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Azine-bridged binuclear metallophthalocyanines functioning photophysical and photochemical-responsive

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ABSTRACT

The new phthalodinitrile containing azine-bridged (**3**) was prepared by the reaction of 4-nitrophthalonitrile (**2**) and 4,4′-(1E,1'E)-hydrazine-1,2-diylidenebis(methan-1-yl-1-ylidene)diphenol (**1**). The new binuclear asymmetric type zinc(II) (**5**), oxotitanium(IV) (**6**), tin(II) (**7**), cobalt(II) (**8**), copper(II) (**9**) and nickel(II) (**10**) phthalocyanine complexes containing azine moiety were synthesized by the cyclotetramerization of azine containing phthalonitrile (**3**) and unsubstituted phthalonitrile (**4**). The aggregation behaviors of these compounds were investigated at different concentrations in dimethylsulfoxide (DMSO). Furthermore, the photophysical (fluorescence quantum yields and lifetimes) and photochemical properties (singlet oxygen and photodegradation quantum yields) were studied for zinc(II) (**5**), oxotitanium(IV) (**6**) and tin(II) (**7**) phthalocyanine complexes in DMSO. The synthesized cobalt (**8**), copper (**9**) and nickel (**10**) phthalocyanine complexes were not evaluated for this purpose due to transition metal and paramagnetic behavior of central metals in the phthalocyanine cavity.

1. Introduction

Phthalocyanines (Pcs) are important class of compounds for many technological applications in different scientific areas such as chemical sensors [1–3], electrochromic displaying systems [4], non-linear optics [5], solar cells [6], molecular electronics [7], semiconductors [8], liquid crystals [9], optical storage devices [10], laser dyes [11], catalyst [12] and photodynamic therapy (PDT) [13]. Binuclear phthalocyanines have two phthalocyanine units connecting one another via covalently bonding. Many researchers have been focused on their metal complexes due to their different electrical and spectroscopic properties [14–16].

Main drawback of phthalocyanines is aggregation causing low photosensing ability in technological applications. Aggregation decreases the solubility of the phthalocyanines in many organic solvents or water. The substitution of Pcs with different bulky organic groups or cationic and anionic species or axially substitution on the central metal ions can increase the solubility of these compounds [17–20]. Especially bulky peripheral substituents decrease the aggregation, hindering the π–π stacking between planar phthalocyanine rings. Additionally, bulky peripheral substitutions of phthalocyanines increase their solubility in common organic solvents. Generally, it's known that organic solvents decrease the aggregation, while aqueous solvents increase it. Furthermore the type of solvent is important factor on the photophysical and photochemical properties of MPc complexes [21–25].

The highest absorption band of phthalocyanines in visible region is Q band and this band occurs because of the transition between the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital). The most important advantage of Pcs compared with porphyrins is their Q bands which have more intense and longer wavelengths than that of porphyrins. Therefore some phthalocyanines show higher biological activity against tumors than porphyrins due to long wavelength absorption [26,27].

In heterocyclic chemistry, although the term of azine is used for description of six-membered ring system such as pyrazines, pyrimidines, in acyclic chemistry, azines are non-heterocyclic compounds which are synthesized one mol hydrazine hydrate reaction with 2 mol aldehyde. Additionally this compound class is called “aldazines” when an aldehyde is used as carbonyl compound [28,29]. Some azines are biological active compounds having antitumor [30], antibacterial [31] and antifungal activity [32].

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Many researchers have been focused on binuclear phthalocyanines and their metal complexes due to their different electrical and spectroscopic properties. The objectives of this research are to determine whether new peripherally azine-bridged binuclear phthalocyanines have potential for photodynamic therapy of cancer. The azine moiety is symmetrical molecule with high conjugation providing chemical stability. The chemical stability is important parameter in the photochemical studies. Furthermore, in literature there isn't any study on synthesis, photophysical and photochemical characterisation of the phthalocyanine derivatives having azine moieties. In this study, new phthalonitrile derivative (**3**) consisting of two phthalonitrile unit and its zinc(II) (**5**), oxotitanium(IV) (**6**), tin(II) (**7**), cobalt(II) (**8**), copper(II) (**9**) and nickel(II) (**10**) phthalocyanine derivatives were synthesized and characterized. The aggregation behaviors of these dimeric metallophthalocyanines (**5**–**10**) were investigated at different concentration in DMSO. The photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen and photodegradation quantum yields) properties were investigated for zinc(II) (**5**), oxotitanium(IV) (**6**), tin(II) (**7**) phthalocyanine complexes in DMSO. The investigation of the photophysical and photochemical properties of phthalocyanine complexes are very useful for photocatalytic applications such as photodynamic therapy of cancer.

2. Experimental

2.1. Materials

All reactions were carried out under dry and oxygen-free nitrogen atmosphere using standard Schlenk techniques. 1,3-diphenylisobenzofuran (DPBF) and 1,8-diazabycyclo[5.4.0]undec-7-ene (DBU) were purchased from Fluka. Unsubstituted phthalonitrile (**4**) was purchased from Merck. Unsubstituted ZnPc was purchased from Aldrich. All solvents were dried and purified as described by Perrin and Armarego [33] before use. 4,4′-(1E,1′E)-hydrazine-1,2-diylidenebis(methan-1-yl-1-ylidene)diphenol (**1**) [34] and 4-nitrophthalonitrile (**2**) [35] were prepared according to the literature.

