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Synthesis and photophysical characterization of dimethylamine-derived Zn(II)Phthalocyanines: exploring their potential as selective chemosensors for trinitrophenol

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We report a novel synthetic approach, with good yields, for the synthesis of selective dimethylamine-substituted phthalonitriles (1-3) in the presence of triethyl phosphite and dimethylformamide at 160 °C. The peripherally-modified dimethylamine substituted Zn(II)phthalocyanines (ZnPc1-3) with varied number and position of dimethylamine groups were prepared for a systematic investigation on the effect of the substituents on their electronic and spectroscopic properties. Compounds show strong aggregation behaviour in methanol and this behaviour decreasing with the increase of the alkyl chain of the alcohol solvents (i.e., from methanol to octanol). The fluorescence quantum yields of ZnPc1-3 showed an excellent correlation with the extent of the molecular aggregation. The versatility of the ZnPc1-5 compounds possessing both electron donating and electron withdrawing substituents at their periphery is investigated towards the detection of nitroaromatic compounds (NACs) in solution and in the vapour phase. It was found that ZnPc1-5 exhibit high selectivity towards trinitrophenol (TNP). A good linearity of the fluorescence detection using ZnPc3 as the fluorescent probe was observed in the concentration range of 5×10^-6-450×10^-6 M in chloroform, with a detection limit (LOD) of 11±2 ppm. Stern-Volmer (SV) and DFT studies reveal that the fluorescence quenching behaviour occurs through photo-induced electron transfer from the excited state of ZnPc3 to TNP with static quenching behaviour occurring in a predominant fashion. The formation of porous morphology of ZnPc3 thin film promotes high selectivity and accessibility to TNP vapours (7.7×10^{-3} ppb).

1. Introduction

Considerable interest has recently been focused in the design of stimuli-responsive smart materials with tuneable photophysical properties. Phthalocyanines (Pcs) and related cyclic tetrapyrrolic macrocycles comprise a highly conjugated π-electron family that exhibit strong absorption of light in the 600-700 nm spectral.\(^2\) In this sense, the unique optical properties of these compounds are explored in different applications acting as functional materials.\(^3\) The low solubility of un-substituted phthalocyanine in organic solvents or water limits, however, their practical application. Hence, a number of phthalocyanine derivatives have been synthesized bearing modified peripheral substituents with π-conjugation and with a wide range of functional groups so to enhance its solubility.\(^4,6\) Various metal ions can also be inserted at the central core of the ring resulting in the formation of metallophthalocyanines as monomers/dimers with transition/pseudo metals, and double decker type phthalocyanines with some lanthanide metal ions.\(^7,9\) The development of novel strategies for the rational design of absorption properties of Pcs using simple synthetic methods with high solubility remains a challenge in phthalocyanine chemistry. The molecular tolerability via chemical modification and compatibility with the flexible substrates of Pcs render them ideal organic semiconductor materials as active layers for organic field effect transistors and photosensitizers in photodynamic therapy (PDT) applications.\(^10-12\) Phthalocyanines were employed as active chemosensor materials in the development of electronic conductance, mass-sensitive, surface acoustic-wave (SAW) and optical sensors.\(^13-16\) Several studies have investigated their sensing ability by changing both the central metal of the Pc core and the peripheral substituents for an effective detection of toxic vapours like NO\(_2\), NH\(_3\), SO\(_2\), ethanol and hazardous metal ions.\(^17-19\) The sensing mechanism was correlated with the response behaviour by formation of hydrogen bonds and the basicity of the analyte. Our recent efforts in this field have focused on the synthesis of novel porphyrins and Pcs bearing different ligands which act as molecular probes for the recognition of anions.\(^20\) We reported a novel peripherally-substituted 2,3,9,10,16,17,23,24-octatosylamino-phthalocyanine which acts as a viable chromogenic anion chemosensor with high affinity towards fluoride ion.\(^21\) Suitable modification of Pcs with functional ligands results in significant change of their optical properties. Liu \textit{et al.} have developed highly selective phthalocyanine-thymine conjugates to act as selective...
chemosensors for Hg\textsuperscript{2+}-based on target induced aggregation behaviour with fluorescence quenching.\textsuperscript{22} Fluorogenic chemosensor based on 4-[2-(4-nitrophenoxo)ethoxy]phthalocyanine was developed for the detection of Zn\textsuperscript{2+} in dimethyl sulfoxide-acetonitrile medium.\textsuperscript{23} The high planar nature of phthalocyanines promotes strong interactions (van der Waals forces, π-stacking interactions, hydrogen bonding and solvent effect) with nucleobase units, fulleren, and other π-electron acceptor molecules by formation of strong charge-transfer complexes.\textsuperscript{24} The formation of such complexes leads to dramatic changes in the Q-band spectral pattern and show quenching of the fluorescence emission behaviour.

Nitroaromatic compounds (NACs) are a class of electron-deficient compounds (known as explosive materials) who have received great attention in recent years due to homeland security threats and to their high toxicity to the environment.\textsuperscript{25-27} Owing to their significant toxicity, ultrasensitive and selective detection of NACs is, thus, of prevalent issue. Organic thin film transistors developed with peroxide vapours with high selectivity. Organic thin film transistors developed with peroxide vapours with high selectivity. Organic thin film transistors developed with peroxide vapours with high selectivity. Organic thin film transistors developed with peroxide vapours with high selectivity.

