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Mini Review

A new approach to photophysical properties control of main group element π -electron compounds based on the coordination number changeShigehiro Yamaguchi^{a,b,*}, Seiji Akiyama^a, Kohei Tamao^{a,*}^a Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan^b PRESTO, Japan Science and Technology Corporation (JST), Uji, Kyoto 611-0011, Japan

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Dedicated to Emeritus Professor Makoto Kumada and Professor Reinhard Schmutzler for their outstanding achievements in the fields of organosilicon chemistry and organophosphorus chemistry.

Abstract

We have explored a new possibility of controlling the properties of the main group element π -electron compounds based on a change in the coordination states of the elements. In a series of trianthryl derivatives of boron, silicon, and phosphorus, various control modes of the properties have been achieved depending on the element. Thus, in the case of the Group 13 boron, the change from tri-coordinate tri(9-anthryl)borane to the corresponding tetra-coordinate fluoroborate results in a significant change in the absorption property associated with the color change from orange to colorless. In the case of the Group 14 silicon, the change from tetra-coordinate tri(9-anthryl)fluorosilane to the corresponding penta-coordinate difluorosilicate causes a significant enhancement in the fluorescence of about 20 fold for the quantum yield. In the case of the Group 15 phosphorus, the fluorescence property is changed in multi-stages from tri-coordinate tri(9-anthryl)phosphine to the corresponding tetra-coordinate phosphonium salt and phosphine oxide, and to the penta-coordinate difluorophosphorane. These results demonstrate the significant potential of the present approach as a new molecular design for the functional main group element compounds. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Coordination number; UV–vis absorption spectra; Fluorescence spectra; Boron; Silicon; Phosphorus

1. Introduction

There has been a new trend in the main group organic chemistry towards materials science, especially for photonic and electronic applications. The incorporation of the main group elements into the π -conjugated framework enables access to new π -electron systems with intriguing photophysical and electronic properties and functions [1–4]. One advantage of the utilization of the main group elements is a possible properties control based on a change in the valence states or coordination states of the elements. For example, the nature of the π -electron systems can be modified by changing the

valence states of the elements. It has been reported that the π -electron-excessive nature of oligothiophenes can be changed to a π -electron-deficient nature by the oxidation of thiophene moieties to thiophene dioxides [5] or monooxides [6]. A similar approach has also been applied to the phosphole-containing π -electron systems [7]. On the other hand, we have explored the new possibility of property control by changing the coordination states of the elements. This concept is based on the change in the orbital interaction via through-bond and/or through-space upon changing the coordination number and thus the geometry from tri-coordinate planar (or pyramidal) to tetra-coordinate tetrahedral to penta-coordinate trigonal bipyramidal (Fig. 1). This idea has been realized by some trianthryl derivatives of Group 13 boron [8], Group 14 silicon [9] and Group 15 phosphorus [10]. This paper describes our recent results

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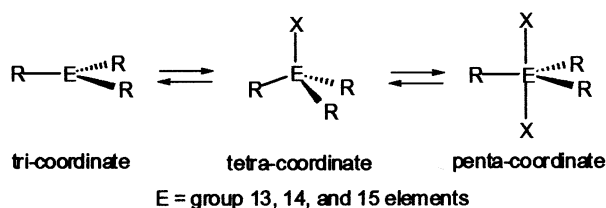


Fig. 1. Various coordination states of main group element compounds.

for the coordination number-based properties control of a series of trianthryl main group element compounds.

2. Trianthryl-boron series

Triarylboranes bearing three identical aryl groups on a boron atom have a unique lowest unoccupied molecular orbital (LUMO) in which π -conjugation effectively extended over three aryl groups due to the $p_{\pi}-\pi^*$ conjugation through the vacant p-orbital of the boron atom [2k]. Our idea to achieve the properties control for this class of boron compounds is based on the switching of the through-bond orbital interaction by the coordination number change, as shown in Fig. 2. Thus, the change from the tri-coordinate borane to tetra-coordinate borate by the addition of an external anion X would interrupt the π -conjugation in the LUMO, leading to a significant change in the absorption spectra. We applied this idea to the tri(9-anthryl)borane derivatives **1** and **2** (Chart 1) [8] which have been recently prepared by us [2k].