2.2. Equipment

^{1}H NMR and ^{13}C NMR (for phthalonitrile compound **3**) spectra were recorded on a Varian XL-200 NMR spectrophotometer in $CDCl_3$ and chemical shifts were reported (δ) relative to Me_4Si as internal standard. FT-IR spectra were recorded on a Perkin–Elmer Spectrum one FT-IR spectrometer in KBr pellets. The mass spectra were measured with a Micromass Quattro LC/ULTIMA LC- MS/MS spectrometer using chloroform–methanol as solvent system and a linear mode Bruker Microflex LT MALDI-TOF mass spectrometer using nitrogen laser accumulating 50 laser shots in dihydroxybenzoic acid (DHB) as MALDI matrix. All experiments were performed in the positive ion mode. Elemental analyses were performed on a Costech ECS 4010 instrument; the obtained values agreed with the calculated ones. Melting points were measured on an electrothermal apparatus and are uncorrected. Absorption spectra in the UV–visible region were recorded with a Shimadzu 2101 UV–Vis spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm path length cuvette at room temperature. General Electric quartz line lamp (300 W) was used for photo-irradiation studies. A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiations. An interference filter (Into, 670 nm with a band width of 40 nm) was additionally placed in the light path before the sample. Light intensities were measured with a POWER MAX5100 (Molelectron detector incorporated) power meter.

2.3. Photophysical parameters

2.3.1. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) were determined by the comparative method using equation (1) for zinc(II) (**5**), oxotitanium(IV) (**6**) and tin(II) (**7**) phthalocyanine complexes [36].

$$\Phi_F = \Phi_F(\mathrm{Std}) \frac{F \cdot A_{\mathrm{Std}} \cdot n^2}{F_{\mathrm{Std}} \cdot A \cdot n_{\mathrm{Std}}^2} \tag{1}$$

where F and F_{Std} are the areas under the fluorescence emission curves of the samples [zinc(II) (**5**), oxotitanium(IV) (**6**) and tin(II) (**7**) phthalocyanines] and the standard, respectively. A and A_{Std} are the respective absorbances of the samples and standard at the excitation wavelengths, respectively. n and n_{std} are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc (**Std-ZnPc**) ($\Phi_F = 0.20$) [37] was employed as the standard in DMSO. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05

Natural radiative lifetimes (τ_0) were determined using PhotochemCAD program [38] which uses the Strickler–Berg equation. The fluorescence lifetimes (τ_F) were evaluated using equation (2).

$$\Phi_F = \frac{\tau_F}{\tau_0} \tag{2}$$

2.4. Photochemical parameters

2.4.1. Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_Δ) determinations were carried out using the experimental set-up described in literature [39–41] for zinc(II) (**5**), oxotitanium(IV) (**6**) and tin(II) (**7**) phthalocyanine complexes in DMSO. Typically, a 3 cm^3 portion of the respective zinc(II) (**5**), oxotitanium(IV) (**6**) and tin(II) (**7**) phthalocyanine solutions ($C = 1 \times 10^{-5}$ M) containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation set-up described in references [39–41]. Singlet oxygen quantum yields (Φ_Δ) were determined in air using the relative method with unsubstituted ZnPc (**Std-ZnPc**) as reference in DMSO. DPBF was used as chemical quencher for singlet oxygen quantum yield determinations. Equation (3) was employed for the calculations:

$$\Phi_\Delta = \Phi_\Delta^{\mathrm{Std}} \frac{R \cdot I_{\mathrm{abs}}^{\mathrm{Std}}}{R^{\mathrm{Std}} \cdot I_{\mathrm{abs}}} \tag{3}$$

where $\Phi_\Delta^{\mathrm{Std}}$ is the singlet oxygen quantum yield for the standard unsubstituted ZnPc ($\Phi_\Delta^{\mathrm{Std}} = 0.67$ in DMSO) [42]. R and R_{Std} are the DPBF photobleaching rates in the presence of the respective samples [zinc(II) (**5**), oxotitanium(IV) (**6**) and tin(II) (**7**) phthalocyanines] and standard, respectively. I_{abs} and $I_{\mathrm{abs}}^{\mathrm{Std}}$ are the rates of light absorption by the samples and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [43], the concentration of quenchers was lowered to $\sim 3 \times 10^{-5}$ M. Solutions of sensitizer (1×10^{-5} M) containing DPBF were prepared in the dark and irradiated in the Q band region using the photo-irradiation set-up and degradation of DPBF at 417 nm was monitored. The light intensity 6.45×10^{15} photons s^{-1} cm^{-2} was used for Φ_Δ determinations.

2.4.2. Photodegradation quantum yields

Photodegradation quantum yield (Φ_d) determinations were carried out using the experimental set-up described in literature [39–41]. Photodegradation quantum yields were determined using equation (4),

$$\Phi_d = \frac{(C_0 - C_t) \cdot V \cdot N_A}{I_{\mathrm{abs}} \cdot S \cdot t} \tag{4}$$

where C_0 and C_t are the samples [zinc(II) (**5**), oxotitanium(IV) (**6**) and tin(II) (**7**) phthalocyanines] concentrations before and after irradiation respectively, V is the reaction volume, N_A is the Avogadro's constant, *S* is the irradiated cell area, *t* is the irradiation time and I_{abs} is the overlap integral of the radiation source light intensity and the absorption of the samples. A light intensity of 2.15×10^{16} photons s^{-1} cm^{-2} was employed for Φ_d determinations.