The NMR (\textit{H}, \textit{C}) spectra were recorded on Bruker 300 MHz, (\textit{H}, J = 6 Hz), 3.08 (s, 6H). \textsuperscript{19}F NMR (282.28 MHz, CDCl\textsubscript{3}) δ 137.67 (t, J = 19.7 Hz, 1F). \textsuperscript{13}C NMR (75.47 MHz, CDCl\textsubscript{3}) δ 42.02 (-N(CH\textsubscript{3})\textsubscript{2}), 107.12, 115. 6, 121.1, 143.5, 147.4, 154.9. ESI-MS: m/z calculated for C\textsubscript{47}H\textsubscript{38}N\textsubscript{2}: 250.26; found: 250.18. FT-IR spectra were recorded from dry KBr pellets (infra-red spectroscopy grade, BDH Spectrosol) using a Bruker Tensor 27 spectrometer. Typically 2 mg of the sample was mixed in a mortar with ca. 200 mg of KBr. UV-Vis absorption spectra were recorded on a Shimadzu UV-2501 PC UV-Vis spectrometer. Absorption spectra in solution were recorded in CHCl\textsubscript{3} (conc. 2×10\textsuperscript{-6} mol/L) and the spectra in the solid state were recorded by producing thin films of ZnPcs on quartz substrate.

Steady-state fluorescence emission studies were carried out with Jobin-Yvon fluoroMax 3. Fluorescence quenching experiments were carried out in a quartz cell in chloroform. Stern-Volmer (SV) quenching rate constants were estimated by plotting the ratio of Io/I against the concentration of the quencher [Q], where Io and I are the maximum fluorescence intensity of the ZnPcs before and after the addition of the analyte, respectively. Time-resolved fluorescence measurements were carried out with time-correlated single-photon counting (TCSPC) with a picosecond LED (635 nm, pulse width <200 ps) being used to excite the samples. Electrochemical measurements were carried out using a Metrohm Auto lab potentiosstat instrument (PGSTAT-128N). Three electrode cell configurations were employed. A glassy carbon electrode having 3.0 mm in diameter was used as working electrode. A leak-free saturated Ag/AgCl electrode was employed as the reference and a Pt wire was used as the counter electrode. Tetra(n-buty)ammonium hexa-fluorophosphate (TBAPF\textsubscript{6}) was employed as the supporting electrolyte. Typically, a 0.1 M solution of TBAPF\textsubscript{6} in dimethylformamide containing 0.5 mM of ZnPcs was employed. The solution was purged with nitrogen flow for 3 min and voltammograms were recorded under the flow of nitrogen at ambient temperature with a scan rate of 5 mV s\textsuperscript{-1}.

Thin films were fabricated by taking 0.5 mg of ZnPcs in 0.2 mL of chloroform and spin coating on a quartz plate with a rate of 2000 rpm and annealed at 50 °C for 2 h. The fabricated thin film on the quartz plate was kept directly facing the excitation light source and the emission spectra was then collected. The position of the film was kept constant during each set of measurements. The solid state fluorescence quenching in the vapour phase was tested under saturated vapours of NACs.\textsuperscript{25-27} Scanning electron microscopy (SEM) images were obtained with a JEOL 7600F SEM operating at 2 kV in recorded in gentle beam mode (GB-high).

Geometry optimization of ZnPcs was carried out in the Gaussian 03 package with hybrid basis sets.\textsuperscript{32} Electron density profiles of molecular orbitals were obtained with GaussView 5.0.8.

2.2 Synthesis of 4-fluoro-5-(dimethylamino)phthalonitrile, 1

4,5-Difluorophthalonitrile (492 mg, 3 mmol), dimethylformamide (DMF, 4 mL) and triethyl phosphate (100 mg) were added into a glass tube (50 mL). The glass tube was sealed tightly with a septum and heated to 160 °C for 3 h. The reaction was cool down to ambient temperature and extracted with water and chloroform (3x150 mL). The organic layer was dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and the solution was evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel (dichloromethane: hexane, 1:1) and recrystallized from CHCl\textsubscript{3} and MeOH gave pale yellow solid 1 with ca. 72% yield. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): δ 7.31 (d, 1H, J = 12 Hz), 7.0 (d, 1H, J = 6 Hz), 3.08 (s, 6H). \textsuperscript{13}C NMR (75.47 MHz, CDCl\textsubscript{3}) δ 137.36 (137.60), 121.11 (121.14), 143.92 (143.97), 147.40 (147.43). ESI-MS: m/z calculated for C\textsubscript{47}H\textsubscript{38}N\textsubscript{2}: 222.20; found: 222.12. Scanning electron microscopy (SEM) images were obtained with a JEOL 7600F SEM operating at 2 kV in recorded in gentle beam mode (GB-high).
1469 vs; ν(C-H) = 1424 vs; ν(C-C) = 1389 s; ν(C-N) = 1239 m; ν(C-N) = 1020 m; γ(C-H) = 965 s, 737 w.

**Synthesis of 4-chloro-5-(dimethylamino)phthalonitrile, ZnPc1**

4,5-Dichlorophthalonitrile (586 mg, 3 mmol), dimethylformamide (DMF, 4 mL) and triethyl phosphate (100 mg) were added into a glass tube (50 mL). The glass tube was sealed tightly with a septum and heated to 160 °C for 6 h. After completion of the reaction, the tube was cooled down to ambient temperature and the mixture was washed with water and extracted with chloroform (3x50 mL). The organic layer was dried over anhydrous Na2SO4. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography over silica gel (dichloromethane: hexane; 3:2) and recrystallized from chloroform and methanol producing the yellow solid ZnPc1 with a yield of ca. 76% (467 mg).

H NMR (300 MHz, CDCl3): δ 7.68 (s, 1H), 7.20 (s, 1H), 3.02 (s, 6H, CH3). 13C NMR (75.47 MHz, CDCl3): δ 100.9 m; γ(C(H) = 965 s, 737 w. m/z calculated for C9H6C12N2Zn: 250.1; found: 251.1 [M+H]+. FT-IR (KBr pellet), νmax/cm−1: ν(O-H, water) = 3310 m; ν(C-H) = 2952(2795 w; ν(C=C) = 1627 w; ν(C(H) = 1418 vs; ν(C-C)) = 1514 m; β(C-H) = 1511 s; γ(C-H) = 973 s, 737 w.