Trianthrylborane **1** actually shows a unique UV–vis absorption spectrum, as shown in Fig. 3a [2k]. Thus, in addition to the absorption bands around 350–390 nm attributed to the $\pi-\pi^*$ transitions of the anthracene moieties, a new strong band appears at 470 nm. This band can be ascribed to the transition from the HOMO localized on one anthryl group to the LUMO delocalized over the molecule through the vacant p-orbital of the boron atom. As a consequence, the color of **1** is orange.

We investigated the change in the UV–vis absorption spectra from the borane **1** to the corresponding fluoroborate **1F** by the addition of $n\text{-Bu}_4\text{NF}$ (TBAF) as a

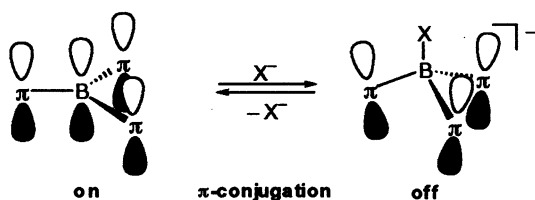


Fig. 2. Schematic representation of the switching of π -conjugation in the LUMO of boron-based π -electron systems: π stands for π -conjugated substituents.

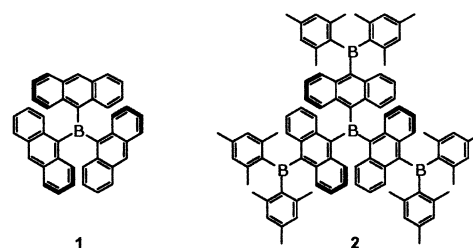


Chart 1.

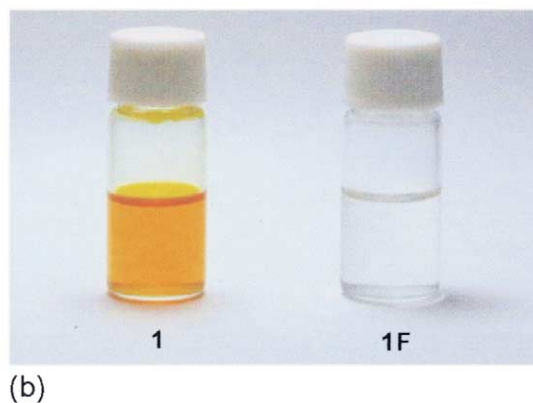
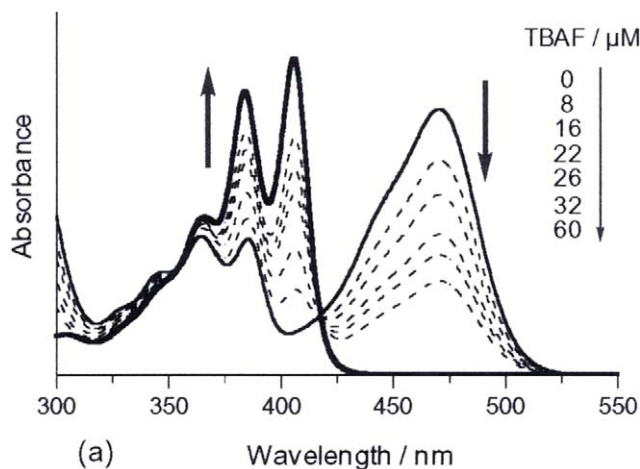
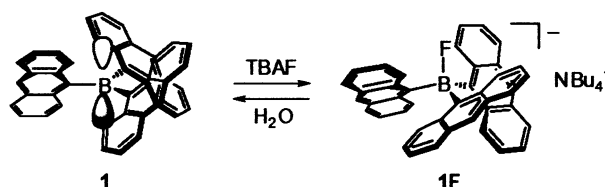


