Porphyrins

Polyfunctional Lewis Acids: Intriguing Solid-State Structure and Selective Detection and Discrimination of Nitroaromatic Explosives

Chinna Ayya Swamy P and Pakkirisamy Thilagar *[a]

Abstract: Synthesis and crystal structures of three porphyrin-based polyfunctional Lewis acids **1–3** are reported. Intermolecular HgCl····HgCl (linear and μ -type) interactions in the solid state of the peripherally ArHgCl-decorated compound **3** lead to a fascinating 3D supramolecular architecture. Compound **3** shows a selective fluorescence quenching response to picric acid and discriminates other nitroaromatic-based explosives. For the first time, an electron-deficient polyfunc-

Introduction

Aryl mercuryl compounds have been used as precursors to synthesize other organometallic compounds through transmetalation reactions.^[1] Recently, multifunctional organomercury compounds have been used as Lewis acid catalysts, receptors for the recognition of anions and neutral Lewis basic species,^[2,3] and as building blocks for supramolecular structures.^[4] In this context, seminal contributions from Kochi and co-workers,^[5a] Dean and Damude^[5b,c] and Olah and co-workers^[5d] are notable. Recently, Gabbaï and co-workers elegantly utilized trimeric perfluoro-o-phenylene mercury as a supramolecular host for several π -conjugated guest molecules.^[6] The work of Jäkle and co-workers on metallocene-based mercuryl compounds is also noteworthy in this context.^[7]

Among various organic π systems, porphyrins^[8g,h] and expanded porphyrins^[8c,k] occupy a special position and have found wide applications in organic light-emitting diodes,^[8d,e,p,q] photodynamic cancer therapy,^[8] photovoltaics,^[8b,n] catalysis,^[8a,f,i,o] and chemosensing.^[8l,m] The *meso*-functionalized porphyrins exhibit different intramolecular electronic coupling and coordination chemistry beyond classical coordination compounds. Despite the vast developments in porphyrin chemistry, surprisingly, the chemistry of peripheral organomercuryl porphyrins has not been reported to date. This may be attributable to difficulties in synthesizing mercury-substituted

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tional Lewis acid is shown to be useful for the selective de-

tection and discrimination of nitroaromatic explosives. The

Stern-Volmer quenching constant and detection limits of

compound **3** for picric acid are the best among the reported

small-molecular receptors for nitroaromatic explosives. The

electronic structure, Lewis acidity, and selective sensing char-

acteristics of 3 are well corroborated by DFT calculations.

 $\label{eq:scheme 1. Synthesis of compounds 1-3. i) HC(OEt)_3/EtOH/HCl (cat.). ii) 1) n-BuLi/Et_2O (-78 °C); 2) Me_3SnCl; 3) 1 % KHSO_4/THF. iii) Pyrrole/BF_3·Et_2O/CHCl_3, DDQ/benzene. iv) Zn(OAc)_2·2H_2O/MeOH; v) HgCl_2/THF/Et_2O.$

porphyrins in good yields. Herein, we report a facile synthetic route to peripherally Hg decorated porphyrin **3** (Scheme 1), which can be regarded as a polyfunctional Lewis acid. Attempts were made to understand the fundamental electronic and solid-state structure of **3** and to utilize of its properties for potential applications.

Recently, fluorescent organic π systems have been comprehensively studied for detection of nitroaromatics.^[9] Nitroaromatics detection is highly relevant to applications related to environmental pollution control, forensic analysis, and for national security (defense and antiterrorism).^[10] Among chemical explosives, trinitrotoluene (TNT) and picric acid (PA) have attracted a lot of attention due to their high energy content.



Particularly in vapor form, they are very hazardous and can cause headache, weakness, anemia, and liver damage.^[11] In general electron-rich conjugated π systems that enable effective π - π stacking with electron-poor quenchers (TNT or PA) have been employed for sensing these explosives.^[12] However, poor selectivity has been observed in general. Both TNT and PA are electron-deficient nitroaromatics and they differ only marginally in their chemical structures. Thus, designing a superior sensor for selective detection of TNT or PA is a topical and challenging area of research.^[13]

It occurred to us that the electron density of a large π system such as a porphyrin could be modulated by decoration with suitable Lewis acid (LA) groups. We anticipated that the modified π cloud of the conjugated molecule may show selectivity towards TNT or PA. We also envisioned that the presence of LAs on the organic π system may facilitate intermolecular hydrogen-bonding interaction with the hydroxyl group of PA and thereby discriminate it from TNT, which is has no hydroxyl group. Our expectation was met by the new chloromercuryl-phenyl metalloporphyrin **3**, which showed a highly selective fluorescence-quenching response towards PA. To the best of our knowledge, this is the first example of a polyfunctional LA-based fluorescence sensor for nitroaromatics.

