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The synthesis and fluorescence behaviour of new unsymmetrically mono-functionalized carboxy Ge, Ti and Sn phthalocynines

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ABSTRACT

This work reports on the synthesis and fluorescence behaviour of novel unsymmetrically substituted monocarboxy germanium ($(OH)_2$GeMCPc, **3**), titanium (OTiMCPc **4**) and tin ($(ac)_2$SnMCPc, **5**) phthalocyanines. The fluorescence quantum yields ranged from 0.09 to 0.14. The fluorescence lifetimes were found to be higher for the complex with higher fluorescence quantum yield value. Higher fluorescence quantum yields and lifetimes were obtained for the $(ac)_2$SnMCPc complex (**5**), followed by OTiMCPc complex (**4**), and the lowest fluorescence quantum yield and lifetime were observed for $(OH)_2$GeMCPc (**3**).

1. Introduction

Metallophthalocyanines (MPcs) show promise for many applications including in: photocatalysis [1–4], photo-electrocatalysis [5] and photodynamic therapy of cancer [6–10]. Mono-functionalized MPc complexes are of great interest since they can be coupled to various substrates by chemically binding one reactive substituent of the Pc, with the other binding sides being blocked with non reactive substituents [11,12]. It is also believed that low symmetry phthalocyanines have less tendencies to form aggregates compared to symmetrically tetrasubstituted Pcs which is a very useful and attractive property for these Pcs for their application as photosensitizers. For a good photosensitizer a molecule is required to be in its monomeric state for successful photo-induced energy and electron transfer [13–15]. Low symmetry bisthienylethene phthalocyanines with photochromic properties have been reported [16,17]. The complexes showed potential for applications in photoswitching devices [17]. Recently our group has reported on selective coupling of a monocarboxy phthalocyanine complex on zinc oxide substrates for solar cells applications [15]. The photo-electrochemical studies of a series of symmetrically carboxy phthalocyanines displayed a lack of selective binding due to the presence of many carboxylic acid groups available for attachment on ZnO. The complexes also showed aggregation when they were bound to ZnO substrate, which lead to low power efficiencies compared to unsymmetrically monosubstituted carboxy Pc [15]. Other studies in our group have shown successful linking of nano particles such as quantum dots to low symmetry amino phthalocyanines for the improvement of Förster resonance energy transfer (FRET) as compared to symmetrically substituted carboxy Pcs [18]. However the disadvantage of working with low symmetry phthalocyanine complexes is the low yield that is obtained during the synthesis of the complexes [19]. The statistical condensation method of making low symmetry phthalocyanines results in a mixture of different compounds depending on the ratio of the two starting material used [20–23]. Separation of the various compounds formed during the synthesis to get the desired mono-functionalized Pc complex is a major and a crucial step during the purification of these complexes, resulting in low yields of the desired product due to loss during the separation. Herein we report on the synthesis and characterization of germanium, titanium and tin phthalocyanine complexes with only one reactive carboxy group as an electrophile. We investigate the fluorescence properties of these compounds in solution. Most low symmetry MPc complexes contain the common central metals such as Zn. In this work we use Ti, Ge and Sn as central metals, the use of the carboxy group is to allow coordination of biological molecules containing amino groups at a later state, the diethylaminoethanethiol substituents were chosen to enhance solubility

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as well as red shifting of the spectra, which are requirements for photosensitizers.

2. Experimental and method

2.1. Materials

Potassium carbonate (K_2CO_3), D_2O, DMSO-d_6, germanium (IV) chloride, titanium (IV) butoxide, tin (IV) acetate, 2-(diethylaminoethanethiol) hydrochloride, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), zinc phthalocyanine and aluminum oxide (WN-3: neutral) for column chromatography were purchased from Sigma–Aldrich. Pentanol was purchased from Saarchem. Dimethylformamide (DMF), dichloromethane (DCM) and dimethyl sulphoxide (DMSO), methanol (MeOH), n-hexane, chloroform ($CHCl_3$), dichloromethane (DCM), tetrahydrofuran (THF), acetone, and ethanol were obtained from Merck and were dried according to reported procedures [24] before use. 4-Carboxyphthalonitrile (**2**) was synthesized in a similar method reported in literature using trimellitic anhydride (Aldrich) as the starting material [4,25]. 4-Nitrophthalonitrile was synthesized as reported in literature [26].

