

Microwave-assisted synthesis of novel nonperipherally substituted metallophthalocyanines bearing (7-(trifluoromethyl)quinolin-4-yl)oxy groups

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Abstract: The synthesis, characterization, and spectroscopic properties of novel nonperipherally tetrasubstituted metallophthalocyanines (zinc, cobalt, copper, manganese, and indium) bearing 4 (7-(trifluoromethyl)quinolin-4-yl)oxy units has been reported. The new compounds have been characterized using UV-Vis, IR, ^1H NMR, ^{13}C NMR, ^{19}F NMR, and mass spectroscopic data. The absorption properties of these new complexes were compared to those of peripherally substituted phthalocyanine derivatives. Based on the structural, spectroscopic, and absorption studies, it was found that the substitution effect altered the electronic structures significantly. The results provide useful information to understand the effect of peripheral or nonperipheral substitution on the properties of this macrocyclic ring. Photophysical properties with zinc(II) phthalocyanine were found, including electronic absorption and fluorescence quantum yield. The fluorescence of the complex was investigated in DMF and it was found that benzoquinone was an effective quencher.

Key words: Aggregation, benzoquinone, fluorescence, microwave, nonperipheral, phthalocyanine, quinoline

1. Introduction

Phthalocyanines (Pcs) are 18 π -electron disk-like aromatic macrocycles with 2D π -electron delocalization over the whole molecule.¹ Since their discovery, Pcs have attracted attention as functional chromophores for various applications such as liquid crystals, chemical sensors, electrochromic compounds, and nonlinear optical and photovoltaic cells.^{2–7} The physicochemical properties of Pcs depend on the nature of the peripheral or nonperipheral functional groups, as well as the electronic properties of the central metal cations in the Pc core.⁸ The substitution by functional groups is advantageous because it gives flexibility in solubility and also efficiently tunes the color of the material.

Pcs are promising second-generation photosensitizers for photodynamic therapy as a result of their strong absorption in tissue-penetrating red light and high efficiency of generating singlet oxygen.^{9,10} Recently, quinoline derivatives are receiving a great deal of attention due to their biological activity. For example, quinoline-related chemical classes are being exploited in cancer chemotherapy and a number of them are in different phases of clinical trials in recent years.^{11,12} In particular, 8-hydroxyquinoline derivatives are potential anticancer drug candidates.¹³

One important problem related to Pc derivatives is their low solubility in several organic media and water because of aggregation phenomena. The solubility of Pc compounds can be improved via nonperipheral or peripheral substitution.^{14–16} Placing substituents on nonperipheral positions of the Pc ring may reduce the detrimental effect of the substituents on the strong π - π interaction between Pc molecules.

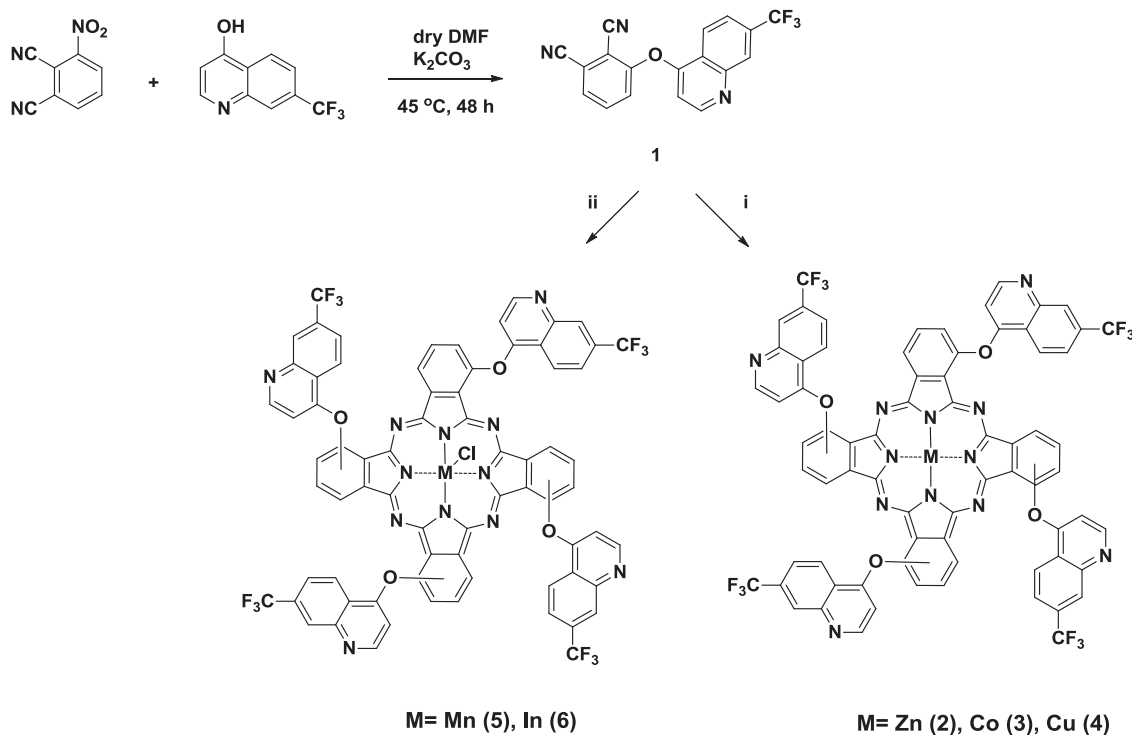
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Traditional synthetic routes to Pcs need long reaction times and very high temperatures. Synthesis of Pcs has been accomplished in minutes by using microwave energy.¹⁷ Microwave irradiation is an alternative to traditional heating, because microwave-assisted synthesis can result in increased yields, lowered reaction times, and reduced side reactions.^{18–21}