2.5. Synthesis

2.5.1. 4,4′-(2,2′-(1E,1′E)-hydrazine-1,2-diylidenebis(methan-1-yl-1-ylidene)bis(2,1-phenylene))bis(oxy)diphthalonitrile (3)

Compound **1** (1.39 g, 5.78 mmol) was added to a solution of 4-nitrophthalonitrile (**2**) (2 g, 11.55 mmol) in dry DMF (20 cm^3) and the temperature was increased up to 55 °C. Finely powdered dry K_2CO_3 (1.60 g, 11.56 mmol) was added to the reaction in eight equal portions at 15 min intervals with efficient stirring and the reaction was stirred at the same temperature for 5 days. The reaction mixture was poured into ice-water and the precipitate was filtered and dried in vacuum over P_2O_5 and recrystallized from ethanol to give dark yellow crystalline powder. Yield: 1.97 g, (69.2%), mp: 214–215 °C. Anal. Calc. for $C_{30}H_{16}N_6O_2$: C, 73.16; H, 3.27; N, 17.06, Found: C, 73.18; H, 3.25; N, 17.09. FT-IR (KBr tablet) υ_{max}/cm^{-1}: 3051 υ(Ar−CH), 2925–2851 υ(aliph. CH), 2227 (C≡N), 1621–1601 υ(C=C), 1505 υ(CH = N), 1270–1253 υ(C−O−C), 982 δ(CH). ^{1}H NMR (DMSO-d$_6$), (δ: ppm): 8.27 (s, 2H, CH = N), 7.89–7.85 (m, 4H/Ar−H), 7.69–7.65 (d, 2H/Ar−H), 7.46–7.43 (m, 4H/Ar−H), 6.99-6.92 (m, 4H/Ar−H). ^{13}C NMR (DMSO-d$_6$), (δ: ppm): 162.21, 160.78, 160.65, 139.75, 134.25, 129.62, 126.13, 124.14, 118.87, 115.89, 115.25, 112.35, 107.84. MS (ESI), (*m*/*z*): Calculated: 492.13; Found: 493.61 [M + H]$^+$.

2.5.2. General procedure for synthesis of dimeric metallophthalocyanines (5–10)

In a glass sealed tube, the mixture of compound **3** (0.20 g, 0.406 mmol), phthalonitrile **4** (0.32 g, 2.489 mmol) and related metal salts [(Zn(Ac)$_2$ (0.149 g, 0.812 mmol); Ti(OBu)$_4$ (0.28 cm^3, 0.812 mmol); SnCl$_2$ (0.472 g, 2.489 mmol); CoCl$_2$ (0.105 g, 0.812 mmol); CuCl$_2$ (0.109 g, 0.812 mmol); Ni(Ac)$_2$ (0.144 g, 0.812 mmol)] in dry n-pentanol (3 cm^3) was heated to 90 °C and 3 drops of 1,8-diazabycyclo[5.4.0]undec-7-ene (DBU) was added and the temperature was increased to 160 °C for 24 h. Then they were precipitated by methanol and then filtered. After washing with hot water, ethanol, acetone and diethyl ether, the precipitates were dissolved in chloroform and filtered. Then chloroform was evaporated under reduced pressure. The pure dimeric metallophthalocyanines (**5**–**10**) were isolated through silica gel column to remove impurities as well as formed symmetrically unsubstituted phthalocyanines. The chemical and physical spectral characteristics of these new products are given below.

*2.5.2.1. Dimeric zinc(II) phthalocyanine (**5**).* Solvent system for column chromatography: Chloroform:methanol (100:3). Yield: 0.05 g, (8.8%), mp:>300 °C (decomposition). Anal. Calc. for $C_{78}H_{40}N_{18}O_2Zn_2$: C, 67.30; H, 2.90; N, 18.11. Found: C, 67.41; H, 2.84; N, 18.19. FT-IR (KBr tablet) υ_{max}/cm^{-1}: 3053 υ(Ar−CH), 2922–2851 υ(aliph. CH), 1616–1607 υ(C=C), 1507 υ(CH = N), 1277–1249 υ(C−O−C), 987 δ(CH). ^{1}H NMR (DMSO-d$_6$), (δ: ppm): 8.97 (s, 2H, CH = N), 7.92–7.85 (m, 10H/Ar−H), 7.72–7.61 (bd, 8H/Ar−H), 7.52–7.38 (m, 10H/Ar−H), 7.11–6.89 (m, 10H/Ar-H). UV−vis (DMSO): λ_{max}/nm (log ε): 672 (5.03), 609 (4.23), 341 (4.53). MALDI-TOF-MS, (*m*/*z*): Calculated: 1392.08; Found: 1393.42 [M + H]$^+$.

*2.5.2.2. Dimeric oxotitanium(IV) phthalocyanine (**6**).* Solvent system for column chromatography: Chloroform:methanol (100:7). Yield: 0.04 g, (7.1%), mp:>300 °C (decomposition). Anal. Calc. for $C_{78}H_{40}N_{18}O_4Ti_2$: C, 67.45; H, 2.90; N, 18.15; Found: C, 67.49; H, 2.94; N, 18.77. FT-IR (KBr tablet) υ_{max}/cm^{-1}: 3045 υ(Ar−CH), 2927–2847 υ(aliph. CH), 1618–1611 υ(C=C), 1503 υ(CH = N), 1269–1252 υ(C−O−C), 981 δ(CH), 953 (Ti=O). ^{1}H NMR (DMSO-d$_6$), (δ: ppm): 8.92 (s, 2H, CH = N), 7.92–7.59 (m, 18H/Ar−H), 7.42–7.03 (bm, 20H/Ar−H). UV−vis (DMSO): λ_{max}/nm (log ε): 689 (4.91), 623 (4.28), 340 (4.64). MALDI-TOF-MS, (*m*/*z*): Calculated: 1389.05; Found: 1389.90 [M + H]$^+$.

