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A novel phthalocyanine conjugated with four salicylideneimino complexes: Photophysics and fluorescence quenching studies

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ABSTRACT

A novel phthalocyanine with four salicylideneimino ligating groups directly conjugated to the macrocyclic core has been synthesized by the condensation of tetramino-phthalocyanine with salicylaldehyde. Complexation on the periphery to obtain pentanuclear complex has been accomplished either directly through the reaction of this phthalocyanine, 8-hydroxyquinoline as the second ON donor ligand and zinc (II) salt or zinc (II) complex of 8-hydroxyquinoline has been isolated first and then it has been reacted with the phthalocyanine carrying salicylideneimino ligating groups. Also a new mixed ligand Schiff base complex of Zn (II) as a model containing salicylaldimine ligand and 8-hydroxyquinoline has been synthesized to compare with the complex. The new compounds have been characterized by elemental analysis FTIR, ^{1}H NMR, UV–Vis spectroscopy and mass spectrometry. General trends are described for fluorescence lifetimes and fluorescence of these compounds in dimethylsulfoxide, dimethylformamide and tetrahydrofurane. The solvent effect on the photophysical parameters of the zinc (II) phthalocyanines and the model zinc (II) complex is also studied. The fluorescence of the substituted zinc (II) phthalocyanine complexes is effectively quenched by 1,4-benzoquinone (BQ) in these solvents.

1. Introduction

The design of novel substituted phthalocyanines (Pcs) closely follows the requirements of their intended applications [1]. The increasing importance and use of phthalocyanines as advanced materials have created impetus for design variables of the central metal ion and peripheral substituents to reach the desired properties [2]. Phthalocyanines are used in a number of applications in many areas such as in medicinal and material science due to their increased stability, architectural flexibility, diverse coordination properties and improved spectroscopic characteristics [3]. The interesting properties of Pcs are the presence of a highly conjugated π-electron system, intense absorption in the red/near-IR (Q band) region [4], capability to exhibit changeable conductivity and photocatalytic effects [5,6]. Some technological applications in fields such as chemical sensors [7], liquid crystals [8], semiconductors [9], non-linear optics [10] and photosensitizers in photodynamic therapy (PDT) [11] have shown the increased importance of these intensely colored macrocyclic compounds. The metallophthalocyanines (MPcs) can be modulated in a number of ways by changing the peripheral or non-peripheral substitution on the Pc ring in addition to changing the central metal ion and the axial ligands [12].

Over the last decade, a substantial number of phthalocyanine-based photosensitizing agents for PDT have been prepared and evaluated for their photodynamic activity with the focus being on silicon, zinc and aluminum analogs as a result of their desirable photophysical properties [13] and their applications for the detection and cure of tumors are under investigation [14].

Coordination compounds from ligand systems capable of binding multiple metal centers are of importance due to their physical properties being totally different than mononuclear systems. One strategy for the design of multimetallic systems has involved the use of polynucleating macrocyclic ligands [15] and, in particular, much work has been devoted to the synthesis of porphyrins [16] and phthalocyanines [17] that have been functionalized with appendages capable of coordinating metal ions as well. Several different approaches in designing polynucleating porphyrins and phthalocyanines have emerged. These include meso substitution with ferrocenes [18] or crown ethers [19] as well as substitution with metal-ion-coordinating pendant-arms and basket-handles [20]. There are also examples of

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meso-tetrapyridylporphyrins that coordinate metal ions peripherally *via* the pyridyl groups [21]. However, for most of these complexes, the extent of electronic interaction between metal sites is quite low.

In a recent review, π- conjugated salen systems have been reported and the related conjugated multi-salphen structures might be considered as complementary systems to phthalocyanines with excellent building block potential [22]. Recently, we have reported Pcs with unsaturated cinnamaldimine moieties attached to the inner core through phenoxy-bridges [23] and a new water-soluble tetra-cationic zinc phthalocyanine [24] which contains four conjugated Schiff's base groups at the peripheral positions. In the present study, we are combining the completely planar 18 π-electron system of aromatic phthalocyanine core with salicylideneimino groups to enhance conjugation. We start with the synthesis of a zinc (II) phthalocyanine containing salicylideneimino moieties on the periphery and subsequently, complexation of its Schiff's base groups with zinc (II) ions in the presence of a second ON donor ligand, 8-hydroxy-quinoline (**4**), pentanuclear zinc (II) complex is isolated. A model compound has been also prepared.