Results and Discussion

Synthesis and structural characterization of 1-3

The synthetic protocol for Zn^{II} 5,10,15,20-tetra(4'-chloromercuriophenyl)porphyrin (3) is shown in Scheme 1. First, 5,10,15,20tetra(4'-trimethylstannylphenyl)porphyrin (1) was prepared by acid-catalyzed condensation reaction between pyrrole and 4-trimethylstannylbenzaldehyde. Treatment of 1 with Zn(OAc)₂·2H₂O in CHCl₃/MeOH (1/1) gave Zn^{II} 5,10,15,20tetra(4'-trimethylstannylphenyl)porphyrin (2) as a purple solid in good yields. Compound 2 was treated with four equivalent of HgCl₂ in THF to give Zn^{II} 5,10,15,20-tetra(4'-chloromercuriophenyl)porphyrin (3) as a dark brown solid. Compounds 1-3 were characterized by NMR spectroscopy (¹H, ¹³C, ¹¹⁹Sn, ¹⁹⁹Hg) and ESI-MS. The molecular structures of 1-3 were confirmed by single crystal X-ray diffraction studies. The ¹H NMR spectra of 1-3 showed a singlet at about 8.86 ppm corresponding to the β -pyrrole proton of porphyrin. The *meso*-phenyl moiety gave rise to two doublets at about 8.20 and about 7.87 ppm, respectively. The ¹¹⁹Sn resonances of 1 and 2 were observed at -25.5 and -25.1 ppm, respectively. The ¹⁹⁹Hg signal of **3** was observed at -1181 ppm. ESI-MS analysis, which showed peaks for **1** at 1272.07 [*M*+H]⁺, 1103.27 [*M*-SnMe₃]⁺ and 941.40 $[M-2SnMe_3]^+$, for **2** at 1330.92 $[M]^+$, 1168.87 $[M-SnMe_3]^+$, 1024.57 $[M-2SnMe_3+Na]^+$ 843.47 $[M^+-3SnMe_3]$, and 679.67 $[M-4SnMe_3]^+$, and for **3** at 1619 $[M^+]$, 1383 $[M^+-HgCl]$, 1150 $[M^+-2HgCI]$, and 679 [M+-4HgCI] confirmed their chemical composition. The experimentally observed and calculated isotopic distributions of the peaks corresponding to fragments were consistent with their m/z values (see the Supporting Information).



Figure 1. Molecular structures of **2** (left) and **3** (right), as determined by single crystal X-ray diffraction studies. Atoms are shown with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

The molecular structures of **1–3** were confirmed by singlecrystal X-ray analysis. The molecular structures of **2** and **3** are shown in Figure 1, and that of **1** is shown in the Supporting information. Compound **2** crystallizes with four H_2O molecules; two of them are bound to Zn and the remaining two are trapped in the crystal lattice. The asymmetric unit of **3** contains four DMF molecules, of which one is attached to Zn center, two to HgCl moieties, while the fourth is encapsulated within the crystal lattice (see Figure 2).



Figure 2. Supramolecular 3D network structure of 3 (bottom left) and 3 with encapsulated DMF (bottom right). Bonding modes of 3 showing μ -type (top right) and linear-type (top left) Hg–l bonding.

The metric parameters of **3** (1.49(3) Å between tetrapyrrole unit and *meso*-phenyl group and 2.08(2) Å between HgCl unit and *meso*-phenyl group) are shorter those of both **1** [1.50(2) and 2.14(2)] and **2** [1.51(1) and 2.146(9)]. The C–C bonds of the porphyrin *meso*-carbon atoms and *meso*-phenyl substituents in **3** are significantly shorter than those observed for **1** and **2**. The dihedral angle between *meso*-phenyl and tetrapyrrole units in **3** (56°) is significantly smaller than those of **1** (90°) and **2** (66°). On the basis of the dihedral angles, one can tentatively conclude that the electronic communication between the porphyrin core and terminal Lewis acid moieties should be stronger in **3** than in **1** and **2**. The Zn center in compound **2** is in octahedral geometry (four pyrrole nitrogen atoms occupy the square plane, and two water molecules the

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axial positions). In **3**, Zn is in square-pyramidal geometry (four pyrrole nitrogen atoms in the square plane and one DMF molecule in an axial position). The Zn atom in **3** lies above the mean plane of the porphyrin ring, in contrast to **2** (see the Supporting Information, Table S1). This is possibly due to the difference in the coordination environment around the Zn center in **2** and **3**.

In the solid state, compound **3** exhibits an interesting supramolecular 3D structure formed by intermolecular Hg-Cl-Hg interactions between adjacent molecules. A closer look at the 3D structure reveals the presence of two different types of Hg-Cl-Hg interactions, that is, linear and μ -type coordinative covalent interaction between neighboring molecules (Figure 2, top). The linear Hg-Cl-Hg bonds appear once after every two adjacent μ type bonds. The chloride ions involved in the μ -type bonding also interact with the *meso*-phenyl hydrogen atoms, whereas those in linear-type bonding interact with β -pyrrole protons of the porphyrin. These multiple interactions generate two different types of infinite tapes (see the Supporting Information, Figure S3). These tapes form a sandwich-herringbone pattern along the *a* axis^[8] (Figure 3). These infinite tapes enclose voids,



Figure 3. Sandwich-herringbone pattern of 3 with DMF solvent molecules.