*2.5.2.3. Dimeric tin(II) phthalocyanine (**7**).* Solvent system for column chromatography: Chloroform:methanol (100:4). Yield: 0.04 g, (6.6%), mp:>300 °C (decomposition). Anal. Calc. for $C_{78}H_{40}N_{18}O_2Sn_2$: C, 62.51; H, 2.69; N, 16.82; Found: C, 62.54; H, 2.64; N, 16.86. FT-IR (KBr tablet) υ_{max}/cm^{-1}: 3052 υ(Ar−CH), 2934–2861 υ(aliph. CH), 1621–1604 υ(C=C), 1512 υ(CH = N), 1275–1242 υ(C−O−C), 986 δ(CH). ^{1}H NMR (DMSO-d$_6$), (δ: ppm): 9.02 (bs, 2H, CH = N), 8.03–7.87 (m, 10H/Ar−H), 7.77–7.65 (bd, 8H/Ar−H), 7.52-7.02 (bm, 20H/Ar−H). UV−vis (DMSO): λ_{max}/nm (log ε): 691 (4.96), 628 (4.26), 342 (4.69). MALDI-TOF-MS, (*m*/*z*): Calculated: 1498.71; Found: 1566.76 [M + 4OH]$^+$.

*2.5.2.4. Dimeric cobalt(II) phthalocyanine (**8**).* Solvent system for column chromatography: Chloroform:methanol (100:5). Yield: 0.08 g, (14.3%), mp:>300 °C (decomposition). Anal. Calc. for $C_{78}H_{40}N_{18}O_2Co_2$: C, 67.93; H, 2.92; N, 18.28; Found: C, 67.81; H, 2.84; N, 18.36. FT-IR (KBr tablet) υ_{max}/cm^{-1}: 3054 υ(Ar−CH), 2924–2847 υ(aliph. CH), 1615-1602 υ(C=C), 1509 υ(CH = N), 1272–1249 υ(C−O−C), 982 δ(CH). UV−vis (DMSO): λ_{max}/nm (log ε): 656 (5.27), 595 (4.63), 325 (5.05). MALDI-TOF-MS, (*m*/*z*): Calculated: 1379.16; Found: 1402.59 [M + Na]$^+$.

*2.5.2.5. Dimeric copper(II) phthalocyanine (**9**).* Solvent system for column chromatography: Chloroform:methanol (100:8). Yield: 0.07 g, (12.4%), mp:>300 °C (decomposition). Anal. Calc. for $C_{78}H_{40}N_{18}O_2Cu_2$: C, 67.48; H, 2.90; N, 18.16; Found: C, 67.53; H, 2.94; N, 18.09. FT-IR (KBr tablet) υ_{max}/cm^{-1}: 3049 υ(Ar−CH), 2921-2844 υ(aliph. CH), 1618–1610 υ(C=C), 1505 υ(CH = N), 1268–1248 υ(C−O−C), 972 δ(CH). UV−vis (DMSO): λ_{max}/nm (log ε): 670 (5.24), 604 (4.53), 332 (4.80). MALDI-TOF-MS, (*m*/*z*): Calculated: 1388.38; Found: 1389.91[M + H]$^+$.

*2.5.2.6. Dimeric nickel(II) phthalocyanine (**10**).* Solvent system for column chromatography: Chloroform:methanol (100:7). Yield: 0.09 g, (16.1%), mp:>300 °C (decomposition). Anal. Calc. for $C_{78}H_{40}N_{18}O_2Ni_2$: C, 67.95; H, 2.92; N, 18.29; Found: C, 67.85; H, 2.82; N, 18.41. FT-IR (KBr tablet) υ_{max}/cm^{-1}: 3049 υ(Ar−CH), 2924-2845 υ(aliph. CH), 1619–1604 υ(C=C), 1501 υ(CH = N), 1267–1244 υ(C−O−C), 976 δ(CH). ^{1}H NMR (DMSO-d$_6$), (δ: ppm): 8.95 (bs, 2H, CH = N), 7.82–7.71 (m, 10H/Ar−H), 7.66–7.35 (bm, 18H/Ar−H), 7.17–6.92 (m, 10H/Ar−H). UV−vis (DMSO): λ_{max}/nm (log ε): 671 (4.91), 605 (4.16), 341 (4.71). MALDI-TOF-MS, (*m*/*z*): Calculated: 1378.68; Found: 1424.54 [M + 2Na]$^{2+}$.

3. Results and discussion

3.1. Outlook of the synthesized compounds

The synthesis route of 4,4′-(2,2′-(1E,1′E)-hydrazine-1,2-diylidenebis(methan-1-yl-1-ylidene)bis(2,1-phenylene))bis(oxy) diphthalonitrile (**3**) and its target binuclear metallophthalocyanine complexes (**5**, **6**, **7**, **8**, **9** and **10**) is shown in Fig. 1. The structures of new compounds have been characterized by a combination of ^{1}H and ^{13}C NMR (for phthalonitrile compound), FT-IR, UV−Vis spectroscopy, elemental analysis and mass spectral data.

Generally, many researchers use substituted phthalonitrile or 1,3-diimino-1*H*-isoindoles to prepare phthalocyanines by cyclotetramerization [44,45]. Base catalyzed nucleophilic aromatic nitro substitution reaction of 4-nitrophthalonitrile has been achieved by many authors [46,47]. In general, nucleophilic displacement of a nitro group from an activated aromatic substrate can be effectively achieved by a variety of strong nucleophiles under dipolar aprotic solvents for example in DMF or DMSO [48,49].

In this respect, we prepared phthalonitrile derivative **3** from the reaction of 4,4′-(1E,1’E)-hydrazine-1,2-diylidenebis(methan-1-yl-1-ylidene)diphenol (**1**) with 4-nitrophthalonitrile (**2**) in the presence of anhydrous K_2CO_3 as basic catalyst under N_2 atmosphere at 55 °C in schlenk system for 5 days in DMF. In the FT-IR spectrum of this compound, the absence of −OH stretching/deformation of compound **1** and the presence of C≡N absorption band at 2227 cm^{-1} clearly proves the formation of compound **3**. In the ^1H NMR spectrum of **3**, OH group of compound **1** disappeared as expected. In the mass spectrum of compound **3**, the presence of molecular ion peaks at $m/z = 493.61$ $[M + H]^+$, confirmed the proposed structures.