**Synthesis of 4,5-bis(dimethylamino)-3,6-difluorophthalonitrile, ZnPc2**

3,4,5,6-Tetrafluorophthalonitrile (600 mg, 3 mmol), dimethylformamide (DMF, 4 mL) and triethyl phosphate (100 mg) were added into a glass tube (50 mL). The tube was sealed tightly with a septum and heated to 160 °C for 6 h. After completion of the reaction, the tube was cooled down to ambient temperature and the mixture was washed with water and extracted with chloroform (3x50 mL). The organic layer was dried over anhydrous Na2SO4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel using a mixture of dichloromethane:hexane (9:3) as eluent. The major yellow compound was identified as compound 3 in 68% yield. The other compound, with a yield of 22%, was identified as 4-(dimethylamino)-3,6-difluorophthalonitrile (4).

**Synthesis of tetrakis[4-fluoro-5-(dimethylamino)phthalocyaninato]zinc(II), ZnPc3**

Zinc dust (0.327 g), 4-fluoro-5-(dimethylamino)phthalonitrile (1 (0.472 g, 2.5 mmol) and 1-chloronaphthalene (10 mL) were stirred and heated under reflux at 200 °C for 48 h in a sand bath. The reaction mixture was cooled down to ambient temperature after which petroleum ether was added. The formed precipitate was filtered and the resulting residue was stirred with 2M hydrochloric acid (50 mL) in order to dissolve the untreated zinc. The residual dark green solid was washed with boiling water, dried, finely powdered and extracted with chloroform (2x100 mL). The solution was evaporated under reduced pressure and purified through silica gel column chromatography with a chloroform:methanol mixture (98:2) to isolate ZnPc3 in 66% yield. H NMR (300 MHz, CDCl3): δ 9.5 (d, J = 12 Hz, 2H, α-Pc), 8.77 (d, J = 9 Hz, 2H, α-Pc), 8.72 (d, J = 3 Hz, 2H, α-Pc), 3.73 (s, -N(CH3)2, 24H). 13C NMR (282.38 MHz): δ 142.1 (t, J = 28.2 Hz, β-F). 13C NMR (75.47 MHz, DMSO-d6): δ 43.9 [M+H]+. FT-IR (KBr pellet), wmax/cm−1: ν(O-H, water) = 3432 m; ν(C-H) = 2926-2804 w; ν(C-C) = 1627 w; ν(C-H) = 1418 vs; ν(C-C) = 1514 m; β(C-H) = 1511 s; γ(C-H) = 973 s, 737 w.

**Synthesis of octakis[4,5-bis(dimethylamino)-3,6-difluorophthalocyaninato]zinc(II), ZnPc4**

A similar procedure as described for ZnPc1 was employed for the preparation of ZnPc3, using 4,5-bis(dimethylamino)-3,6-difluorophthalonitrile as a precursor. Yield: 54%. H NMR (300 MHz, DMSO-d6): δ 8.81-8.72 (m, 2H, α-Pc), 6.87-6.55 (m, 4H, α-Pc), 8.40 (d, J = 12 Hz, 2H, α-Pc), 3.46 (s, 24H, -N(CH3)2). 13C NMR (75.47 MHz, DMSO-d6): δ 43.9 (t, J = 15.1 Hz, -N(CH3)2), 112.2 (d, J = 32.7, 123.7-123.4 (q), 128.3 (t, J = 15.1 Hz, 131.7 (t, J = 40.2 Hz), 137.2-136.3 (m), 151.2-149.6 (m). MALDI-TOF MS: m/z calculated for C40H26F12N12Zn: 820.2; found: 820.2 [M]+. FT-IR (KBr pellet), wmax/cm−1: ν(O-H, water) = 3432 m; ν(C-H) = 2926-2804 w; ν(C-C) = 1627 w; ν(C-H) = 1418 vs; ν(C-C) = 1514 m; β(C-H) = 1511 s; γ(C-H) = 973 s, 737 w.

