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Novel metal(III) and metal free soft phthalocyanine metal ion sensors bearing (1-hydroxyhexan-3-ylthio)-substituents: Synthesis, characterization, aggregation behavior



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ABSTRACT

A new substituted phthalonitrile derivative, 4-(1-hydroxyhexan-3-ylthio) phthalonitrile, was prepared by the nucleophilic displacement reaction between 1-hydroxyhexan-3-ylthio and 4-nitrophthalonitrile. The highly soluble novel metallo phthalocyanines [M: 2H (**2**), Ga(III) (**3**), In(III) (**4**)] with four peripheral 1-hydroxyhexan-3-ylthio groups were synthesized by cyclotetramerization. Purification of these compounds was tedious because of their high solubility and they were purified by column chromatography. They were characterized by elemental analysis, FTIR, ¹H and ¹³C NMR, MALDI-TOF and UV–Vis spectral data. The complexes were soluble in both polar solvents and non-polar solvents, such as MeOH, EtOH, CHCl₃, CH₂Cl₂, benzene, toluene and even hexane. Absorption spectral changes of the functional MPcs during addition of Ag(I) and Pd(II) soft-metal ions were evaluated by UV–Vis spectroscopy, with monomer-dimer formation.

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1. Introduction

Metallophthalocyanines (MPcs), a family of aromatic macrocycles based on an extensive delocalized $18-\pi$ electron system, are known not only as classical dyes in practical use, but also as modern functional materials in scientific research [1]. Phthalocyanines (Pcs) have many considerable physical and chemical features. Therefore, they have attracted many investigators in the science world for decades [2]. Because of these properties, phthalocyanines have been utilized in many fields, such as gas sensors, [3] semiconductor materials [4], photovoltaic cells [5], liquid crystals [6,7], optical limiting devices [8–10], molecular electronics [11], nonlinear optical applications [12], Langmuir–Blodgett films [13], fibrous assemblies [14] and photodynamic therapy [15].

The main disadvantage of phthalocyanines is their insolubility in organic solvents. The lower solubility of phthalocyanines hinders their utilization in many fields. However, the solubility of Pcs is very important for investigating their chemical and physical characteristics [16]. In order to improve the solubility of phthalocyanines, several substituents, such as long alkyl, alkoxy, phenoxy groups and crown ethers, can be added to peripheral or non-peripheral positions of the phthalocyanines [17]. Soluble phthalocyanines with enhanced optical, electronic, redox and magnetic properties are expected to increase their possible application fields [18]. Tetra-substituted phthalocyanines are usually more soluble than the corresponding octa-substituted phthalocyanines due to the formation of constitutional isomers and the high dipole moment that results from the unsymmetrical arrangement of the substituents at the periphery [19].

Aggregation of phthalocyanine compounds is an important phenomenon. Substituted metallophthalocyanines can form two types of aggregations which affect their electronic and optical properties, namely face-to-face H-aggregation and side-to-side J-aggregation [20]. Typically, phthalocyanine aggregation results in a decrease in intensity of the Q-band corresponding to the monomeric species, meanwhile a new, broader and blue-shifted band is seen to increase in intensity. This shift to lower wavelengths indicates H-type aggregation among the phthalocyanine molecules. In rare cases, red-shifted bands have been observed, corresponding to *I*-type aggregation of the phthalocyanine molecules. Generally, J-aggregates of Pcs occur by utilizing coordination of the side substituent from one Pc molecule to the central metal ion in a neighboring molecule [21]. Aggregation is usually depicted as a coplanar association of rings, progressing from monomer to dimer and higher order complexes. It depends on the concentration, nature of the solvent, nature of the substituents, central metal ions and temperature [22].



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Ga(III) and In(III) metals have been chosen as central atoms due to their heavy diamagnetic nature and axial substitution capacity. It is known that axial substitution can introduce a dipole moment perpendicular to the macrocycle and via a steric effect it can alter the spatial relationship between neighboring molecules [9].

It is known that the effect of *S*-donor substitution on the periphery for all phthalocyanines/porphyrazines results in a shift of these intense Q bands to longer wavelenghts as a result of the electrondonating thioether substituents when compared with those of unsubstituted and alkyl or O-substituted derivatives [23].