Fig. 3. Colorimetric change of **1** upon addition of $n\text{-Bu}_4\text{NF}$ (TBAF): (a) UV–vis absorption spectral change of **1** (4.0×10^{-5} M) in THF and (b) visual color change.

fluoride source (Scheme 1). As the amount of TBAF increased, the characteristic absorption band of **1** at 470 nm became weaker and finally disappeared and new



Scheme 1.

bands appeared in the anthracene region (360–400 nm), as shown in Fig. 3a. This spectral change was associated with a dramatic color change from orange to colorless, as shown in Fig. 3b. Thus, the trianthrylborane **1** works as a *colorimetric* fluoride sensor detectable by the naked eye [11]. Notably, this significant color change is unique for the present trianthryl system. While it has already been reported that the change from triphenylborane (λ_{\max} 287 nm) to its acetonitrile complex causes about a 60 nm blue shift of the λ_{\max} [12], this change occurs only in the UV region.

The titration experiment revealed the large binding constant of **1** to the fluoride ion of $2.8 (\pm 0.3) \times 10^5 \text{ M}^{-1}$ at 20 °C in THF. However, the resulting borate **1F** could revert to the starting borane **1** by the addition of water, like other fluoride chemosensors [9,11], probably due to the preferential hydration of the fluoride ion. Notably, compound **1** has a selective sensing ability for the fluoride ion. Thus, compound **1** showed smaller binding constants for AcO^- and OH^- , $1.7 (\pm 0.1) \times 10^3$ and $1.1 (\pm 0.1) \times 10^3 \text{ M}^{-1}$, respectively, by titration with their Bu_4N^+ salts. Furthermore, no sign of complexation with other anions such as Cl^- , Br^- , I^- , ClO_4^- , and BF_4^- was observed in the UV–vis spectra upon the addition of an excess amount of such anionic species as their $n\text{-Bu}_4\text{N}^+$ salts.

We have also prepared an extended π -electron system **2** which has four boron atoms in two different environments, i.e. an internal trianthrylborane moiety and three external dimesitylanthrylborane moieties. This extended system exhibited the multi-stage sensing of the fluoride ions [8]. Thus, the titration of **2** by the addition of TBAF showed the stepwise absorption spectral change in three concentration regions as shown in Fig. 4, suggesting that **2** can capture up to three fluorides. The binding constant with the first fluoride ion, $6.9 (\pm 0.2) \times 10^4$ at 20 °C in THF, is comparable to that of **1**, although those with the second and third fluorides become significantly decreased, $9.0 (\pm 0.6) \times 10^2$ and $2.1 (\pm 0.4) \times 10^2$ at 20 °C in THF, respectively. The final spectrum (Fig. 4) after binding three fluorides is similar in shape and about 25 nm red-shifted compared with that of trianthrylborane **1** (see Fig. 3), suggesting that the complexation of fluoride ions may have occurred not with the internal boron site but with the external three dimesitylanthrylborane sites.

3. Trianthryl-silicon series

In the case of Group 14 silicon compounds, our idea for the properties control is based on the change of the through–space orbital interaction, as shown in Fig. 5 [9]. Thus, the Group 14 compounds having three bulky π -conjugated substituents should have a strong through–space interaction among the substituents in