2.2. Equipment

UV–visible spectra were recorded on a Varian 500 UV–Vis/NIR spectrophotometer. ^{1}H-NMR spectra were recorded using a Bruker EMX 400 MHz NMR spectrometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluoremeter. IR spectra (KBr pellets) were recorded on a Perkin–Elmer spectrum 2000 FTIR spectrometer.

Fluorescence lifetimes were measured using a time correlated single photon counting setup (TCSPC) (FluoTime 200, Picoquant GmbH) with a diode laser (LDH-P-670 with PDL 800-B, Picoquant GmbH, 670 nm, 20 MHz repetition rate, 44 ps pulse width). Fluorescence was detected under the magic angle with a peltier cooled photomultiplier tube (PMT) (PMA-C 192-N-M, Picoquant) and integrated electronics (PicoHarp 300 E, Picoquant GmbH). A monochromator with a spectral width of about 8 nm was used to select the required emission wavelength band. The response function of the system, which was measured with a scattering Ludox solution (DuPont), had a full width at half-maximum (FWHM) of 300 ps. All luminescence decay curves were measured at the maximum of the emission peak and lifetimes were obtained by deconvolution of the decay curves using the FLUOFIT software program (PicoQuant GmbH, Germany). The support plane approach [27] was used to estimate the errors of the decay times.

Mass spectral data were collected with a Bruker AutoFLEX III Smartbeam TOF/TOF Mass spectrometer. The instrument was operated in positive ion mode using an m/z range of 400–3000. The voltage of the ion sources were set at 19 and 16.7 kV for ion sources 1 and 2 respectively, while the lens was set at 8.50 kV. The reflector 1 and 2 voltages were set at 21 and 9.7 kV respectively. The spectra were acquired using dithranol as the MALDI matrix, using a 355 nm nitrogen laser.

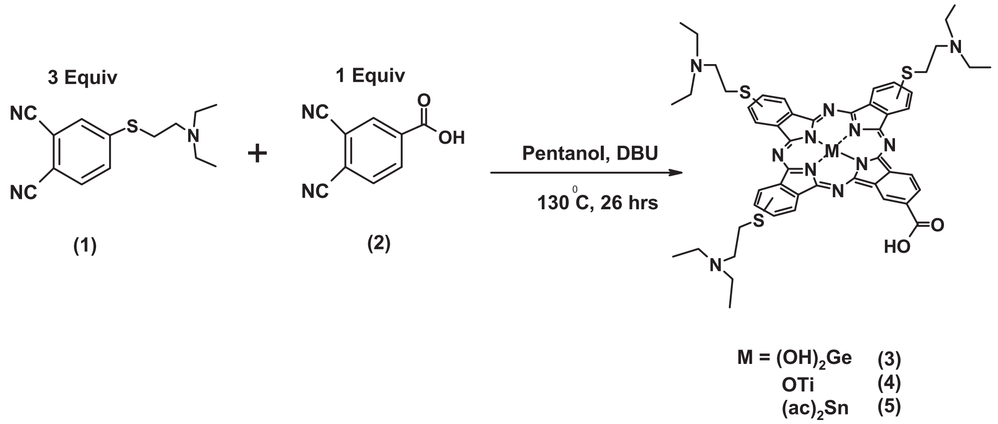
2.3. Synthesis

The synthesis of 4-carboxyphthalonitrile (**2**) has been reported before [25].

