metal in pentanol and metal salt in quinoline generates 2H-PyzPz **4** and M-PyzPz **5a-d** products, respectively.

IR spectral data of precursor **3** shows an intense bands at 2228, 1515 and 1613 cm^{-1} for C≡N, (C=N) and (C=C) groups, respectively. In accordance with this structure, the ^1H NMR spectrum revealed a singlet at δ = 7.62 (d) and 1.67 (s) assignable to aromatic and aliphatic protons, respectively. Elemental analytical results and ^{13}C NMR spectral data of the new dinitrile**3** are consistent with the assigned formulation (see experimental, scheme 1). IR spectrum of 2H-PyzPz **4** shows a broad band at 1521 cm^{-1}, which is assignable to the stretching vibration of the C=N bond. The absorption values of the C=N vibration at 1515, 1509, 1512, and 1511 cm^{-1} for Co-PyzPz**5a**, Ni-PyzPz**5b**, Zn-PyzPz**5c** and Cu-PyzPz**5d** respectively, are lower by about 6-12 cm^{-1} than those for the metal free 2H-PyzPz **4**, which indicate the coordination of azomethine nitrogen atom to metal ions in the complexes. Moreover, there is a broad band at 3356 cm^{-1}, assignable to the stretching vibration of the N-H bond in free metal pyrazinoporphyrazine complex 2H-PyzPz **4**.

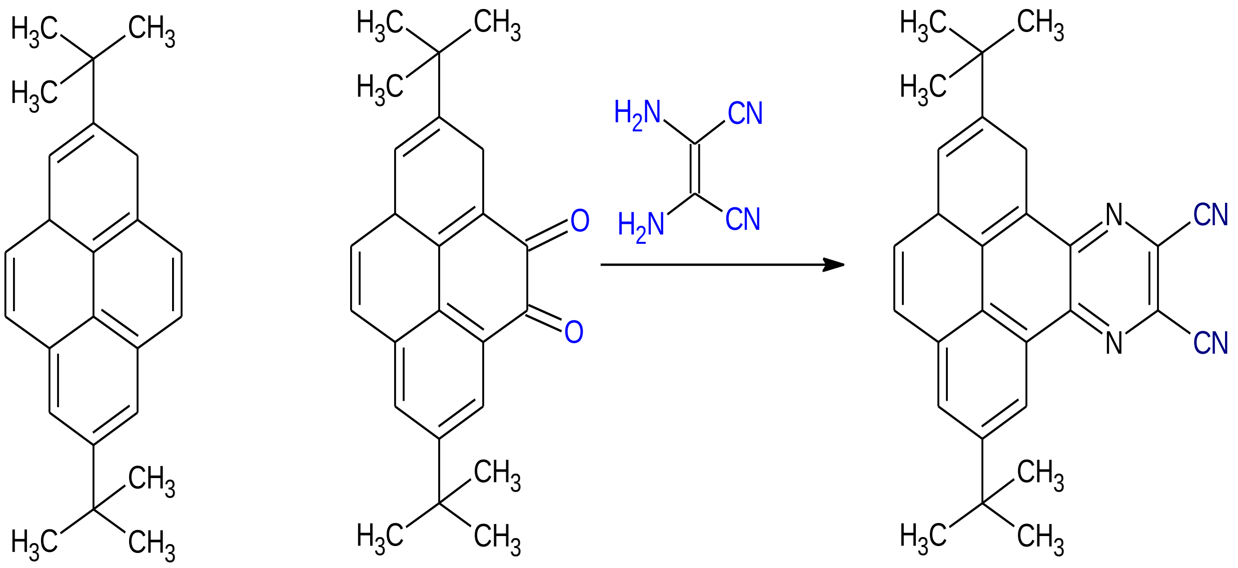
This stretching vibration of the N-H bond does not appear in the spectra of metal complexes **5a-d** which means that NH group is involved in metal-ligand formation. UV-Vis spectrum of 2H-PyzPz **4** in dichloromethane solution shows a strong Soret bands at 344nm and 438 nm. The Q bands attributable to the difference between the highest occupied molecular orbital (HOMO) energy level and the lowest unoccupied molecular orbital (LUMO) energy, that is, the π-π^* transitions in 2H-PyzPz **4** are observed at 637 and 692 nm. These bands are in a good agreement with the absorption spectra reported in the literature (Kim *et al.*, 2008).

The electronic absorption spectra of the metal complexes **5a-d** illustrated in experimental. Two transitions are dominated at higher-energy B-band (broad band around 362 nm and shoulder band around 447 nm) which can be assigned to the π-π^* and/or d-π^* transitions in the fusedpyrolopyrazine ring structure (J-Joung *et al.*, 1998, Puigdollers *et al.*, 2006). Two characteristic well developed intense lower-energy, Q-bands, (around 659 nm and 709 nm) are observed. The shoulder band is usually attributed to the 1s → 4d transition (Wizel *et al.*, 1999).