The dimeric metallophthalocyanine complexes (**5**–**10**) were synthesized by statistical cross-condensation of a 1:6.13 M ratio of phthalonitriles **3** and **4** and corresponding metal salts in the presence of DBU by heating under reflux for 24 h in n-pentanol. For SnPcs, the reaction of phthalonitrile with $SnCl_2$ may produce Sn(II) Pc or $Cl_2Sn(IV)$Pc species. The amount of $SnCl_2$ used in the reaction determines the type of the product. The Sn(II)Pc derivatives can be prepared by the use of excess amount of $SnCl_2$. In this study, Sn(II) Pc derivative was synthesized in the presence of excess amount of $SnCl_2$ [50].

Generally, statistical cross-condensations of phthalonitriles are used to prepare different asymmetrical Pcs. However, this method gives the mixture of phthalocyanines [51,52]. According to the statistical considerations, if two phthalonitrile compounds (A and B) having same chemical reactivity react together in the ratio of 3:1, they will give a mixture of the symmetric Pc (AAAA), and the desired asymmetric Pc (AAAB) and other cross-condensation products [53,54]. In our research, excess of phthalonitrile (A) was used in the reaction media, so there were mixture of mainly two products; unsubstituted symmetric Pc (AAAA) and desired asymmetric Pc (AAAB). It is known that the solubility of unsubstituted Pc (AAAA) in common organic solvents is very low. The crude product washed with chloroform and then filtered off for separating the formed unsubstituted Pc derivatives. The filtrate was evaporated and purified by column chromatography [55].

The spectroscopic characterization of the newly synthesized phthalocyanine compounds includes ^1H NMR, FT-IR, UV/Vis and mass spectral methods, and the results are in accordance with the proposed structures. The products (**5**–**10)** obtained by the cyclotetramerization reaction of phthalodinitrile **3** and phthalonitrile **4** were confirmed in their FT-IR spectra by the disappearance of the sharp C≡N vibration at around 2227 cm^{-1}. The rest of the spectra of Pcs were similar to that of **3**. The ^1H NMR spectra of **8** and **9** could not be determined because of the presence of paramagnetic cobalt and copper atoms in the cavity [56]. The ^1H NMR spectra of other MPcs (**5**, **6**, **7** and **10**) were not very different than that of the compound **3** except the broadness of the signals because of probable aggregation at the concentration for NMR measurements [57]. In the mass spectra of compounds **5**–**10**, the parent molecular ion peaks were observed at $m/z = 1393.42$ $[M + H]^+$ for **5**, 1389.90 $[M + H]^+$ for **6**, 1566.76 $[M + 4OH]^+$ for **7**, 1402.59 $[M + Na]^+$ for **8**, 1389.91[M + H] for **9** and 1424.59 $[M + 2Na]^+$ for **10**, these peaks have verified the proposed structures.

3.2. UV–Vis absorption spectra and aggregation studies

The electronic spectra of the phthalocyanine complexes (**5**–**10**) showed characteristic absorption in the Q band region at around 656–691 nm in DMSO, Table 1. The B-bands were observed at around 325–341 nm. The spectra showed monomeric behavior for

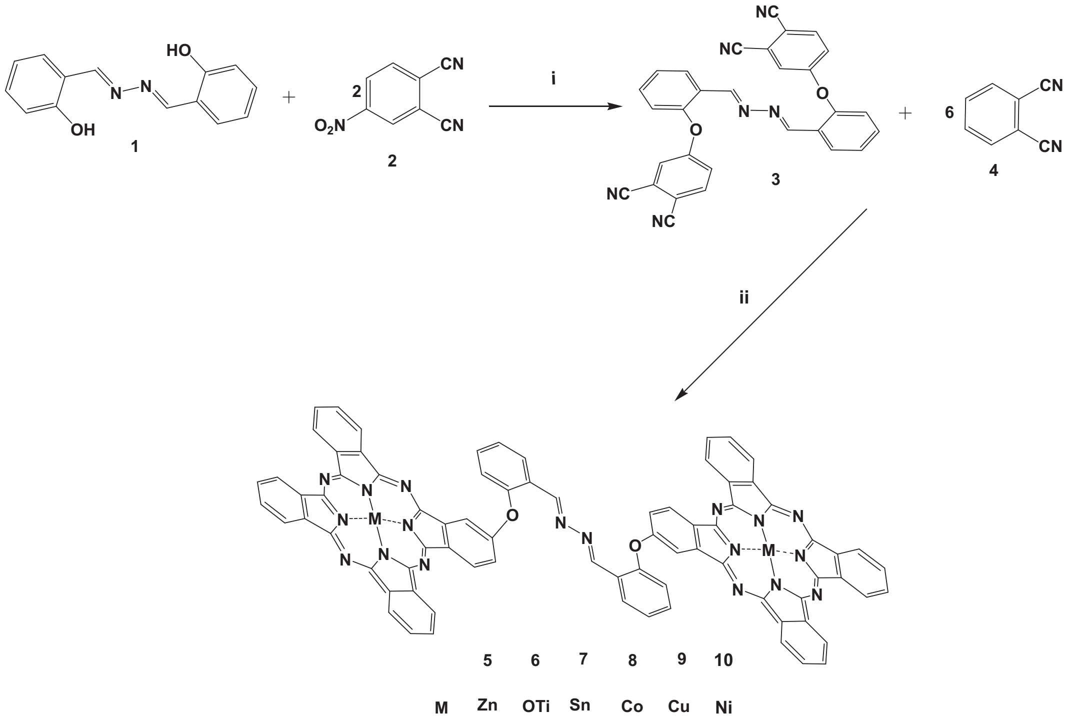

Fig. 1. Synthetic route of novel phthalocyanine compounds. (i) dry DMF, anhydrous K_2CO_3, N_2, 5 days, 55 °C. (ii) dry n-pentanol, DBU, N_2, $Zn(OAc)_2$, $Ti(BuO)_4$, $SnCl_2$, $CoCl_2$, $CuCl_2$ or $Ni(OAc)_2$.

