

The coordination number–photophysical properties relationship of trianthrylphosphorus compounds: doubly locked fluorescence of anthryl groups

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Abstract

A series of tri(9-anthryl)phosphorus compounds including tri(9-anthryl)methylphosphonium iodide (**2b**), tri(9-anthryl)phosphine oxide (**2c**), and tri(9-anthryl)difluorophosphorane (**2d**) have been newly synthesized from the already reported tri(9-anthryl)phosphine (**2a**) and their photophysical properties including UV–vis absorption and fluorescence spectra have been determined in order to elucidate their coordination number–properties relationships. It has been found that their characteristic fluorescence properties are highly dependent on the coordination number of the central phosphorus atom. Thus, while the tri-coordinate phosphine **2a** and the tetra-coordinate phosphonium salt **2b** and phosphine oxide **2c** show no and weak ($\Phi_f < 0.01$) fluorescence, respectively, the penta-coordinate phosphorane **2d** exhibits intense fluorescence ($\Phi_f = 0.28$) which is comparable to that of the parent anthracene. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

π -Electron systems containing main group elements have attracted increasing attention because of their unusual photophysical and electrical properties dependent on the nature of the element. In particular, the modulation approach changing the coordination or valence states of the elements represents a new and powerful way to control the properties of the π -electron systems through the intrinsic electronic effect as well as structural changes [1–6]. As one example, we have recently reported a dramatic change in the fluorescence properties from the tetra-coordinate trianthrylfluorosilane (**1a**) to the corresponding penta-coordinate trianthryldifluorosilicate (**1b**). The structural change from the tetrahedral silane to the trigonalbipyramidal silicate induces a perturbation on the through-space interaction among the three anthracene moieties, resulting in a significant enhancement of the fluorescence quantum

yields by about 20 times (Fig. 1) [5]. In order to extend this concept to elements of other groups [6], we have now studied their Group 15 analogs, the trianthrylphosphorus compounds **2**. Unlike the silicon case, three coordination states are available in the phosphorus case, including the tri-coordinate phosphine **2a** [7,8], the tetra-coordinate phosphonium salt **2b** and phosphine oxide **2c**, and the penta-coordinate phosphorane **2d** (Chart 1). Reported herein are the syntheses and elucidation of the coordination number–properties relationship of the trianthrylphosphorus compounds [9].

2. Results and discussion

2.1. Synthesis

The synthesis of a series of trianthrylphosphorus compounds **2** is shown in Scheme 1. Trianthrylphosphine **2a** was prepared by modifying the method originally reported by Schmutzler and coworkers [7]. Thus, 9-anthryllithium, generated from bromoanthracene

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with *n*-BuLi in ether, was rapidly added to PCl_3 at 0 °C, followed by stirring at room temperature for 1.5 h. Recrystallization from toluene gave **2a** as red crystals

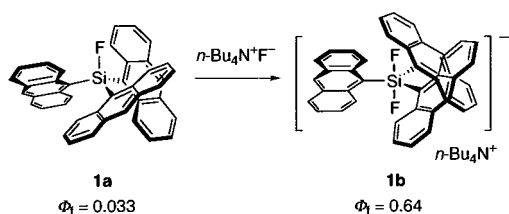
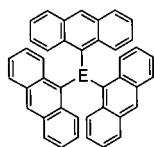
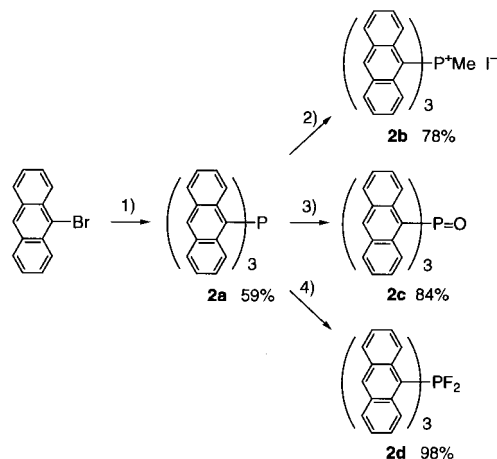


Fig. 1. Fluorescence change by the coordination number change in trianthrylsilane derivatives **1**.



2a (E = P)
2b (E = P⁺Me⁻)
2c (E = P=O)
2d (E = PF₂)

Chart 1.



Scheme 1. Synthesis of a series of trianthrylphosphorus compounds. Reagents and conditions: (1) *i*: *n*-BuLi (1.0 mol. amt.), Et₂O, -78–0 °C. ii: PCl_3 (0.3 mol. amt.), 0 °C–r.t.; (2) MeI (2.0 mol. amt.), DMF, 90 °C; (3) H_2O_2 , C_6H_6 -MeOH, r.t.; (4) XeF_2 (1.2 mol. amt.), CH_2Cl_2 , 0 °C. Mol. amt., molar amount.