In the present article, the ligand 4-(1-hydroxyhexan-3-ylthio)phthalonitrile was prepared according to the procedure reported in the literatüre [24], and its tetra-substituted metal free and metallophthalocyanines (M = 2H, Ga(III) and In(III)) are described, Also their soft metal ion (Ag(I) and (Pd(II)) binding properties were investigated and evaluated.

2. Experimental

2.1. Materials and methods

Chloroform (CHCl₃), tetrahydrofuran (THF), 4-nitrophthalonitrile, GaCl₃ and lnCl₃ were purchased from Merck and Alfa Aesar, and used as received. All other reagents were obtained from Fluka, Aldrich and Alfa Aesar Chemical Co. and used without purification. The purity of the products was tested in each step by TLC (SiO₂, CHCl₃/MeOH and THF/MeOH). FT-IR spectra were recorded on a Perkin-Elmer FT-IR spectrophotometer, where samples were dispersed in KBr. Chromatography was performed with silica gel (Merck grade 60) from Aldrich. All reactions were carried out under a dry N₂ atmosphere. Elemental analysis (C, H and N) was performed at the instrumental analysis laboratory of Marmara University. Time- and applied-resolved UV-Vis array spectra were recorded. ¹H and ¹³C NMR spectra were recorded on a Bruker 300 spectrometer instrument. Matrix-assisted laser desorption/ ionization time-of-flight (MALDI-TOF) mass spectra (MS) were measured using a Bruker Autoflex III mass spectrometer equipped with a nitrogen UV-Laser operating at 337 nm. The MALDI matrix, α -cyano-4-hydroxy-cinnamic acid (CHCA) was chosen as the best one.

2.2. Synthesis

2.2.1. 4-(1-Hydroxyhexan-3-ylthio)phthalonitrile (1)

This compound was prepared according to the procedure reported in the literature [24].

2.2.2. 2(3),9(10),16(17),23(24)-Tetrakis(1-hydroxyhexan-3-ylthio)phthalocyaninato metal-free) (2)

Compound 1 (0.150 g, 0.405 mmol) and anhydrous 4-(1hydroxyhexan-3-ylthio)phthalonitrile were heated to reflux in a sealed tube under a N₂ atmosphere for 6 h. The color of the mixture turned green-blue during the course of the reaction. Heating was continued for an additional 2 h, then the green-blue product was cooled to room temperature, after which the mixture was diluted with petroleum ether. The crude product was washed several times successively with first *i*-PrOH, and then cold CH₃CN to remove impurities. Finally, the product was further purified by silica gel chromatography {using THF-MeOH (50:1 v/v) and then CHCl₃/MeOH (20:1 v/v). The resulting oily product was washed with copious amounts of hexane, diethyl ether and finally *i*-PrOH, and then dried in vacuo. This product is soluble in MeOH, EtOH, THF, DMF, DMSO and pyridine. Yield 0.025 g (16%), mp > 200 °C. Anal. Calc. for C₅₆H₆₄N₈O₄S₄ (1040 g/mol): C, 59.08; H, 4.66; N, 7.26; S, 16.57. Found: C, 58.75; H, 4.78; N, 7.16; S, 16.22%. FT-IR (KBr) ν, cm⁻¹: 3365, 3230 (Ar–OH), 3089, 3020 (Ar–H), 2933, 2873 (Aliph–H), 1639, 1595, 1442, 1390, 1321, 1209, 1145, 1097, 1037, 920, 808, 740. ¹H NMR (DMSO-d₆) δ, ppm: 8.10–7.76 (m, 12H, br, phenyl H3, H5, H6), 5.20 (s, t, br, $-CH_2$ –OH, D₂O exchangeable), 4.16 (t, br, 8H, $-CH_2$ OH), 3.40 (m, br, 4H, CH₂*CH*(–S–)CH₂), 3.33 (DMSO), 1.80–1.70 (m, 8H, CH₂*CH*₂CH), 1.47–1.32 (m, 8H, CH₂*CH*₂CH₃), 0.98 (t, 12H, CH₃).¹³C NMR (300 MHz, DMSO-d₆) δ, ppm: 149.35 (S–Ar–C4), 133.11 (Ar–C6), 132.25 (Ar–C5), 131.03 (Ar–C3), 116.85 (Ar–C3), 116.03 (Ar–C2), 115.16 (Ar–CN), 114.56 (Ar–CN), 110.25 (Ar–C1), 58.46 (–CH₂OH), 40.26 (DMSO), 39.87 (S–CH–), 38.11 (*CH*₂CH₂OH), 36.12 (S*CH*₂CH₂CH₃), 20.56 (*CH*₂CH₃), 14.23 (CH₃). UV–Vis (THF): λ_{max} , nm: 713 (Qx), 680 (Qy), 623 (n– π^*), 345 (B) (Q). MS (MALDI–TOF–MS, α–cyano–4–hydroxycinnamic acid (CHCA) as matrix): 1041.5 [M+H]^{*}.