which are occupied by DMF molecules, which are not bound to Hg or Zn atoms). The guest DMF molecules are non-innocent and form weak C-H-Cl-Hg interactions with *meso*-C₆H₄HgCl units of neighboring molecules and augment the 3D supramolecular structure. The bond lengths and bond angles of coordinative covalent interactions are in line with the literature reports.^[7a, 14]

Photophysical properties

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The absorption spectra of compounds 1-3 show Soret and Q bands (Figure 4) typical of a porphyrin core. The spectral features are compared with those of the model tetraphenylporphyrin compounds TPP and TPP+Zn in Figure 4, top). Interestingly, the absorption maxima (Soret bands) of 1-3 are redshifted compared to TPP and Zn-TPP. Compound 3 shows



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Figure 4. Normalized absorption spectra of 1–3 compared with those of TPP and TPP+Zn [Soret bands (a) and Q-bands (b) recorded for 10^{-6} M solutions]. Normalized fluorescence spectra of 1–3 compared to those of TPP and TPP+Zn [(c), λ_{ex} =420 nm, 10^{-6} M DMF as solution].

the largest redshift (ca. 17 nm). The Q bands of compounds 1-3 are also redshifted with respect to the model compounds. The significantly larger redshift of absorption features observed for 3 can be tentatively explained in terms of the dihedral angle between the tetrapyrrole unit and the heavy-metal-containing meso-phenyl unit. This dihedral angle in compound 3 (56°) is smaller than that of 2, as a result of which the interaction between the tetrapyrrole unit and the heavy metal is more favored in the former compared to the latter. On excitation at 420 nm, compounds 1-3 exhibited typical porphyrin and metalloporphryin (TPP and Zn-TPP) PL features. However, the emission peaks of 1-3 are redshifted compared to TPP and Zn-TPP. As in the absorption spectra, the redshift of 3 is larger than those of 1 and 2. The quantum yields of 1 (5.8%), 2 (3.4%), and 3 (2.1%) are significantly lower than those of the respective model compounds TPP and Zn-TPP. These results are in line with values reported for heavy metal substituted porphyrins and metalloporphyrins^[15] (Table 1).

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Table 1. Ph							
Compound	Absorption [nm] (ɛ)	Emission [nm] (λ _{ex} =420 nm)	Quantum yield ^(b) [%] $(\lambda_{ex} = 420$ nm)				
1	422 (0.65×10 ⁶); 554 (2.2×10 ⁴); 592 (1.3×10 ⁴); 646 (0.4×10 ⁴).	651, 714	5.8				
2	424 (0.58×10 ⁶); 550 (4.0×10⁴); 588 (1.0×10⁴).	601, 647	3.4				
3	435, (0.61×10 ⁶); 566 (1.3×10 ⁴); 604 (9.1×10 ³).	608, 658	2.1				
ТРР	$\begin{array}{l} 418 \; (0.71 \times 10^6); 512 \\ (4.0 \times 10^5); 551 \; (3.2 \times 10^4); 592 \\ (2.0 \times 10^4); 647 \; (1.4 \times 10^4). \end{array}$	651, 711	11.3				
TPP + Zn	420 (0.82×10 ⁶); 549 (3.8×10 ⁵), 588 (1.0×10 ⁴).	591, 638	6.4				
[a] All given data are for 10 μ M DMF solutions. [b] Quantum yields were calculated by using quinine sulfate (0.1 M H ₂ SO ₄ , λ_{ex} =420 nm $\Phi_{\rm F}$ =57.7%) solution as reference (R) and using the following formula $\Phi = (\Phi_{\rm F}/I_{\rm B})(A_{\rm B}/A)(\eta^2/\eta_{\rm B}^2)$, where Φ = quantum yield, <i>I</i> = emission intensit							

 $\Phi = (\Phi_{\text{F}}/\eta_{\text{R}})(\eta_{\text{R}}/\eta_{\text{R}})$, where $\Phi = \text{quantum yield}$, $\eta = \text{emission interm}$ $A = \text{absorbance at } \lambda_{\text{ext}}$ and $\eta = \text{refractive index of solvent.}$

Titration studies

The nitroaromatics-sensing ability of **3** was evaluated by titrating it against various nitroaromatics. As hypothesized above, compound **3** discriminates TNT and shows very high selectivity towards PA. This result is remarkable because the redox potentials of TNT and PA are similar^[9] and in general organic π systems such as porphyrin^[16] interact with both TNT and PA and cannot distinguish between them. The selective discrimination in the present instance is possibly due to the presence of Lewis acidic HgCl groups at the porphyrin π system. The Lewis acidic functional groups in **3** can distinguish the minor difference in functional groups between TNT and PA.

