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# The synthesis, spectroscopic and thermal properties of phenoxycyclotriphosphazenyl-substituted phthalocyanines

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**Abstract**

Novel phthalocyanines with four hexa(phenoxy)cyclotriphosphazene groups, appended through ether linkages were synthesized. Two hexa (phenoxy)cyclotriphosphazene derivatives, a substituted phthalonitrile derivative and metal-free, Ni and Zn phthalocyanines were characterized by elemental analysis, mass spectrometry, IR, $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectroscopies. The synthesis and spectroscopic properties of hexa(phenoxy)cyclotriphosphazenyl-substituted metal-free, Ni and Zn phthalocyanines are reported for the first time; their thermal stability, electronic absorption and fluorescence spectral properties are reported. The phthalocyanines displayed monomeric behaviour in $CHCl_3$; fluorescence quantum yields and lifetimes were determined using DMSO solutions of the compounds.


*Keywords:* Phthalocyanine; Cyclotriphosphazene; Thermal stability; Photophysics; Fluorescence; NMR

## 1. Introduction

Phthalocyanines, which were first developed as industrial pigments, have been actively explored in various technological applications [1] such as optical recording photovoltaics, photocopying, gas sensing, liquid crystal and photodynamic therapy. The ring substitution improves phthalocyanines' useful characteristics and frequently enhances their solubility. Ring substituted phthalocyanine derivatives may be useful for various applications such as chemical sensors [2], liquid crystals [3], semiconductors [2b], non-linear optics [4] and photodynamic therapy (PDT) [5]. Their photophysical and photochemical properties can be fine-tuned by changing the metal and/or nature of substituents [1,6]. Tetrasubstituted phthalocyanines are usually more soluble than the corresponding octa-substituted phthalocyanines due to the formation of constitutional isomers and the high dipole moment that results from the unsymmetrical arrangement of the substituents at the periphery [7,8]. According to their substituent positions, two types of tetrasubstituted macrocycles which show significant differences in their chemical and physical behaviour can be distinguished. Substitution at the more sterically crowded α (non-peripheral) position causes reduced aggregation tendencies more than substitution at β (peripheral) position [9].

Cyclotriphosphazenes, $(N{=}PR_2)_n$, are an important class of inorganic heterocyclic ring systems and their physical and chemical properties can be tailored by the choice of appropriate substituted (R) groups on phosphorus atoms [10]. They are usually prepared by nucleophilic substitution reactions of alkoxides, aryloxides, or amines on halocyclotriphosphazenes or high polymers as side groups [11]. The design of materials containing cyclotriphosphazenyl groups has attracted attention because of their special properties such as thermal stability, catalytic properties, electrical conductivity, liquid crystal and biomedical activity [12]. The thermal behaviour and decomposition of a variety of polyphosphazenes have been studied in some detail [13–15]. At elevated temperatures, the thermal

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response depends on the types of side groups present. The thermal stability and flame resistance of polyphosphazenes that bear aryloxy side groups are especially well documented, and aryloxyphosphazene polymers have been developed commercially as foams for electrical, heat, and sound insulation [16]. Cyclotriphosphazenes have also been investigated as flame retardant additives to organic polymers. Compositions that contain cyclotriphosphazenes or cyclotetraphosphazenes with commercial polymers are relatively easy to prepare, and flame retardant polyaramids [17], polyesters [18], rayon [19], and various other polymers [20] have been produced in this way. One of the reasons cyclotriphosphazenes has excellent flame retardant properties is the presence of phosphorus and nitrogen in the backbone. Recently, several reports have also appeared concerning the stereoisomerism of cyclotriphosphazene derivatives [21]. There are a few studies about the fluorescence behaviour of the cyclotriphosphazene derivatives [22].

According to our best knowledge, there is just one report that synthesis of polyphosphazene being linked to phthalocyanines as side groups [23]. The nature of substituents can strongly influence essential parameters of a phthalocyanine, such as its solubility, thermal stability, electronic absorption and fluorescence spectral properties. Therefore, we want to investigate the effects of four cyclotriphosphazenyl-rings substituted on peripheral position of a phthalocyanine macrocycle. In this work, we report the molecular design, synthesis of the metal-free, Ni and Zn phthalocyanines **6**–**8** with four hexa(phenoxy)cyclotriphosphazene groups (Fig. 1). The effects of ring substitution and metal atom on the spectroscopic and aggregation properties of phthalocyanine derivatives **6**–**8** in different solvents (toluene, dichloromethane, chloroform, THF, and DMSO) were studied. Fluorescence quantum yields and lifetimes of these compounds were also investigated in DMSO.

## 2. Results and discussion

### 2.1. Synthesis and characterization

Generally, substituted phthalocyanines are prepared by cyclotetramerization of substituted phthalonitriles or 1,3-diimino-1*H*-isoindoles. 2(3),9(10),16(17),23(24)-Tetrasubstituted phthalocyanines can be synthesized from 4-substituted phthalonitriles while 1(4),8(11),15(18),22(25)-tetrasubstituted phthalocyanines are obtained from 3-substituted analogues [24]. In both cases, a mixture of four possible structural isomers is obtained. The four probable isomers can be designed by their molecular symmetry as $C_{4h}$, $C_{2v}$, $C_s$ and $D_{2h}$. The 2(3)-substituted compounds always occur in the expected statistical mixture of 12.5% $C_{4h}$-, 25% $C_{2v}$-, 50% $C_s$- and 12.5% $D_{2h}$-isomer. But for the 1(4)-substituted ones the composition depends on the central metal ion and the structure of the peripheral substituent [25]. We expect that synthesized phthalocyanine compounds were prepared as a statistical mixture of four regioisomers due to the various possible positions of the cyclotriphosphazenyl side chains relative to one another. No attempt was made to separate the isomers of complexes **6**–**8**.

The synthetic route of the compounds presented in this work is shown in Scheme 1. Compound **1** was synthesized [26] by the reaction of phenol with hexachlorocyclotriphosphazene. Phenoxy substituted group was selected because of its solubility effect on a cyclotriphosphazene ring and easily

