Electronic Supplementary Material (ESI) for Analytical Methods.

Electronic Supplementary Information (ESI)

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

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General Aspects: Dry tetrahydrofuran (THF) was freshly distilled over sodium prior to use. High quality triarylphosphines, **TPHP**, **TOTP** and **TPTP**, were purchased from Sigma-Aldrich and used without further purification. All compounds are substantially soluble in common organic solvents such as dichloromethane, chloroform, acetonitrile, THF and dioxane, but insoluble in methanol and water. Thus, the aggregates were prepared by addition distilled water into the dilute THF solution of the luminogen of interest since THF and water are miscible with each other at room temperature. Both anhydrous and aqueous analyte solutions were visually transparent and homogenous, *viz*. no precipitate was observed even at high fractions of water added (THF-water, 5:95, v/v). All compounds studied herein are proved to be air and moisture stable, thus all measurements were done under ambient conditions unless stated otherwise. UV−vis absorption spectra were recorded on a Varian Cary 100 UV/Visible spectrometer in THF and aqueous-THF solutions. Photoluminescence spectra and intensity measurements were made on a Varian Cary Eclipse Fluorescence Spectrophotometer with excitation and emission slits set to 2.5 nm. The PL quantum yields (ϕ_{PL}) were evaluated using biphenyl (ϕ_{PL} = 18% in cyclohexane at λ_{ex} = 233 nm) as a standard by using the equation below:

$\phi_u = \phi_s(I_u/I_s)(A_s/A_u)(\eta_u/\eta_s)^2$

with the subscripts “s” and “u” referring to standard and unknown samples, A_u and A_s to absorbance at the excitation wavelength, I_u and I_s to the integrated emission intensities (i.e., areas under the emission curves), and η_u and η_s to the refractive indexes of the corresponding solutions.

Surface morphology was investigated with a Jeol S-3000 H-scanning electron microscopy (SEM), and the sample was prepared by dropping a small quantity of the THF-water (5:95, v/v) solution of analyte on a copper stub and air dried. The particle size analysis/dynamic light scattering (DLS) experiment was performed on a Malvern particle size analyser with a scattering angle of 45°. Especially the THF solution of none of the triarylphosphines afforded a signal in this analysis indicating no particle in anhydrous medium. The $^{31}P\{^{1}H\}$ NMR spectra were measured with a BRUKER-Avance 400 MHz, Multi nuclei facilities in $CDCl_3$-CD_3OD solvents. Chemical shifts (*δ*) are reported in parts per million and are referenced to the residual protiated solvent.

Preparation of Chlorine water or aq. Cl_2:

Chlorine water was prepared and its concentration estimated iodometrically by following the procedures described in Vogels′ textbook of practical organic chemistry.[1] As the colour of *Chlorine water* rapidly bleached from yellow into colourless on standing in sunlight at 20 °C, a fresh solution was prepared before each titration experiment and stored at 0 °C in a darkroom.

Fluorescence titrations between triarylphosphines vs. aq. Cl_2:

The solution of triarylphosphine (0.1 mM) was prepared in THF-water (5:95, v/v) mixture and the chlorine water (ca. 2.3 mM) was prepared in distilled water. The fluorescence spectra of these solutions were recorded upon gradual addition of aq. Cl_2 up to 0.41 μM to the luminogen solution. The reaction between Cl_2 and triarylphosphine leads to the phosphonium salts as realized from the decrease of the fluorescence intensity and ^{31}P NMR analysis. All fluorescence traces were corrected to eliminate the Raman and solvent emissions. The corrected spectra were used to draw the plot between changes in PL intensity at 300 nm against $[Cl_2]$.

The *ortho*-CH_3 substituents in **TOTP** sterically protect the phosphorus atoms and as a result the reaction with Cl_2 was very slow at room temperature, however, at 60 °C the reaction proceeds smoothly in the presence of an excess quantity of Cl_2 water.

1 B. S. Furniss, A. J. Hannaford, P. W. G. Smith, A. R. Tatchell, *Textbook of Practical Organic Chemistry*, 1989, John Wiley & Sons, New York.