Table 1
Absorption, excitation and emission spectral data for unsubstituted zinc(II) (**Std-ZnPc**) binuclear zinc(II) (**5**), oxotitanium(IV) (**6**), tin(II) (**7**), cobalt(II) (**8**), copper(II) (**9**) and nickel(II) (**10**) phthalocyanine complexes in DMSO.

Compound	Q band λ_{max}, (nm)	log ε	Excitation λ_{Ex}, (nm)	Emission λ_{Em}, (nm)	Stokes shift Δ_{Stokes}, (nm)
5	672	5.03	673	680	7
6	689	4.91	689	699	10
7	691	4.96	690	693	3
8	656	5.27	–	–	–
9	670	5.24	–	–	–
10	671	4.91	–	–	–
ZnPc[a]	672	5.14	672	682	10

[a] Data from ref. [63].

studied Pc complexes evidenced by a single (narrow) Q band, typical of metalated Pc complexes [58]. The Q band of the tin(II) phthalocyanine complex (**7**) was red-shifted when compared to the corresponding other studied phthalocyanine complexes in DMSO, suggesting that the non-planar effect of the bigger lead as central metal atom. The B-bands were broad due to the superimposition of the B1 and B2 bands in the ~320–340 nm regions.

In this study, the aggregation behaviors of studied phthalocyanine complexes (**5**–**10**) were also investigated at different concentrations in DMSO. The Beer–Lambert law was obeyed for all of these complexes at concentrations ranging from 1.2 × 10^{-5} to 2 × 10^{-6} M. All the studied phthalocyanine complexes did not show aggregation at these concentrations ranging in DMSO (Fig. 2).

3.3. Fluorescence spectra

Fig. 3 shows fluorescence emission, absorption and excitation spectra of complex **5** in DMSO as an example for the studied phthalocyanine complexes. Fluorescence emission peak values were listed in Table 1. The observed Stokes shifts were 10 nm for complex **5**, 7 nm for complex **6** and 3 nm for complex **7** in DMSO. Zinc(II) (**5**) and oxotitanium(IV) (**6**) phthalocyanine complexes showed similar fluorescence behavior in DMSO (Fig. 3 as an example for complex **5**). The excitation spectra were similar to absorption spectra and both were mirror images of the fluorescent spectra for zinc(II) (**5**) and oxotitanium(IV) (**6**) phthalocyanine complexes in DMSO. The proximity of the wavelength of each component of the Q band absorption to the Q band maxima of the excitation spectra for zinc(II) (**5**) and oxotitanium(IV) (**6**) phthalocyanine complexes suggest that the nuclear configurations of the ground and excited states are similar and not affected by excitation. For studied tin(II) phthalocyanine complex (**7**), the shape of excitation spectrum was different from the absorption spectrum in that the Q band of the excitation was observed as a split band in DMSO. This suggests that there are changes in the molecules following excitation most likely due to loss of symmetry, or change in aggregation status following excitation. Thus, the Q band maxima of the excitation and absorption spectra were different due to the differences in the ground and excited state species. The difference in the behavior of tin(II) phthalocyanine complex (**7**) on excitation could be due to the larger tin metal being more displaced from the core of the Pc ring, and the displacement being more pronounced on excitation hence a loss of symmetry.

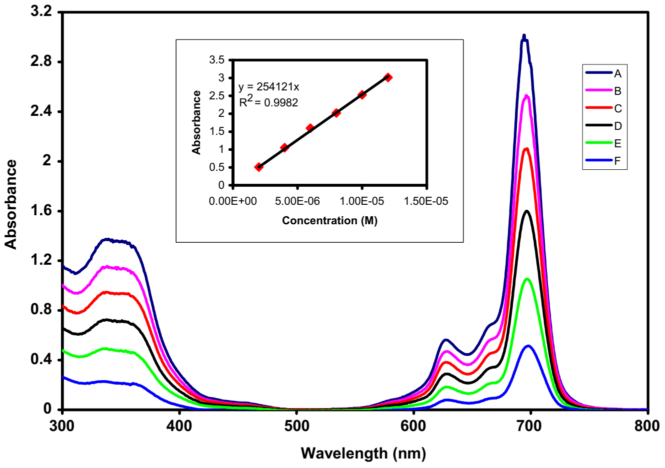

Fig. 2. Absorption spectral changes for complex **7** in DMSO at different concentrations: 12 × 10^{-6} (A), 10 × 10^{-6} (B), 8 × 10^{-6} (C), 6 × 10^{-6} (D), 4 × 10^{-6} (E), 2 × 10^{-6} (F) M. (Inset: Plot of absorbance versus concentration).

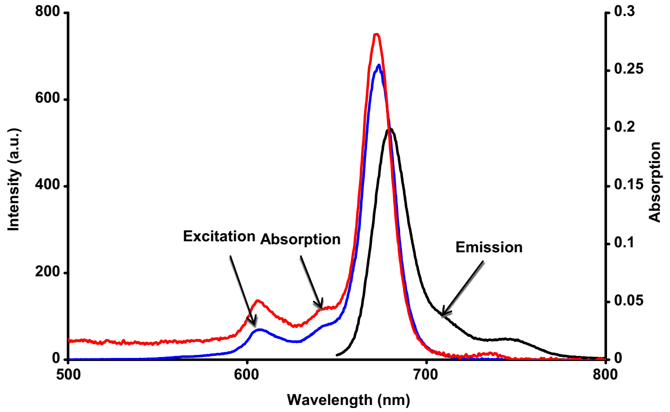

Fig. 3. Absorption, excitation and emission spectra of the complex **5** in DMSO. (Excitation wavelength = 673 nm).