**3. Results and discussion**

The synthetic route employed for the preparation of new peripheral dimethyamine substituted ZnPc3 is depicted in Scheme 1. An interesting finding was noted while optimizing the reaction conditions for the nuclophilic substitution of phthalonitriles with triethyl phosphate. The treatment of 4,5-difluorophthalonitrile with triethyl phosphate in DMF at 160 °C leads to formation of 4-fluoro-5-(dimethylamino)phthalonitrile (1) in good yield. Reaction of 3,4,5,6-tetrafluorophthalonitrile forms 4,5-bis(dimethylamino)-3,6-difluorophthalonitrile as a secondary product (4) with yield of 22%. The formation of dimethyamine substitution on phthalonitriles could involve the reaction of substrate with DMF followed by the loss of carbon monoxide or nuclophilic substitution of dimethyamine formed by the decomposition of DMF. We have discovered that...
triethyl phosphite acts as a catalyst for the fast decomposition of DMF ultimately promoting the nucleophilic substitution of the dimethylamine groups on the phthalonitrile. Under similar experimental conditions, in the absence triethyl phosphite and the use of other bases such as Na$_2$CO$_3$, K$_2$CO$_3$ and Cs$_2$CO$_3$, the formation of the corresponding dimethylamine-substituted phthalonitrile derivatives are typically observed with very low yields in the range of 10-26% for a total reaction time of 24 h. Table S1 summarizes the experimental reaction conditions and use of different amounts of triethyl phosphite, and other bases, for the formation of dimethylamine phthalonitriles from the corresponding phthalonitriles. Increasing the amount of triethyl phosphite in the reaction medium promotes a great enhancement of the product conversion rate. We note that the dimethylamination of aromatic compounds with DMF has been reported to be dependent on the employed temperature. At elevated temperatures, fluoro/chloro groups undergo nucleophilic substitution that depends on the activation of the fluoro/chloro groups induced by the cyano group of phthalonitriles. As the fluoro/chloro groups exert its strong electron withdrawing effect, dimethylamination occurs only at the β-position while halogens at α-positions are unaffected. In short, the results herein presented clearly demonstrate that a combination of DMF and triethyl phosphite could serve as a better and more efficient approach to produce selective dimethylamine phthalonitriles when treated with halogenated phthalonitriles. The NMR ($^1$H, $^{13}$F and $^{19}$F), ESI-MS spectra (Figs. S1-S11, ESI$^1$) and single-crystal X-ray diffraction studies corroborate in tandem the structural features of the prepared dimethylamine-substituted phthalonitriles. Good quality single-crystals suitable X-ray diffraction studies were obtained by slow solvent evaporation of a solution of each pure compound in a chloroform-methanol (1:1) mixture at ambient temperature. Fig. 1 depicts the molecular structures as derived from these studies for 1 to 3. Zinc(II) phthalocyanines (ZnPcs) were prepared via a cyclotetramerization reaction of the respective phthalonitriles and metallic zinc in 1-chloronaphthalene at 200 °C. The cyclotetramerization of the dimethylamine-substituted precursors 1 and 2 in the presence of anhydrous ZnCl$_2$ in 1-chloronaphthalene inevitably led to the formation of ZnPc1 and ZnPc2 as mixtures of four regioisomers having C$_{2v}$, C$_{2}$, C$_{1}$ and D$_{2h}$ point symmetry. The structures of the target compounds were confirmed from FT-IR (Figs. S12-13, ESI$^1$), NMR ($^1$H, $^{13}$C and $^{19}$F) and MALDI-TOF-mass spectroscopic techniques (Figs. S14-S24, ESI$^1$). The FT-IR spectra of ZnPc1-3 exhibit major bands arising from the central aromatic Pc macrocycle including the wagging and torsion vibrations of C−H groups $ca.$ 2943−2795 cm$^{-1}$, C=C modes in the range $ca.$1609-1627 cm$^{-1}$, and C–C isodineole ring stretching vibrations in the range $ca.$ 1321-1389 cm$^{-1}$. In addition, the absence of C=N peaks at $ca.$ 2220 cm$^{-1}$ in the spectra clearly indicated that the precursor phthalonitriles 1–3 were converted into ZnPc1-3. The $^1$H NMR spectra of ZnPc1 show four doublet peaks in the range $δ$ 9.15-8.82 ppm arising from the resonances of the α-protons corresponding to the four isomers; the dimethylamine (−N(CH$_3$)$_2$) protons appear as a singlet peak at $δ$ 3.37 ppm. $^{19}$F NMR shows a triplet with $J = 28.3$ Hz. ZnPc3 shows only −N(CH$_3$)$_2$ protons at $δ$ 3.43 ppm, while the $^{19}$F NMR is dominated by a triplet peak centred at $δ$ 131.45 with $J = 14.1$ Hz corresponds to the α-F atoms. The mass spectra of all ZnPcs exhibit an intense cluster corresponding to aggregates of molecular ion peaks centred at m/z 820.2 for ZnPc1,
polarities. In addition to the position of the absorption, the band peaks at 691, 682 and 704 nm in THF with a refractive index of 1.406, and at 700, 695 and 722 nm, respectively, in solvents with a higher refractive index resulting in a red shift.

The width of the Q-band in the range of 440–530 nm is attributed to the presence of the dimethylamine (–N(CH3)2) groups with this property being exhibited in various solvents such as tetrahydrofuran (THF), acetone, dichromethane (DCM), chloroform (CHCl3), dimethyl-sulfoxide (DMSO) and DMF, with this property being attributed to the presence of the dimethylamine (–N(CH3)2) groups in the periphery of the macrocycle. Fig. 2b depicts the variation in colour of ZnPc1–3 in CHCl3.

The intensity of the Q-band was quantified by the molar extinction coefficient (ε). The ε values were determined and summarized in Table S1. An interesting feature was observed in the Q-band of ZnPc1–3 in protic solvents. In methanol solution, the intensity of the Q-band decreases dramatically and shows a broad absorption with an overlap of the peak at 630 nm. Such spectral features are typical for Pc dimers or aggregates. The intensity of the Q-band increases as the length of alkyl chain of the protic solvents is also increased (i.e., from methanol to octanol). Fig. 2d shows the change in the absorption spectral pattern of ZnPc2 in different protic solvents. The absorption of Q-band shows a red shift of 8–10 nm with a dramatic increase in the absorption coefficient value in respect to the increase of the alkyl chain length of the solvent, going from methanol to octanol. The absorption spectra of other ZnPcs in different solvents are depicted in Fig. S25 (ESI†). The aggregation behaviour of ZnPc1–3 was studied by collecting the concentration-dependent UV-Vis spectra in chloroform (Fig. S26, ESI†). Fig. 3 shows the representative concentration dependent absorption spectra of ZnPc2 in chloroform.