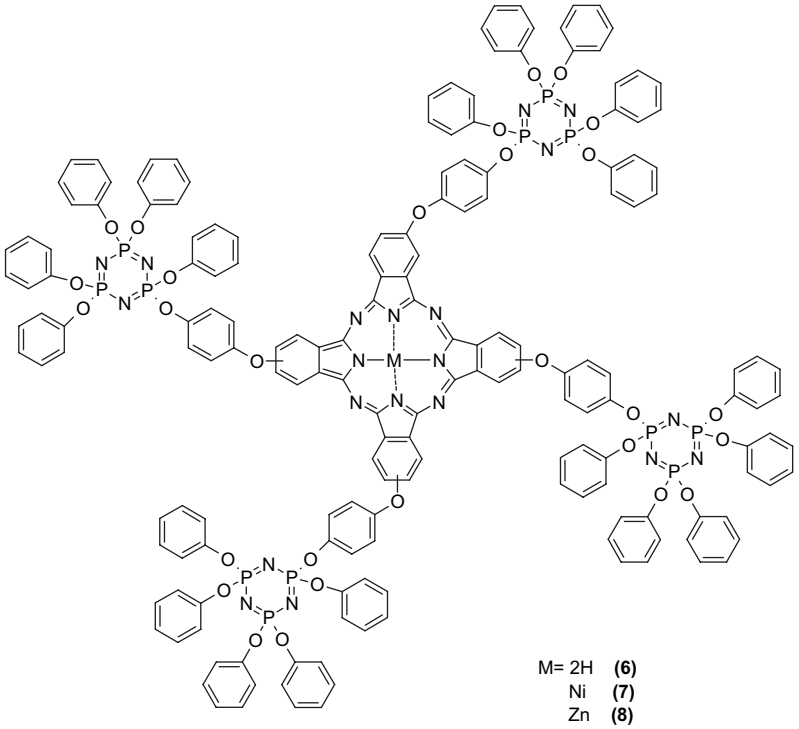
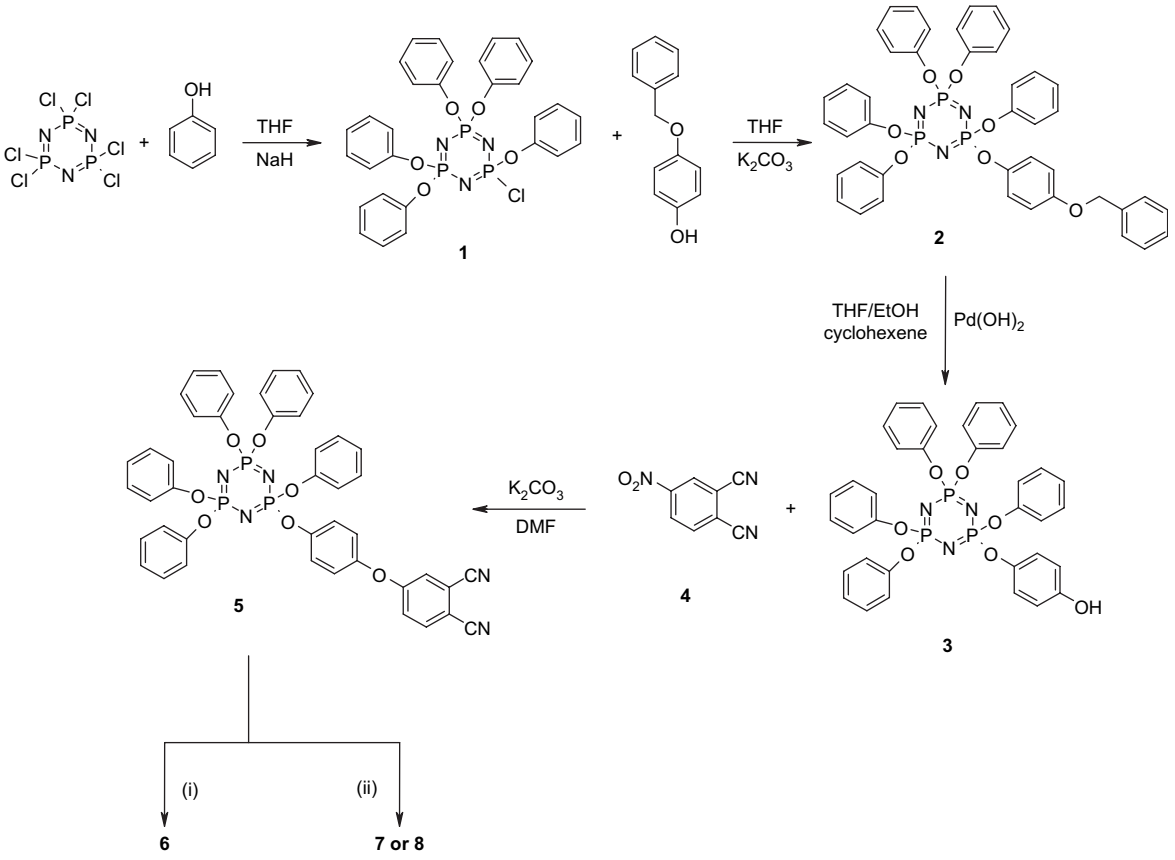



Fig. 1. Structure of phthalocyanine derivatives **6**, **7** and **8**.




Scheme 1. Chemical structure and synthetic pathway of compounds **1**–**8**. (i) 2-(Dimethylamino)ethanol (DMAE), 6 h for $H_2Pc$, (ii) Metal salt [$NiCl_2$ or $Zn(AcO)_2$], DBU, 1-pentanol, 7 h for MPcs.

allows the preparation of 1,1,3,3,5-pentaphenoxy-5-chlorocyclotriphosphazatriene (**1**). Compound **1** was reacted with 4-benzyloxyphenol in the presence of $K_2CO_3$ in THF to obtain compound **2**. The 4-benzyloxyphenoxy unit of compound **2** was converted to 4-hydroxyphenoxy group with cyclohexene in a mixture of THF/ethanol, in the presence of $Pd(OH)_2$ as a catalyst [27] to give compound **3**. Compound **5** was obtained from a nucleophilic displacement reaction of **3** on 4-nitro phthalonitrile (**4**) [28–30]. The reaction was carried out in dimethyl formamide (DMF) at 50 °C with potassium carbonate which was used as the base.

The preparation of phthalocyanine derivatives from the aromatic nitriles occurs under different reaction conditions [1]. A convenient high-yield synthesis is required for the further considerations. For various substituted dinitriles, the reaction in the presence of strong non-nucleophilic bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) either in 1-pentanol or in bulk is most efficient in comparison to other methods [31]. In addition, these reactions are easy to perform, work under relatively mild conditions and yield pure phthalocyanines. Therefore, the metal phthalocyaninates **7** and **8** were obtained by using the anhydrous metal salts [$NiCl_2$ or $Zn(AcO)_2$] in 1-pentanol in the presence of a strong organic base such as DBU at reflux temperature (Scheme 1). Also, the tetrasubstituted metal-free phthalocyanine derivative **6** was accomplished by the cyclotetramerization of the mono-cyclotriphosphazenyl-substituted phthalonitrile derivative **5** in 2-(dimethylamino)-ethanol at reflux temperature (Scheme 1). Purification was achieved by successive preparative thin layer chromatography.

All new compounds **2**, **3** and **5**–**8** were characterized by IR, $^1H$, $^{13}C$ and $^{31}P$ NMR, mass spectrometry and elemental analysis. All the results were consistent with the predicted structures as shown in Section 3. The IR spectra of all these compounds feature peaks at around 1200 $cm^{-1}$ (br) (P═N) and 960 $cm^{-1}$ (P–O) for a phosphazene ring as expected [32]. The aliphatic C–O stretching peak of compound **2** was observed at 1103 $cm^{-1}$ and this peak disappears after hydrolysis. Also the sharp peak for the C≡N vibrations of phthalonitrile **5** at around 2230 $cm^{-1}$ disappeared after conversion, indicative of phthalocyanine formation. The IR spectra of phthalocyanine derivatives **6**–**8** are very similar except for the NH band at 3300 $cm^{-1}$ which was observed in the spectrum of the metal-free phthalocyanine **6**. These protons are also very well characterized by the $^1H$ NMR which shows a peak at $\delta = -3.22$ ppm as a result of the magnetic anisotropy created by the 18 π-electron system of phthalocyanine ring. The NH signal disappears by deuterium exchange. The $^1H$ NMR spectra of tetrasubstituted phthalocyanine derivatives **6**–**8** show complex patterns owing to the mixed isomer character of these compounds. The complexes were found to be pure by $^1H$ NMR spectra with all the substituents and ring

protons observed in their respective regions. The $^{1}$H NMR spectra of metal-free **6** and metallated **7** and **8** phthalocyanines are almost identical, the only difference being the appearance of the broad NH protons of **6**. The resonances belonging to ring protons were observed in the range 7.43–8.79 ppm for **6**, 7.41–8.82 ppm for **7** and 7.60–8.80 ppm for **8** as three different multiplets, integrating for a total of 12 protons for both peripheral and non-peripheral protons. The phenoxy ring protons were observed in the range 6.86–7.16 ppm for **6**, 6.82–7.11 ppm for **7** and 6.85–7.24 ppm for **8**, integrating for a total of 116 protons for each as expected. Although the presence of isomers as well as phthalocyanine aggregation at the concentrations used for the NMR measurements may lead to broadening of the aromatic signals [33], the observed spectra of all the complexes were relatively well resolved.

