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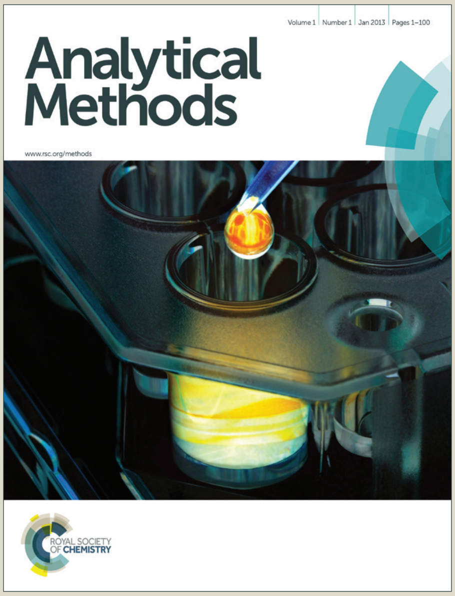

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Palani Natarajan*

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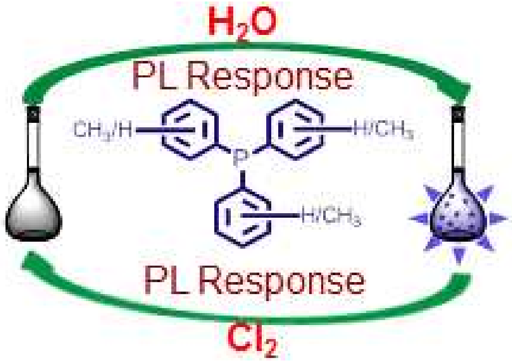

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Luminescence of Triarylphosphines and their Application to Detection of Elemental Chlorine in Aqueous Solution†

Palani Natarajan*

The concept of aggregation induced emission has been utilized to raise luminescence of triarylphosphines for the first time. Appreciable emission in the aggregated state as well as Lewis basic character of these compounds were capitalized to demonstrate functional utility as fluorescent chemosensors for elemental chlorine, Cl_2, in aqueous solution.

Among phosphorus compounds, phosphines[1] have widely been employed in biology, nature and chemical industries as antioxidants, insecticides, herbicides, flame-retardants, catalysts, surfactants, nerve agents, energy transporters, semiconductors, dopants, plastics and so on. Curiously, the luminescence characteristics of phosphines have not been reported to date.[1,2] The possible reasons for this are free rotation of the substituents in the phosphine scaffold, and inversion of the lone-pair of electrons on the phosphorus atom.[3] As these procedures readily extinguish the emission of any fluorophore through electron transfer quenching[4] and\or depopulation of the excited states via non-radiative mechanisms by internal conversions.[5]

Almost all non-radiative decay processes can be overcome readily by adopting suitable experimental conditions.[4,5] For example, the amino-functionalized anthracenes are weakly emissive in acetonitrile solution, however their photoluminescence quantum yields (ϕ_{PL}) are raised by more than 200-fold by protonation of the amino-group/s.[4] Likewise, tetraphenylethene and its derivatives are found to be faintly emissive or nonemissive in dilute solutions, at room temperature, due to the active intramolecular motions of the multiple aryl rotors with respect to the central olefinic double bond. The ϕ_{PL} value has been shown to be increased by 5-150-fold by restriction of the rotation of aryl rings through aggregation[5,6] or encapsulation.[7]

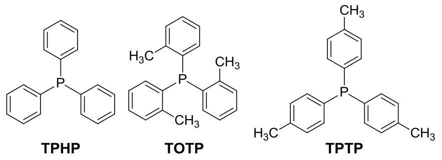

Chart 1 Chemical structure of propeller-shaped TPPs investigated.

As luminescence materials[2,4-6,8] find many applications in dyes, optical sensors, molecular electronics, nonlinear optics, light emitting diodes, photovoltaic cells, field-effect transistors, etc., the present study was aimed at exploring the luminescence characteristics of triarylphosphines (TPPs, Chart 1) in particular. The interest in TPPs was spurred by the fact that they are available readily in pure form,[1] insensitive to water and oxygen at ambient conditions,[1,2] fluorescent in the solid state as revealed by emission with a hand-held UV lamp, and should be expected to exhibit aggregation behaviour in polar solvents due to their hydrophobic nature. In addition, TPPs are powerful nucleophiles, and may form complexes with suitable analytes leading to changes in photophysics. Herein, I report the absorption and photoluminescence (PL) properties of three TPPs (Chart 1) in anhydrous- as well as aqueous tetrahydrofuran (THF) and in the solid state. Also, the study accounts for the sensing activities of these TPPs for the detection of elemental chlorine. To the best of my knowledge, emission features of phosphine derivatives have not been heretofore investigated in detail.[1,2,9]

The optical properties of TPPs (Chart 1) were investigated by UV-vis absorption and fluorescence spectroscopy and the details are summarized in Table 1.