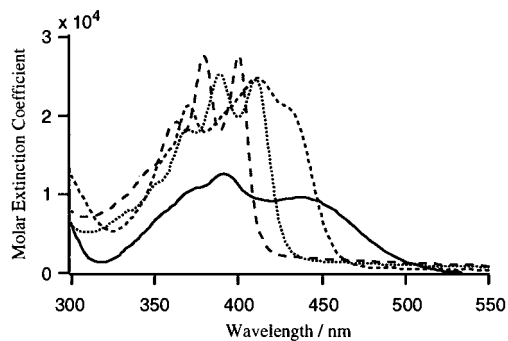


Fig. 2. UV–vis absorption spectra of trianthrylphosphorus compounds: **2a** (—), **2b** (---), **2c** (···), and **2d** (- -) in THF.

Table 1

UV–vis absorption data for trianthrylphosphorus compounds **2**^a

Compound ^b	λ_{max} (nm) (log ϵ)
Ant ₃ P	2a 437 (3.99), 392 (4.10)
Ant ₃ P ⁺ MeI ⁻	2b 430 (sh, 4.32), 412 (4.39), 371 (4.33)
Ant ₃ P=O	2c 411 (4.39), 390 (4.40), 370 (4.25)
Ant ₃ PF ₂	2d 401 (4.42), 380 (4.42), 364 (4.25)

^a In THF.

^b Ant, 9-anthryl.

in 59% isolated yield. Further traditional transformations from **2a** with MeI, H_2O_2 , and XeF_2 successfully afforded the corresponding methylphosphonium iodide **2b**, phosphine oxide **2c**, and difluorophosphorane **2d**, in 78, 84, and 98% yields, respectively. All these compounds are air-stable in the solid state except for **2d**, which is gradually decomposed in air to form the phosphine oxide **2c**.

2.2. UV–vis absorption spectra

The UV–vis absorption spectra of **2a–2d** are shown in Fig. 2 and their data are summarized in Table 1. In the UV–vis absorption spectra, trianthrylphosphine **2a** shows a broad absorption band around 390 nm due to the π - π^* transition of the anthracene moieties and, in addition, a new band with the maximum at 437 nm probably due to the extended π -conjugation through the lone-pair electrons on the phosphorus atom [10]. While the phosphonium salt **2b** also shows broad absorption bands, the phosphine oxide **2c** and phosphorane **2d** have absorption bands with vibronic fine structures like the parent anthracene, but their λ_{0-0} values are longer by 35 and 25 nm, respectively, than that of anthracene (λ_{0-0} 376 nm). These bathochromic shifts may be ascribed to the inductive effects of the phosphorus moieties, P=O and PF_2 , respectively, as well as the through-space interaction among the anthracene moieties.

2.3. Fluorescence spectra

In the fluorescence spectra, a more significant dependence on the nature of the central phosphorus atom has been observed. Their fluorescence spectra and the corresponding data are summarized in Fig. 3 and Table 2, respectively. While the tri-coordinate **2a** has almost no fluorescence, the tetra-coordinate **2b** and **2c** show weak fluorescence with relatively large Stokes shifts. In sharp contrast to these results, the penta-coordinate **2d** shows an intense fluorescence with a small Stokes shift, which quantum yield is about 30–100 times greater than those of **2b** and **2c** and comparable to that of the parent anthracene itself ($\Phi_f = 0.29$).

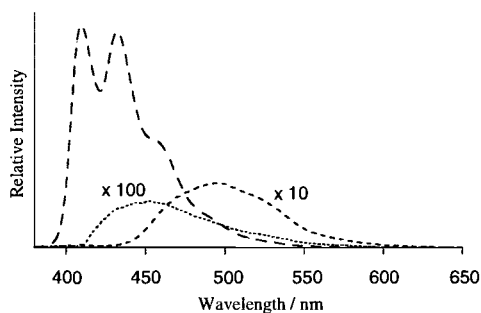


Fig. 3. Fluorescence spectra of trianthrylphosphorus compounds: **2b** (---), **2c** (···), and **2d** (- · -) in THF.

Table 2
Fluorescence data for trianthrylphosphorus compounds **2**^a

Compound ^b	λ_{em} (nm) ^c	Φ_f ^d
Ant ₃ P	2a	—
Ant ₃ P ⁺ MeI ⁻	2b	7.7×10^{-3}
Ant ₃ P=O	2c	$< 10^{-3}$
Ant ₃ PF ₂	2d	2.8×10^{-1}

^a In THF.

^b Ant, 9-anthryl.

^c Excited at 366 nm.