4-(2-Diethylaminoethanethiol) phthalonitrile (**1**) was synthesized according to the literature method [28]. Briefly 4-nitrophthalonitrile (3.05 g, 17.6 mmol) was dissolved in anhydrous DMF (150 ml) under argon and 2-diethylaminoethanethiol hydrochloride (9 g, 53.0 mmol) was slowly added. The mixture was left stirring at room temperature, and after 20 min finely ground anhydrous K_2CO_3 (29.3 g, 212.0 mmol) was added in portions over a period of 2 h with stirring. The reaction mixture was constantly stirred at room temperature for a period of 48 h under argon. Then the solution was poured into ice (900 g) for precipitation. The precipitate was filtered off, washed with water, until the filtrate was neutral. The pure product was then dried in air. Yield: (82.30%). IR (KBr) mmax/cm^{-1}: 3098 (Ar–C–H), 2956 (CH_2), 2234 (CN), 742 (C–S–C), 714, 624, 550. ^{1}H-NMR (CDCl3) δ :7.74–7.62 (m, 3H, Ar–H), 3.21–3.04 (t, 2H, SCH_2), 2.84–2.73 (t, 2H, NCH_2), 2.37–2.18 (qnt, 4H, CH_2C), 1.16–1.08 (t, 6H, CH_3) ppm.

2.3.1. *Tris {9 (10), 16 (17), 23 (24)-4-(2-diethylaminoethanethiol)-2-(4-carboxyphthalonitrile) phthalocyaninato} germanium (IV) dihydroxy (Scheme 1, (GeMCPc (**3**)))*

A mixture of 4-carboxyphthalonitrile (**2**) (0.22 g, 1.3 mmol) and 4-(2-diethylaminoethanethiol) phthalonitrile (**1**) (0.99 g, 3.9 mmol) was firstly finely ground and homogenized and placed in a round bottom flask that contained pre-heated pentanol. The mixture was then stirred under reflux at 160 °C for 26 h in an argon atmosphere in the presence of excess germanium (IV) chloride as a metal salt and DBU as a catalyst. Thereafter, the mixture was cooled to room temperature and dropped in n-hexane to precipitate. The green solid product precipitated and was collected by centrifugation and washed with n-hexane and dried in air. Purification was achieved using column chromatography with neutral alumina as column material and DCM:MeOH:THF (10:3:3) as eluent, followed by drying. The desired product was further washed with ethanol,



Scheme 1. Schematic representation of the statistical synthetic route used for the synthesis of low symmetry monocarboxy phthalocyanine complexes: $(OH)_2$GeMCPc (**3**), OTiMCPc (**4**) and $(ac)_2$SnMCPc (**5**). ac = acetate.

acetone, n-hexane and diethylether in a Soxhlet extraction apparatus. Yield: (10.44%). IR (KBr, cm^{-1}): 3447(O–H), 3123(C–H), 2854–2969 (carboxylic acid OH), 1559(C=C), 1447, 1348, 1128, 843, 748 (C–S–C), 701(Ge–O), 610, 543. ^{1}H-NMR (DMSO-d_6): δ, ppm 9.17–9.19 (9H, m, Pc-H), 8.27–8.29 (3H, br, Pc-H), 4.73–4.78 (2H, br, OH) 3.37 (12H, m, S–CH_2), 2.13–2.24 (12H, q, N–CH_2), 1.67–1.74 (18H, dd, CH_3). UV/Vis (DMF) λ_{max} nm (log ε): 350 (3.26), 695 (4.87). Calc. for $C_{51}N_{11}H_{57}O_4S_3Ge$: C 57.98, N 14.59, H 5.39, S 9.11; Found: C 56.32, N 13.17.H 5.39, S 10.47. MALDI TOF MS m/z: Calcd: 1055.59. Found: $[M - 3H]^+$ 1053.18.