Fig. 1 shows the absorption spectrum of **TPHP** (1×10^{-4} M) in THF and water-THF mixture containing different water fractions from 10 to 95%. Independent to the medium very similar wavelengths of absorption (λ_{ab}) were observed, however, profile shapes were found to be broader and the absorption tails extended to the long wavelength region in aqueous-THF mixture. Similar phenomena were noticed from **TOTP** and **TPTP** as well, indicating luminogens aggregated into nanoparticles in the aqueous-THF mixture as the Mie effect of nanoparticles known to cause such tail levelling-off in the absorption spectra.[5,6,10] From the onset of the absorption profile, the band gap was estimated to be 4.3-4.42 eV, 4.26-4.32 eV and 4.28-4.38 eV, respectively, for **TPHP**, **TOTP** and **TPTP**.

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Table 1 Optical properties of **TPHP**, **TOTP** and **TPTP** in THF, water-THF mixture and solid states

luminogen	$\lambda^{a}_{ab,s}$ (nm)	$\lambda^{b}_{ab,a}$ (nm)	E_g ^{c} (eV)	λ^{f}_{em} (nm) soln.^{g}	aggr.^{h}	frozen^{i}	film^{j}	$\phi^{k}_{PL,s}$ (%)	$\phi^{l}_{PL,a}$ (%)	d_H ^{m} (nm)
TPHP	234, 255, 260, 266, 272	234, 261, 266, 273	4.42^{d} 4.30^{e}	293	304	303	308	4	32	440
TOTP	229, 264, 271, 279	227, 264 272, 279	4.32^{d} 4.26^{e}	299	308	308	309	7	28	301
TPTP	234, 258, 264, 271, 275	233, 263, 269, 275	4.38^{d} 4.28^{e}	294	303	305	304	5	35	373

Abbreviations: $\lambda^{a}_{ab,s}$ absorption wavelengths in THF, $\lambda^{b}_{ab,a}$ absorption wavelengths in THF-water (5:95, v/v) mixture, E_g^{c} band gap (eV) estimated from the onset of absorption spectra, ^{d}in THF, ^{e}in THF-water (5:95, v/v) mixture, λ^{f}_{em} maximum emission wavelength measured at excitation wavelength of 240±5 nm, ^{g}in THF, ^{h}in THF-water (5:95, v/v) mixture, ^{i}in methylcyclohexane rigid glass at 77 K, ^{j}in film spin-casted on quartz substrate, $\phi^{k}_{PL,S}$ fluorescence quantum yield in THF estimated using biphenyl[11] (ϕ_{PL} = 18% in cyclohexane at λ_{ex} = 233 nm) as standard, $\phi^{l}_{PL,a}$ fluorescence quantum yield in THF-water (5:95, v/v) estimated using biphenyl[11] (ϕ_{PL} = 18% in cyclohexane at λex = 233 nm) as standard, ^{m}hydrodynamic radius (d_H) measured in THF-water (5:95, v/v) mixture. soln; solution, aggr; aggregate.

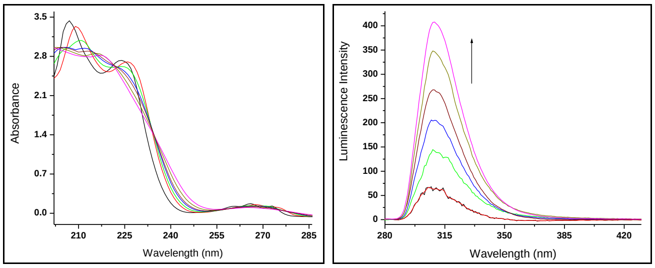

Fig. 1 UV−vis (left) and PL (right) spectra of **TPHP** (0.1 mM) measured in THF (black) and THF-water mixtures, v/v; 9:1 (red), 8:2 (green), 6:4 (blue), 4:6 (wine), 2:8 (dark yellow), 0.5:9.5 (magenta) at ambient conditions.