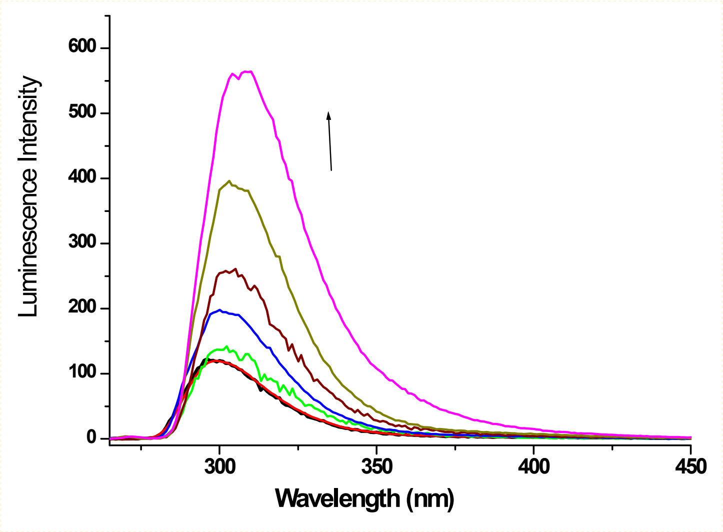

Fig. S1 The PL spectra of **TOTP** (0.1 mM) measured in THF (black) and THF-water mixtures, v/v; 9:1 (red), 8:2 (green), 6:4 (blue), 4:6 (wine), 2:8 (dark yellow), 0.5:9.5 (magenta) at ambient conditions.

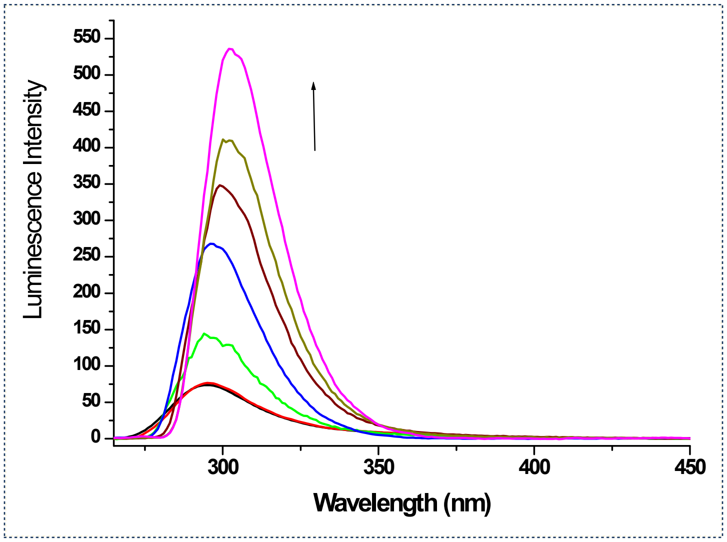

Fig. S2 The PL spectra of **TPTP** (0.1 mM) measured in THF (black) and THF-water mixtures, v/v; 9:1 (red), 8:2 (green), 6:4 (blue), 4:6 (wine), 2:8 (dark yellow), 0.5:9.5 (magenta) at ambient conditions.

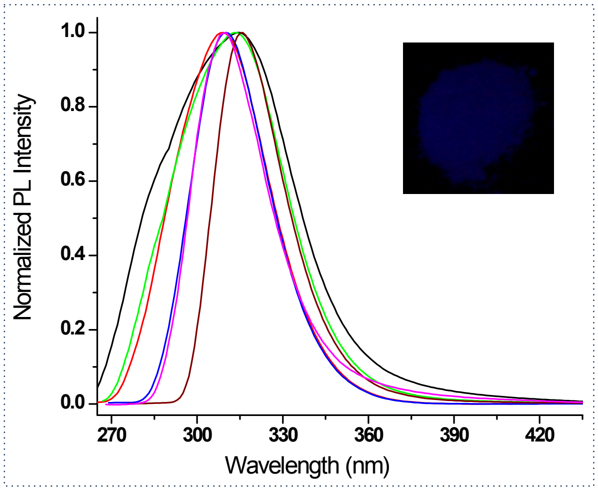

Fig. S3 Photoluminescence spectra measured for thin-film of **TPHP** (black), **TPOP** (red) and **TPTP** (green), as well as frozen solution of **TPHP** (blue), **TPOP** (wine) and **TPTP** (magenta) with a excitation wavelength of 240±5 nm. In the inset is shown the photograph of emission from the **TPHP** powder taken while illuminated with a hand-held UV-lamp.