On gradual addition of PA to a DMF solution of 3, the initial fluorescence intensity of the 3 was quenched rapidly (Figure 5), but there was no change in the shape of the emission spectra. We believe that the observed quenching of fluorescence intensity is due to complex formation between 3 and PA (Figure 5). A linear Stern-Volmer plot was obtained from the fluorescence-quenching titration profile, and Stern-Volmer quenching constants K_{SV} were determined from the slope of the plot (see the Supporting Information). The K_{sv} value of $1.6 \times 10^7 \,\mathrm{m^{-1}}$ is higher than those obtained for other PA chemosensors.^[13c, 17] A linear Stern–Volmer relationship can be obtained for a static or dynamic quenching process. The static quenching mechanism involves the formation of a groundstate nonfluorescent charge-transfer complex, whereas dynamic quenching involves excited-state electron transfer from the fluorophore to the quencher. The electronic absorption spectroscopic studies and excited-state lifetime measurement in response to PA concentrations clearly indicate the formation of a ground-state complex between Lewis acid 3 and PA (Figure 5 and Supporting Information). On addition of PA, the intensity of Soret band at 435 nm decreased with concomitant redshift by 10 nm. The considerable change in absorption in-



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Figure 5. a) The absorption bands of **3** are redshifted in the presence of PA ($\lambda_{ex} = 425 \text{ nm}, 10^{-6} \text{ M}$ solution in DMF). The inset shows the changes associated with the Q bands of **3** in the presence of PA. b) The fluorescence intensity of **3** decreased linearly with increasing equivalents of PA. The changes saturate at 15 equiv of PA. Concentrations of solutions of **3** and PA were 10^{-6} M and 10^{-4} M respectively. For fluorescence studies, **3** was excited at 425 nm.

tensity of **3** on the gradual addition of PA is consistent with the formation of a ground-state complex between **3** and the PA quencher. Fluorescence lifetime studies on **3** with variable concentrations of PA showed no significant change in lifetime, which strongly suggested that the complex (**3** + PA) was formed in the ground state.^[18]

We also investigated the effect of other electron-deficient aromatic compounds on the fluorescence profile of 3 (Figure 5). Clearly 3 shows very high selectivity towards PA over other tested analytes such as dinitrobenzene, dinitrotoluene (DNT), benzoguinone, tetrachlorobenzoguinone (chloranil), and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The reduction potential of these and PA do not differ significantly, the observed higher quenching response for PA is presumably due to the interaction between Cl in 3 and OH of PA. To validate the above hypothesis, the picric-acid binding event was monitored by ¹H NMR spectroscopy. On addition of PA, three major chemical shift changes were observed in the ¹H NMR spectrum: 1) The phenolic proton of PA shifted downfield from $\delta = 5.1$ to 5.6 ppm, 2) the β -pyrrole protons of **3** shifted downfield from $\delta = 8.76$ to 8.95 pm, and 3) the *meso*-phenyl protons of compound **3** shifted downfield from $\delta = 7.81$ and 8.10 ppm to 7.93 and 8.25 ppm, respectively. There were no significant chemical

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shift changes on addition of other nitroaromatics such as TNT, DNT, and nitrobenzene or benzoquinone to compound **3** (see the Supporting Information). The binding event was also monitored by observing the ¹⁹⁹Hg NMR chemical shift of compound **3** in the presence of various nitroaromatics. Only on addition of PA did the ¹⁹⁹Hg signal at $\delta = -1186$ ppm shift downfield to -1160 ppm. Very little change in the chemical shift was observed in the presence of dinitrophenol. These results directly corroborated that the interaction between the phenolic OH and C₆H₄HgCl groups could be a possible reason for the selective detection of PA.

Furthermore, compound **3** was titrated against the PA analogue dinitrophenol (DNP), and the changes in emission profile were monitored by fluorescence spectroscopy. As observed in the case of titrations with PA, noticeable fluorescence quenching of **3** was observed on gradual addition of DNP (K_{sv} = 4.16 × 10⁴ M⁻¹), but the magnitude of quenching was less for DNP (71% decrease in fluorescence intensity) compared to PA (94% decrease in fluorescence intensity). Under similar conditions, **3** showed negligible fluorescence-quenching response to other phenols such as 4-*tert*-butylphenol, 3-methoxyphenol, 4-nitrophenol, and 4-methoxyphenol. This clearly suggests that **3** can be used as a selective sensor for PA-based explosives (Figures 6



Figure 6. Fluorescence quenching efficiency of **3** (10–5 M) for various nitroaromatics ($\lambda_{ex} = 425$ nm, 10⁻⁶ M solution in DMF). From left to right: 4-aminophenol (1), 4-*tert*-butylphenol (2), 4-cresol (3), 3-cresol (4) 4-fluorophenol (5), benzoquinone (6), naphthalene monohydrate (7) nitrobenzene (8), 1,4-dinitrobenzene (9), 1,3-dinitrobenzene (10), 1,2-dinitrobenzene (11), nitrotoluene (12), 2,4-dinitrotoluene (13), TNT (14), nitrophenol (15), 2,4-dinitrophenol (16), and PA (17) (10⁻³ M). From this data one can conclude that compound **3** is a selective fluorogenic sensor for trinitrophenol and dinitrophenol.

and 7). To probe the role of the Lewis acidity of Hg^{\parallel} in 3, we performed fluorescence titrations for model compounds TPP and Zn–TPP and complexes 1 and 2 with nitroaromatics under similar titration conditions. In all these cases, the changes in the emission feature were insignificant. Despite the structural similarity of 1 and 2 to 3, changes in emission spectra on addition of nitroaromatics are very small, which may be due to the high Lewis acidity of 3 compared to 1 and 2 and model compounds (TPP and Zn–TPP).