2.3.2. Tris {9 (10), 16 (17), 23 (24)-4-(2-diethylaminoethanethiol)-2-(4-carboxyphthalonitrile) phthalocyaninato} titanium (IV) oxide (Scheme 1, (TiMCPc (4)))

The synthesis and purification of the low symmetry titanium (IV) phthalocyanine complex (**4**) was as outlined for the low symmetry germanium (IV) phthalocyanine complex (**3**), except that 0.8 mL titanium (IV) butoxide was employed as a metal source instead of germanium (IV) chloride. Purification procedure and the amounts of the rest of the reagent were as outlined for (**3**).

Yield: (8.15%). IR (KBr, cm^{-1}): 3439(O–H), 3213(C–H), 2850–3000 (carboxylic acid OH), 1491(C=C), 1353, 1238, 987(Ti=O), 962, 742 (C–S–C), 572. ^{1}H-NMR (DMSO-d_6): δ, ppm 8.91–8.99 (9H, m, Pc-H), 8.57–8.62 (3H, br, Pc-H), 3.58–3.60 (12H, m, S–CH_2), 2.96–3.01 (12H, m, N–CH_2), 1.98–2.01 (18H, dd, CH_3). UV/Vis (DMF) λ_{max} nm (log ε): 340 (3.31), 734 (4.91). Calc. for $C_{51}N_{11}H_{55}O_3S_3Ti + H_2O$: C 59.32, N 15.20, H 5.52, S 9.32; Found: C 58.69, N 14.43, H 4.29, S 8.73. MALDI TOF MS m/z: Calcd: 1012.88 Da. Found: $[M + H]^+$ 1013.58 Da.

2.3.3. Tris {9 (10), 16 (17), 23 (24)-4-(2-diethylaminoethanethiol)-2-(4-carboxyphthalonitrile) phthalocyaninato} tin (IV) acetate (Scheme 1, (SnMCPc (5)))

The synthesis and purification of the low symmetry tin (IV) phthalocyanine complex **(5)** was as outlined for the low symmetry germanium (IV) phthalocyanine complex (**3**), except that excess tin (IV) acetate was employed as a metal salt instead of germanium (IV) chloride. Purification procedure and the amounts of the rest of the reagent were as outlined for (**3**).

Yield: (8.21%). IR (KBr, cm^{-1}): 3439(O–H), 3213(C–H), 2824–2897 (carboxylic acid OH), 1587(C=C), 1326, 1335 (C–O), 1265, 829, 758 (C–S–C), 673, 559 (Sn–O). ^{1}H-NMR (DMSO-d_6): δ, ppm 9.10–9.19 (9H, m, Pc-H), 8.64–8.67 (3H, br, Pc-H), 4.15–4.22 (6H, m, ac-CH_3) 3.81–3.88 (12H, m, S–CH_2), 3.14–3.20 (12H, q, N–CH_2), 2.10–2.16 (18H, dd, CH_3). UV/Vis (DMF) λ_{max} nm (log ε): 330 (3.47), 720 (4.90). Calc. for $C_{51}N_{11}H_{55}O_2S_3Sn$: C 57.52, N 14.43, H 5.51, S 9.01; Found: C 57.74, N 13.55.H 6.39, S 8.52. MALDI TOF MS m/z: Calcd: 1185.71. Found: $[M - 1H]^+$ 1184.80.

2.4. Fluorescence behaviour

The fluorescence quantum yields (Φ_F) were obtained by comparative method [29] using Equation (1)

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

where F and F_{Std} are the areas under the fluorescence curves of the MPc derivatives and the used standard. A and A_{Std} are the absorbances of the sample and reference at the excitation wavelength, and n and n_{Std} are the refractive indices of solvents used for the sample and standard, respectively. ZnPc in DMSO was used as a standard, $\Phi_F = 0.2$ [30]. For each study at least two independent experiments were performed for the quantum yield determinations. Both the sample and the standard were excited at the same relevant wavelength.