The high solubility of the phthalocyanines has enabled us to obtain $^{13}$C NMR spectra. The peaks in the aromatic region were assigned using a conventional additivity law. The attached proton test (APT) indicates the presence of the monoprotonated carbons in the aromatic region for dinitrile derivative **5**. The results were in agreement with those previously found for tetrasubstituted phthalocyanines [30a]. The $^{13}$C NMR spectrum of **5** shows 30 different signals for aromatic carbons between 161.88 and 109.17 ppm, two arising from C–C≡N (115.24 and 115.69 ppm) as expected. After conversion of the dinitrile compounds into phthalocyanine derivatives, the characteristic feature of the $^{13}$C NMR spectra of the phthalocyanine derivatives is the disappearance of the chemical shifts of nitrile carbons' (C≡N) signals and the appearance of the new resonance related to the phthalocyanine ring carbons (N–*C*=N). The resonances belonging to phthalocyanine ring carbons (N–*C*=N) were observed as follows: 171.10 ppm for **6**, 171.21 ppm for **7** and 171.24 ppm for **8**. The chemical shifts of the phenyl carbons on cyclotriposphazene group are very close to each other. Therefore in $^{13}$C NMR spectra of phthalocyanine derivatives **6**–**8**, less signals were observed for these carbons than expected.

To obtain good resolved $^{31}$P NMR spectra a diluted solution in $CDCl_3$ (5 mg per 0.7 ml) was used. However, 2(3)-tetrasubstituted phthalocyanines and 3(4)-tetrasubstituted naphthalocyanines exhibit broad signals in the $^{1}$H NMR spectra [34] and also $^{31}$P NMR, as known in general for many substituted phthalocyanines this not only causes difficulties for the characterization of the phthalocyanines but also prevents the determination of the symmetry of these molecules. The broad signals and their high field shift in the $^{1}$H and $^{31}$P NMR spectra could be due to aggregation of the molecules in solution and very short relaxation times $T_1$ and $T_2$ for phthalo- and naphthalocyanines. This problem has been solved using very dilute solutions of phthalocyanines for $^{31}$P NMR measurements.

In particular, most $^{31}$P NMR spectra were analyzed as $AB_2$ spin systems and the $^{31}$P NMR chemical shifts and $^{2}J_{PNP}$ of compounds **1**–**3** and **5**–**8** are summarized in Table 1. The proton-decoupled $^{31}$P NMR spectrum of compound **1** is shown as the expected $A_2X$ spin system. Signal assignment is straightforward with the triplet ($^{1}$P) at ca. 23 ppm belonging to >P(PhO)(Cl) and the doublet (2P) at ca. 7.90 ppm to >P(PhO)$_2$. Compounds **2**, **3** and **5**–**8** have similar spectra, though there are small differences in chemical shifts and geminal coupling constants. As an example, the proton-decoupled $^{31}$P NMR spectrum of compound **6** is shown as the expected typical $AB_2$ pattern in Fig. 2. The resonances belonging to phosphorous atoms were observed at ca. 9.9 ppm for >P(PhO)$_2$ and at ca. 10.26 ppm for >(OPh)$_2$OPc. The difference of magnitude of the $^{2}J_{PNP}$ is small for compounds **2**, **3** and **5**–**8** and especially the phthalocyanine derivatives **6**–**8** have very similar coupling constants as 87.5, 87.9 and 87.8 Hz, respectively.

Table 1
$^{31}$P NMR parameters of compounds **1**–**3** and **5**–**8**[a]

| Compounds | Chemical shifts (ppm) | | | $^{2}J_{PNP}$ (Hz) |
|---|---|---|---|---|
| | >P(PhO)$_2$ | >P(PhO)(X) | X | |
| **1**[b] | 7.88 | 23.17 | Cl | 82.7 |
| **2** | 9.89 | 10.40 | OPhOCH$_2$Ph | 89.2 |
| **3** | 9.84 | 10.02 | OPhOH | 86.8 |
| **5** | 9.62 | 10.21 | OPhOPh(CN)$_2$ | 89.9 |
| **6** | 9.85 | 10.26 | OPhOPc(2H) | 87.5 |
| **7** | 9.98 | 10.35 | OPhOPc(Ni) | 87.9 |
| **8** | 9.73 | 10.11 | OPhOPc(Zn) | 87.8 |

[a] $^{31}$P NMR (202.38 MHz) measurements in $CDCl_3$ solutions at 293 K. Most spectra were analyzed as $AB_2$ spin systems.
[b] Compound **1** was analyzed as $A_2X$ spin system.

In addition to the elemental analysis results, the mass spectral data for the newly synthesized dinitrile derivative **5** and tetrasubstituted phthalocyanines **6**–**8** were consistent with the assigned formulations. The mass spectra of these compounds were obtained by Electron Spray Ionization (ESI) technique. The molecular ion peaks showing parent ions at *m*/*z* 836, 3348, 3404 and 3411 have been found for **5**, **6**, **7** and **8**, respectively (see Section 3).

Low-molecular-weight phthalocyanines exhibit excellent thermal stability. Especially, substituted phthalocyanines decompose without sublimation. According to thermal analyses, temperatures of 450–600 °C are the limit of thermal treatment under inert gas [35,36]. The thermal properties of the cyclotriphosphazenyl-substituted phthalocyanine derivatives **6**–**8** and

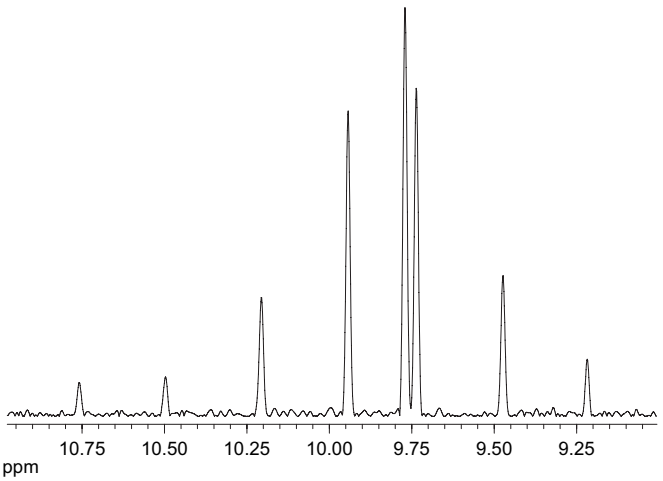



Fig. 2. Proton-decoupled $^{31}$P NMR spectrum of compound **6** in $CDCl_3$ solution.