3.4. Fluorescence quantum yields and lifetimes

The fluorescence quantum yield (Φ_F) values of zinc(II) (**5**) and oxotitanium(IV) (**6**) phthalocyanine complexes were similar but the Φ_F value of tin(II) phthalocyanine complex (**7**) was lower than these complexes (Table 2). The Φ_F values of the binuclear phthalocyanine complexes (**5**–**7**) were lower compared to unsubstituted zinc(II) phthalocyanine (**Std-ZnPc**) in DMSO. The Φ_F value of the tin(II) phthalocyanine complex (**7**) was the lowest among the studied Pc complexes could be due to heavy metal effect of tin.

Lifetimes of fluorescence (τ_F, Table 2) were calculated using the Strickler–Berg equation. Using this equation, a good correlation has been found for the experimentally determined fluorescence lifetimes and the theoretically determined lifetimes for the unaggregated molecules as is the case in this work [36]. Thus we believe

Table 2
Photophysical and photochemical data for unsubstituted zinc(II) (**Std-ZnPc**) binuclear zinc(II) (**5**), oxotitanium(IV) (**6**) and tin(II) (**7**) phthalocyanine complexes in DMSO.

Compound	Φ_F	τ_F (ns)	τ_0 (ns)	[a]k_F (s^{-1}) (x10^8)	Φ_d (x10^{-5})	Φ_Δ
5	0.17	1.04	6.14	1.62	1.10	0.40
6	0.12	0.64	5.30	1.89	3.11	0.55
7	0.02	0.10	5.45	1.83	44.35	0.59
ZnPc	0.20[b]	1.22[c]	6.80[c]	1.47[c]	2.61[c]	0.67[d]

[a] k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$.
[b] Data from Ref. [37].
[c] Data from Ref. [63].
[d] Data from Ref. [42].

that the values which obtained using this equation are a good measure of fluorescence lifetimes.

The τ_F values were within the range reported for MPc complexes [59,60]. The τ_F values were lower for zinc(II) (**5**), oxotitanium(IV) (**6**) and tin(II) (**7**) phthalocyanine complexes when compared to unsubstituted zinc(II) phthalocyanine (**Std-ZnPc**) (Table 2) suggesting quenching of fluorescence by the ring substituents. However, the τ_F values are typical for zinc(II) (**5**) and oxotitanium(IV) (**6**) phthalocyanine complexes [59,60]. The τ_F values of zinc(II) (**5**) and oxotitanium(IV) (**6**) phthalocyanine complexes were higher than tin(II) (**7**) complex because of the tin is heavy atom, Table 2.

The rate constants for fluorescence (k_F) values of zinc(II) (**5**), oxotitanium(IV) (**6**) and tin(II) (**7**) phthalocyanine complexes were higher than unsubstituted zinc(II) phthalocyanine (**Std-ZnPc**). The natural radiative lifetime (τ_0) value of studied zinc(II) (**5**) phthalocyanine was longer than for the other complexes (**6**, **7** and **Std-ZnPc**) in DMSO. The τ_0 values among substituted complexes decrease as follows: **5** > **Std-ZnPc** > **7** > **6**, Table 2.

3.5. Singlet oxygen quantum yields

The quantity of the singlet oxygen quantum yield (Φ_Δ) is a sign of the capability of the compounds as photosensitizers in photocatalytic applications for instance PDT. The Φ_Δ values were determined in DMSO using a chemical method and DPBF used as a quencher. The disappearance of DPBF absorbance at 417 nm was monitored using by UV–*vis* spectrophotometer (Fig. 4 for complex **5** as an example).

Energy transfer between the triplet state of photosensitizers and ground state molecular oxygen cause to generation of singlet oxygen. There is a necessity of high efficiency of transfer of energy between excited triplet state of MPc and ground state of oxygen to generate large amounts of singlet oxygen, essential for PDT. The singlet oxygen quantum yields (Φ_Δ), give an indication of the potential of the complexes as photosensitizers in applications where singlet oxygen is required such as Type II mechanism.

There were no changes in the Q band intensities during the Φ_Δ determinations, confirming that complexes were not degraded during singlet oxygen studies (Fig. 4 as an example for complex **5**). The Φ_Δ values of the newly synthesized phthalocyanine complexes (**5**–**7**) were given in Table 2. All studied Pc complexes showed lower Φ_Δ values than unsubstituted zinc (II) Pc complex (**Std-ZnPc**) in DMSO. The tin(II) phthalocyanine complex (**7**) showed the highest Φ_Δ value among the studied Pc complexes (Table 2). The Φ_Δ value of binuclear zinc(II) Pc complex (**5**) was lower than other Pc complexes (**6** and **7**).