In a previous work, the synthesis and the characterization of tetra-substituted metal-free and metallophthalocyanines carrying 4 trifluoromethyl-quinoline units on the periphery were described.²² The wavelength of the absorption of the Q-band, the solubility, and the aggregation properties of the compounds were also investigated. In this regard, we report herein the synthesis of metallophthalocyanines (**2–6**) carrying 4 trifluoromethyl-quinoline groups on the nonperipheral positions. The spectroscopic characterization and the electronic and aggregation behaviors of these newly synthesized complexes are also presented. Furthermore, the fluorescence quenching of the zinc Pc (**2**) in DMF solution using benzoquinone (BQ) as a quencher is reported.

2. Results and discussion

The synthesis of substituted phthalonitrile derivatives is an important step in Pc synthesis. Nonperipherally substituted phthalonitrile derivatives are synthesized through reactions between 3-nitrophthalonitrile and O-, S-, or N-nucleophiles.^{23–25} Using this synthetic strategy, the synthesis and characterization of metallophthalocyanines **2–6** and their precursor **1** are reported. The synthesis of 3-((7-(trifluoromethyl)quinolin-4-yl)oxy)phthalonitrile (**1**) was achieved in 74% yield through base-catalyzed aromatic displacement of 3-nitrophthalonitrile with 4-hydroxy-7-(trifluoromethyl)quinoline using K_2CO_3 as the base in dry DMF. The reaction was carried out at 45 °C under N_2 atmosphere for 48 h. The synthetic route is shown in the Scheme.



Scheme. Synthesis of phthalonitrile derivative **1** and phthalocyanines **2–6**. (i) Metal salts ($Zn(CH_3COO)_2$, $CoCl_2$, $Cu(CH_3COO)_2$), n-pentanol (or DMAE), DBU, 3–10 min, 350 W, 135–165 °C. (ii) Metal salts ($MnCl_2$, $InCl_3$), n-hexanol (or DMAE), DBU, 3–10 min, 350 W, 135–165 °C.

Cyclotetramerization of compound **1** to obtain the nonperipherally tetra-substituted phthalocyanines (**2–6**) was accomplished in the presence of metal salts ($\text{Zn}(\text{CH}_3\text{COO})_2$, CoCl_2 , $\text{Cu}(\text{CH}_3\text{COO})_2$, MnCl_2 , InCl_3) and a suitable nitrogen-donor base (1,8-diazabicyclo[5.4.0]undec-7-ene, DBU) in n-pentanol (n-hexanol or DMAE) by using microwave irradiation (Scheme). Tetra-substituted Pcs were obtained as mixtures of 4 structural isomers with D_{2h} , C_{4h} , C_{2v} , and C_s symmetries, respectively.^{26,27} These isomers have been separated in the past using chromatographic methods.^{28,29} In this study, the novel tetra-substituted metallophthalocyanines **2–6** are obtained as expected isomer mixtures. No attempt was made to separate the isomers of **2–6**. The metallophthalocyanines (**2**, **3**, and **4**) were purified by column chromatography, whereas compounds **5** and **6** were purified by washing with diethyl ether, hexane, and cold methanol. They were obtained in good yields (45% for **2**, 30% for **3**, 26% for **4**, 36% for **5**, and 39% for **6**) and were characterized by elemental analysis and by their spectral data (^1H NMR, ^{13}C NMR, ^{19}F NMR, IR, mass, and UV-Vis spectra). The data are consistent with the assigned structures.