cyclotriposphazene derivatives **2** and **3** were investigated by thermogravimetric analysis. The initial and main decomposition temperatures are given in Table 2. Generally, initial decomposition of the phthalocyanine compounds corresponding to the substituted group (crown ether [37], alkyl chains [38], alkylsulfonyl [29], sulfonyl chains [39] and azamacrocycle [40]) occurs at ca. 200–350 °C and the extensive decomposition appears at temperature range between 320 and 450 °C. Phthalocyanine derivatives **6–8** substituted with four hexa(phenoxy)cyclotriphosphazene groups, showed a weight loss corresponding to moisture at 100–140 °C. The initial and extensive decompositions occur at ca. 420–440 °C and 530–550 °C. These temperatures are higher than those found for different organic substituted groups containing phthalocyanine complexes [29,37–40]. Thus, the substitution of phthalocyanine core with cyclotriphosphazenyl ring increases significantly the thermal stability of the present phthalocyanine compounds **6–8**, according to other phthalocyanines substituted with different organic groups.

### 2.2. Ground state electronic absorption spectra

The ground state electronic spectra of the complexes showed characteristic absorption in the Q band region at 702 and 666 nm for **6**, 673 nm for **7** and 680 nm for **8** in $CHCl_3$, Table 3. The B band region was observed around 330–355 nm in $CHCl_3$ (Fig. 3a). The spectra showed monomeric behaviour evidenced by a single (narrow) Q band, typical of metallated phthalocyanine complexes for **7** and **8** in $CHCl_3$ which depict the monomeric nature of these complexes in this solvent. The metal-free phthalocyanine complex **6** gives a doublet (narrow) Q band as a result of the $D_{2h}$ symmetry [41]. Complex **7** showed bands around 650 nm due to the aggregation while complex **8** did not show aggregation in DMSO. Complex **6** showed a small broadness around 650 nm in DMSO suggesting minimal aggregation (Fig. 3b). The results of the UV–vis measurements from nickel (**7**) and zinc (**8**) phthalocyanines are compared with each other and zinc phthalocyanine **8** is found that it has 7 nm higher in absorbance value than the corresponding nickel phthalocyanine **7** in $CHCl_3$ (Fig. 3a). The B-bands are broad due to the superimposition of the $B_1$ and $B_2$ bands in the 330–355 nm region.

Aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes. It is dependent on the concentration, nature of the solvent, nature of the substituents, complexed metal ions and temperature [42]. In the aggregated state the electronic structure of the complexed phthalocyanine rings is perturbed resulting in alternation of the ground and excited state electronic structures [43]. In this study, the aggregation behaviour of the phthalocyanines (**6–8**) is investigated in different solvents (chloroform, dichloromethane, DMF, DMSO, THF, and toluene) (Table 3). While complexes **6** and **7** did not showed aggregation in chloroform, DCM, THF and toluene, they show aggregation in DMF and DMSO (Fig. 4 for complex **7** in chloroform, DMF and DMSO) as judged by the broadening of the Q band and peak around 650 nm insignificant for complex **6**. In general, DMSO and DMF are strong

Table 2
Thermal properties of compounds **2**, **3**, and **6–8**

| Compound | Initial dec. temp (°C) | Main dec. temp (°C) |
|---|---|---|
| **2** | 370 | 424 |
| **3** | 375 | 518 |
| **6** | 438 | 528 |
| **7** | 436 | 545 |
| **8** | 421 | 535 |

Table 3
UV–vis spectral data of phthalocyanines **6**, **7** and **8** in toluene, DCM, THF, $CHCl_3$ and DMSO

| Compounds | Solvent | Q band (nm) | B band (nm) | N band (nm) |
|---|---|---|---|---|
| **6** | Toluene | 702, 666 | 342 | – |
| | DCM | 703, 664 | 342 | – |
| | THF | 699, 664 | 341 | – |
| | $CHCl_3$ | 702, 666 | 342 | 270 |
| | DMSO | 699, 669 | 340 | – |
| **7** | Toluene | 674 | 335 | – |
| | DCM | 672 | 331 | 286 |
| | THF | 671 | 332 | – |
| | $CHCl_3$ | 673 | 332 | 284 |
| | DMSO | 673 | 333 | – |
| **8** | Toluene | 681 | 349 | – |
| | DCM | 681 | 345 | 290 |
| | THF | 675 | 348 | – |
| | $CHCl_3$ | 680 | 349 | 289 |
| | DMSO | 680 | 354 | – |

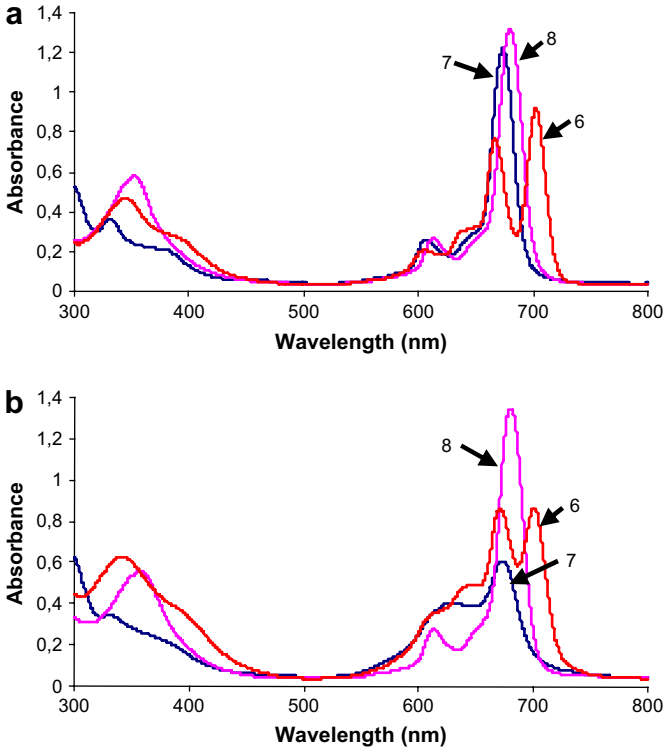



Fig. 3. Absorption spectra of the compounds **6**, **7** and **8** (a) in $CHCl_3$, (b) in DMSO. Concentration = $4 \times 10^{-6}$ mol dm$^{-3}$.

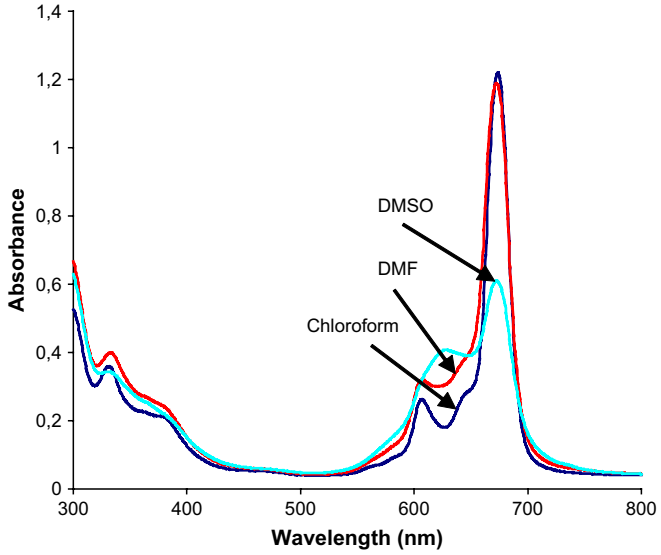



Fig. 4. Absorption spectra of the compound **7** in different solvents. Concentrations = $4 \times 10^{-6}$ mol dm$^{-3}$.