The intensity of Q-band increases gradually with the increase of the concentration without any appearance of new absorption bands. This process followed the Beer-Lambert law, which is characteristic of non-aggregated Pcs, in the concentration range from 2x10^-7 to 3x10^-6 mol dm^-3. The inset in Fig. 3 shows the linear increase in the absorbance as a function of the concentration. Steady-state fluorescence emission studies provide information on the fluorescence excitation and emission wavelengths, Stokes shift and the fluorescence quantum yields. Fig. 4a shows the emission spectra of ZnPcs in chloroform under excitation at 630 nm. ZnPcs shows a red shifted emission spectra with an emission shift of ca. 20 nm and 24 nm in comparison with ZnPc1 and ZnPc2, respectively. It was found that while increasing the number of dimethylamine groups on ZnPcs, the emission spectral pattern is more red shifted comparing to the absorption spectra. In DMSO, ZnPc1–3 exhibits a red shifted emission when compared with other
solvents. The emission spectra of all complexes show emission bands that are typical for phthalocyanines with Stokes shift ranging from 5-20 nm. The fluorescence emission spectra of ZnPc1-3 were performed in different solvents. The emission maximum was found to vary according to the solvent polarity. In methanol, ZnPcs exhibit very low fluorescence emission intensity. This arises because of the formation of aggregates as clearly observed in the absorption spectra.

Aggregates of Pcs are known to quench the fluorescence emission because aggregation lowers the fluorescence intensity of molecules through dissipation of energy. The emission intensity increases with increasing the alkyl chain of the alcohol medium (Fig. S27, ESI†). A study of the dependence of the emission with the concentration reveals that the emission maximum is red shifted. For example, the emission maxima of ZnPc3 show a gradual red shift as a function of the concentration (1x10⁻⁶-6x10⁻⁶ M) and starts decreasing in intensity without any change in the spectral pattern (Fig. S28, ESI†). This indicates the formation of molecular aggregates of ZnPcs at this concentration level. The fluorescence quantum yields of ZnPc1-3, in different solvents were measured using ZnPc as the reference. The compounds exhibit fluorescence quantum yields in the range 0.02-0.15 in different solvents. We note that the very low quantum yields were observed for ZnPc1-3 in methanol. The fluorescence lifetime with time-correlated single photon counting (TCSPC) method was measured for ZnPc1-3, with the values showing single exponential emission decays with lifetimes of ca. 1.85 ns, 2.81 ns and 3.22 ns for ZnPc1, ZnPc2 and ZnPc3, respectively. ZnPc3 exhibits longer lifetime than ZnPc1 and ZnPc2 because of its more symmetrical nature and increased donating strength. The fluorescence rate constants (kᵣ = Φᵣ/τᵣ) and non-radiative rate constants (kᵣᵣ = (1−Φₑ)/τₑ) were calculated and the photophysical data of ZnPc1-5 in chloroform are summarized in Table 1.

Table 1. Summary of photophysical data of ZnPc1-3 in chloroform.

<table>
<thead>
<tr>
<th>Compd.</th>
<th>Abs, nm (log ε)ᵃ</th>
<th>Emission nmᵇ</th>
<th>Stokes shift (nm)</th>
<th>Q.Y.ᶜ (Φₑ)</th>
<th>Lifetime τₑ (ns)</th>
<th>Kᵣ (s⁻¹) (10⁸)ᵈ</th>
<th>Kᵣᵣ (s⁻¹) (10⁸)ᵉ</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnPc1</td>
<td>359 (4.44), 636 (4.11), 701 (5.49)</td>
<td>717, 783</td>
<td>16</td>
<td>0.12</td>
<td>1.85</td>
<td>64.86</td>
<td>475.67</td>
</tr>
<tr>
<td>ZnPc2</td>
<td>347 (5.16), 621 (4.83), 693 (5.50)</td>
<td>713, 784</td>
<td>20</td>
<td>0.12</td>
<td>2.81</td>
<td>35.58</td>
<td>320.28</td>
</tr>
<tr>
<td>ZnPc3</td>
<td>358 (5.06), 646 (4.65), 720 (5.27)</td>
<td>737, 813</td>
<td>17</td>
<td>0.16</td>
<td>3.22</td>
<td>49.68</td>
<td>260.86</td>
</tr>
</tbody>
</table>

ᵃ log ε represents the molar absorption coefficients; ᵇ Excitation at λₑx: 630 nm; ⁣ᶜ reference to ZnPc (Φₑ) = 0.20; ⁣ᵈ Kᵣ = Φₑ/τₑ; ⁣ᵉ Kᵣᵣ = 1- Φₑ/τₑ.
A number of reports have appeared in the literature describing the ability of ZnPcs in electron transfer processes with acceptors. The formation of donor-acceptor charge transfer complexes could involve π-π stacking and intra/inter molecular interactions. Nitroaromatic compounds (NACs) are known to behave as good acceptors, and detection of NACs has recently attracted increased attention. We further tested the usage of ZnPcs towards the detection of NACs through fluorescence quenching in solution and in the solid state. To demonstrate the ability of ZnPcs for detection of NACs we first performed fluorescence quenching studies of ZnPcs with different NACs such as 4(nitrobenzene (NB), 4-nitrotoluene (NT), 4-nitrophenol (NP), 2,4-dinitrotoluene (DNT), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), 2,4,6-trinitrotoluene (TNT), nitromethane (NM) and other aromatic electron-deficient compounds such as benzoquinone (BQ) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in chloroform. According to the undertaken study, ZnPcs exhibit good fluorescence quenching behaviour towards trinitrophenol (TNP). To corroborate the selectivity of ZnPcs for the detection of NACs, we have carried out fluorescence titration experiments with other electron-deficient aromatic compounds. Interestingly, ZnPcs showed differential fluorescence quenching responses among the various tested analytes. Fig. 6a shows the emission spectra of ZnPc3 upon the gradual addition of different concentrations of TNP under excitation at 630 nm. The emission maxima of ZnPc3 at 737 nm depleted with the increased concentration of TNP in solution, showing 80% quenching at 450 µM of TNP concentration (~103±2 ppm). ZnPc1 and ZnPc2 show 41% and 58% of quenching efficiency for TNP, respectively. These results indicate that the increase in the number of dimethylamine groups on the ZnPc enhances the electron donating strength of the macrocycle ultimately showing a high quenching efficiency. To further understand this phenomenon, we have studied two model compounds consisting of t-butyl substituted groups at peripheral positions of ZnPc as more electron donating (ZnPc4) and highly electron withdrawing perfluoro substituted groups (ZnPc5) (see Scheme 1) with NACs. Under similar experimental conditions, ZnPc4 and ZnPc5 show only 36% and 21% of quenching efficiency for TNP. The high electron donating strength of dimethylamine groups in ZnPc1–3 show higher sensitivity than ZnPc4. The less quenching efficiency ZnPc5 arises due to the high electron withdrawing tendency of fluorine making ZnPc5 a more electron-deficient compound than other ZnPcs used in this work, and also exhibiting weak interactions with NACs (Figs. S29-33, ESI†). These results are consistent with the observations for other fluoro-derivatives of porphyrins treated with different nitrated derivatives. Fig. 6b depict the quenching efficiency of ZnPcs when treated with different NACs. Results show that ZnPcs exhibit high selectivity towards trinitrophenol with ZnPc3 showing a superior selectivity than other ZnPc derivatives. Quantitative evaluation of the solution phase quenching of fluorescence was performed using the Stern–Volmer (SV) equation, where Io and I are the fluorescence intensities in the absence and in the presence of the analyte, respectively, Q is the analyte concentration and KSV is the Stern–Volmer rate constant. The steady-state Stern–Volmer plots provide more insight so to understand the quenching mechanism is static or dynamic. The static quenching was formed by ground state complex
between ZnPcs and NACs and dynamic quenching was formed by excited state collisions.