In recent years, microwave-assisted organic synthesis has emerged as a valuable technology among synthetic organic chemists. However, replacing the oil bath with a dedicated microwave reactor provides the opportunity to perform reactions in dramatically shortened time periods as well as increasing yields by using conditions not attainable under conventional heating.^{18–21} Attempts to synthesize compounds **2–6** in a conventional way have failed, and therefore we have adopted microwave-assisted reactions instead. The microwave experiments in the present study were performed in a CEM Discover SP microwave system. Using 350 W of power for irradiation, the temperature was raised to 135–165 °C, the reactions were completed in 3–10 min, and compounds **2–6** were obtained in good yields, whereas the reactions were completed in 24 h with the conventional method.²² Consequently, the microwave irradiation method provided nearly the same or higher product yields in a very short period of time as compared with the conventional heating-based cyclotetramerization method. These results suggest that the microwave irradiation method was more useful than the conventional method due to shorter reaction time and energy savings.

In the IR spectrum of compound **1**, stretching vibrations of $\text{C}\equiv\text{N}$ groups at 2240 cm^{-1} and aromatic groups at 3070 cm^{-1} appeared at expected frequencies. The ^1H NMR spectrum of **1** in d_6 -DMSO showed signals with ranging from 8.99 to 7.22 ppm belonging to aromatic protons. In the ^{13}C NMR spectrum of compound **1**, protonated and unsaturated benzene and quinoline carbon atoms appeared at 158.56–108.55 ppm, while nitrile carbons were observed at 116.44 and 115.36 ppm. ^{19}F NMR spectroscopy has been a very useful technique for investigating the fluorine-substituted compounds. In the ^{19}F NMR spectrum of compound **1**, a signal was observed at –61.35 ppm as a singlet. Literature data suggests that fluorine shifts, when present in an aromatic group, are observed between –54 and –80 ppm; therefore, the observed shift confirms the presence of an aryl-trifluoromethyl-substituted molecule. In the EI^+ -GCMS spectrum of **1**, the molecular ion peak at $m/z = 339$ was easily identified.

Cyclotetramerization of phthalonitrile derivative **1** was confirmed by the disappearance of the sharp $\text{C}\equiv\text{N}$ vibration at 2240 cm^{-1} . The IR spectra of Pcs **2–6** are very similar to each other. The ^1H NMR spectra of compounds **2** and **6** are consistent with the proposed structure. In the ^1H NMR spectra of ZnPc (**2**) and InPc (**6**) in d_6 -DMSO, the aromatic and Pc protons resonated between 8.90 and 7.45 ppm for **2** and between 9.24 and 7.17 ppm for **6**, integrating for 32 protons for each complex. The ^1H NMR spectra of compounds **2** and **6** are somewhat broader than the corresponding signals in the dinitrile derivative **1**. Compounds **3**, **4**, and **5** have paramagnetic atoms (Co^{2+} , Cu^{2+} , and Mn^{3+}) in the inner core. If the compound is diamagnetic (like

compounds **2** and **6**), then it can be characterized with NMR easily. Paramagnetic compounds would affect the magnetic shimming. For this reason, paramagnetic compounds generally are not characterized via NMR. The ^1H NMR spectra of the paramagnetic phthalocyanines (**3**, **4**, and **5**) were not measured.

In the mass spectra of compounds **2–6**, the presence of the characteristic molecular ion peaks at $m/z = 1421.92$ $[\text{M}]^+$ for phthalocyanine **2**, $m/z = 1417.07$ $[\text{M}]^+$ for **3**, $m/z = 1420.83$ $[\text{M}]^+$ for **4**, $m/z = 1447.19$ $[\text{M}]^+$ for **5**, and $m/z = 1507.05$ $[\text{M}]^+$ for **6** confirmed the proposed structure.

The electronic absorption spectra of Pcs **2–6** showed characteristic intense Q bands at 685 (**2**), 675 (**3**), 685 (**4**), 731 (**5**), and 707 (**6**) nm in THF. The B bands were observed around 320–350 nm. The wavelengths of the absorption of the Q band of **2–6** follow the order of $\text{Mn} > \text{In} > \text{Zn}, \text{Cu} > \text{Co}$, due to the nature of the central metal ion. The order shows that the cobalt Pc (**3**) has the largest blue shift while manganese Pc (**5**) has the largest red shift as compared to the other metal complexes, **2**, **4**, and **6**.^{30,31} Furthermore, MnPc (**5**) shows an absorption at 567 nm, which was interpreted as a charge transfer absorption (phthalocyanine \rightarrow metal, LMCT).^{32,33} These observations are characteristic for Mn(III)Pc complexes. The UV-Vis spectra of compounds **2–6** in THF are shown in Figure 1. The Q bands of the nonperipherally substituted Pcs (**2–6**) are red-shifted when compared to the corresponding peripherally substituted complexes in THF.²² The bathochromic shifts are 15 nm between nonperipheral and peripheral substituted derivatives. The observed red-shifts are typical of Pcs with substituents at the nonperipheral positions.^{34,35}