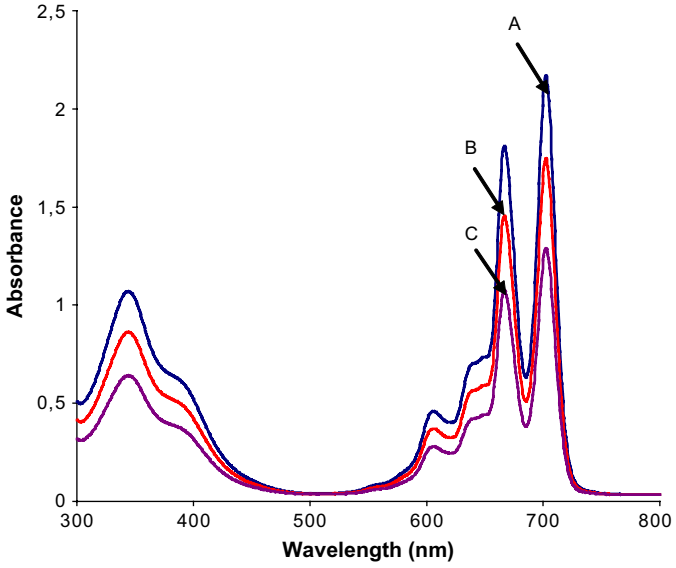



Fig. 6. Absorption spectra of **6** in $CHCl_3$ at different concentrations: $14 \times 10^{-6}$ (A), $10 \times 10^{-6}$ (B), $6 \times 10^{-6}$ mol dm$^{-3}$ (C).

coordinating solvents since they are known as the aggregation preventing solvents. However, complexes **6** and **7** showed aggregation in these solvents and the same effect has been observed in the literature [44]. The addition of Triton X-100 (a surfactant) to the DMSO solutions of the substituted Ni(II) phthalocyanine **7** resulted in reduction of aggregation, as evident by the sharp increase in the intensity of the monomer peak (673 nm) and a decrease in the intensity of the dimer peak (622 nm) (Fig. 5) [45]. However, the disappearance of the peak due to the aggregate is not complete as judged by the persistence of the peak at 622 nm even after addition of Triton X-100. Complex **8** did not show aggregation in all solvents studied as judged by a single narrow band of the Q band.

The aggregation behaviour of the phthalocyanines **6**, **7** and **8** was also investigated at different concentrations in $CHCl_3$ (Fig. 6 for complex **6**). In $CHCl_3$, as the concentration was increased, the intensity of absorption of the Q band also increased and there were no new bands (normally blue shifted) due to the aggregated species for all phthalocyanines (**6**, **7** and **8**) (Fig. 6 for complex **6**). The phthalocyanine derivatives **6**, **7** and **8** did not show aggregation in $CHCl_3$ at different concentrations. When the concentrations change from $1.4 \times 10^{-5}$ to $6 \times 10^{-6}$ mol dm$^{-3}$ all of these compounds obeyed Beer–Lambert law.

### 2.3. Fluorescence spectra

Fig. 7 shows the fluorescence emission spectra for compounds **6**, **7** and **8**. While the phthalocyanines **6** and **8** are fluorescent, the phthalocyanine **7** does not show fluorescence at this excitation wavelength (645 nm) [46]. The phthalocyanines **6** and **8** showed similar fluorescence behaviour in $CHCl_3$. In $CHCl_3$, emission peaks were observed at: 708 nm (**6**) and 693 nm (**8**) (Table 4). The excitation spectra were similar to absorption spectra and both were mirror images of the fluorescence spectra in $CHCl_3$ [47] (Fig. 8). The proximity of the wavelength of each component of the Q band absorption to the Q band maxima of the excitation spectra for phthalocyanines **6** and **8** suggests that the nuclear configurations of the

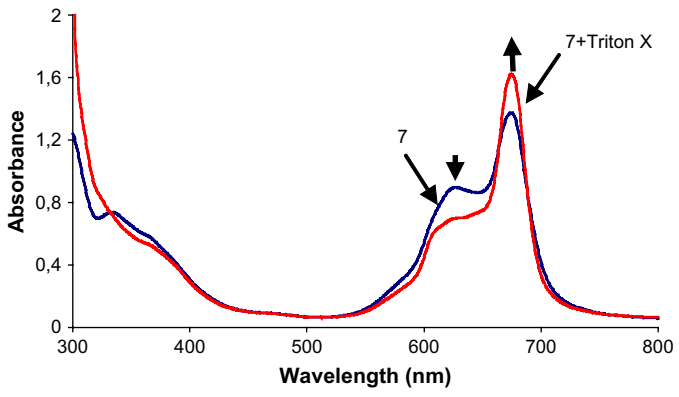



Fig. 5. Absorption spectral changes for phthalocyanine **7** observed on addition of Triton X-100 in DMSO.

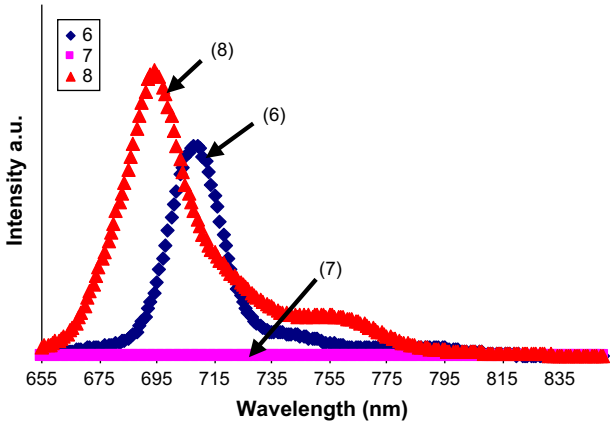



Fig. 7. Emission spectra of **6**, **7** and **8** in $CHCl_3$. Concentration = $4 \times 10^{-6}$ mol dm$^{-3}$. Excitation wavelength = 645 nm.

Table 4
Absorption, excitation and emission spectral data for phthalocyanines **6**, **7** and **8** in $CHCl_3$

| Compound | Q band, $\lambda_{max}$ (nm) | log $\varepsilon$ | Excitation $\lambda_{Ex}$ (nm) | Emission $\lambda_{Em}$ (nm) | Stokes shift $\Delta_{Stokes}$ (nm) |
|---|---|---|---|---|---|
| **6** | 702, 666 | 5.04, 4.97 | 704, 667 | 708 | 6 |
| **7** | 673 | 5.14 | – | – | – |
| **8** | 680 | 4.99 | 680 | 693 | 13 |

ground and excited states are similar and not affected by excitation in $CHCl_3$. The observed Stokes shifts (Table 4) were typical of phthalocyanine complexes in $CHCl_3$.