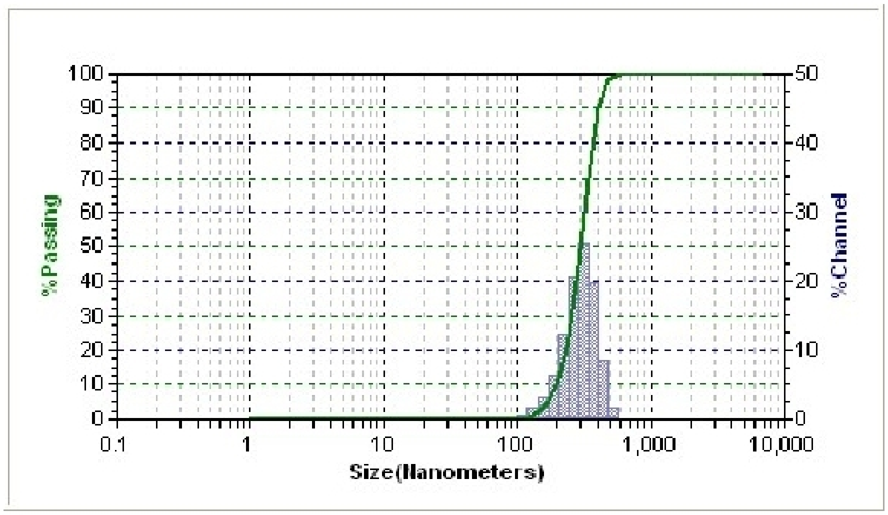

Fig. S4 DLS profile of **TPTP** in THF-water mixture (5:95, v/v) measured at ambient conditions.

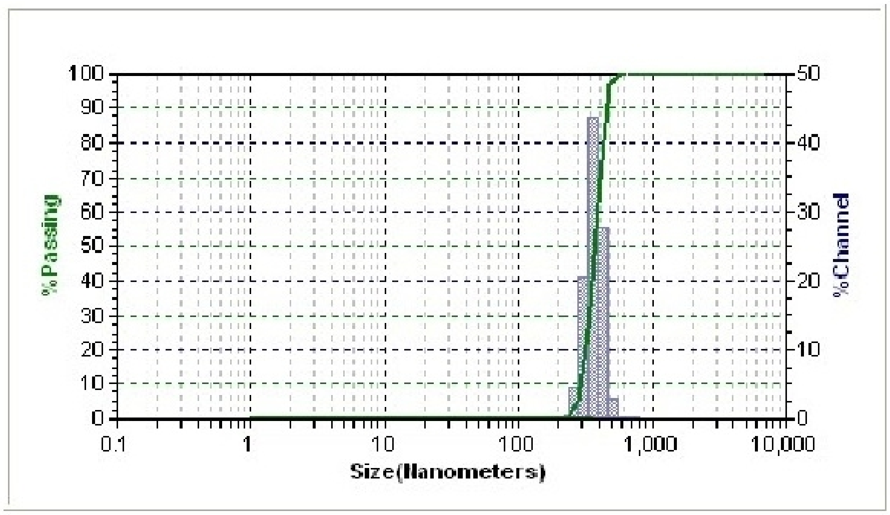

Fig. S5 DLS profile of **TOTP** in THF-water mixture (5:95, v/v) measured at ambient conditions.

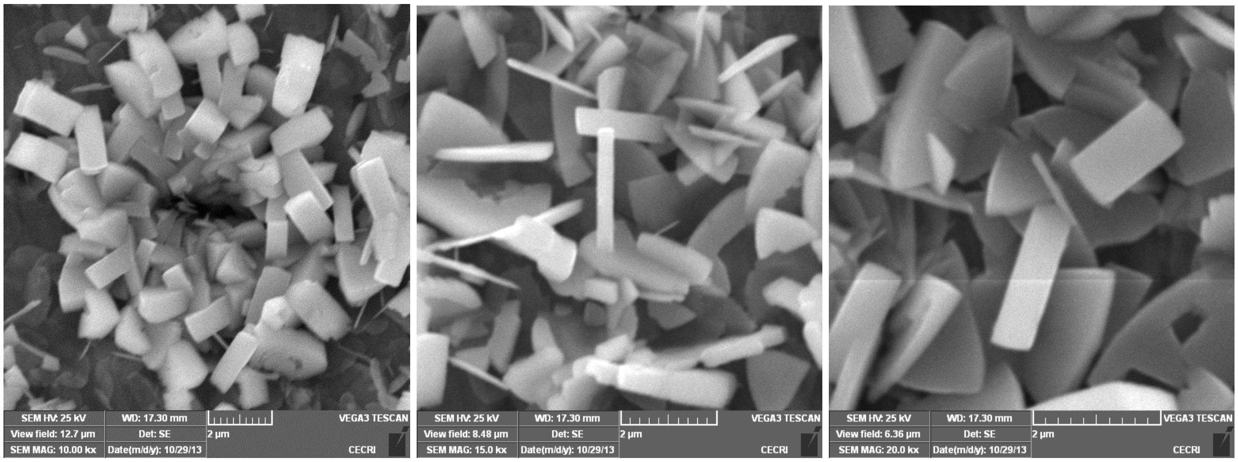

Fig. S6 The SEM images of aggregates of **TPHP** in THF-water (5:95, v/v) mixture.