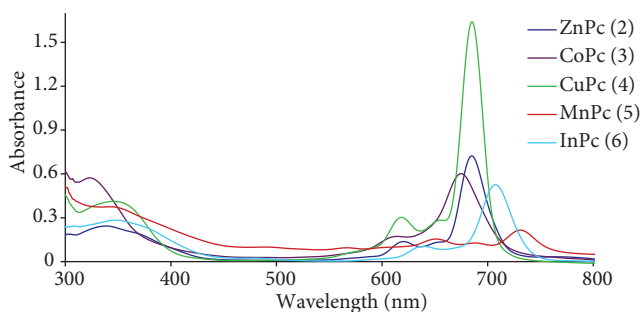


Figure 1. Electronic absorption spectra of **2–6** in THF. Concentration: 1.00×10^{-5} M.

In this study, the aggregation behavior of complexes **2–6** was examined at different concentrations in THF (Figure 2 shows the series of spectra for complex **2**) and the results were compared with the aggregation behavior of the already prepared peripherally substituted derivatives in the literature.²² As the concentration was increased, the intensity of absorption of the Q band also increased. No new band due to the formation of aggregated species was observed.^{36,37} This means that the Pc derivatives (**2–6**) did not show aggregation in THF and the Beer–Lambert law was obeyed for all these compounds for concentrations ranging from 4.00×10^{-6} to 14.00×10^{-6} M. Both nonperipherally and peripherally substituted phthalocyanines do not show aggregation in THF and they obey the Beer–Lambert law. It was observed that the position of the substitution does not affect the aggregation properties of the nonperipherally and peripherally substituted phthalocyanines.

Figure 3 shows the absorption, fluorescence emission, and excitation spectra for zinc Pc (**2**) in DMF. Fluorescence emission peaks were observed at 721 nm for ZnPc (**2**) in DMF. Fluorescence quantum yields (Φ_F) were determined by the comparative method [Eq. (1)]. Both the sample and the standard were excited at the same wavelength. The fluorescence quantum yield was calculated as 0.048. Φ_F values of zinc Pc (**2**) are lower than that of unsubstituted ZnPc ($\Phi_F = 0.17$) in DMF.³⁸

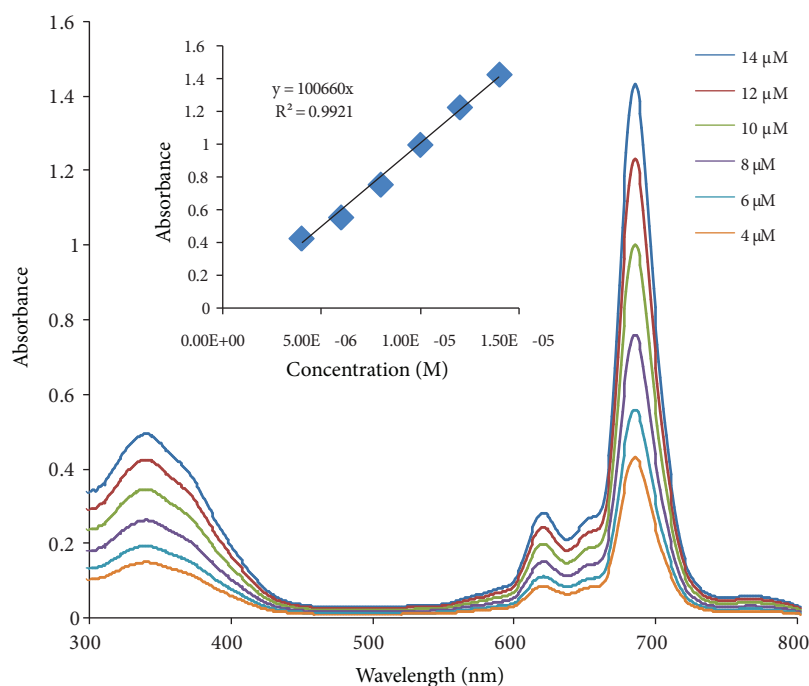


Figure 2. Aggregation behavior of **2** in THF at different concentrations.

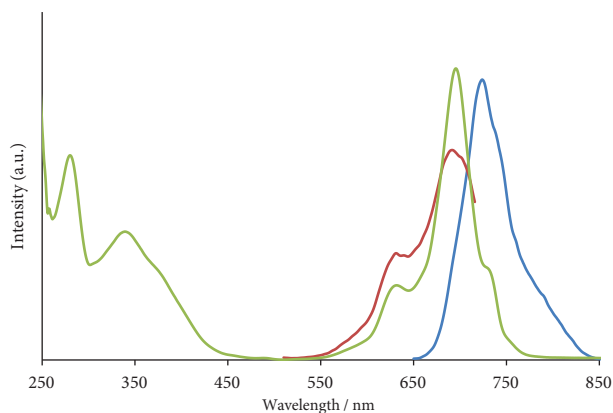


Figure 3. Absorption (green), excitation (red), and emission (blue) spectra for compound **2** in DMF. Excitation wavelength = 630 nm.