### 2.4. Fluorescence quantum yields and lifetimes

Fluorescence quantum yield ($\Phi_F$) is the fraction of molecules in the excited singlet state that are deactivated radiatively. Factors like temperature, molecular structure and solvent parameters (polarity, viscosity, refractive index and the presence of heavy atoms in the solvent molecule) are widely known to influence the values of $\Phi_F$.

The fluorescence quantum yields ($\Phi_F$) of **6** and **8** were similar and typical of MPc complexes, Table 5. The $\Phi_F$ values of **6** and **8** were lower than unsubstituted ZnPc in DMSO. When $\Phi_F$ values of **6** and **8** were compared, the substituted ZnPc complex **8** was larger than substituted unmetallated phthalocyanine **6** in DMSO due to the minimal aggregation in this solvent. Aggregation reduces the likelihood of radiative deactivation (fluorescence) through dissipation of energy by the aggregates.

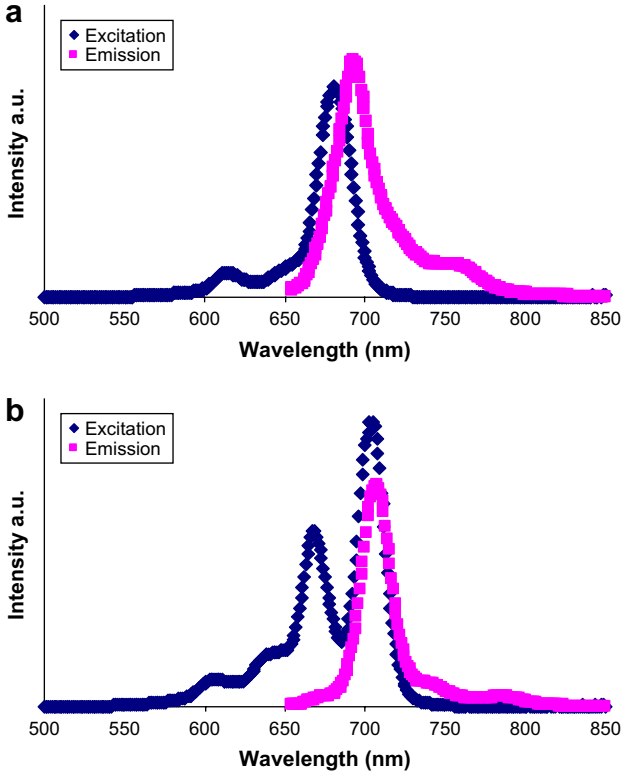



Fig. 8. Fluorescence emission and excitation spectra of the compounds **8** (a) and **6** (b) in $CHCl_3$. Excitation wavelength = 645 nm.

Table 5
Fluorescence data for phthalocyanines **6** and **8** and unsubstituted ZnPc as reference in DMSO

| Compound | Fluorescence quantum yield ($\Phi_F$) | Fluorescence lifetime $\tau_F$ (ns) | Natural radiative lifetime $\tau_0$ (ns) | $k_F$[a] ($s^{-1}$) ($\times 10^7$) |
|---|---|---|---|---|
| **6** | 0.14 | 1.36 | 9.59 | 10.42 |
| **8** | 0.17 | 2.17 | 12.38 | 8.07 |
| ZnPc | 0.18 | 1.22 | 6.80 | 14.71 |

[a] $k_F$ is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$.

Fluorescence lifetimes ($\tau_F$) were calculated by using the Strickler–Berg equation [48] which gave a good correlation between experimentally and theoretically determined lifetimes. $\tau_F$ values of **6** and **8** are longer when compared with unsubstituted zinc phthalocyanine in DMSO suggesting the substitution effect. $\tau_F$ value of substituted zinc phthalocyanine complex **8** is longer when compared with substituted unmetalled phthalocyanine **6** in DMSO. The values of natural radiative lifetime ($\tau_0$) for substituted complexes **6** and **8** are longer than unsubstituted zinc phthalocyanine complex in DMSO. $\tau_0$ value is longer for substituted zinc phthalocyanine complex **8** as compared with substituted unmetalled phthalocyanine **6** in DMSO. Values of the fluorescence rate constant ($k_F$) for **6** and **8** are shorter than that of unsubstituted zinc phthalocyanine complex in DMSO. $\tau_F$ value of substituted zinc phthalocyanine complex **8** is shorter compared with substituted $H_2Pc$ **6** in DMSO.

## 3. Experimental

### 3.1. Materials

Hexachlorocyclotriphosphazene (Otsuka Chemical Co. Ltd) was purified by fractional crystallization from *n*-hexane. The deuterated solvent ($CDCl_3$) for NMR spectroscopy and the following chemicals were obtained from Merck; cyclohexene, ethanol, phenol, $Pd(OH)_2$, $K_2CO_3$, NaH, acetone, triethylamine, silica gel 60, tetrahydrofuran, DMSO, 2-dimethylamino-ethanol (DMAE), nickel(II) chloride, zinc(II) acetate, DBU, 1-pentanol and 4-(benzyloxy)-phenol (>99%). All other reagents and solvents were reagent grade quality and were obtained from commercial suppliers.

### 3.2. Equipment

Elemental analyses were obtained from Thermo Finnigan Flash. UV–vis spectra were recorded with a Shimadzu 2001 UV Pc spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. Infrared spectra were recorded on a Bio-Rad FTS 175C FT-IR spectrophotometer using KBr pellets. Mass analyses were recorded on an HP G1800A GC–MS spectrometer using the HP-5 column by APCI (Atmospheric Pressure Chemical Ionization) technique and on a Thermo LCQ DECA XP-Max spectrometer by ESI (Electron Spray Ionization) technique.

Analytical thin layer chromatography (TLC) was performed on Silica gel plates (Merck, Kieselgel 60, 0.25 mm thickness) with $F_{254}$ indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 230–400 mesh; for 3 g crude mixture, 100 g silica gel was used in a column of 3 cm in diameter and 60 cm in length) and preparative thin layer chromatography was performed on silica gel 60P $F_{254}$. $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectra were recorded in $CDCl_3$ solutions on a Varian 500 MHz spectrometer. Thermogravimetric analysis (TGA) was carried out with a Mettler Toledo thermal analysis system TGA/SDTA 851 at a heating rate of 10 °C $min^{-1}$ in a nitrogen flow (50 ml $min^{-1}$).

### 3.3. Photophysical parameters

#### 3.3.1. Fluorescence quantum yields

Fluorescence quantum yields ($\Phi_F$) were determined by the comparative method (Eq. (1)) [48],

$$\Phi_F = \Phi_F(\mathrm{Std})\frac{FA_{\mathrm{Std}}\eta^2}{F_{\mathrm{Std}}A\eta^2_{\mathrm{Std}}} \quad (1)$$

where $F$ and $F_{Std}$ are the areas under the fluorescence emission curves of the samples (**6** and **8**) and the standard, respectively. $A$ and $A_{Std}$ are the respective absorbances of the samples and standard at the excitation wavelengths, respectively. The refractive indices of the solvents were employed in calculating fluorescence quantum yields in different solvents. Unsubstituted ZnPc (in DMSO) ($\Phi_F = 0.18$) [49] was employed as the standard. Both the samples and standard were excited at the same wavelength. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

Fluorescence lifetimes ($\tau_F$) were determined using PhotochemCAD Program which uses the Strickler–Berg equation [50] and natural radiative lifetimes radiative ($\tau_0$) are given by Eq. (2).

$$\Phi_F = \frac{\tau_F}{\tau_0} \quad (2)$$

Using the $\tau_F$ values, rate constants for fluorescence ($k_F$), intersystem crossing ($k_{ISC}$), internal conversion ($k_{IC}$) and photodegradation ($k_d$) were estimated.