3. Results and discussion

3.1. Synthesis and characterization

Scheme 1 shows the synthetic route employed for the mono-functionalized carboxy Ge (**3**), Ti (**4**) and Sn (**5**) phthalocyanines. The most common strategy for synthesizing the low symmetry Pc's is statistical condensation reactions using two different precursors. Thus in this work, phthalonitrile **1** (A) and **2** (B), Scheme 1 were employed to form an expected mixture of compounds with AAAA, AAAB, AABB, ABAB, ABBB, and BBBB structures as previously described in literature [20–23,31,32]. Phthalonitrile **1** was substituted with bulky groups to enhance the solubility of the low symmetry phthalocyanines which improves the separation of the various compounds formed. However the separation of the different structures formed was extremely challenging since it required different solvent ratios with various polarity to elute each compound. In forming the desired mono-functionalized carboxy phthalocyanine (AAAB type), the synthetic method was optimized in statistical terms by adjusting the ratio to 3:1 mol equivalence of the phthalonitrile (**1** and **2**) precursors. Chromatographic separation of the desired product from the other products was then undertaken successfully. The AAAB will also contain structural isomers.

The desired mono-functionalized carboxy complexes were obtained in relatively low yields, with complex (**3**) having a slightly higher yield of 10.44% and complexes **4** and **5** with a yield of 8.15 and 8.21%, respectively. The structural analyses of all the three (complex **3, 4** and **5**) newly synthesized compounds were consistent with the predicted structures as shown in the experimental section. The complexes were successfully characterized with spectroscopic techniques such as the UV–vis, Maldi–TOF MS, IR, proton NMR and by elemental analyses. The formation of phthalocyanine complexes (**3**–**5**) was characterized by the disappearance CN vibration in the 2200–2250 cm^{-1} region. The ^{1}H-NMR spectra of all the complexes showed aromatic Pc ring protons between 8 and 10 ppm. Phthalocyanine aggregation at the concentrations used for the ^{1}H-NMR measurements leads to broadening of the aromatic signals [33], all the proton NMR peaks integrated correctly giving the expected total number of protons for each complex (**3, 4** and **5**), confirming the relative purity of the complexes as shown in the experimental section.

All the other characterization techniques confirmed the structures for each compound as presented in the experimental section.

3.2. Ground state UV–visible spectral characterization

The ground state absorption spectra for complexes **3**–**5** are shown in Fig. 1a. The broadening of the Q band in symmetrical Pcs is usually associated with aggregation [34–36], however for unsymmetrically substituted phthalocynines, loss of symmetry will also result in broadening or splitting of spectra. A clear splitting of the Q band was observed for SnPc derivative (**5**), the TiPc derivative (**4**) did not show splitting but the spectrum was broadened. Less broadening was seen for the GePc derivative (**3**). Fig. 2 shows that as the concentration was increased for complex (**4**), the intensity of the absorption of the Q band maxima also increased and there were no new bands normally blue shifted due to the aggregated species. Same trend was also observed with complex which did not show aggregation in DMF. Beer–Lambert's law was obeyed for all of these complexes in the concentrations ranging from 2×10^{-6} to 14×10^{-6} mol dm^{-3}. These studies confirm that the broadness is not due to aggregation, but most likely due to the low symmetry nature of the complexes especially for complexes **4** and **5**. OTiPc complexes are known to have a slightly square pyramidal structure