2.2.3. [Ga] 2(3),9(10),16(17),23(24)-tetrakis(1-hydroxyhexan-3ylthio) phthalocyanine (**3**)

Compound of 1 (0.25 g, 0.96 mmol) and DBU (0.05 cm³) were pulverized in a sealed tube and heated with efficient stirring at 160 °C for 0.5 h under an inert N₂ atmosphere, then anhydrous GaCI₃ (0.04 g, 0.22 mmol) was added. After heating and stirring for 8 h, the deep green-blue product was cooled to room temperature and the solid was washed successively with hot heptane, a mixture of isopropanol and water, and then cold acetonitrile to remove impurities until the filtrate was clear. The green-blue product was isolated by silica gel column chromatography with THF-MeOH (50/1 v/v) as the eluent. Complex **3** was purified again with a second column chromatography over sephadex (5% CH₃OH/ CHCl₃, eluent) and then dried in vacuum. Complex **3** is moderately soluble in CH₃CN, CHCl₃, CH₂Cl₂, THF, *i*-PrOH, MeOH, EtOH, DMF, DMSO, DMAA and pyridine. Yield 0.087 g (32.80%), mp > 200 °C. Anal. Calc. for C₅₆H₆₄N₈O₄S₄GaCI (1145.2 g/mol): C, 60.81; H, 5.79; N, 10.14. Found: C, 59.08; H, 5.83; N, 9.60%. IR (KBr) v, cm⁻¹: 3351 (br, OH), 3059 (Ar-H), 2956, 2872 (Aliph-H), 1726 (w, H-O...H, weak), 1664, 1599, 1582, 1463, 1431, 1338, 1307, 1255, 1214, 1189, 1068, 919, 870, 830, 745, 644, ¹H NMR $(DMSO-d_6) \delta$, ppm: 8.12–7.74 (m. br. 12H, phenvl H3, H5, H6). 5.12 (s. t. br. 4H. -CH₂-OH. D₂O exchangeable). 3.82 (t. br. 8H. -CH2OH), 3.47 (m, br, 4H, CH2CH(-S-)CH2), 3.30 (DMSO), 1.80-1.71 (m, 8H, CH₂CH₂CH), 1.42-1.37 (m, 8H, CH₂CH₂CH₃), 0.98 (t, 12H, CH₃). ¹³C NMR (300 MHz, DMSO-d₆) δ, ppm: 149.15 (S-Ar-C4), 133.51 (Ar-C6), 130.87 (Ar-C5), 131.23 (Ar-C3), 115.11 (Ar-C3), 115.07 (Ar-C2), 114.98 (Ar-CN), 114.01 (Ar-CN), 109.32 (Ar-C1), 57.31 (-CH₂OH), 40.85 (DMSO), 39.98 (S-CH-), 37.56 (CH₂CH₂OH), 35.98 (SCH₂CH₂CH₃), 20.25 (CH₂CH₃), 14.01 (CH₃). UV–Vis (THF) λ_{max} , nm: 707 (Q), 636 (n– π^* , sh), 341 (B). MS (MALDI-TOF-MS, α -cyano-4-hydroxycinnamic acid (CHCA) as matrix): 1146.5 [M+H]+.