Fig. 7 (a) The Stren-Volmer (SV) plot of ZnPc1-5 treated with different concentrations of TNP. (b) The SV plot of ZnPc3 upon addition of different NACs at different concentration levels.

Fig. 7a shows the SV plot of ZnPcs treated with different concentrations of TNP. All ZnPcs exhibit a linear increase in the Io/I values with respect to the degree of fluorescence quenching, indicating a static quenching by formation of ground state complexes between ZnPcs and TNP. Among all ZnPcs studied, ZnPc3 shows the higher quenching rate constant of 2.99x10^4 M^-1 with the order of reactivity being ZnPc3> ZnPc2> ZnPc1> ZnPc4> ZnPc5 for TNP. The significant high magnitude of Ksv for ZnPc3 when compared to ZnPc1 and ZnPc2 is attributed to the additional supra-molecular interactions. Fig. 7b shows the SV plot ZnPc3 for different NACs. Table S4 (ESI†) summarizes the SV rate constants of ZnPcs with different NACs. The formation of static quenching was further confirmed by UV-Visible titration of ZnPcs with TNP. For instance, when adding different concentrations of TNP to ZnPc3, the intensity of the Q-band peak at ca. 720 nm decreases as a function of the concentration, while the intensity of the peak at ca. 640 nm gradually increases. The high selectivity towards TNP arises due to its absorption at ca. 340 nm, which overlaps with the absorption spectra of the soret band of ZnPcs. The intensity of the Soret increases with the increase of the concentration of TNP (Fig. S35, ESI†) indicating the formation of charge-transfer complexes by axial coordination of the TNP molecules to ZnPcs, in a similar fashion to the reported axial coordination of Zn(II)porphyrins with NACs alongside with the formation of strong intermolecular π-π stacking interactions by co-facial geometry. On the other hand, ZnPcs exhibit moderate quenching of the fluorescence by other electron-deficient compounds (benzoquinone, DDQ and aromatic solvents such as benzene and toluene) and their quenching efficiency is quite low in magnitude when compared to all nitroaromatics. The stoichiometric binding constants of ZnPcs treated with different concentrations of TNP were determined by using the Benesi–Hildebrand equation. The observed linear fits with TNP indicate formation of 1:1 adducts and ZnPc3 show high binding affinity (Fig. S34, ESI†).

Based on the collected photophysical studies, we observe that there is no spectral overlap between the absorption spectrum of TNP and the emission spectra of ZnPcs, thus indicating that the main quenching mechanism is due to photo-induced charge transfer between the excited states of the ZnPcs to NACs. Furthermore, so a favourable electron to be transferred from the excited state of sensor to the analyte leads to observed fluorescence quenching. This can be understood better one needs to take a close look at the energy levels of ZnPcs and NACs. Density Functional Theory (DFT) calculations were carried out using Gaussian03 with basis set as B3LYP/6-31g* with LANL2DZ. Tetra-substituted ZnPcs were isolated as different regioisomers with C4h, D2h, C2v, and Ci symmetries. Spectroscopic data show, however, 50% probability of obtaining the C4h symmetry as stable conformer with high yield. Therefore, all ZnPcs were optimized with point C4h symmetry for better correlation of ZnPc1, ZnPc2 and ZnPc3. The optimized structures are in good agreement with similar structures obtained from experimental studies. Frequency calculations were carried out for the optimized structures in order to confirm that all structures considered are minima on the potential energy surface.