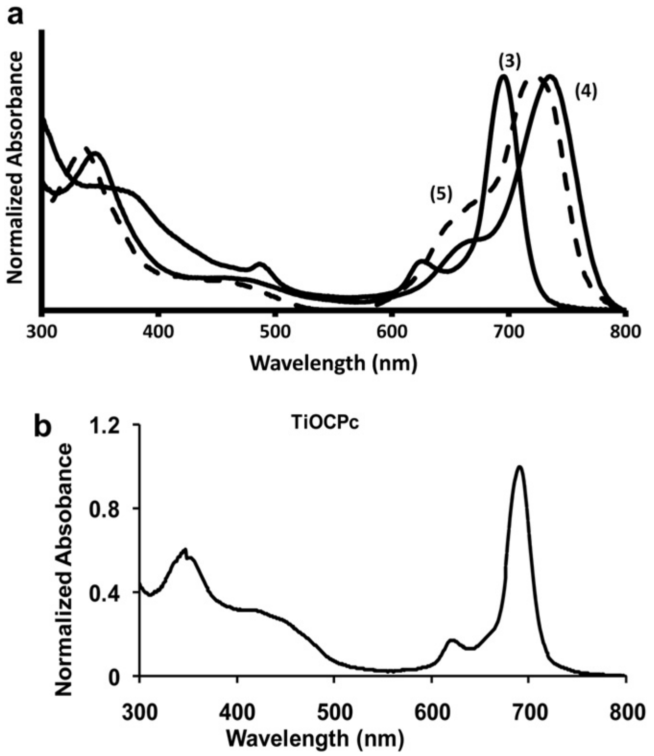


Fig. 1. Ground state electronic absorption spectra of (a) GeMCPc (**3**), TiMCPc (**4**) and SnMCPc (**5**) in DMF and (b) OTiOCPc in pH 10 buffer.

[37], hence do not fit perfectly into the center of the ring. Sn is a large metal hence it also does not fit into the Pc ring. This may explain why both TiPc and SnPc derivatives show more broadening in the spectra due to the effects of both the central metal and the unsymmetric nature of the substituents. The corresponding symmetrical octacarboxy phthalocyanines (MOCPc) did not show the broadening in spectra (see for example Fig. 1b for OTiOCPc) [36,38] observed for complexes **4** and **5**, hence exhibited no aggregation as is typical of MOCPc complexes. These complexes are not aggregated even in aqueous media where in general phthalocyanines are aggregated. Phthalocyanines containing diethylaminoethanethiol substituents also show a narrow Q band typical of phthalocyanines [39].

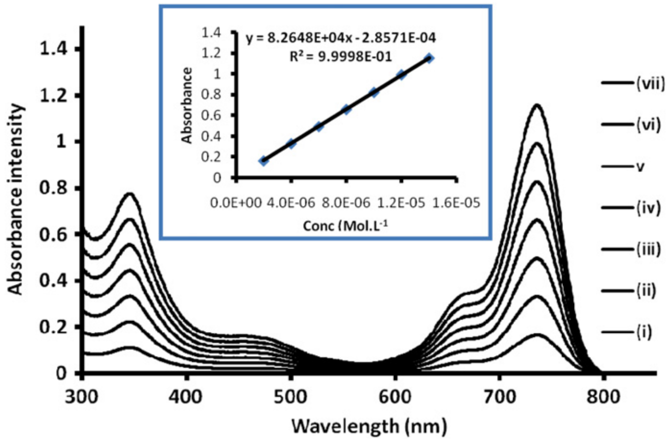


Fig. 2. Ground state electronic absorption spectra of TiMCPc at various concentrations: (i) 2×10^{-6}, (ii) 4×10^{-6}, (iii) 6×10^{-6}, (iv) 8×10^{-6}, (v) 10×10^{-6}, (vi) 12×10^{-6} and 14×10^{-6} mol dm^{-3} in DMF.

The Q band absorption maxima in DMF (Fig. 1a) of the various monocarboxy Pc's were observed at completely different wavelengths. As shown in Table 1, complex **4** (Q band at 734 nm) and complex **5** (Q band at 720 nm) were red shifted relative to complex **3** (Q band at 695 nm). The shift in spectra has been explained in terms of conformational distortion caused by the stress of the substituents in MPc complexes [40]. And have also been attributed to coordination of certain ligands to the central metals leading to enlargement of the π-system of the Pc [37,41]. However certain central metals such as Ti and Sn are known to result in red shift of the Q band [42]. In this work, the red shifting of the Q band of these low symmetry phthalocyanine complexes was strongly influenced by the electron donating nature of the diethylaminoethanethiol substituents.

Charge transfer bands were observed for all the three complexes in a region from 400 to 500 nm, with complex (**3**) showing the most prominent charge transfer band compared to complex (**4** and **5**) in DMF.