2.2.4. [In] 2(3),9(10),16(17),23(24)-tetrakis(1-hydroxyhexan-3ylthio) phthalocyanine (**4**)

Compound **1** (0.25 g, 0.96 mmol), anhydrous InCl₃(0.03 g, 0.13 mmol) and DBU (0.05 cm³) were pulverized in a sealed tube under a N₂ atmosphere, then immediately covered. The temperature of the reaction mixture was raised to 150–160 °C and maintained for 8 h. After cooling to room temperature and diluting with 2-propanol, the reaction mixture was filtered. The dark green–blue crude product formed during the reaction was treated with 2-propanol several times and filtered off. It was then successively washed with CH₃CN and dried, followed by further purification by column chromatography (flash column) with silica gel (CHCl₃/MeOH as the eluent, 5/100%) and dried *in vacuo* to give **4**. The blue phthalocyanine **4** is soluble in THF, MeOH, EtOH, DMF and DMSO. Yield 0.07 g (27.30%), mp > 200 °C. *Anal.* Calc. for C₅₆H₆₄N₈O₄S₄InCl (1190.6 g/mol): C, 61.15; H,5.82; N, 10.19. Found: C, 60.36; H, 5.50; N, 9.62. IR (KBr) *v*, cm⁻¹: 3229 (H-bonded,



Scheme 1. Synthetic route to 2,9,16,23-tetrakis{1-hydroxyhexan-3-ylthio phthalocyanine M{Pc[S-CH(CH₂CH₂CH₃)-(CH₂CH₂OH)]₄} (M = 2H (**2**), Ga(III) (**3**), In(III) (**4**)}. (i) K₂CO₃, 3-mercapto-1-hexanol, DMF, 40 °C, 2 days. (ii) Without metal salt, ca. 160–170 °C, for 6 h DBU. (iii) Anhydrous GaCl₃, InCl₃, 160–170 °C, for 8 h DBU.



Fig. 1. UV-Vis spectra of 2, 3 and 4 in THF.

OH), 2955 (Ar–H), 2950, 2851 (Aliph-H), 1645, 1572, 1463, 1364, 1261, 1109, 1023, 984, 801, 720, 691, 613. ¹H NMR (DMSO-d₆) δ , ppm: 8.10-7.75 (m, br, 12H, phenyl H3, H5, H6), 5.09 (s, t, br, 4H, -CH₂–OH, D₂O exchangeable), 3.84 (t, br, 8H, –CH₂OH), 3.45 (m, br, 4H, CH₂CH(–S–) CH₂), 3.28 (DMSO), 1.79–1.72 (m, 8H, CH₂CH₂CH), 1.58–1.46 (q, 8H, CH₂CH₂CH–), 1.43–1.35 (m, 8H, CH₂CH₂CH₃), 0.96 (t, 12H, CH₃).¹³C NMR (300 MHz, DMSO-d₆) δ , ppm: 149.81 (S–Ar–C4), 133.67 (Ar–C6), 130.98 (Ar–C5), 130.14 (Ar–C3), 115.19 (Ar–C3), 115.26 (Ar–C2), 114.97 (Ar–CN), 114.26 (Ar–CN), 109.66 (Ar–C1), 57.84 (–CH₂OH), 40.84 (DMSO), 39.91 (S–CH–), 37.54 (CH₂CH₂OH), 36.33 (SCH₂CH₂CH₃), 20.12 (CH₂CH₃), 14.86 (CH₃). UV–Vis (THF) λ_{max} , nm: 708 (Q), 631 (n– π^* , sh), 378 (B).



Fig. 2. UV–Vis spectra of **2** in THF during titration with Ag(I) (A) and Pd(II) (B) ions in MeOH. The variation of the absorbance at 713 and 680 nm during the titration of **2** in THF with Na₂PdCl₄ in MeOH (C).

MS (MALDI-TOF-MS, α -cyano-4-hydroxycinnamic acid (CHCA) as matrix): 1192 [M+H]⁺.



Fig. 3. UV–Vis spectra of **3** in THF during titration with Ag(I) (A) and Pd(II) (B) ions in MeOH. The variation of the absorbance at 707 and 669 nm during the titration of **3** in THF with Na₂PdCl₄ in MeOH (C).