It was already demonstrated in early theoretical work, (Cory and Zerner, 1991), that exchange coupling of the metal centre with ligand states gives rise to spin-allowed transitions at low energy. It will be shown that there are states in the range of 443-451 nm below the Q-band excitation for all of the M-PyzPzproducts. These states arise from d–d excitations and ligand–metal exchange coupling. There is a little difference among the spectra of various metal pyrazinoporphyrazines. It has been suggested that both Q and B bands can be influenced by the metal-to-ligand charge-transfer bands (Chen *et al.*, 1995). It is clear that the absorption bands for metal complexes, extends beyond 800 nm. So, these pyrazinoporphyrazines could be useful in the field of optical data storage and for security printing which require absorbance in the near infrared.

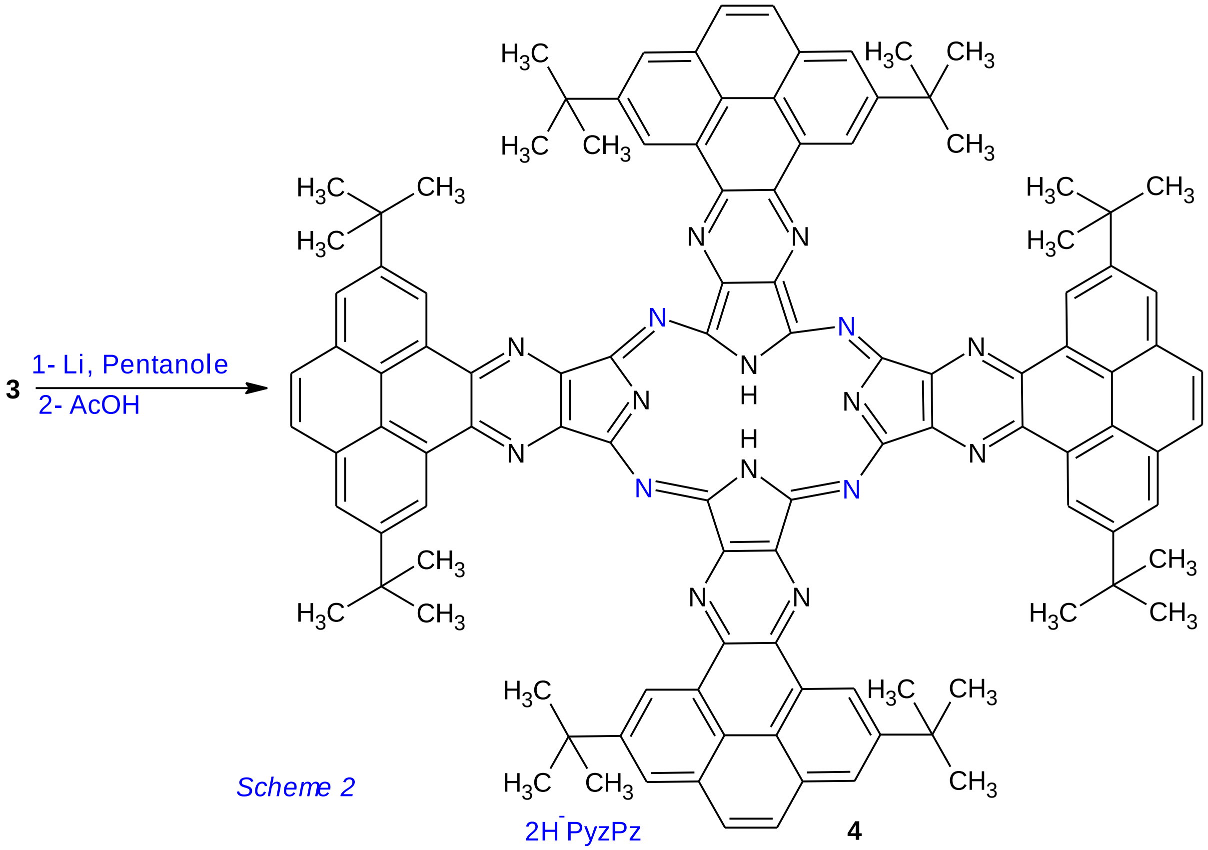
^{1}H-NMR spectrum of 2H-PyzPz **4** reveals signals at δ = 9.73 (s, H, NH), 7.68 (s, aromatic-H), 7.62 (d, aromatic-H), 1.41 (s, aliphatic-H). The presence of signal at δ = 9.73 assignable to NH proton in 1H-NMR spectrum of 2H-PyzPz **4** gives direct evidence of the formation of an unsymmetrical tetradentate ligand. On the formation of metal complexes **5a-d** the signal of the NH groups disappear. All metal complexes show signals around δ = 8.35 and 1.40 assignable to aromatic and aliphatic protons, respectively (see experimental, scheme 1. Elemental analyses for the prepared products show that the amount of carbon within products is consistent with their idealised structures represented in scheme 1. The experimental values of carbon content of the prepared products are consistent with that calculated for the product. Also, the experimental values of metal content (see experimental) of the prepared products are consistent with that calculated for the product.