2. Experimental

2.1. Instruments and chemicals

All chemicals used were of reagent grade quality. The solvents were dried over molecular sieves (4 Å). 4-Nitrophthalonitrile, [2,9,16,23-tetra-(4-nitro)-phthtalocyaninatozinc(II)] (**npc**), [2,9,16,23-tetra-(4-amino)-phthtalocyaninatozinc(II)] (**1**) and 2-[(E)-(phenylimino)methyl]-phenol (**8**) were synthesized according to the methods described previously in the literature, respectively [14,23,25,26]. The compounds **2**, **4** and **7** were used as supplied commercially. All reactions were carried out under dry argon atmosphere unless otherwise noted. Column chromatography was performed on silica gel 60 (Merck, 0.040–0.063 mm) for purification of the complexes. The progress of the reactions and the homogeneity of the products were monitored in each step by TLC (SiO_2). IR spectra were recorded on a Perkin Elmer Spectrum One FTIR (ATR sampling accessory) spectrophotometer; electronic spectra in the UV–Vis region were recorded with an Agilent 8453 UV/Vis spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. ^{1}H NMR spectra were recorded in *d*-tetrahydrofuran on a Varian UNITY INOVA 500 MHz spectrophotometer using TMS as internal reference. Mass spectra were performed on a Bruker microflex LT MALDI-TOF MS. Melting points were determined on an Electrothermal Gallenkamp apparatus. Elemental analyses were performed on a Thermo Flash EA 1112.

2.2. Synthesis

2.2.1. [2,9,16,23-tetra-(salicylaldimino)phthtalocyaninatozinc(II)] (*3*)

A solution of **1** (150.4 mg, 0.236 mmol) in dry THF (10 mL) was added dropwise to a solution of salicylaldehyde (**2**) (115.2 mg, 0.943 mmol) in dry THF (5 mL) and the mixture was heated under reflux under argon for 20 h. The solvent was evaporated to 1/10 of the initial volume and the reaction mixture was precipitated by adding methanol at room temperature. The product was separated by filtration as a green solid. The precipitate was washed successively with cold water, methanol and ethanol to remove the unreacted starting materials and dried *in vacuo*. The dark green product was isolated from the crude residue by column chromatography over silica gel using $CHCl_3$: THF (1:10, v/v) as eluent. Compound **3** is fairly soluble in THF, acetone, DMF, DMSO and $CHCl_3$. Yield: 86 mg (35%); m.p. > 200 °C. FTIR υ_{max}/cm^{-1}: 3430 (Ar–OH, m), 3058 (Ar–H, w), 2921–2840 (–CH, m), 1619 (–N=C, s), 1568, 1490 (Ar C=C); ^{1}H NMR (DMSO-d_6) δ, ppm: 13.56 (s, 4H, –OH, D-exchangeable), 8.90 (s, 4H, –N=CH), 9.42, 8.51–7.01 (m, 28H, Ar–H); UV–Vis (THF): λ_{max}/nm (log ε, L. mol^{-1} cm^{-1}): 694 (5.08), 629 (4.48), 356 (4.88); (DMF): λ_{max}/nm (log ε, L. mol^{-1} cm^{-1}): 698 (5.06), 632 (4.46), 361 (4.86); (DMSO): λ_{max}/nm (log ε, L. mol^{-1} cm^{-1}): 702 (5.06), 637 (4.50), 361 (4.89); Anal. Calc. for $C_{60}H_{36}N_{12}O_4Zn$ (1054.4148 g/mol): C, 68.35; H, 3.44; N, 15.94; Found: C, 68.11; H, 3.02; N, 15.70; MS (MALDI-TOF): *m*/*z* (100%) 1054.607 $[M]^+$, 844.51 $[M-(C_7H_6NO)-(C_6H_5O)]^+$, 916.59 $[M\text{-}4OH\text{-}(C_6H_5)+2H]^+$, 948 $[M-(C_7H_6O)-2H]^+$, 1018 $[M-2OH-4H]^+$.