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Figure 7. Digital photographs of **3** with various nitroaromatics. From left to right: **3** (1) 4-aminophenol (2), 4-*tert*-butylphenol (3), 4-cresol (4), 3-cresol (5) 4-fluorophenol (6), benzoquenone (7), nitrobenzene (8), 1, 4-dinitrobenzene (9), 1, 3-dinitrobenzene (10), 1, 2-dinitrobenzene (11), nitrotoluene (12), 2, 4-dinitrotoluene (13), TNT (14), nitrophenol (15), dinitrophenol (16), and PA (17)]. The photographs clearly indicate that, on addition of 2,4-dinitrophenol or PA to compounds, the fluorescence intensity decreased, whereas for other nitroaromatics there was no change.

The detection limits of compound **3** with PA and dinitrophenol were determined from the fluorescence-quenching titration data. The *x*-axis intercept (here [X], X = PA or DNP) was obtained by plotting $(I_{max} - I)/(I_{max} - I_{min})$ versus lg[PA], where I_{max} , *I*, and I_{min} are the initial fluorescence intensity, intensity at a particular concentration, and intensity at saturation point, respectively. Detection limits were calculated by the formula ([X]×MWX)/1000 (multiplied by 10⁹ to give values in ppm), where MWX is the molecular weight of PA or DNP and the related spectrum shown in the Supporting Information. The detection limits for compound **3** were found to be 18 and 140 ppb for PA and DNP, respectively. The molecular probes **3** showed much lower detection limits compared to reported small-molecular probes for PA (Table 2).^[9e, 19]

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Table 2. Quenching efficiencies, quantum yields, and detection limits of $1-3$, TPP, and Zn-TPP with PA.										
1 12 7 7.2 7.2 n.d. Icl n.d. 2 15 6 3.4 3.4 n.d. n.d. 3 94 71 0.01 0.25 18 140 TPP 9 4 11.2 11.2 n.d. n.d. Zn-TPP 11 5 5.4 5.4 n.d. n.d.	Compound	Quenchin PA	g efficiency [%] (I ₀ —I/ I ₀)×100 DNP	Qua yiel PA	antum d [%] DNP	Dete limit PA	ction [ppb] DNP				
3 94 71 0.01 0.25 18 140 TPP 9 4 11.2 11.2 n.d. n.d. Zn-TPP 11 5 5.4 5.4 n.d. n.d.	1	12 15	7 6	7.2 3.4	7.2 3.4	n.d. ^[c] n.d.	n.d. n.d.				
	3 TPP Zn–TPP	94 9 11	71 4 5	0.01 11.2 5.4	0.25 11.2 5.4	18 n.d. n.d.	140 n.d. n.d.				

[a] All given data are for 10 μ M DMF solutions. [b] Quantum yields were calculated by using quinine sulfate (0.1 μ H₂SO₄, λ_{ex} =420 nm, Φ_{F} =57.7%) solution as reference (R) and using the following formula: $\Phi = (\Phi_{F} I/I_{R})(A_{R}/A)(\eta^{2}/\eta_{R}^{2})$, where $\Phi =$ quantum yield, I = emission intensity, A = absorbance at λ_{exv} and $\eta =$ refractive index of solvent. [c] Not detectable.

Computational studies

To gain further insight into the photophysical behavior of **1–3**, DFT calculations were performed. The hybrid B3LYP functional was used in all calculations, as implemented in the Gaussian 09 package,^[20] mixing the exact Hartree–Fock-type exchange with Becke's expression for the exchange functional and that proposed by Lee–Yang–Parr for the correlation contribution. We used the LANL2DZ basis set for Sn, Hg, and Zn and 6-31G for the rest of the atoms (C, N, H, Cl). All of the energy calculations were performed with 10^{-8} density-based convergence criterion. The MOs were generated from corresponding cube files by

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Figure 8. Selected MOs of **3** and Zn–TPP (left). In **3**, HOMO and LUMO are mainly centered on the porphyrin π system. The LUMO + 1 and LUMO + 2 are centered only on the HgCl unit. In Zn–TPP, HOMO, LUMO + 1, and LUMO + 2 are localized on the porphyrin unit. Right: MOs of **3** and Zn–TPP. For **3**, LUMO and LUMO + 2 are doubly degenerate orbitals, whereas in Zn–TPP LUMO and LUMO + 1 have similar energy but are not degenerate due to its C_{2h} symmetry.