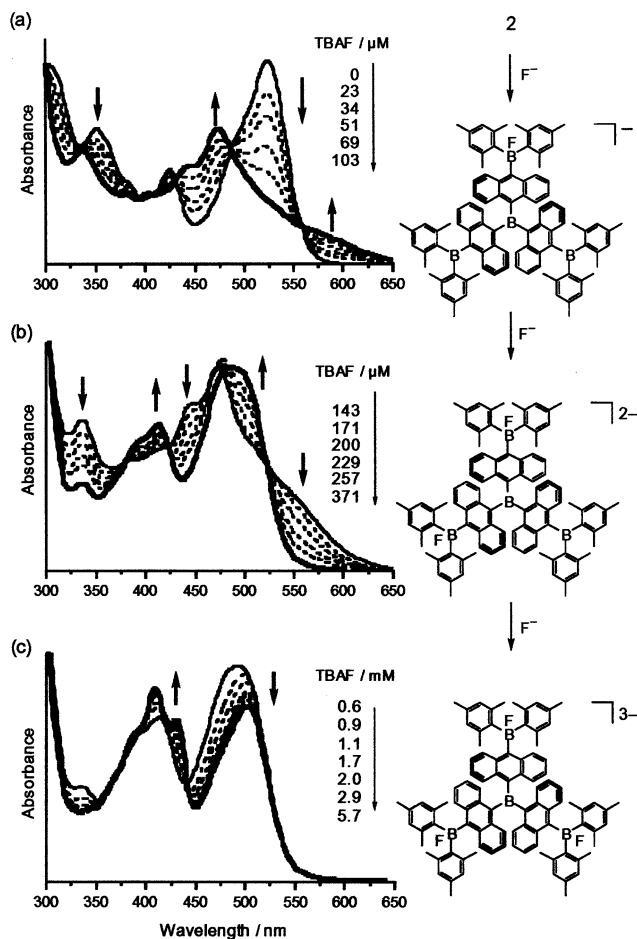


Fig. 4. Spectral change of a THF solution of **2** ($4.0 \times 10^{-5} \text{ M}$) upon addition of $n\text{-Bu}_4\text{NF}$ (TBAF).

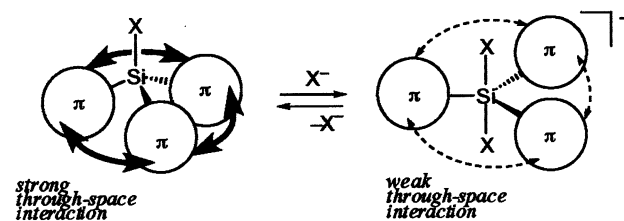


Fig. 5. Schematic representation of the change in the through–space interaction between π -conjugated substituents by penta-coordination of the central silicon atom.

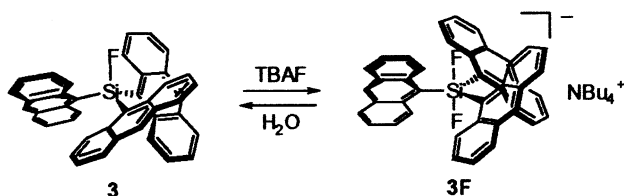
the tetra-coordinate tetrahedral structure. Upon the addition of an external anion X, the structural change from tetrahedral to trigonal bipyramidal by penta-coordination would cause a change in the through–space interaction, leading to the change in the photo-physical properties, especially the fluorescence. The key point to achieve this properties control is the choice of the π -conjugated substituent which should be bulky enough to interact with one another in the tetrahedral structure. We chose the anthryl group as the bulky

substituent and we have investigated the photophysical properties change from tri(9-anthryl)fluorosilane **3** to the corresponding difluorosilicate **3F** by the addition of a fluoride ion [9].

The titration experiment using the fluorescence spectral technique was carried out by the addition of TBAF to a THF solution of trianthrylfluorosilane **3** (Scheme 2). Upon the formation of the penta-coordinate trianthryldifluorosilicate **3F**, the fluorescence intensity was significantly increased, as shown in Fig. 6a. In terms of the quantum yield, about a 20 fold increment was observed from **3** ($\Phi_f = 0.033$) to **3F** ($\Phi_f = 0.64$). This notable change is visualized in Fig. 6b. This result means that the turning ‘off/on’ of the fluorescence of the anthracene π -system is controlled by the coordination number of the central silicon atom.