Fig. 8 Energy minimized structure of ZnPc3 and its adduct (1:1) with TNP optimized at B3LYP/6-31g* basis set. The Figure also depicts the electron density profiles of HOMO and LUMO orbitals of ZnPc3 and ZnPc3-TNP. The representative optimized structures of ZnPc3 and of the adduct with TNP are shown in Fig. 8, alongside with their frontier molecular orbital electron density profiles. The HOMO orbitals of ZnPcs are centred on the phthalocyanine core with substantial contribution being observed from the dimethylamine groups. The LUMO energy levels are double degenerate with only one of the states shown for each system. The calculated LUMO energy levels of the ZnPcs are very close to the experimental ones determined from the cyclic voltammetry measurements. The HOMO-LUMO gap was found to decrease with the increase in the number of dimethylamine groups showing 2.02 eV, 2.03 eV and 1.90 eV for ZnPc1, ZnPc2 and ZnPc3, respectively. The decrease in the HOMO–LUMO gap for ZnPc3 arises due to a considerable
electronic coupling between the donor part of the dimethylamine groups and the phthalocyanine core. These results are in agreement with the HOMO–LUMO gap obtained from absorption and electrochemical studies. The LUMO energy level of \textit{ZnPc3} is close to the LUMO energy level of TNP results efficient electron transfer process for high selectivity. The calculated binding energy (\(\Delta E\)) of binding to TNP, whereas for \textit{ZnPc1} and \textit{ZnPc2} treated with TNP.

LUMO of TNP. Similar results were obtained for other \textit{ZnPcs} with TNP. The frontier molecular orbitals of the \textit{ZnPc3} TNP adduct show that the electron density of the HOMO orbital is localized on the phthalocyanine ring while the LUMO orbitals are instead localized on the TNP molecules. This indicates that an efficient electron transfer process occurs by excited-state electron transfer from the lower lying LUMO level of \textit{ZnPcs} to the LUMO of TNP. Similar results were obtained for other \textit{ZnPcs} treated with TNP.

![Figure 9](image-url)

**Fig. 9** (a) Time dependent fluorescence quenching of \textit{ZnPc3} thin film upon exposure to the saturated vapours of TNP (7.7×10\(^{-3}\) ppb). The inset shows the variation in the Stern-Volmer plot of \textit{ZnPc1-5} to the saturated vapours of TNP at different time intervals. (b) Variation in the quenching efficiency of \textit{ZnPc1-5} to the saturated vapours of different NACs for a total exposure of 10 min.

Towards the practical use of \textit{ZnPcs} as potential chemosensors, thin films were prepared by spin coating on a quartz substrate with a rate of 2000 rpm and a solution with concentration of 0.5 mg/0.2 mL in chloroform. The obtained thin films were annealed at 50 °C for 2 h. The absorption spectra of \textit{ZnPcs} thin films show broad Soret and Q-bands. The emission spectra of the thin films further depict similar behaviour as that of the solution spectra (Fig. S36, ESI†). Solid-state fluorescence quenching of the prepared thin films was obtained by exposing them to saturated vapours of NACs over time. \textit{ZnPc3} is highly sensitive towards the saturated vapours of TNP when compared with the same results for other \textit{ZnPc} films. A high quenching response (76%) was obtained for 720 seconds of exposure time. Interestingly, \textit{ZnPc4} show only 5-15% decrease in the fluorescence emission intensity. To understand the role of electron donating groups contributing to the enhanced sensitivity, fluorescence quenching studies were carried out with \textit{ZnPc5} under similar conditions. The thin film of \textit{ZnPc5} only showed 8% decrease in the fluorescence quenching for TNP vapours at 600 sec of exposure time. Fig. 9 shows that \textit{ZnPc3} is highly selective towards TNP while other \textit{ZnPcs} only show a 5-21% decrease in the quenching efficiency; the order of reactivity is as follows: \textit{ZnPc3} > \textit{ZnPc2} > \textit{ZnPc1} > \textit{ZnPc4} > \textit{ZnPc5}. Fig. S37 and S38 (in the ESI†) show the fluorescence quenching behaviour of \textit{ZnPc1-5} towards saturated vapours of other NACs. The decrease in fluorescence intensity of thin films of \textit{ZnPcs} upon exposure to the nitroaromatic vapors is ascribed to the charge-transfer complex formation between the electron rich phthalocyanines to the electron-deficient nitroaromatics through strong intermolecular interactions. In addition, steric effects may also influence the sensor behaviour. Therefore, morphological studies of the thin films were carried out with field emission scanning electron microscope (FE-SEM) to investigate structural integrity and homogeneity (Fig. 10). The samples for SEM were prepared by depositing the solutions of \textit{ZnPcs} onto a SiO\(_2\)/Si substrate (1x1 cm\(^2\)).

![Figure 10](image-url)

**Fig. 10** Scanning electron microscope (SEM) images of \textit{ZnPc} thin films prepared from chloroform: (a) \textit{ZnPc1} (b) \textit{ZnPc2} and (c) \textit{ZnPc3}. (d) SEM of \textit{ZnPc3} thin films obtained from methanol.

The morphology of the \textit{ZnPc3} thin films obtained from chloroform exhibit highly ordered porous nature with variation in the pore size. The \textit{ZnPc1} film shows cluster of aggregates and that of \textit{ZnPc2} a more ordered crystalline morphology. In general, the formation of such porous structures for thin films were typically obtained from carbon-rich materials, polymers and other inorganic materials.\(^{49}\) The formation of such morphology for phthalocyanines is, to the best of our knowledge, rare opening interesting possibilities for optoelectronic applications. We note that the morphology of the
thin films was largely influenced by the solvent employed. ZnPc3 shows porous structures when dichloromethane and chloroform are used, while employing instead methanol promotes the formation of spherical aggregates (Fig. 10d). The use of mixed solvents such as dichloromethane-hexane and dichloromethane-methanol, promotes the collapse of the porous film morphology with the formation of spherical crystallites. This is a clear indication that the solvent polarity plays an important role to obtain the desired porous morphology (Fig. S39, ESI†). ZnPc1 and ZnPc2 also promote the formation of spherical crystalline morphologies in methanol and in mixed solvents. The morphological results of the thin films ascribe the variation in the sensing behaviour of the different molecular structures. For example, the ZnPc3 thin film obtained from methanol shows only 46% quenching of fluorescence for TNP vapour. It is worthy of noting that the highly ordered porous structure of ZnPc3 can easily allow the diffusion of the vapours of NACs which, in turn, has a direct consequence in the observed selectivity and efficient binding of TNP.