using Gaussview 5.0 with isovalue = 0.02. The structural parameters of DFT optimized structures closely resemble those obtained from single-crystal X-ray analysis, with slight differences in the values of the dihedral angles. The optimized structure of compound **3** shows an C-Hg-Cl bond angle of about 180° and C-Hg bond length of 2.195 Å. The phenyl rings are bent by 70° with respect to the porphyrin plane. The MOs of compound 3 and Zn–TPP are completely different from each other. As shown in Figure 8, the HOMO (-4.95 eV) of Zn-TPP is completely localized on the porphyrin, and LUMO (-2.17 eV) and LUMO+1 (-2.17 eV) are also concentrated on the porphyrin unit, which has same energy but nondegenerate orbitals due to its C_{2h} symmetry. However, LUMO + 2 (-0.64 eV) is localized more on the porphyrin and moderately on the meso-phenyl units, whereas the HOMO (-5.59 eV) of 3 is comparatively concentrated on the porphyrin unit, the LUMO (-2.78 eV), which is doubly degenerate, is followed by LUMO + 1 (-2.04 eV) and LUMO + 2 (-2.04 eV), three molecular orbitals having same energy, which are mostly spread over the mercury and chlorine atoms. The participation of the atomic orbitals of the peripheral organometallic moiety in electronically important energy levels may be responsible for the redshift observed in the Soret band of compound 3 (Figure 4, top). It also indicates redistribution of electrons from the core towards the periphery on electronic excitation, which can be useful if explored further for photonic applications. These calculations show that there should be a considerable redshift in absorption bands on going from Zn-TPP to 3, which was clearly observed experimentally, and also possible participation of peripheral organometallic moieties in extending the conjugation in excited states, which results in the stabilization of LUMO + 1 and LUMO+2 compared to Zn-TPP. Whereas compound 2 is not much different from Zn-TPP in the localization of orbitals (HOMO, LUMO, LUMO+1 and LUMO+2), compound 2 has lower-energy frontier MOs than Zn-TPP (see the Supporting Information).



Figure 9. ESP surfaces of 3 and 2. The potentials clearly indicate that 3 is a stronger Lewis acid than 2.

The stronger Lewis acidity of the divalent organometallic Hg moieties compared to SnMe₃ groups can be well understood from their electrostatic potential (ESP) surface maps (Figure 9). The high charge separation near the (meso-phenyl)C-Hg-Cl motifs in compound 3 demonstrates the Lewis acidity of the Hg centers. Due to the ionic nature of the Hg-Cl bonds, the terminal chlorine atoms are electron-rich centers that may be the driving force in controlling the interactions of the compounds with electron-deficient nitroaromatics. The charge separation in the C-Hq-Cl motifs can also explain the nature of the bonding interactions observed in the solid-state structure of 3. The Cl--Hg--Cl and Hg--Cl--Hg bonding patterns in the solidstate structure of compound 3 presumably result from the intermolecular Hg---Cl electrostatic interactions. In 3, the peripheral Lewis acidic units are also electronically important and strongly participate in forming the low-lying vacant orbitals (see the Supporting Information). As discussed above, LUMO and LUMO+2 forms two degenerate energy levels in compound 3, which are mostly concentrated on the terminal HgCl units (Figure 9), and thus they are expected to participate actively in controlling the optical properties of compound 3.

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In addition, to get further insight into the nature of the interaction of PA with 3 and possible modes of interactions, detailed computational investigations were performed. Due to the large size of compound **3**, which was originally kept in D_{2d} symmetry, the optimizations of its interactions with picric acid in C_1 symmetry did not converge. To overcome this problem, optimizations were performed by considering fragment models, that is, Zn^{II}-porphyrin core and Ph-Hg-Cl (see the Supporting Information). Optimizations of the individual systems and their PA complex showed that the terminal C-Hg-Cl-aromatic (PA) interactions are more favorable (43.87 kJ mol⁻¹) than π (porphyrin)···· π (PA) interactions (15.87 kJ mol⁻¹). The terminal C-Hg-Cl-aromatic (PA) interactions are partially electrostatic in nature and enhance the intermolecular interaction between PA and 3 (see the Supporting Information). The terminal interactions can be also corroborated by the downfield shift of the ¹H NMR signal of OH (PA) observed for 3 + PA complexes in the ¹H NMR titrations.

Conclusion

For the first time, we have synthesized and structurally characterized a series of heavy-metal-decorated metalloporphyrins 1-3. Solid-state structural analysis revealed that compound 3 shows a very exciting 3D supramolecular structure through intermolecular coordinative covalent interactions between Hg and Cl. For the first time, we have shown that a polyfunctional Lewis acid can be used for selective detection of PA. The fluorescence studies demonstrated that 3 is a highly selective and sensitive chemosensor for phenolic nitroaromatic explosives such as PA and DNP. The manifestation of Lewis acidity in 3 (charge separation in Hg-Cl motifs) and thus its selective fluorescent sensing of electron-deficient nitrophenols (PA and DNP) was validated by DFT calculations. The presence of LA groups on the periphery of the metalloporphyrin modulated the electron density of the porphyrin π system and endowed compound 3 with a special ability to discriminate PA over TNT. Such discrimination has not been reported for LA-based sensors and has seldom been realized with other fluorescence chemosensors.

Experimental Section

Caution! The nitroaromatic compounds used in this study, especially TNT and PA, are very powerful explosives. They must be handled with care and also in very small quantities.