### 3.4. Synthesis

The 1,1,3,3,5-pentaphenoxy-5-chlorocyclotriphosphazatriene (**1**) [26] and 4-nitro phthalonitrile (**4**) [51] were prepared according to the literature procedure.

#### 3.4.1. Synthesis of compound 2

4-(Benzyloxy)phenol (0.7 g, 3.49 mmol) and dry and finely powdered potassium carbonate (0.44 g, 3.18 mmol) were dissolved in dry THF (10 ml) under argon atmosphere. The solution was transferred into a 50 ml dropping funnel and slowly dropped to the solution of 1,1,3,3,5-pentaphenoxy-5-chlorocyclotriphosphazatriene (2 g, 3.15 mmol) (**1**) in 10 ml of dry THF under argon atmosphere in a 50 ml three-necked round-bottomed flask. The reaction mixture was refluxed under argon atmosphere for 24 h and followed by TLC indicating no starting material remaining. The precipitated salt (KCl) was filtered off and the solvent was removed under reduced pressure. The crude product was purified by column chromatography [silica gel 60 (70–230 mesh) as adsorbent and dichloromethane/*n*-hexane (1:2) as the eluent]. 1,1,3,3,5-Pentaphenoxy-5-[(4-benzyloxy)phenoxy]cyclotriphosphazene (**2**) was obtained as viscous oil; yield: 1.86 g (74%). (Found: C 64.40, H 4.58, N 5.20%. $C_{43}H_{36}N_3O_7P_3$ (799) requires C 64.58, H 4.54, N 5.25%.) FT-IR $\nu_{max}/cm^{-1}$ (KBr pellet): 3035 (ArCH), 2866 (CH), 1626–1604 (ArC=C), 1260–1211 (P=N), 1103 (C–O), 956 (P–O). $^{1}H$ NMR ($CDCl_3$) $\delta = 6.71$–$7.50$ (m, 34H, ArH), 5.02 (br s, 2H, $CH_2$). $\{^{1}H\}^{13}C$ NMR ($CDCl_3$) $\delta = 153.41$ (ArC), 149.20 (ArCH), 143.30 (ArC), 138.41 (ArC), 129.81 (ArCH), 128.12 (ArCH), 126.40 (ArCH), 125.22 (ArCH), 123.81 (ArCH), 121.23 (ArCH), 70.01 ($CH_2$). MS (APCI) *m/z* (%): 800 (100) $[M+1]^+$.

#### 3.4.2. Synthesis of compound 3

1,1,3,3,5-Pentaphenoxy-5-[(4-benzyloxy)phenoxy]cyclotriphosphazatriene (**2**) (1 g, 1.25 mmol) was dissolved in 10 ml of dry THF under argon atmosphere, and 10 ml of cyclohexene, palladium hydroxide (20 wt% on carbon, 0.4 g) and 10 ml of ethanol were added to the above solution. The mixture was refluxed for 24 h under argon atmosphere and filtered. All of the solvents were removed under reduced pressure. 1,1,3,3,5-Pentaphenoxy-5-[(4-hydroxy)phenoxy]cyclotriphosphazene (**3**) was obtained by crystallization in dichloromethane/*n*-hexane (1:1); yield: 0.79 g (90%), m.p. 107 °C. (Found: C 60.87, H 4.29, N 5.36%. $C_{36}H_{30}N_3O_7P_3$ (709) requires C 60.94, H 4.26, N 5.92%.) FT-IR $\nu_{max}/cm^{-1}$ (KBr pellet): 3610 (OH), 3040 (ArCH), 1592 (ArC), 1271–1179 (P=N), 961 (P–O). $^{1}H$ NMR ($CDCl_3$) $\delta = 6.51$–$7.22$ (m, 29H, ArCH), 5.23 (s, 1H, OH). $\{^{1}H\}^{13}C$ NMR ($CDCl_3$) $\delta = 153.10$ (ArC–OH), 150.82 (ArC), 144.30 (ArC), 129.62 (ArCH), 125.12 (ArCH), 122.32 (ArCH), 121.33 (ArCH), 116.14 (ArCH). MS (APCI) *m/z* (%): 710 (100) $[M+1]^+$.

#### 3.4.3. Synthesis of compound 5

4-Nitrophthalonitrile (**4**) (0.125 g, 0.72 mmol) and compound **3** (0.510 g, 0.72 mmol) were dissolved in anhydrous dimethyl formamide (DMF) (5 ml) under argon atmosphere. After stirring for 15 min at 40 °C, dry and finely powdered potassium carbonate (0.150 g, 1.08 mmol) was added portionwise over 15 min with efficient stirring. The reaction mixture was stirred under argon at 50 °C for 24 h. Then water (50 ml) was added and the aqueous phase extracted with chloroform (3 × 25 ml). The combined extracts were treated with water and dried over anhydrous sodium sulfate and then filtered. Solvent was evaporated and the product was purified by preparative TLC on silica gel using dichloromethane/methanol (100:1) as the eluent. Compound **5** is viscous oil; yield: 0.480 g (80%). (Found: C 61.85, H 3.75, N 8.64%. $C_{44}H_{32}N_5O_7P_3$ (835) requires C 61.99, H 3.84, N 8.21%.) FT-IR $\nu_{max}/cm^{-1}$ (KBr pellet): 3042 (ArCH), 2233 (C≡N), 1592 (ArC=C), 1490, 1267, 1200–1150 (C–O–C), 951, 770. $^{1}H$

NMR ($CDCl_3$) $\delta = 7.54$ (d, $J = 8.51$ Hz, 1H, ArH), 6.77–7.18 (m, 31H, ArH). $\{^1H\}^{13}C$ NMR-APT ($CDCl_3$) $\delta = 161.88$ (ArC–O–phenyl), 150.97 (ArC), 150.94 (ArC), 150.92 (ArC), 150.78 (ArC), 150. 67 (ArC), 150.44 (ArC), 148.59 (ArC), 135.73 (ArCH), 130.10 (ArCH), 130.02 (ArCH), 129.86 (ArCH), 129.83 (ArCH), 129.79 (ArCH), 125.42 (ArCH), 125.35 (ArCH), 125.31 (ArCH), 123.48 (ArCH), 123.45 (ArCH), 121.82 (ArCH), 121.73 (ArCH), 121.37 (ArCH), 121.34 (ArCH), 121.31 (ArCH), 121.28 (ArCH), 121.26 (ArCH), 121.25 (ArCH), 121.23 (ArCH), 117.87 (ArC–C≡N), 115.69 (C≡N), 115.24 (C≡N), 109.17 (ArC–C≡N). MS (ESI) *m/z* (%): 836 (100) $[M + 1]^+$.