Fluorescence lifetime is the average time a molecule stays in its excited state before fluorescence. Natural radiative lifetimes (τ_o) were calculated using the PhotochemCAD program, which uses the Strickler–Berg equation.³⁹ The fluorescence lifetimes (τ_F) and natural radiative lifetimes (τ_o) of the ZnPc (**2**) were calculated as 0.49 and 10.30 ns, respectively.

Fluorescence quenching by BQ of zinc phthalocyanine (**2**) is a popular and important method to study the energetics of the excited states.^{40,41} In the presence of a quencher (BQ), energy transfer occurs between the fluorophore [the excited Zn(II) phthalocyanine, **2**] and the quencher. In this study, the fluorescence of compound **2** was effectively quenched by BQ in DMF. There is a progressive decrease in fluorescence intensity as the concentration of BQ increases. Quinone derivatives have high electron affinities, and their involvement in electron transfer processes is well documented.⁴⁰ It is known that the energy of the lowest excited state

for quinones is greater than the energy of the excited singlet state of Pcs.⁴¹ The fluorescence quenching of Zn(II) Pc (**2**) by BQ obeyed Stern–Volmer kinetics. This is consistent with diffusion-controlled bimolecular reactions. Figure 4 shows the fluorescence of ZnPc (**2**) in the presence of varying concentrations of BQ. The slopes of the plots shown in Figure 5 give the Stern–Volmer constant (K_{SV}) values ($K_{SV} = 56.73 \text{ M}^{-1}$).^{42,43} The bimolecular quenching constant (kq) value of the substituted zinc Pc (**2**) was calculated as $11.5 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

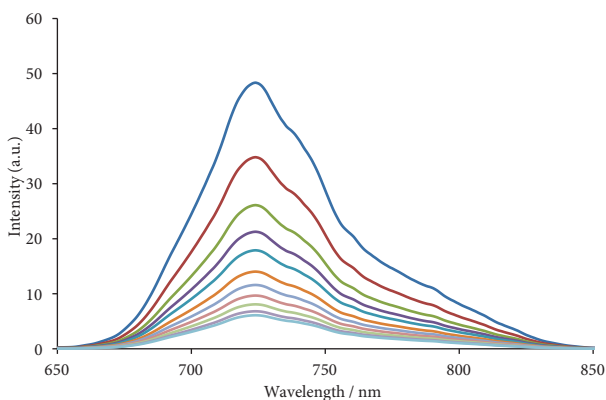


Figure 4. Fluorescence emission spectral changes of **2** ($4.00 \times 10^{-6} \text{ M}$) on addition of different concentrations of BQ in DMF. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 M.

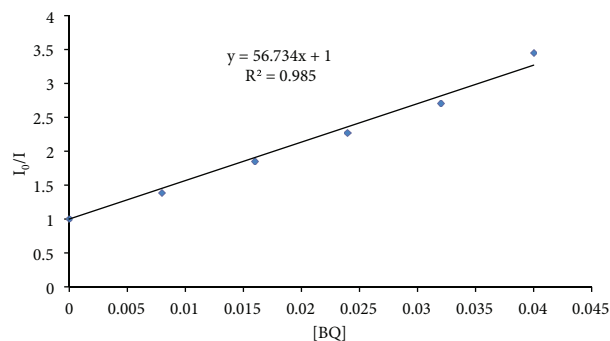


Figure 5. Stern–Volmer plots for benzoquinone (BQ) quenching of **2** [ZnPc] = $4.00 \times 10^{-6} \text{ M}$ in DMF. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.04 M.

Tetrasubstituted Pcs usually show a higher solubility than octasubstituted derivatives because of the mixture of regioisomers.^{44–46} Pcs **2–6** having CF_3 groups show excellent solubility in common organic solvents when compared with quinolinoxy-substituted Pcs reported in the literature.⁴⁷ Compounds **2–6** are soluble in chloroform, dichloromethane, tetrahydrofuran, dimethylformamide, dimethylsulfoxide, and toluene. Manganese (**5**) and indium (**6**) Pcs also show good solubility in methanol and acetone. Nonperipherally (**2–6**) and peripherally substituted phthalocyanines carrying CF_3 groups are soluble in same solvents and the position of substitution did not change the solubility of trifluoromethyl-quinoline substituted Pcs.²²