^d Determined with reference to anthracene.

These characteristic fluorescence properties can be rationalized as follows: (1) the non-fluorescent nature of **2a** is ascribed to the effective quenching by the loosely bound lone-pair electrons on the phosphorus atom. Actually, it has already been reported that Ph₂ArP (Ar = naphthyl, anthryl, etc.) has no fluorescence, whereas the corresponding phosphine oxides show intense fluorescence [11–13]; (2) the quantum yields of the tetra-coordinate **2b** and **2c** are still moderate, despite the fact that the phosphorus lone-pair electrons are no longer present. These results may result from the through-space interaction among the three anthryl groups arranged in a trigonal–pyramidal fashion, as demonstrated in the case of trianthrylsilane **1a** [5]; (3) the strong fluorescence is observed only in the case of **2d**, in which the lone-pair electrons are no

longer present and the three anthryl groups are arranged in a trigonal–planar fashion.

These results clearly demonstrate that in the trianthrylphosphorus framework, the fluorescence of the anthracene π -system is doubly locked in terms of two factors, i.e. the availability of the lone-pair electrons and the pyramidal arrangement of the three anthracene moieties. This behavior is compared with that of a Group 14 analog, the trianthrylsilanes **1**, as summarized in Fig. 4. Thus, while in the case of **1** the fluorescence of the anthracene moieties is simply controlled by the coordination number of the silicon atom, tetra- or penta-coordinate [5], in the present phosphorus case, multi-stage control of the fluorescence properties can be achieved. These results demonstrate a clear-cut example of the element-dependent properties-control based on the coordination number change and suggest that various modes of property-control can be accessible depending on the elements to be employed. Further studies to extend this idea to other element analogs are now in progress.

3. Experimental

3.1. General

Melting point (m.p.) determination was performed by using a Yanaco MP-S3 instrument. ¹H-, ¹³C-, ¹⁹F-, and ³¹P-NMR spectra were measured with a JEOL EX-270 (270 MHz for ¹H, 67.8 MHz for ¹³C, 254 MHz for ¹⁹F, and 109.25 MHz for ³¹P) spectrometer in appropriate solvents. Chemical shifts are reported in δ (ppm) with reference to the residual protio solvent peak for ¹H, solvent peak for ¹³C, CFCl₃ for ¹⁹F, and to H₃PO₄ for ³¹P. UV–vis absorption and fluorescence spectra were measured with a Shimadzu UV-3100PC spectrometer and Perkin–Elmer LS50B spectrometer, respectively, using degassed spectral grade THF as a solvent. Diethyl ether (Et₂O) was distilled from Na–benzophenone before use. Other all solvents were dried over appropriate desiccants and distilled under nitrogen.

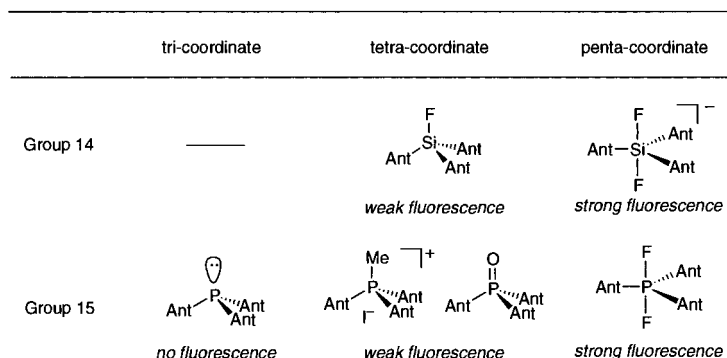


Fig. 4. Coordination number–fluorescence relationship of trianthryl derivatives of Group 14 and 15 elements (Ant, 9-anthryl).

3.2. Tri-9-anthrylphosphine (**2a**)

To a Et₂O (40 ml) solution of 9-bromoanthracene (5.1 g, 20 mmol) was added a C₆H₁₄ solution of *n*-BuLi (1.6 M, 12.5 ml, 20 mmol) at -78°C . After stirring at 0°C for 2 h, the reaction mixture was added to a Et₂O (20 ml) solution of PCl₃ (824 mg, 6.0 mmol) at 0°C , followed by stirring at room temperature (r.t.) for 1.5 h. The resulting red precipitates were collected by filtration and washed with Et₂O (10 × 3 ml). Recrystallization from dry C₆H₅CH₃ gave pure **2a** (1.98 g, 3.5 mmol) in 59% yield as red crystals. The spectral data essentially coincide with those reported in the literature [7].