According to the titration, the binding constant of **3** with the fluoride ion is $2.8 (\pm 0.2) \times 10^4 \text{ M}^{-1}$ at 20 °C in THF [13]. When other anionic species such as Cl^- , Br^- , I^- , ClO_4^- , and BF_4^- as their $n\text{-Bu}_4\text{N}^+$ salts were added to the silane **3** in place of TBAF, no changes were observed in the fluorescence spectra. These results apparently rely on the specific affinity of the silicon atom with the fluorine atom. The produced difluorosilicate **3F** can be changed back to the fluorosilane **3** by washing with excess water without any decomposition, like the trianthrylboranes. These features demonstrate that the present trianthrylsilane works as a selective fluorescent sensor of the fluoride ion [14].

The dramatic fluorescence change observed for **3** and **3F** originated from the extremely low quantum yield of the former ($\Phi_f = 0.033$), which is about 1/10 that of the parent anthracene ($\Phi_f = 0.29$) [15]. This is in contrast to the high quantum yields of other anthrylsilane analogs, di(9-anthryl)phenylfluorosilane ($\Phi_f = 0.17$) and (9-anthryl)diphenylfluorosilane ($\Phi_f = 0.86$) [16]. Notably, the fluorescence quantum yield significantly decreases as the number of anthryl groups increased. In addition, no striking changes in the fluorescence quantum yields were observed for di(9-anthryl)phenylfluorosilane and (9-anthryl)diphenylfluorosilane upon penta-coordination [9]. These results clearly demonstrate that the fluorescence change observed from **3** to **3F** is due to the change not of the through-bond orbital interaction or the electronic effect of the silicon moiety but of the



Scheme 2.

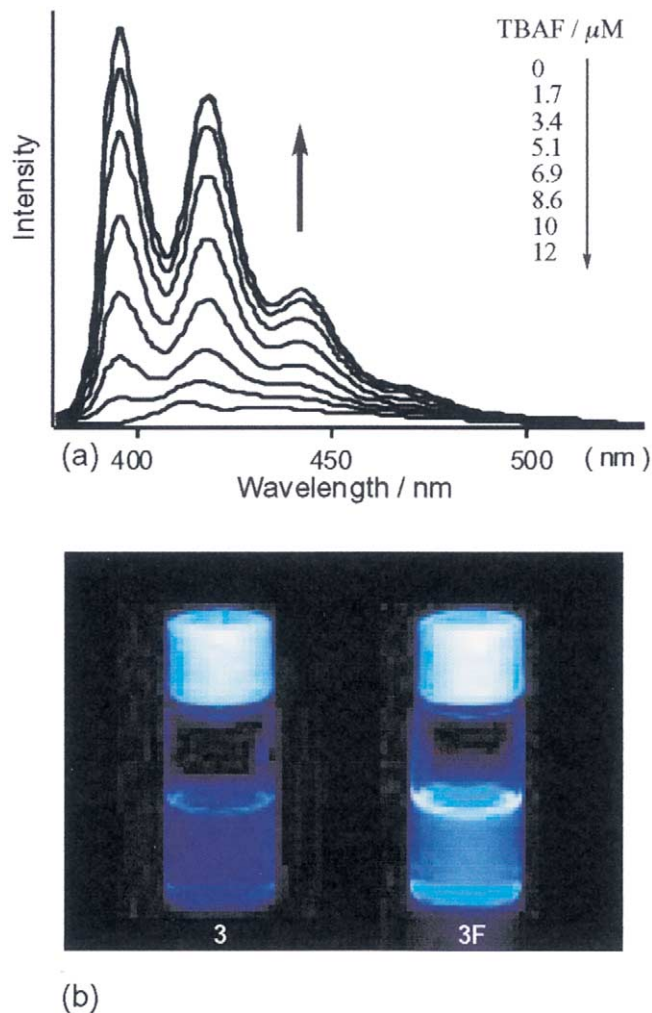


Fig. 6. Fluorescence change upon the addition of $n\text{-Bu}_4\text{NF}$ (TBAF) to **3** in THF: (a) fluorescence spectra: **3**, 0.2 μM and (b) a picture of THF solutions of **3** (left) and **3F** (right) under irradiation of light at 365 nm.

through-space interaction among the three anthryl groups, as expected.