Fig. 4. UV-Vis spectra of **4** in THF during titration with Ag(1)(A) and Pd(II)(B) ions in MeOH. The variation of the absorbance at 708 and 668 nm during the titration of **4** in THF with Na_2PdCl_4 in MeOH (C).



Fig. 5. Absorption spectra of 2 and 3 in THF at different concentrations (inset: plot of absorbance versus concentration).

3. Results and discussion

3.1. Synthesis and characterization

In this study, the metal ion sensor ligand 4-(1-hydroxyhexan-3-ylthio)phthalonitrile **1**, its metal free, gallium(III) and indium(III) phthalocyanines, **2**, **3** and **4**, were prepared. The synthesis of the related Pcs **2–4** was accomplished by heating a pulverized mixture of 4-(1-hydroxyhexan-3-ylthio)phthalonitrile with anhydrous GaCl₃, InCl₃ and/or without metal salt at *ca*. 160–170 °C under a

 N_2 atmosphere in the presence of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) for 6-8 h (Scheme 1).

3.2. Spectroscopic characterization

The structure of phthalocyanines **2**, **3** and **4** were verified by FT-IR, ¹H NMR and UV–Vis spectroscopic methods, as well as by elemental analysis. All the analytical spectral data are consistent with the predicted structures.



Fig. 6. (A) AFM images of 3, (B) AFM images of 4, (C) AFM images of 3 + Pd(II), (D) AFM images of 4 + Pd(II), prepared from THF.

Cyclotetramerization of the 4-(1-hydroxyhexan-3-ylthio)-phthalonitrile to phthalocyanines **2–4** was confirmed by the disappearance of the sharp $-C \equiv N$ vibration at 2223 cm⁻¹. The IR spectra of the phthalocyanines are very similar, with the exception of small stretching shifts.

The ¹H NMR spectrum of **2** is somewhat broader than the corresponding signals in the starting 4-(1-hydroxyhexan-3-ylthio)phthalonitrile derivative (**1**). This broadening is likely to be due to chemical exchange caused by an aggregation-disaggregation equilibria and the fact that the product obtained in these reactions is a mixture of positional isomers which are expected to show chemical shifts that differ slightly from each other. The isoindole protons in **2** show a singlet in high field region at -1.35 ppm due to strong shielding. The peripheral -OH protons at 4.50-4.70 ppm in **2-4** were easily identified in the ¹H NMR spectra with a broad chemical shift and this signal disappears on deuterium oxide, D₂O, exchange [25]. The other resonances related to OCH₂, CH₂, SCH₂ and Ar–H protons in the ¹H NMR spectra of **2-4** are very similar to that of the 4-(1-hydroxyhexan-3-ylthio)phthalonitrile.

The UV/Vis spectra of the phthalocyanine complexes **2–4** exhibited characteristic absorptions in the Q-band region at around 650–700 nm, attributed to the π – π * transition from the HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital) of the Pc^{2–} ring, and in the B band region (UV region) at around 300–400 nm, arising from deeper π – π * transitions. The Q-band absorptions of the π – π * transitions for all the phthalocyanines in THF were observed as a single band of high intensity at 713(Qx), 680 (Qy) for **2**, 707 nm for **3** and 708 nm for **4**. There was also a shoulder at the slightly higher energy side of the Q band for each phthalocyanine (Fig. 1.). In the phthalocyanines bearing sulfanyl substituted moleties on the periphery, the Q band absorption was shifted to the lower energy side as a result of the electron-donating thioether containing substituents compared to that of phthalocyanines bearing oxa substituted moieties, whereas the position of the soret-like $\pi - \pi^*$ bands of all the phthalocyanines were only slightly shifted. Any increase in the concentration results in a little bit of aggregation of the phthalocyanine molecules, which is accompanied by a little blue shift of the Qband with a decrease in intensity.