3. Experimental

3.1. Materials and equipment

All chemicals and reagents were purchased from Merck Chemicals and Sigma-Aldrich Chemicals and used without any further purification. All reported ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Agilent VNMR5 500 MHz spectrometer. Chemical shifts (δ , ppm) were determined with TMS as the internal reference. IR spectra were recorded on a PerkinElmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer; electronic spectra were recorded on a Scinco Lab Pro Plus UV/Vis spectrophotometer. Fluorescence spectra were recorded on a PerkinElmer LS55 fluorescence spectrophotometer. Mass spectra were measured on a Bruker microflex LT MALDI-TOF MS spectrometer and PerkinElmer Clarus 500 gas chromatograph-mass spectrometer. The isotopic patterns for all assigned signals are in agreement with the calculated natural abundance. Data have been given for the most abundant isotope only. A single-mode microwave reactor (CEM Discover SP) was used for carrying out the synthesis of metallophthalocyanines. Silica gel (Kieselgel 60, 200–400 mesh) and aluminum oxide 90 active neutral were used in the separation and

purification of compounds by column chromatography. The homogeneity of the products was tested in each step by TLC. The purity of all new compounds was checked with their ^1H NMR spectra and elemental analysis.

3.2. Synthesis

3.2.1. 3-((7-(Trifluoromethyl)quinolin-4-yl)oxy)phthalonitrile (1)

3-Nitrophthalonitrile (1 g, 5.78 mmol) was dissolved in 40 mL of dry DMF and 4-hydroxy-7-(trifluoromethyl)quinoline (1.80 g, 8.45 mmol) was added. After stirring for 15 min, 2.35 g of finely ground anhydrous K_2CO_3 (17.3 mmol) was added in small portions for 2 h with efficient stirring. The reaction mixture was stirred under nitrogen at 45°C for 48 h. The mixture was then poured into 200 mL of ice-water mixture and the precipitate was filtered off, washed with water until the filtrate was neutral, and dried in vacuo. Finally, a white product was crystallized from ethanol. Yield: 1.44 g, (74%). Mp: 213°C ; anal. calcd. for $\text{C}_{18}\text{H}_8\text{F}_3\text{N}_3\text{O}$: C, 63.72; H, 2.38; N, 12.39%; found: C, 63.50; H, 2.31; N, 12.22%; IR $\nu_{\text{max}}/\text{cm}^{-1}$: 3070 (C-H, aromatic), 2240 ($\text{C}\equiv\text{N}$), 1606, 1508, 1474, 1458, 1367, 1299, 1245, 1198 cm^{-1} ; ^1H NMR (d_6 -DMSO): δ , ppm: 8.99 (d, 1H, Ar-H), 8.53–8.47 (m, 3H, Ar-H), 8.13 (d, 1H, Ar-H), 8.01 (m, 1H, Ar-H), 7.88 (d, 1H, Ar-H), 7.22 (d, 1H, Ar-H) ppm; ^{13}C NMR (d_6 -DMSO): δ , ppm: 158.56 (quinoline C-O), 156.39 (aromatic C-O), 153.41 (quinoline CH), 148.25 (quinoline C), 136.46 (aromatic CH), 130.89 (quinoline C), 130.82 (aromatic CH), 130.57 (quinoline CH), 126.55 (aromatic CH), 126.51 (C-F), 125.97 (quinoline CH), 124.84 (quinoline CH), 123.49 (quinoline C), 122.42 (aromatic C), 116.44 ($\text{C}\equiv\text{N}$), 115.36 ($\text{C}\equiv\text{N}$), 112.72 (quinoline CH), 108.55 (aromatic C); ^{19}F NMR (d_6 -DMSO): δ , ppm: -61.35 (s, 3F, CF_3); MS (ESI): m/z 339.9 $[\text{M}]^+$, 338.8 $[\text{M}-1]^+$, 269.9 $[\text{M}-1-\text{CF}_3]^+$.

3.2.2. 1,8(11),15(18),22(25)-Tetrakis-[(7-(trifluoromethyl)quinolin-4-yl)oxy] phthalacyaninatozinc (II) (2)

Compound **1** (0.30 g, 0.88 mmol), anhydrous $\text{Zn}(\text{CH}_3\text{COO})_2$ (0.04 g, 0.22 mmol), and a catalytic amount of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in 1-pentanol (2 mL) were irradiated in a microwave oven at 145°C and 350 W for 10 min under nitrogen. After cooling to room temperature, the reaction mixture was precipitated by the addition of methanol:water (1:1, 15 mL). The precipitate was centrifuged and washed with the same mixture, then dried in vacuo. Finally, the green compound was chromatographed on silica gel and eluted with THF. Yield: 0.13 g (45%). Mp: $>200^\circ\text{C}$; anal. calcd. for $\text{C}_{72}\text{H}_{34}\text{F}_{12}\text{N}_{12}\text{O}_4\text{Zn}$: C, 63.63; H, 2.52; N, 12.37%; found: C, 63.54; H, 2.47; N, 12.35%; IR $\nu_{\text{max}}/\text{cm}^{-1}$: 3067 (C-H, aromatic), 1598, 1508, 1483, 1430, 1382, 1296, 1260, 1197 cm^{-1} ; UV-Vis (THF): $\lambda_{\text{max}}/\text{nm}$: 338, 685 nm; ^1H NMR (d_6 -DMSO): δ , ppm: 8.90–7.45 (m, 32H, Ar-H); MS (MALDI-TOF): m/z 1421.92 $[\text{M}]^+$.