The PL spectrum of **TPHP** (1×10^{-4} M) in THF and water-THF mixture containing different water fractions from 10 to 95% is shown in Fig. 1. Analogues spectra for **TOTP** and **TPTP** are provided in Figs. S1 and S2, ESI†. Notice that all of the compounds were weakly luminescence in THF, but the emission intensity gradually intensified with increasing water content and reaches a maximum value at water content of 95% in the THF-water mixture. The emission intensities of **TPHP**, **TOTP** and **TPTP**, respectively, in THF-water (5:95, v/v) mixture are 8-, 4- and 7-fold higher than those found in anhydrous-THF. To have a quantitative picture, the ϕ_{PL} was estimated with respect to biphenyl[11] (ϕ_{PL} = 18% in cyclohexane at λ_{ex} = 233 nm) as the standard, to the amounts of 4%, 7% and 5% (Table 1) in anhydrous-THF and 32%, 28% and 35% (Table 1) in THF-water (5:95, v/v) mixture, respectively, for **TPHP**, **TOTP** and **TPTP**. In THF, all TPPs are soluble completely (not a suspension) as a result they undergo internal conversions (motions/rotations) without any constraint leading to poor luminescence activities.[5,6] In aqueous-THF solution, however, TPPs aggregate themselves into lumps (Fig. 1) due to their hydrophobic nature.[1,2] As a consequence, non-radiative relaxations that happen by internal conversion are ceased.[5-7] It was confirmed by low temperature- and solid state PL measurements as well, vide infra.

The internal conversions of flexible system are insignificant at low temperature as well as in the condensed phase.[2,12] Thus PL emission of TPPs has been investigated at liquid N_2 temperature (77 K) and in the solid thin film. In both of these experiments, all compounds (Chart 1) show intense emission with λ_{em} centred between 303-309 nm (Fig. S3, ESI†). So it is reasonable to state that the intense emission (Table 1) detected from TPPs in the aqueous medium is by the effect of aggregation, through self-assembly, which facilitates radiative transitions.[5,6] However, the detailed mechanism for the aggregation induced emission of triarylphosphine not identified. Doing that may help to enable phosphines to practical applications including in light emitting devices.[6b] Therefore the structure of TPPs shown in Chart 1 are novel aggregation induced emitters as analogues to well-known tetraphenylethenes[6] that show promising emission in condensed phase than in solutions.

A dynamic light scattering experiment (DLS) was used to investigate the size of the aggregates of **TPHP**, **TOTP** and **TPTP** assembled in THF-water (5:95, v/v) mixture. A typical unimodal distribution was observed with an average particle size, in terms of the hydrodynamic radius (d_H), are 440 nm, 301 nm and 373 nm (Fig. 2, and Figs. S4 and S5, ESI†), respectively, for **TPHP**, **TOTP** and **TPTP**. Indeed particles were found to be relatively stable, as d_H values were almost unchanged over a week.

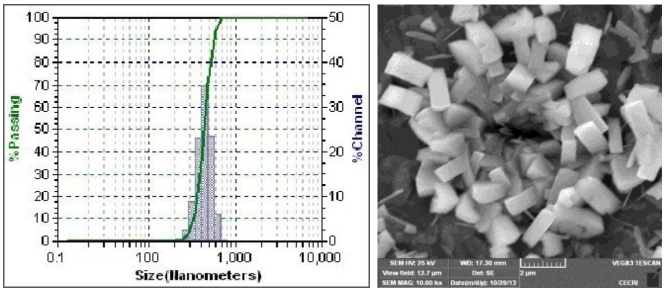

Fig. 2 Typical DLS profile (left) and the SEM image (right) of **TPHP** in THF-water mixture (5:95, v/v) measured at ambient conditions.

The scanning electron microscopy (SEM) was used to explore the morphology of particles of **TPHP**, a representative example, organized in THF-water (5:95, v/v) mixture. Interestingly **TPHP** aggregated into bricks like structure (Fig. 2 and Fig. S6, ESI†) with average size of 450-500 nm as similar to that noticed from DLS analysis.