3.3. Fluorescence spectra and properties

Shown in Fig. 3, are the absorption, fluorescence excitation and emission spectra of the complexes **3**–**5** in DMF. The fluorescence excitation of GeMCPc (complex **3**, Fig. 3a) was observed as mirror image of both the absorption and the excitation spectra, and hence the excitation was similar to the absorption spectra typical of MPcs. However there was a disagreement of the absorption, fluorescence excitation and emission of complexes **4** and **5** (Fig. 3b and c). The deviation of the spectra could be due to size of the central metal in particular for SnMCPc (**4**) which showed a more pronounced splitting upon excitation, due to loss of symmetry. The loss of symmetry or disagreement of the spectral properties has been documented before (i.e on InPc [43] and SnPc [44] derivatives) and it was found to be due to the fact that Sn and In are metals with large atomic numbers that can be easily displaced from the core of the Pc ring on excitation, hence resulting into a loss of symmetry.

For TiMCPc, the excitation spectrum was red shifted and narrower compared to absorption spectrum, and the emission spectrum was a mirror image of the excitation spectrum, Fig. 3b. The red shift and narrowing in the excitation spectrum compared to absorption spectrum for complex **4** suggests aggregation with only the monomer fluorescing. This confirms that in Fig. 1, the observed broadening in the absorption spectrum includes contribution from the aggregate even though Beer's law was obeyed in the concentration range of Fig. 2. Stokes shifts for complexes **4** and **5** were larger than is typical of MPc complexes [45,46]. For symmetrically substituted OTiOCPc, the absorption and excitation spectra were similar and mirror images of emission spectrum due to lack of aggregation [36].

Fig. 4 shows the time-resolved florescence decay curve for SnMCPc (**5**) in DMF, indicaticating a mono-exponential decay. A mono-exponential decay was observed for all the complexes (**3, 4** and **5**) in DMF suggesting only one fluorescing species present in each solution. The fluorescence lifetimes (Table 1) were obtained

Table 1
Fluorescence and UV–visible spectral data for $(OH)_2$GeMCPc, $(ac)_2$SnMCPc and OTiMCPc in DMF.

Compound	Q-band wavelength (nm)	Emission wavelength (nm)	Fluorescence Life time (τ_F) (ns)	Fluorescence quantum yield (Φ_F)
$(OH)_2$GeMCPc (**3**)	695	700	1.61	0.09
OTiMCPc (**4**)	734	765	1.84	0.11
$(ac)_2$SnMCPc (**5**)	720	748	2.35	0.14