Fig. 11 Reversibility of the ZnPc3 thin film exposed to the saturated vapours of TNP.

An important consideration to design a real time, practical, and reusable sensor is the ability to release the analyte vapours after the exposure and quickly recover the fluorescence emission of the films. There are, nevertheless, only a handful of reports that show the recovery of the fluorescence after exposure to the analyte vapour, which may be due to the fact that recovery is often a slow process.⁴⁶ Fig. 11 shows the reversibility of the ZnPc3 film towards the exposure of TNP vapour. The film was exposed to saturated vapours of TNP at ambient temperature for 300 s. The emission spectrum of the film was collected through front face technique and compared with the emission spectrum of the virgin film. The thin film was washed with water and dried under nitrogen flow and the emission spectrum was recorded and the whole process was repeated. The results show that the initial fluorescence intensity was significantly retained after several cycles, ultimately confirming the high photostability of the fabricated thin film.

4. Conclusions

In conclusion, we have developed a novel method for the selective substitution of dimethylamine derivatives on phthalonitriles. Cyclic tetramerization of dimethylamine phthalonitriles with ZnCl₂ in 1-chloronaphthalene at 200 °C forms Zn(II)phthalocyanines in 65±3% yield. It was found that increasing the number of dimethylamine groups at the peripheral positions decreases the HOMO-LUMO gap. The absorption spectra of ZnPc1-3 in aprotic solvents exhibits a typical behaviour of monomeric form and the observed variation in the Q-band position is mainly due to solvent permittivity. In methanol, compounds show strong intermolecular aggregation with the propensity to aggregate decreasing with the increase of the alkyl chain length of the employed solvent (from methanol to octanol). We further found that the choice of the solvent has a strong impact on the observed photophysical properties, being observed a correlation between the fluorescence quantum yield and the extent of aggregation. We successfully demonstrated that ZnPc derivatives endowed with both electron rich and electron deficient compounds at the periphery show selective detection towards TNP. ZnPc3 exhibits, furthermore, an efficient fluorescent chemosensor-type behaviour for TNP with a rate constant of Kq = 2.99x10⁴ M⁻¹ with LOD of 11±2 ppm. The order of reactivity was found to be ZnPc3>ZnPc2>ZnPc1>ZnPc4>2Pc5. Time-resolved fluorescence emission and UV-Visible titration studies reveal that a static quenching phenomena is predominant by axial coordination of TNP molecules to ZnPcs derivatives, and also with the formation of strong inter-molecular π-π interactions. DFT studies indicate that the electron transfer occurs from the photo-excited ZnPcs to the electron deficient NACs. The solid state fluorescence of ZnPc3 thin films with a typical honeycomb pore distribution exhibits 76% of quenching efficiency in 720 sec towards saturated vapours of TNP. The pore distribution for the ZnPc3 thin films seems to enhance the diffusion of saturated vapours of TNP, ultimately leading to the observed high selectivity. The high reversibility and photostability of ZnPc3 film demonstrating promising practical application potential in solid state sensors for selective detection of TNP.

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Notes and references

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† Electronic Supplementary Information (ESI) available: spectral characterization (1H, 13C and 19F NMR), FT-IR, absorption and fluorescence emission in different solvents, interaction of ZnPcs with NACs in solution and in the vapour state, single-crystal X-ray diffraction technical details. See DOI: 10.1039/b000000x/
§ Crystal data for I: C23H6F2N6, M = 189.19, triclinic, space group P-1, Z = 2, a = 6.4282(18) Å, b = 8.584(2) Å, c = 8.968(3) Å, α = 108.015(10)°, β = 103.788(10)°, γ = 92.762(10)°. F = 453.0(2) Å⁻³, μMo-Kα = 0.102 mm⁻¹, Dc = 1.387 g cm⁻³, yellow block, crystal size of 0.20x0.12x0.08
mm. A total of 13052 reflections collected, 1636 were independent (Rint = 0.0774). Final R1 = 0.0553 [I > 2σ(I)] and wR2 = 0.1244 (all data).

Data completeness to theta = 25.2°, 98.5%. CCDC 1023883.

Crystal data for 2: C12H12ClIN, M = 205.64, triclinic, space group P-1, Z = 2, a = 7.0606(4) Å, b = 7.0918(4) Å, c = 10.4983(6) Å, α = 76.075(3)°, β = 71.330(3)°, γ = 77.999(3)°, V = 478.45(5) Å³, μ(Mo-Kα) = 0.358 mm⁻¹.

Of a total of 16051 reflections collected, 2568 were independent (Rint = 0.0254). Final R1 = 0.0345 [I > 2σ(I)] and wR2 = 0.0897 (all data).

Data completeness to theta = 25.2°, 99.7%. CCDC 1023885.

Crystal data for 3: C10H8F4N8, M = 250.26, monoclinic, space group P21/n, Z = 4, a = 6.7161(18) Å, b = 16.551(5) Å, c = 11.136(3) Å, β = 92.593(10)°, V = 1236.6(6) Å³, μ(Mo-Kα) = 0.106 mm⁻¹.

D₁ = 1.427 g cm⁻³, colourless block, crystal size of 0.19×0.18×0.04 mm. Of a total of 16051 reflections collected, 2568 were independent (Rint = 0.0254). Final R1 = 0.0345 [I > 2σ(I)] and wR2 = 0.0897 (all data).

Data completeness to theta = 25.2°, 99.6%. CCDC 1023883.