General information

*n*BuLi (1.6 \mbox{m} in hexane), 4-bromobenzaldehyde, and DDQ were purchased from Sigma-Aldrich and used as received without any further purification. Triethyl orthoformate and pyrrole were purchased from Merck. All reactions were carried under an atmosphere of pure N₂ by using standard Schlenk techniques. Solvents were redistilled by known laboratory procedures prior to use. All 400 MHz ¹H NMR, 100 MHz ¹³C NMR, 149 MHz ¹¹⁹Sn NMR, 71 MHz ¹⁹⁹Hg NMR were recorded on a Bruker Advance 400 MHz NMR spectrometer. Solution ¹H and ¹³C NMR spectra were recorded with residual

proton signals of deuterated solvents as internal reference. Mass spectral data were recorded on a Bruker Esquire 6000 ESI-MS spectrometer in standard spectroscopic-grade solvents. IR spectra were recorded on a Bruker ALPHA FTIR spectrometer. Electronic absorption spectra were recorded on a PerkinElmer LAMBDA 750 UV/Vis spectrophotometer. Solutions were prepared by using a microbalance (\pm 0.1 mg) and volumetric glassware and then charged in quartz cuvettes with sealing screw caps. Fluorescence emission studies were carried out on a Horiba JOBIN YVON Fluoromax-4 spectrometer. DFT calculations were performed with the B3LYP functional, as implemented in the Gaussian 09^[20] software package. For C, H, N, and Cl atoms the 6-31G(d) basis set was used, whereas for the Zn, Sn, and Hg centers, the LANL2DZ pseudopotential (pseudo=read) basis was used to generate high-quality results on moderately shorter timescales.

X-ray diffraction studies

Single crystal X-ray data were collected on a Bruker SMART APEX CCD diffractometer by using the SMART/SAINT software². Intensity data were collected with graphite-monochromatized $Mo_{K\alpha}$ radiation (0.71073 Å) at 90 K. The structures were solved by direct methods by using the SHELX-97² program incorporated in WinGX².

Synthesis

(4-Bromophenyl)-1,3-dioxolane (a): 4-Bromobenzaldehyde (9.5 g, 51.4 mmol) was dissolved in ethanol (100 mL) followed by subsequent addition of triethyl orthoformate (16.75 g, 113 mmol) and a catalytic amount of conc. HCl. The reaction mixture was heated under reflux for 4 h and cooled. The reaction mixture was extracted with EtOAc. The organic layers were combined, washed with brine and dried over anhydrous Na₂SO₄ followed by evaporation under vacuum to give **a** as a colorless oil. Yield: 98%.¹H NMR (400 MHz, CDCl₃): δ =7.49 (d, *J*=6.8 Hz 2H), 7.35 (d, *J*=8 Hz 2H), 5.46(s, 1H), 3.63–3.49(m, 4H), 1.24 ppm (t, *J*=6.8 Hz, 7.2 Hz 6H).

4-Trimethylstannylphenylbenzaldehyde (b): n-Butvllithium (19.28 mL, 1.6 m in hexane) 30.86 mmol) was added to a solution of a (7.23 g, 28.05 mmol) in Et_2O (to give 100) mL) over 30 min at -78°C. After 1 h, a THF solution of trimethyltin chloride (5 mL, 28.05 mmol) was added over 25 min. The reaction mixture was allowed to warm to room temperature and stirred overnight. A mixture of 30 mL THF and 30 mL of 1% aqueous KHSO₄ was added and the reaction mixture was stirred for a further 4 h. The resulting mixture was partitioned between Et₂O and water. The organic layers were combined, washed with brine, and dried over anhydrous sodium sulfate (Na₂SO₄). Subsequent evaporation and purification (neutral alumina column) gave b as a colorless liquid. Yield: 81 %. ¹H NMR (400 MHz, CDCl₃) δ 9.96 (s, 1 H), 7.78 (d, J=8 Hz 2 H), 7.65 (d, J=8 Hz 2 H), -2.75 (br, 2 H) 0.30 ppm [satellite 0.58 (J = 26.4 Hz), 0.45 ppm (J = 26.4 Hz)].

5,10,15,20-Tetrakis(4'-trimethylstannylphenyl)porphyrin (1): Freshly distilled pyrrole (0.27 mL, 3.70 mmol) was added to a chloroform (30 mL) solution of **b** (1.0 g, 3.70 mmol)and the resulting solution was degassed by purging N₂ for 30 min. Then, BF₃·Et₂O (0.05 mL, 0.37 mmol) was added dropwise and the reaction mixture was stirred until **b** was completely consumed (as observed by TLC). Then, a solution of DDQ (0.84 g 3.70 mmol) in benzene (40 mL) was added to the reaction mixture over 30 min. The solution was stirred at room temperature overnight. The resulting mixture was filtered, concentrated, and purified on a neutral alumina column (petroleum ether/chloroform). The product **1** was obtained as a purple solid. Yield: 21%. UV/Vis (in dichloromethane): λ_{max} [nm] (ε [m⁻¹ cm⁻¹]): 420 (1.0×10⁶); 451 (2×10⁵); 517 (3.9×10⁴);