2.2.2. Chloroaqua-8-hydroxyquinolinatozinc(II) (*6*)

$ZnCl_2$ (93.7 mg, 0.69 mmol) in ethanol (10 mL) was added to a solution of 8-hydroxyquinoline (100 mg, 0.69 mmol) in ethanol (20 mL). The resulting reaction mixture was stirred under reflux for 4 h under a nitrogen atmosphere. During this time a solid precipitated formed. The reaction mixture was cooled to room temperature and the precipitate was isolated by vacuum filtration and washed with water and ethanol. Yield: 85 mg (47%); m.p. 290 °C (dec). FTIR υ_{max}/cm^{-1}: 3432–3352 (H_2O, br), 3049 (Ar–H, w), 1578 (–N=CH, s), 1498, 1463, (Ar C=C), 1378, 1316, 1271, 1107 (ph C–O, s), 821, 732. ^{1}H NMR (DMSO-d_6) δ, ppm: 8.80–6.20 (m, 6H, Ar–H), 3.50 (broad, s, 2H, $-OH_2$), UV–Vis (DMSO): λ_{max}/nm (log ε, L. mol^{-1} cm^{-1}): 323 (3.94), 398 (3.64); Anal. Calc. for $C_9H_8ClNO_2Zn$ (263.0279 g/mol): C, 41.10; H, 3.07; N, 5.32; Found: C, 41.24; H, 3.70; N, 5.26. ESI-MS $[M + H]^+$: 264.2418 *m*/*z* (100%).

2.2.3. [2,9,16,23-tetra-{8-hydroxyquinolinato-salicydenaminatozinc (II)} phthtalocyaninato-zinc (II)] (*5*)

2.2.3.1. Method I. Compound 3 (70 mg, 0.066 mmol) and 8-hydroxyquinoline (4) (38.6 mg, 0.264 mmol) were added successively with constant stirring to dry THF (15 mL). After complete dissolution, $Zn(CH_3COO)_2$ (0.048 mg, 0.264 mmol) was added and the mixture was heated under reflux for 24 h and then allowed to stand at room temperature under argon stream. The progress of the reaction was monitored by TLC. The solvent was evaporated to 1/10 of the initial volume and the reaction mixture was precipitated by adding methanol at room temperature. The resulting precipitate was filtered, washed several times with 50% (v/v) ethanol-water to remove any traces of unreacted materials, then washed with methanol and ethanol and dried in a vacuum desiccator over anhydrous calcium chloride. Yield: 56 mg (45%); m.p. > 200 °C.

2.2.3.2. Method II. Compound **3** (60 mg, 0.057 mmol) and chloroaqua-8-hydroxyquinolinatozinc(II) (**6**) (59.9 mg, 0.228 mmol) were added successively with constant stirring to dry DMSO (20 mL) and the reaction mixture was stirred at 85 °C for 48 h under argon stream. The progress of the reaction was monitored by TLC. The solvent was evaporated to 1/10 of the initial volume and the reaction mixture was precipitated by adding methanol at room temperature. The resulting precipitate was filtered, washed several times with water, ethanol and methanol to remove any traces of unreacted materials and dried in a vacuum desiccator over anhydrous calcium chloride. Yield: 42 mg (39%); m.p. > 200 °C.

The products obtained in both cases are identical and they are insoluble in most common organic solvents but soluble in THF, DMF and DMSO. FTIR υ_{max}/cm^{-1}: 3052 (Ar–H, w), 1604 (–N=CH, s), 1579, 1497, 1466 (Ar C=C), 1048, 940, 825, 743, 742; ^{1}H NMR (DMSO-d_6) δ, ppm: 8.65 (s, 4H, N=C–H), 8.95, 8.45–6.20 (m, 52H, Ar–H); UV–Vis (THF): λ_{max}/nm (log ε, L. mol^{-1} cm^{-1}): 705 (5.11), 640 (4.75), 347 (5.02); (DMF): λ_{max}/nm (–log ε, L. mol^{-1} cm^{-1}): 715 (5.12), 649 (4.78), 352 (5.02); (DMSO): λ_{max}/nm (–log ε, L.