To elucidate how big a structural change is responsible for this fluorescence change, the crystal structural analyses have been carried out for the tetra-coordinate **3** and the penta-coordinate **3F** isolated as a K^+ /[2.2.2]cryptand salt [17], as shown in Fig. 7 [9,15]. As an index to estimate the distance between the anthryl groups, the $\text{C}_{\text{ipso}}\text{--}\text{C}_{\text{ipso}}$ non-bonded distances between the anthryl groups are compared. In the tetra-coordinate silane **3**, the average distance is about 3.18 Å, and the distance in the difluorosilicate **3F** is about 3.28–3.45 Å. Thus, the penta-coordination elongates the length by about 0.1–0.2 Å. In addition, the arrangement of the three anthracene rings is changed from trigonal pyramidal in **3** to trigonal planar in **3F**. It is these structural changes that induce the significant fluorescence change.

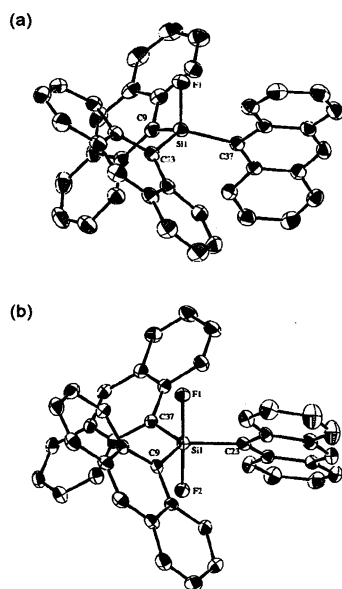


Fig. 7. ORTEP drawing of (a) **3** and (b) $3\text{F}\cdot\text{K}^+ / [2.2.2]\text{cryptand}$ (50% probability for thermal ellipsoids). One of two crystallographically independent molecules for **3F** is shown here and $\text{K}^+ / [2.2.2]\text{cryptand}$ as the counterion is omitted for clarity. Selected bond lengths (\AA) and bond angles ($^\circ$): **3**, Si1–F1 1.615(1), Si1–C9 1.883(2), C9–Si1–C23 115.48(9), C9–Si1–C37 115.24(10), C23–Si1–C37 114.94(9), F1–Si1–C9 102.62(9); $3\text{F}\cdot\text{K}^+ / [2.2.2]\text{cryptand}$, Si1–F1 1.716(2), Si1–F2 1.710(2), Si1–C9 1.955(3), F1–Si1–F2 176.59(9), C9–Si1–C23 114.1(1), C9–Si1–C37 122.7(1), C23–Si1–C37 123.2(1), F1–Si1–C9 91.48(10).

4. Trianthryl-phosphorus series

Unlike the boron and silicon cases, the phosphorus compounds can adapt three coordination states from tri-coordinate to penta-coordinate states. To elucidate the coordination number-property relations for this phosphorus case, a series of tri(9-anthryl)phosphorus compounds, including the tetra-coordinate phosphonium salt **4b** and phosphine oxide **4c**, and the penta-coordinate phosphorane **4d**, have been synthesized from the known tri-coordinate phosphine **4a** (Chart 2) [18,19] and their photophysical properties have been compared with one another [10].

Their fluorescence spectra and the corresponding data are summarized in Fig. 8 and Table 1, respectively. While the tri-coordinate **4a** has almost no fluorescence, the tetra-coordinate **4b** and **4c** show weak fluorescence with relatively large Stokes shifts. In sharp contrast to these results, the penta-coordinate **4d** shows an intense fluorescence with a small Stokes shift, whose quantum

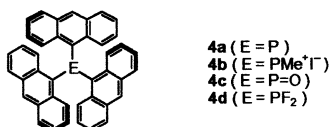


Chart 2.