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554 (2.2×10⁴); 592 (1.3×10⁴); 666 (2.4×10⁴); ¹H NMR (400 MHz, CDCl₃): δ = 8.86 (s, 8H), 8.20 (d, *J* = 8 Hz 8H), 7.87 (d, *J* = 7.6 Hz 8H), 0.51 ppm [satellites: 0.58 (*J* = 26.4 H), 0.45 (*J* = 26.4 Hz)]. ¹³C NMR (100 MHz, CDCl₃): δ = 142.1, 141.4, 134.6, 134.0, 131.1, 127.7, 126.7, 120.2, -9.2 ppm [satellites: -7.6 (d, *J* = 167 Hz), -11.0 (d, *J* = 174 Hz)]; ¹¹⁹Sn NMR (149 MHz, CDCl₃): δ = -26 ppm; ESI-MS: *m*/*z* = 1272.07 [*M*+2H]⁺, 1103.27 [*M*-SnMe₃]⁺ and 941.40 [M-2 SnMe₃]⁺.

Zinc(II) 5,10,15,20-tetrakis(4'-trimethylstanylphenyl)porphyrin (2): A solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.17 g, 0.78 mmol) in MeOH (20 mL) was added to a solution of 1 (0.20 g, 0.16 mmol) in 100 mL of chloroform, and the reaction mixture was stirred for 6 h at room temperature. The resulting reaction mixture was concentrated in vacuum and further purified on a basic alumina column (petroleum ether/dichloromethane). The desired product 2 was obtained as a purple solid. Yield: 95%. UV/Vis (in dichloromethane): λ_{max} [nm] $(\varepsilon [M^{-1} cm^{-1}])$: 422 (1.0×10^{6}) ; 549 (4.0×10^{4}) ; ¹H NMR (400 MHz, $CDCl_3$): $\delta = 8.89$ (s, 8H), 8.14 (d, J = 8 Hz 8H), 7.85 (d, J = 8 Hz 8H), 0.44 ppm (satellites: 0.51 (J = 26 Hz,) 0.37 (J = 23 Hz); ¹³C NMR $(100 \text{ MHz}, \text{CDCl}_3)$: $\delta = 150.3$, 142.5, 141.8, 140.1, 134.8, 132.1, 126.6, 121.6, 7.6 (d J=166 Hz), -9.30, -10.96 ppm (d, J=166 Hz); $^{119}\mathrm{Sn}$ NMR (149 MHz, CDCl₃): $\delta = -25$ ppm; ESI-MS: m/z = 1330.92 [M]⁺, 1168.87 $[M-SnMe_3]^+$, 1024.57 $[M-2SnMe_3+Na]^+$, 843.47 $[M-3 \text{SnMe}_3]^+$, 679.67 $[M-4 \text{SnMe}_3]^+$.

Zinc(II) 5,10,15,20-Tetrakis(4'-chloromercuriophenyl)porphyrin (3): HgCl₂ (36 mg, 0.13 mmol) was dissolved in THF (10 mL) and the solution added to a solution of 2 (20 mg, 0.015 mmol) in Et₂O (20 mL). The reaction mixture was stirred at room temperature for 4 h. The solvent was removed under reduced pressure and the residue was washed with water $(4 \times 10 \text{ mL})$ and dried. Subsequent washing with Et_2O (4×5 mL) and drying gave **3** as a purple solid. Yield: 66%. UV/Vis (in dichloromethane): λ_{max} [nm] (ε [M^{-1} cm⁻¹]): 428, (1.9×10^5) ; 557 (1.3×10^4) ; 600 (9.1×10^3) ; 662 (1.0×10^5) ; 662 (1.0×10^5) ; 661 (1.0×10^5) ; 662 10^4).¹H NMR (400 MHz, [D₆]DMSO): $\delta = 8.76$ (s 8H), 8.10 (d, J = 8 Hz, 8H), 7.85 ppm (d, J = 7.6 Hz 8H); ¹³C NMR (100 MHz, [D₆]DMSO): 142.84, $\delta = 151.17$. 149.71. 135.31. 134.50, 132.01. 120.57 ppm;¹⁹⁹Hg NMR (71 MHz, [D₆]DMSO): $\delta = -1181$ ppm; ESI-MS: $m/z = 1619 [M]^+$, 1383 $[M-HgCl]^+$, 1150 $[M-2HgCl]^+$ 679 [M-4HgCl]⁺.

CCDC 996313, 996314 and 996315 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: Lewis acids • mercury • porphyrinoids • sensors • supramolecular chemistry

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FULL PAPER

Porphyrins

C. A. Swamy P, P. Thilagar *

Polyfunctional Lewis Acids: Intriguing Solid-State Structure and Selective Detection and Discrimination of Nitroaromatic Explosives



Mercurial porphyrin: The synthesis and crystal structure of a polyfunctional Lewis acid based on mercury-decorated porphyrin are reported. The presence of Lewis acidic groups on the periphery of the metalloporphyrin modulated the electron density of the porphyrin π system and endowed the compound with the ability to discriminate picric acid from trinitrotoluene (see figure).