*3.4.4. Synthesis of compound* **6** *($H_2Pc$)*

A solution of **5** (0.135 g, 0.162 mmol) in dry 2-(dimethylamino)ethanol (DMAE) (0.4 ml) was refluxed under argon atmosphere for 6 h and then the solvent was removed under reduced pressure. The crude product was dissolved in dichloromethane and filtered. This mixture was passed through a silica gel column using a mixture of $CH_2Cl_2$/MeOH (100:1) as eluent. Furthermore this product was purified by preparative TLC on silica gel using $CH_2Cl_2$/*n*-hexane (100:1) as the eluent. Yield: 0.03 g (22%). (Found: C 63.32, H 3.55, N 8.42%. $C_{176}H_{130}N_{20}O_{28}P_{12}$ (3345) requires C 63.20, H 3.92, N 8.38%.) IR $\nu_{max}/cm^{-1}$ (KBr pellet): 3300 (NH), 3040 (ArCH), 1592 (ArC=C), 1491, 1268, 1380, 1330, 1280, 1210–1120 (C–O–C), 950, 880, 767, 687. $^1H$ NMR ($CDCl_3$) $\delta = 8.79$–$8.72$ (m, 4H, ArH), 8.51–8.34 (m, 4H, ArH), 7.55–7.43 (m, 4H, ArH), 7.16–6.86 (m, 116H, ArH), −3.22 (br s, 2H, NH). $\{^1H\}^{13}C$ NMR ($CDCl_3$) $\delta = 171.10$, 159.89, 159.58, 154.41, 154.03, 151.04, 150.88, 147.16, 146.89, 138.13, 137.91, 129.76, 129.71, 129.66, 129.63, 125.21, 125.15, 125.09, 121.49, 121.22. MS (ESI) *m/z* (%): 3348 (100) $[M + 3]^+$.

*3.4.5. Synthesis of compound* **7** *(NiPc)*

Compound **5** (0.12 g, 0.144 mmol), DBU (35 μl), anhydrous $NiCl_2$ (0.04 g, 0.31 mmol) and dried 1-pentanol (2.2 ml) were refluxed with stirring under argon atmosphere for 7 h. After cooling to room temperature it was treated with ethanol (5 ml) and the product was filtered off and washed with the same solvent. The dark green crude product was purified by preparative TLC on silica gel, using $CH_2Cl_2$/methanol (100:1) as the eluent. The dark green compound was soluble in $CH_2Cl_2$, $CHCl_3$, THF, DMSO and DMF. Yield: 0.025 g (20%). (Found: C 62.05, H 3.75, N 8.25%. $C_{176}H_{128}N_{20}NiO_{28}P_{12}$ (3401) requires C 62.15, H 3.79, N 8.24%.) IR $\nu_{max}/cm^{-1}$ (KBr pellet): 3040 (ArCH), 1593 (ArC=C), 1490, 1410, 1333, 1268, 1208–1160 (C–O–C), 950, 881, 768, 688. $^1H$ NMR ($CDCl_3$) $\delta = 8.82$–$8.78$ (m, 4H, ArH), 8.48–8.39 (m, 4H, ArH), 7.51–7.41 (m, 4H, ArH), 7.11–6.82 (m, 116H, ArH). $\{^1H\}^{13}C$ NMR ($CDCl_3$) $\delta = 171.21$, 159.76, 159.55, 154.71, 154.13, 151.23, 151.25, 147.22, 146.64, 138.26, 138.12, 130.75, 129.71, 129.65, 129.59, 125.32, 125.19, 125.06, 121.65, 121.13. MS (ESI) *m/z* (%): 3404 (100) $[M + 3]^+$.

*3.4.6. Synthesis of compound* **8** *(ZnPc)*

Compound **5** (0.12 g, 0.144 mmol), DBU (35 μl), anhydrous $Zn(AcO)_2$ (0.03 g, 0.163 mmol) and dried 1-pentanol (2.2 ml) were refluxed with stirring under argon atmosphere for 7 h. After cooling to room temperature it was treated with ethanol (5 ml) and the product was filtered off and washed with the same solvent. The dark green crude product was purified by preparative TLC on silica gel, using $CH_2Cl_2$/methanol (100:1) as the eluent. The dark green compound was soluble in $CH_2Cl_2$, $CHCl_3$, THF, DMSO and DMF. Yield: 0.030 g (24%). (Found: C 61.99, H 3.65, N 8.45%. $C_{176}H_{128}N_{20}O_{28}P_{12}Zn$ (3408) requires C 62.03, H 3.79, N 8.22%.) IR $\nu_{max}/cm^{-1}$ (KBr pellet): 3043 (ArCH), 1592 (ArC=C), 1490, 1410, 1330, 1267, 1208–1160 (C–O–C), 950, 881, 769, 688. $^1H$ NMR ($CDCl_3$) $\delta = 8.80$–$8.68$ (m, 4H, ArH), 8.48–8.39 (m, 4H, ArH), 7.71–7.60 (m, 4H, ArH), 7.24–6.85 (m, 116 H, ArH). $\{^1H\}^{13}C$ NMR ($CDCl_3$) $\delta = 171.24$, 159.86, 159.68, 154.70, 154.03, 151.04, 150.85, 147.11, 146.79, 138.06, 138.01, 129.75, 129.70, 129.66, 129.62, 125.20, 125.12, 125.10, 121.50, 121.20. MS (ESI) *m/z* (%): 3411 (100) $[M + 3]^+$.

## 4. Conclusions

In summary, we have synthesized and characterized three new tetra-cyclotriphosphazenyl-substituted unmetallated, nickel and zinc phthalocyanines for the first time. All phthalocyanines (**6**, **7** and **8**) exhibited excellent solubility in organic solvents and they do not aggregate in $CHCl_3$. The UV–vis spectra of the complexes **7** and **8** showed a single (narrow) Q band typical of metallated phthalocyanine complexes as a result of the $D_{4h}$ symmetry. The metal-free phthalocyanine complex **6** gives a doublet (narrow) Q band as a result of the $D_{2h}$ symmetry. Nickel phthalocyanine complex **7** showed aggregation in DMSO and DMF. The addition of Triton X-100 to the DMSO solutions of the aggregated specie **7** resulted in reduction of aggregation. Although the unmetallated and zinc phthalocyanine complexes showed fluorescence emission, the nickel complex **7** showed no fluorescence at this excitation wavelength. The fluorescence quantum yields ($\Phi_F$) of compounds **6** and **8** were similar and typical of MPc complexes. The substituted zinc phthalocyanine complex **8** has larger $\Phi_F$ value than substituted unmetallated complex **6** in DMSO. Fluorescence lifetime ($\tau_F$) value of substituted zinc phthalocyanine complex **8** is longer when compared to substituted unmetallated phthalocyanine derivative **6** in DMSO suggesting more quenching of zinc phthalocyanine complex **8**. In comparison with the substituted phthalocyanine derivatives containing different types of organic groups, the thermal stabilities of the cyclotriphosphazenyl-substituted phthalocyanine compounds **6–8** are higher. Thus, cyclotriphoshazenyl groups on phthalocyanine ring have a stabilizing effect on the thermal property. The thermal stability of cyclotriphosphazenyl-substituted phthalocyanine derivatives should widen the opportunities for the use in a variety of fire-resistant or flame retardant application.

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