3.2.3. 1,8(11),15(18),22(25)-Tetrakis-[(7-(trifluoromethyl)quinolin-4-yl)oxy] phthalacyaninatocobalt(II) (3)

A mixture of dinitrile **1** (0.30 g, 0.88 mmol) and anhydrous cobalt(II) chloride (0.03 g, 0.22 mmol) was ground together in a microwave oven and 2-(dimethylamino)ethanol (DMAE) (2 mL) was added. The reaction mixture was irradiated in a microwave oven at 135°C and 350 W for 6 min. The resulting blue suspension was cooled to room temperature and the crude product was precipitated by the addition of methanol:water (1:1, 15 mL). The precipitate was collected by filtration, washed with ethanol and methanol, and then dried. The blue product was further purified by chromatography on alumina using methanol as eluent. Yield: 0.095 g (30%). Mp:

>200 °C; anal. calcd. for $C_{72}H_{32}CoF_{12}N_{12}O_4$: C, 60.79; H, 2.27; N, 11.82%; found: C, 60.45; H, 2.30; N, 11.77%; IR ν_{max}/cm^{-1} : 3071 (C-H, aromatic), 1568, 1509, 1468, 1431, 1381, 1296, 1231, 1196 cm^{-1} ; UV-Vis (THF): λ_{max}/nm : 323, 675 nm; MS (MALDI-TOF): m/z 1417.07 $[M]^+$.

3.2.4. 1,8(11),15(18),22(25)-Tetrakis-[(7-(trifluoromethyl)quinolin-4-yl)oxy] phthalocyaninatocopper(II) (4)

The synthesis of compound **4** was similar to that of **3**, except that $Cu(CH_3COO)_2$ (0.04 g, 0.22 mmol) was employed instead of $CoCl_2$. After 6 min the resulting suspension was cooled and then precipitated by the addition of methanol:water (1:1, 15 mL). The blue solid was filtered off and then dried. Finally, the pure phthalocyanine was obtained by column chromatography on silica gel using THF as eluent. Yield: 0.08 g (26%). Mp: >200 °C; anal. calcd. for $C_{72}H_{32}CuF_{12}N_{12}O_4$: C, 61.07; H, 2.28; N, 11.87%; found: C, 61.08; H, 2.21; N, 11.47%; IR ν_{max}/cm^{-1} : 3067 (C-H, aromatic), 1567, 1506, 1484, 1430, 1381, 1295, 1263, 1231, 1196 cm^{-1} ; UV-Vis (THF): λ_{max}/nm : 345, 685 nm; MS (MALDI-TOF): m/z 1420.83 $[M]^+$.

3.2.5. 1,8(11),15(18),22(25)-Tetrakis-[(7-(trifluoromethyl)quinolin-4-yl)oxy] phthalocyaninato (chloro)manganese(III) (5)

A mixture of **1** (0.30 g, 0.88 mmol) and anhydrous manganese(II) chloride ($MnCl_2$) (0.09 g, 0.22 mmol) was heated in DMAE (2 mL) at 135 °C under N_2 by the irradiation of a microwave oven for 5 min. The resulting brown suspension was cooled to room temperature and the product was precipitated by the addition of methanol:water (1:1, 15 mL). The desired product was washed with diethyl ether, hexane, and cold methanol and then dried in vacuo. Yield: 0.11 g (36%). Mp: >200 °C; anal. calcd. for $C_{72}H_{32}ClF_{12}MnN_{12}O_4$: C, 59.74; H, 2.23; N, 11.61%; found: C, 59.56; H, 2.21; N, 11.58%; IR ν_{max}/cm^{-1} : 3068 (C-H, aromatic), 1567, 1508, 1465, 1430, 1382, 1297, 1234, 1196 cm^{-1} ; UV-Vis (THF): λ_{max}/nm : 343, 567, 731 nm; MS (MALDI-TOF): m/z 1447.19 $[M]^+$, 1412.98 $[M-Cl]^+$.