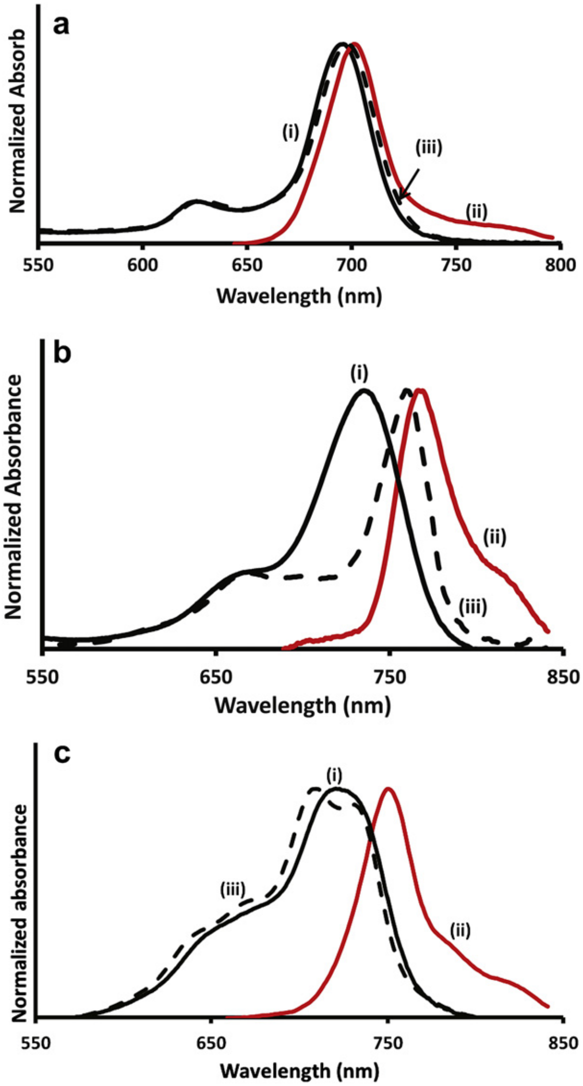


Fig. 3. UV–vis absorption (i), fluorescence emission (ii) and excitation (ii) spectra of (a) GeMCPc (**3**), (b) TiMCPc (**4**) and (c) SnMCPc (**5**) in DMF.

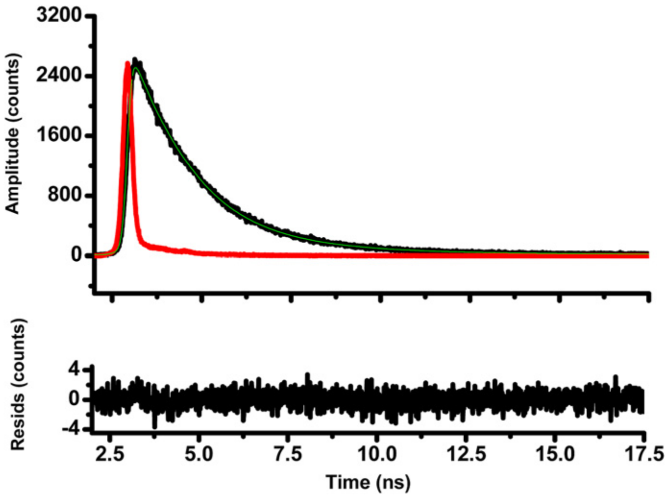


Fig. 4. Photoluminescence decay curve of complex SnMCPc (**5**) in DMF.

from the photoluminescence decay curves and all the lifetimes showed an increase with the increase in fluorescence quantum yield. Complex (**3**) showed the lowest fluorescence quantum yield (Φ_F) and lifetime of 0.09 and 1.61 ns in DMF, followed by complex (**4**) with 0.11 fluorescence quantum yield and a life time of 1.84 ns and complex **5** showed the highest yield and lifetime of 0.14 and 2.35 ns respectively. The fluorescence quantum yield values were within a range reported for MPcs in general [45,46]. The Φ_F value for symmetrically substituted $(OH)_2GeOCPc$ of 0.19 in DMSO has been reported [38]. In aqueous media a $\Phi_F = 0.07$ for OTiOCPc was reported [36] with a fluorescence lifetimes of 1.59 ns. Thus in terms of the fluorescence parameters, the unsymmetrically substituted complexes reported in this work do not differ much from their symmetrical counterparts.

4. Conclusions

The synthesis and characterization of novel low symmetrically substituted carboxy phthalocyanines was successfully achieved. Spectral changes upon excitation were observed for complex **4** and **5** due to their sizes and the nature of the axial ligands. The fluorescence behaviour of the complexes was successful investigated, and an increase in fluorescence lifetimes was observed with increase in fluorescence quantum yield. The trend of the fluorescence behaviour (lifetimes and quantum yields) of all the compounds can be summarized in the form of an increasing order as follows; $(OH)_2GeMCPc < OTiMCPc < (ac)_2SnMCPc$ respectively. The presence of one carboxy group makes these molecules ideal for coordination to biological molecules and quantum dots since a more defined coordination is achieved. Thus the use of these molecules in applications such as photodynamic therapy when coordinated to cancer specific molecules will be explored in the future in comparison with their symmetrically substituted counterparts.

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