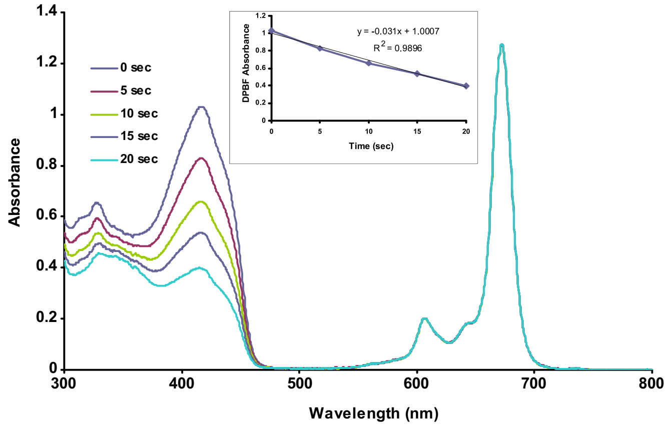

Fig. 4. Absorption changes during the determination of singlet oxygen quantum yield. This determination was for compound **5** in DMSO at a concentration of 1 × 10^{-5} M. (Inset: Plot of DPBF absorbance versus time).

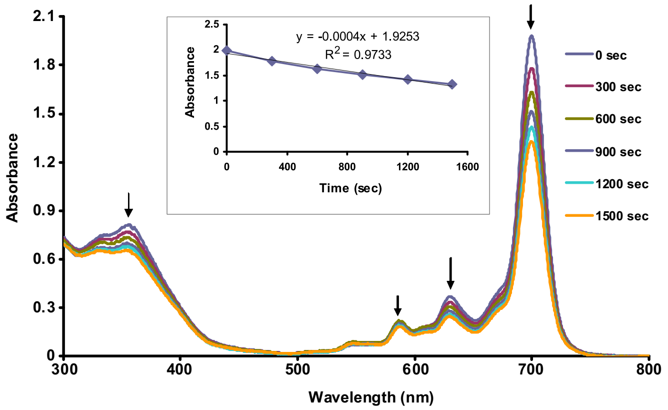

Fig. 5. Absorption changes during the photodegradation studies of compound **7** in DMSO showing the disappearance of the Q band at 10 min intervals. (Inset: Plot of absorbance versus time).

3.6. Photodegradation studies

Photodegradation is the oxidative degradation that a photosensitizer molecule is allocated to over time lower molecular weight fragments under light [43]. Photodegradation is related to the concentration of the molecule, structure, light intensity and solvent. Photodegradation is a singlet oxygen mediated process, as singlet oxygen has highly reactive and capability reacts with phthalocyanines [61]. Largely, phthalimide residual was found to be the photooxidation crop following degradation of phthalocyanines [62]. The stability of Pc complexes are low when the photodegradation quantum yield values are high. This property makes them suitable for use as photocatalysts (such as photosensitizers).

The spectral changes observed for all studied complexes (**5**–**7**) during light irradiation are as shown in Fig. 5 (using complex **7** as an example in DMSO) and hence confirm photodegradation occurred without phototransformation. The Φ_d values, found in this study, are similar to Pc derivatives having different metals and substituents on the Pc ring in literature [59,60]. Stable studied Pc molecules show Φ_d values as low as 10^{-6} and for unstable molecules, values of the order of 10^{-3} have been reported [59]. Table 2 shows that studied oxotitanium(IV) (**6**) and tin(II) (**7**) phthalocyanine complexes were less stable to degradation under light irradiation compared to unsubstituted (**Std-ZnPc**) and substituted (**5**) zinc Pc complexes in DMSO. The tin(II) phthalocyanine complex (**7**) was least stable when compared to the other studied binuclear complexes (**5** and **6**) due to the larger tin metal being more displaced from the core of the Pc ring.

4. Conclusion

In the presented work, the synthesis of new binuclear zinc(II), oxotitanium(IV), tin(II), cobalt(II), copper(II) and nickel(II) (**5**–**10**) phthalocyanine complexes were described and these new complexes were characterized by elemental analysis, FT-IR, ^{1}H NMR, ^{13}C NMR (for compound 3), UV–Vis and mass spectra. Aggregation behaviors of all studied complexes were investigated in DMSO at different concentrations. The spectra showed monomeric behavior evidenced by a single (narrow) Q band, typical of metalated phthalocyanine complexes at concentration range 1.2 × 10^{-6}–2 × 10^{-6} M. The Q band of the tin(II) phthalocyanine complex (**7**) was red-shifted in DMSO due to the non-planar effect of the bigger tin as central atom. The photophysical and photochemical properties of newly synthesized phthalocyanine complexes (**5**–**7**) were also described in DMSO for comparison of the effect of metal atoms on the Pc framework. Binuclear zinc(II) (**5**) and oxotitanium(IV) (**6**) phthalocyanine complexes showed similar and typical fluorescence behavior in DMSO. But the shape of excitation spectrum was different from the absorption spectrum for studied binuclear tin(II) phthalocyanine complex (**7**) in DMSO. The fluorescence quantum yield (Φ_F) values of binuclear zinc(II) (**5**) and oxotitanium(IV) (**6**) phthalocyanine complexes were found similar but the Φ_F value of binuclear tin(II) phthalocyanine complex (**7**) was lower than these complexes. The difference in the behavior of tin(II) phthalocyanine complex (**7**) on excitation could be due to the larger tin metal being more displaced from the core of the Pc ring. The τ_F values were found lower for binuclear phthalocyanine complexes (**5**–**7**) when compared to respective unsubstituted zinc phthalocyanine (**Std-ZnPc**). The τ_F values of binuclear zinc(II) (**5**) and oxotitanium(IV) (**6**) phthalocyanine complexes were found higher than binuclear tin(II) phthalocyanine complex (**7**) in DMSO because of the tin is heavy metal. All newly synthesized binuclear phthalocyanine complexes (**5**–**7**) showed lower Φ_Δ values than unsubstituted zinc (II) Pc complex (**Std-ZnPc**) in DMSO but the singlet oxygen generation of these phthalocyanine complexes still enough for photocatalytic application such as PDT. Generally, the Φ_d values of studied binuclear phthalocyanine complexes (**5**–**7**) were similar to MPc complexes.

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