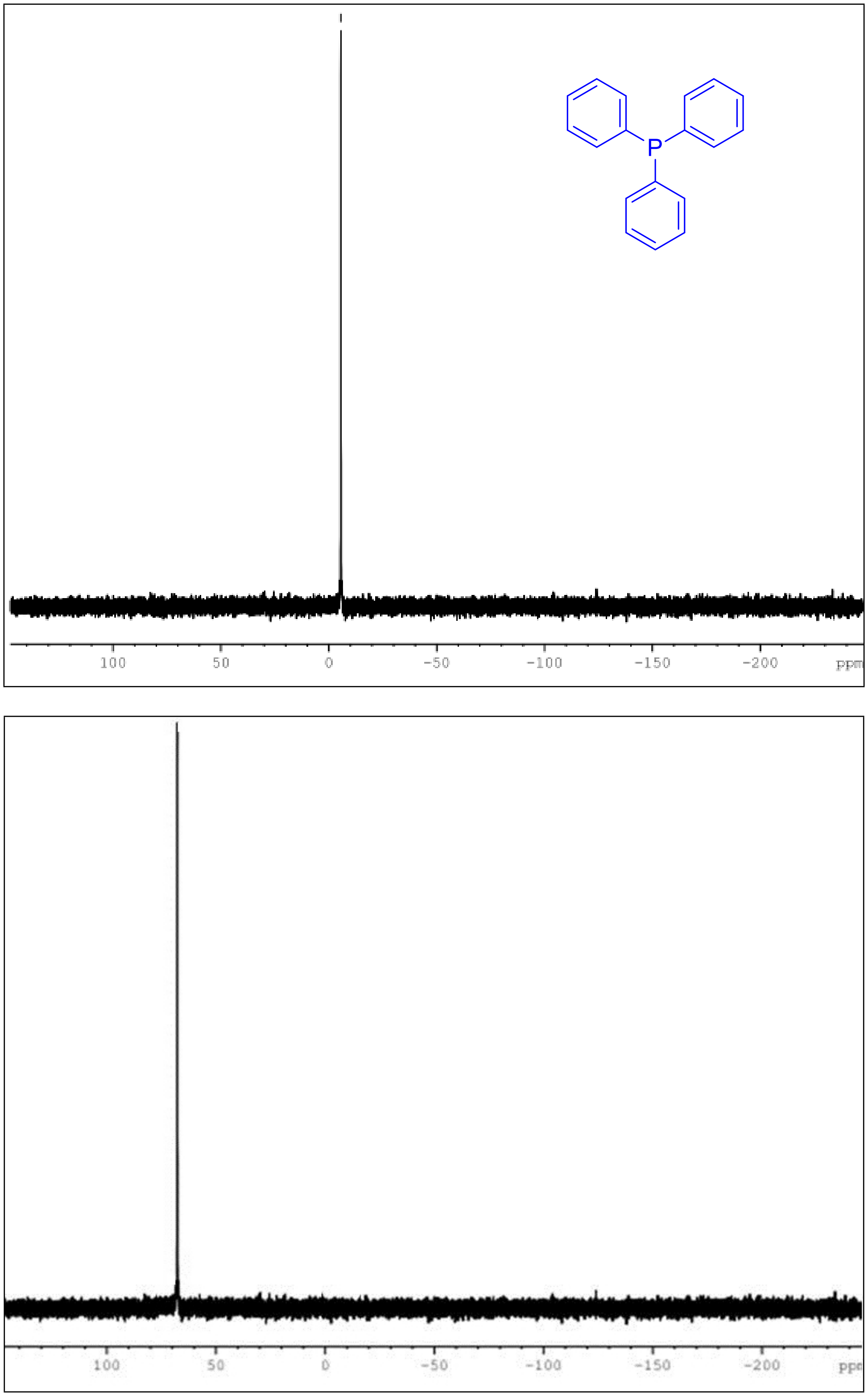

Fig. S7 The $^{31}P\{^{1}H\}$ NMR spectra of **TPHP** measured before (top) and after (bottom) Cl_2 addition. Notice that the ^{31}P NMR signal shifted downfield (+67.4 ppm) after chlorination.