Moreover, metal content and high molecular masses of the synthesized products confirm the efficiency of tetramerization and complexation reactions. The high molar mass and good solubility of these products allow conventional solution-based product processing techniques. These pyrazinoporphyrazines have push-pull intramolecular charge-transfer chromophoric systems in which the pyrene and the pyrazine rings work as a donor group and an acceptor group, respectively. So these products materials exhibit high electrical conductivity. The special conjugation in pyrazinoporphyrazines enables the electrons to delocalize throughout the whole system to make them conductive. When the electrons are removed from the backbone, resulting in cations or added to the backbone resulting in anions, the product can be transformed into a conducting form. Anions and cations act as charge carriers, hopping from one site to another under the influence of an applied electrical field, thus increasing conductivity. It is universally agreed that the doping process is an effective method to produce conducting products because it allows electrons to flow through the conduction bands. As doping occurs, the electrons in the conjugated systems, which are loosely bound, are able to jump around the productsystem.



1 Scheme 1 **2** **3**

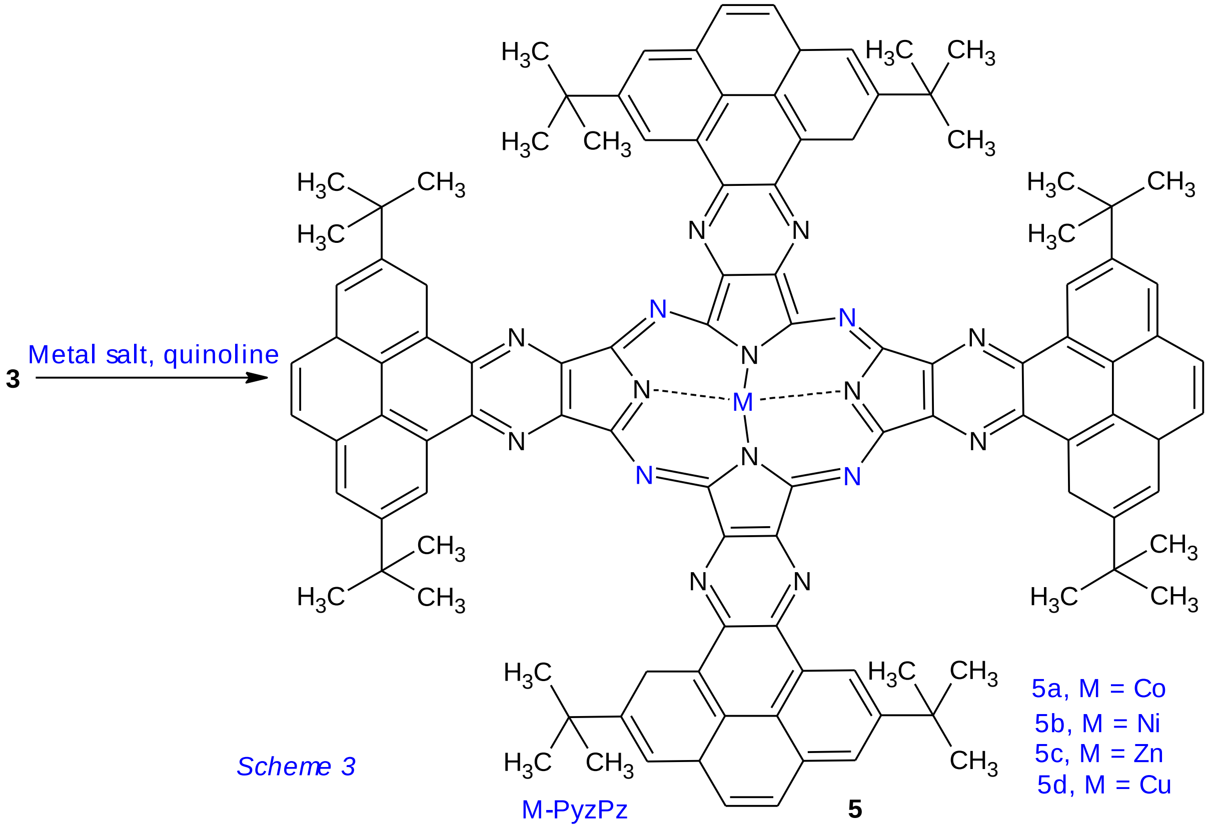
Scheme 1: The rout of formation of dinitrile



Scheme 2

$2H^-PyzPz$ **4**

Scheme 2: Cyclotetramerization of dinitrile to 2H-Pyrazinoporphyrazine



Scheme 3: Cyclotetramerization of dinitrile to M-Pyrazinoporphyrazines

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