The appreciable emission of the aggregate state as well as the nucleophilic nature of the phosphorus atom of TPPs encouraged exploring them as probes for sensor applications. Thus, the aqueous solution[13] of all compounds (Chart 1) was titrated with various di- and tri-valent (Mn^{3+}, Fe^{3+}, Bi^{3+}) transition metal cations as well as Cl_2 and CO_2 gases, which are having detrimental effects on humans and the environment.[14] Chlorine gas (Cl_2) readily affected the PL emission intensities of TPPs significantly, whereas, neither CO_2 nor metal cations impacted the photophysics of the triarylphosphine luminogens at ambient conditions. Thus, the emission response against the quantity of Cl_2 was investigated intricately to gain insight on the interactions between Cl_2 and TPPs (Chart 1) as inhaling or taking Cl_2 above 30 ppm cause eyes irritation, lung damage and aggravates the respiratory system by reaction with cells.[14,15]

As depicted in Fig. 3, the initial emission of nanoaggregates of **TPHP** (0.1 mM) in THF-water mixture (5:95, v/v) weakened gradually with the addition of chlorine-water (ca. 2.3 mM), and attains a constant value (no further enhancement or loss) at 0.41 µM concentration of Cl_2. The plots between changes in fluorescence intensity (I_{PL}) at 300 nm versus [Cl_2] are shown in Fig. 3. The limit of detection (LOD) and limit of quantitation (LOQ) were found at 0.015 ± 0.002 µM (±SD, n = 3) and 0.052 ± 0.006 µM (±SD, n = 10), respectively, suggesting the high sensitivity of the luminogen towards Cl_2 detection. A similar behaviour was observed from **TPTP** as well, c.f. Fig. 3.[16] Phosphines are known to react with halogens, alkyl halides, etc., yielding respective phosphonium salts.[17] Equally, **TPHP** and **TPTP** afforded the corresponding phosphonium salts, $Ar_3PCl^+Cl^-$, with the application of Cl_2 as examined by $^{31}P\{^1H\}$ NMR spectroscopy analysis (Fig. S7, ESI†). The $^{31}P\{^1H\}$ NMR spectrum of the parent **TPHP** resonates at −6.2 ppm, and was shifted to +67.4 ppm (deshielded) after reaction with Cl_2. The genuine dissolution of the phosphonium salt of the luminogen (Chart 1) in aqueous medium tone up the non-radiative transitions or weaken the PL emission intensity (Fig. 3).[5,6] Thus the TPPs (Chart 1) investigated herein are novel fluorescence chemodosimeters for elemental chlorine.

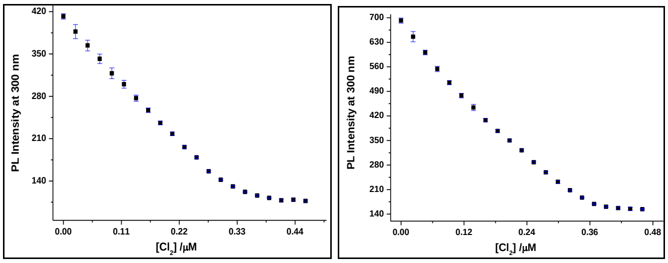

Fig. 3 Changes of fluorescence intensity of **TPHP** (left)/**TPTP** (right) at 300 nm as a function of [Cl_2].

In summary, the optical and sensor properties of three TPPs were studied in solution and solid states. Independent to their structure all are fairly luminescent in anhydrous THF, nevertheless, but exhibit moderate to good emission in THF-water mixtures at room temperature. The detailed analysis shows that, in anhydrous solution, all luminogens undergo internal conversion that depopulate excited state through non-radiative pathways, whereas, in aqueous-THF, they aggregate themselves into nanoparticles of size between 300-440 nm, established by DLS and SEM analyses, which facilitate radiative transitions. It was verified by low temperature- and solid state photoluminescence experiments. In a remarkable manner, the luminescence of nanoaggregates of TPPs is sensitive to the elemental chlorine. Since such a character not readily feasible either from classical luminophores[2] such as naphthalene, anthracene, pyrene, etc., or with familiar aggregation induced emitters[5] such as triphenylethylenes, tetraphenylethylenes, siloles and cyano distyrylbenzenes, suggesting an advantage of electron rich phosphorous atom in phosphine scaffolds reported here. Therefore present investigations may serve as basis for future works aimed at detection and quantification of Cl_2 generated in neutrophils and design of novel functional materials based on phosphines for applications to solid state light emitting devices and molecular electronics.

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