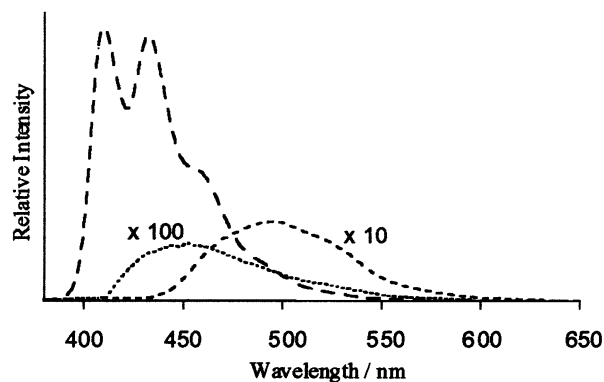


Fig. 8. Fluorescence spectra of trianthrylphosphorus compounds: **4b** (---), **4c** (·····), and **4d** (- · -) in THF.

Table 1

Fluorescence spectral data for trianthrylphosphorus compounds **4**^{a,b}

Compound	λ_{em} (nm) ^c	Φ_f ^d
4a	None	
4b	494	7.7×10^{-3}
4c	452	$< 10^{-3}$
4d	410	2.8×10^{-1}

^a See Ref. [10].

^b In THF.

^c Excited at 366 nm.

^d Determined with reference to anthracene.

yield is about 30–100 times greater than those of **4b** and **4c** and comparable to that of the parent anthracene itself ($\Phi_f = 0.29$).

The non-fluorescent nature of trianthrylphosphine **4a** results from the effective quenching by the lone-pair electrons on the phosphorus atom. Actually, it has already been reported that Ph_2ArP (Ar = naphthyl, anthryl, etc.) has no fluorescence, whereas the corresponding phosphine oxides show intense fluorescence [20]. In contrast, in the present trianthryl series, the quantum yields of tetra-coordinate phosphonium salt **4b** and phosphine oxide **4c** are still moderate, despite the fact that the lone-pair electrons are not available. These results can be ascribed to the through-space interaction among the three anthryl groups arranged in the trigonal-pyramidal fashion, as demonstrated by the trianthrylsilane **3** [9]. It should be noted that the strong fluorescence is observed only in the case of the difluorophosphorane **4d**, in which the lone-pair electrons are no longer available and the three anthryl groups are arranged in a trigonal-planar fashion. These results clearly demonstrate that in the trianthryl-phosphorus 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 arrangement of the three anthracene moieties.

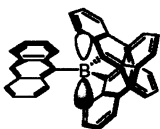
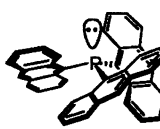
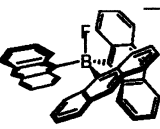
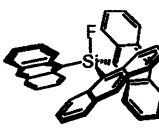
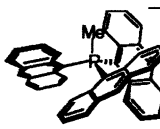

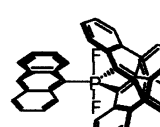
	Group 13	Group 14	Group 15
tri-coordinate	 orange	—	 no fluorescence
tetra-coordinate	 colorless	 weak fluorescence	 weak fluorescence
penta-coordinate	—	 strong fluorescence	 strong fluorescence

Fig. 9. The coordination number–photophysical property relationships for trianthryl derivatives of boron, silicon, and phosphorus.

5. Conclusion

We have described the coordination number–photophysical property relationships of the trianthryl main group element compounds with Group 13 boron, Group 14 silicon, and Group 15 phosphorus as the central element. As summarized in Fig. 9, various modes of properties control have been achieved by employing the trianthryl framework. Thus, for the Group 13 boron, the change from the tri-coordinate to tetra-coordinate state results in a change in the absorption properties. For the Group 14 silicon, the change from the tetra-coordinate to penta-coordinate state leads to a significant increase in the fluorescence intensity. For the Group 15 phosphorus, the fluorescence properties are changed in multi-stages from tri-coordinate to tetra-coordinate to penta-coordinate states. Among these results, it should be particularly noted that the trianthrylborane and the trianthrylsilane have different functions as the colorimetric and fluorescent sensors of the fluoride ion, respectively. These results demonstrate clear-cut examples of the *element-dependent* properties-control based on the coordination number change. The present approach may have a great potential as a new molecular design for the functional organoelement compounds.

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