3.2.6. 1,8(11),15(18),22(25)-Tetrakis-[(7-(trifluoromethyl)quinolin-4-yl)oxy] phthalocyaninato (chloro)indium(III) (6)

Compound **1** (0.30 g, 0.88 mmol), indium(III) chloride (0.05 g, 0.22 mmol), and a catalytic amount of DBU in 1-hexanol (2 mL) were irradiated in microwave oven at 165 °C for 3 min under nitrogen. The resulting brown suspension was cooled to room temperature and then precipitated by the addition of methanol:water (1:1, 15 mL). The precipitate was filtered off and washed with diethyl ether, hexane, and cold methanol and then dried in vacuo. Yield: 0.13 g (39%). Mp: >200 °C; anal. calcd. for $C_{72}H_{32}ClF_{12}InN_{12}O_4$: C, 57.37; H, 2.14; N, 11.15%; found: C, 57.32; H, 2.11; N, 11.09%; IR ν_{max}/cm^{-1} : 3071 (C-H, aromatic), 1566, 1508, 1466, 1430, 1382, 1296, 1230, 1195 cm^{-1} ; UV-Vis (THF): λ_{max}/nm : 347, 707 nm; 1H NMR (d_6 -DMSO): δ , ppm: 9.24–7.17 (m, 32H, Ar-H); MS (MALDI-TOF): m/z 1507.05 $[M]^+$, 1471.43 $[M-Cl]^+$.

3.3. Photophysical parameters

3.3.1. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) were determined by the comparative method [Eq. (1)] using unsubstituted ZnPc ($\Phi_F = 0.17$ in DMF) as the standard.^{38,48}

$$\Phi_F = \Phi_F(Std)(FA_{Std}\eta^2/F_{Std}A\eta_{Std}^2), \quad (1)$$

where F and F_{Std} are the areas under the fluorescence emission curves of the zinc Pc and the standard, respectively. A and A_{Std} are the respective absorbances of the samples and standard at the excitation wavelength, and η and η_{Std} are the respective refractive indices of solvent ($\eta_{DMF} = 1.496$) used for the sample and standard. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

Natural radiative lifetimes (τ_0) were determined using the PhotochemCAD program, which uses the Strickler–Berg equation.³⁹ The fluorescence lifetimes (τ_F) were evaluated using Eq. (2).

$$\Phi_F = \tau_F/\tau_0 \quad (2)$$

3.3.2. Fluorescence quenching by BQ

Fluorescence quenching experiments on the substituted zinc Pc (**2**) were carried out by the addition of different concentrations of BQ to a fixed concentration of the complex, and the concentrations of BQ in the resulting mixtures were 0, 0.008, 0.016, 0.024, 0.032, and 0.040 M. The fluorescence and absorbance spectra of ZnPc (**2**) at each BQ concentration were recorded, and the changes in fluorescence intensity were related to BQ concentration by the Stern–Volmer equation [Eq. (3)]:⁴⁹

$$I_0/I = 1 + K_{SV}[BQ], \quad (3)$$

where I_0 and I are the fluorescence intensities of fluorophore in the absence and presence of the quencher, respectively. $[BQ]$ is the concentration of the quencher; K_{SV} is the Stern–Volmer constant, which is the product of the bimolecular quenching constant (k_q) and τ_F and is expressed as in Eq. (4):

$$K_{SV} = k_q \times \tau_F. \quad (4)$$

The ratios of I_0/I were calculated and plotted against $[BQ]$ according to Eq. (3), and K_{SV} was determined from the slope.

4. Conclusion

In the presented work, the synthesis of novel nonperipherally substituted metallophthalocyanines ($M = \text{Zn, Co, Cu, Mn, and In}$) with 4 (trifluoromethyl)quinoline groups was achieved by microwave irradiation. The characterization, aggregation behavior, and photophysical and photochemical properties of these new metallophthalocyanines were investigated. The Q band absorptions of the synthesized nonperipheral phthalocyanines (**2–6**) shift by 15 nm to a longer wavelength compared to peripherally substituted phthalocyanines. These results show that the position of the substitution affects the electronic properties of Pcs but does not significantly affect the solubility and aggregation properties of Pcs carrying (trifluoromethyl)quinoline groups.

The photophysical and fluorescence quenching properties of the zinc(II) Pc complex (**2**) were investigated in DMF. The fluorescence lifetime is an important parameter for practical applications of fluorescence, such as fluorescence resonance energy transfer and fluorescence-lifetime imaging microscopy. The fluorescence of the substituted zinc(II) Pc complex (**2**) is quenched by quinone derivatives. The fluorescence of the zinc(II) phthalocyanine (**2**) is quenched by BQ in DMF. The linearity of the Stern–Volmer plot (I_0/I) versus the quencher concentration ($[Q]$) indicates that energy transfer occurs between the fluorophore (the excited Zn(II) phthalocyanine) and the quencher (benzoquinone).

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