3.3. Tri(9-anthryl)methylphosphonium iodide (**2b**)

A DMF (8 ml) solution of **2a** (2.25 g, 4.0 mmol) and MeI (1.14 g, 8 mmol) was stirred at 90°C for 14 h. After concentration under reduced pressure, EtOAc was added to the mixture. The insoluble material was collected by filtration and washed with additional EtOAc to afford spectroscopically pure **2b** (2.2 g, 3.1 mmol) in 78% yield: m.p. 212°C (dec.). ¹H-NMR (CDCl₃): δ 3.09 (d, ²J_{HP} = 10.8 Hz, 3H), 6.88 (d, *J* = 9.5 Hz, 3H), 6.95–7.03 (m, 3H), 7.20–7.25 (m, 3H), 7.38–7.45 (m, 3H), 7.49–7.56 (m, 3H), 8.24–8.30 (m, 6H), 8.53 (d, *J* = 9.5 Hz, 3H), 9.13 (s, 3H). ¹³C-NMR (CDCl₃): δ 30.14 (d, ¹J_{CP} = 66.9 Hz), 113.81 (d, ¹J_{CP} = 80.3 Hz), 122.58 (d, ³J_{CP} = 11.1 Hz), 124.10 (d, ³J_{CP} = 7.9 Hz), 125.87, 126.00, 129.69, 129.89, 130.99, 131.08 (d, ²J_{CP} = 12.3 Hz), 131.12, 131.53 (d, ²J_{CP} = 12.3 Hz), 132.73 (d, ³J_{CP} = 8.1 Hz), 135.03 (d, ³J_{CP} = 7.8 Hz), 138.64 (d, ⁴J_{CP} = 4.5 Hz). ³¹P-NMR (C₃H₆O-*d*₆): δ 4.65. Anal. Calc. for C₄₃H₃₀IP as **2b**·H₂O: C, 71.47; H, 4.46. Found: C, 71.33; H, 4.16%.

3.4. Tri(9-anthryl)phosphine oxide (**2c**)

A solution of **2a** (225 mg, 0.4 mmol) in C₆H₆–MeOH 1/1 mixed solvent (12 ml) was added to 30% H₂O₂ aq. solution (20 ml), followed by stirring at r.t. for 4 h. After removal of the aq. layer, the organic layer was washed with water (10 × 2 ml), dried over Na₂SO₄, and concentrated under reduced pressure to give spectroscopically pure **2c** (194 mg, 0.33 mmol) in 84% yield as yellow crystals: m.p. 283°C (dec.). ¹H-NMR (CDCl₃): δ 6.71–6.79 (m, 6H), 7.11–7.19 (m, 6H), 7.88 (d, *J* = 8.4 Hz, 6H), 8.38 (d, *J* = 8.6 Hz, 6H), 8.58 (s, 3H). ¹³C-NMR (CDCl₃): δ 124.92, 126.60, 126.96 (d, ³J_{CP} = 7.3 Hz), 129.20, 131.03 (d, ¹J_{CP} = 95.0 Hz), 131.45 (d, ²J_{CP} = 10.9 Hz), 133.81 (d, ³J_{CP} = 8.5 Hz), 134.02 (d, ⁴J_{CP} = 3.7 Hz). ³¹P-NMR (C₆D₆): δ 25.41. Anal. Calc. for C₄₂H₂₇PO: C, 87.18; H, 4.70. Found: C, 87.02; H, 4.60%.

3.5. Tri(9-anthryl)difluorophosphorane (**2d**)

To a CH₂Cl₂ (2 ml) solution of **2a** (561 mg, 1.0 mmol) was added a CH₂Cl₂ (2 ml) solution of XeF₂ (204 mg, 1.2 mmol) at 0°C . After the addition was completed, the mixture was immediately condensed under reduced pressure to afford spectroscopically pure **2d** (586 mg, 0.98 mmol) in 98% yield: m.p. 268°C (dec.). ¹H-NMR (CD₂Cl₂): δ 6.77–6.85 (m, 6H), 7.23–7.33 (m, 6H), 8.05 (d, *J* = 7.8 Hz, 6H), 8.19 (d, *J* = 8.9 Hz, 6H), 8.78 (s, 3H). ¹³C-NMR (CD₂Cl₂): δ 125.03, 126.59, 128.43–128.66 (m), 129.61, 130.80–131.60 (m), 132.03 (d, ²J_{CP} = 15.8 Hz), 133.25–133.80 (m), 134.22 (d, ³J_{CP} = 3.7 Hz). ¹⁹F-NMR (C₆D₆): δ 2.76 (d, ¹J_{FP} = 673.8 Hz). ³¹P-NMR (C₆D₆): δ -41.45 (t, ¹J_{FP} = 673.8 Hz). HRMS (FAB): Calc. for C₄₂H₂₇F₂P: 600.1812. Found: 600.1810. A satisfactory elemental analysis was not obtained probably due to instability of this compound.

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