3.3. Metal ion binding titration studies

It is well known that sulfur atoms on the periphery of metallo or metal-free phthalocyanine complexes (MPcs) are optically sensitive to soft metal ions, such as Ag(I) and Pd(II). Therefore, we have employed UV-Vis spectroscopy to monitor the metal ion binding capability of the MPcs. Each titration experiment was carried out using a MeOH/THF solution of the MPcs (10/90, v/v) to ensure complete dissolution of the analyte salt in MeOH. The concentration of the metal salt (ca. 10^{-3} mol cm⁻³) was kept higher than those of the MPc (ca. 10^{-5} mol cm⁻³) to diminish the absorption decreases of the bands due to dilution. Gradual addition of Ag(I) to the solutions of **2–4** at room temperature caused a gradual color change, from green to blue, which suggests that the complexes coordinate with Ag(I) to form aggregated species. Interaction of Ag(I) with these complexes decreases the solubility of the dimer, trimer, tetramer.. complexes formed, which results in the observation of a small amount of an intractable product at the end of the titration due to polymerisation. As shown in Fig. 2A (2), 3A (3) and (4), the Ag(I) binding to the donor atoms of the complexes results in pronounced effects on the Q-, B- and shoulder band absorptions $(n-\pi^*)$ transitions: attributed to the non-bonding sulfur electron (n) to the π^* phthalocyanine orbital) [14]. The intensity of the Q and B-bands diminished during the titration with **3** and **4** without shifting. This means that although there was a decrease in absorbance (sensing to Ag(I)), formation of aggregations, both H- and J-, were not observed

The gradual addition of Na_2PdCl_4 in MeOH (in µl portions) to **2**, **3** and **4** in THF at room temperature caused a similar gradual color change {Fig. 2B (**2**), 3B (**3**) and 4B (**4**)}, suggesting *H*-type complex formation in the case compounds **2–4**. These distinctive changes could be attributed to the increase in the intensity of the dimeric H-type aggregates and a decrease in the intensity of the monomers in **2–4**. During the titration, the intensity of the B-bands in **2–4** between 320 and 360 nm decreased and somewhat shifted to longer wavelengths (the CT region).

Figs. 2–4C show the spectroscopic changes of the monomer/ aggregation bands of **2**, **3** and **4** during titration with Pd(II) ions { ε versus the molar amounts of Pd(II)} and the inset plots show the variations in the absolute values with the extinction coefficients (ε) at monomer and dimer wavelengths in response to Pd(II) addition, along with a fit to the ca. 1:4, 1:4 and 1:2 binding isotherms.

In this study, the aggregation behavior of **2**, **3** and **4** was also investigated at different concentrations in THF (Fig. 5). As shown in the figure, the Q band increases in intensity with the increasing concentration of **2**, **3** and **4**. Any new band observed were due to the aggregated species.

3.4. Morphology of the phthalocyanines

Atomic force microscopy (AFM) was also used to investigate the nano morphology of 3 and 4 in THF (Fig. 6). The samples were prepared by drop-casting a concentrated solution of $[MPc(\beta-S CH(CH_2CH_2CH_3)-(CH_2CH_2OH)]_4$ {M = Ga(III), In(III)} in THF (6 mg/ mL) onto a SiO_2 substrate. Evidence for the formation of *H*-type nano morphology structures of 3 and 4 after the gradual addition of Na₂PdCl₄ in THF based on electronic absorption spectroscopy was further strengthened by atomic force microscopy (AFM). Different AFM morphologies of 3 and 4 on Ag(I) and Pd(II) being introduced were strikingly observed [3-Pd(II) (Fig. 6C) and 4-Pd(II) (Fig 6D)]. The distinct morphologies formed from the soft acid (Ag^I or Pd^{II}) soft base (Pcs) interactions also clearly reflect the differences in the self-assembly processes of **3** and **4**, including different molecular packing conformations and morphologies. Bigger closely nano packed pellets, indicating dimeric regular arrangements of Haggregates between 3/4 and Pd(II) ions, can be seen in Fig. 6.

4. Conclusion

We have presented the synthesis and characterization of new metallophthalocyanine soft metal ion sensors (**2–4**) containing 1-hydroxyhexan-3-ylthio substituted groups. The structures of the new compounds were characterized by elemental analysis, FTIR, ¹H and ¹³C NMR, MALDI-TOF, UV–Vis spectral data and AFM images. Their soft metal ion [Ag(I) and (Pd(II)] binding properties and binding ratios were investigated and evaluated by UV–Vis spectroscopy.

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