

## 2P-126

### DFT study of colorimetric fluoride ion sensing by the heterodinuclear main-group/transition-metal complexes through allosteric coordination

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#### [Introduction]

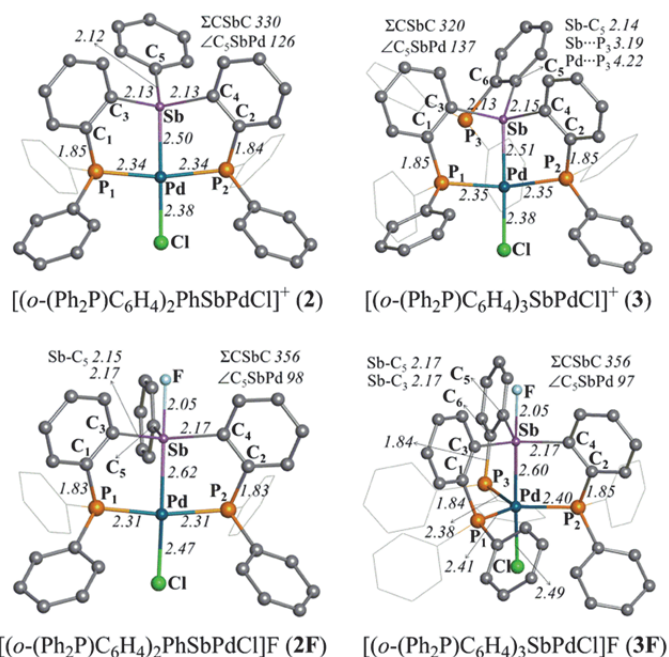
Fluoride anion plays a crucial role in biological process and daily life. However, excessive intake will lead to dental and skeletal fluorosis and even osteosarcoma. Taking into account these adverse effects of fluoride anion, the recognition and sensing of fluoride anions are necessary. For a potential fluoride chemosensor, such factors as large ion affinity, high selectivity, visible photophysical response, and hydrolytic stability must be satisfied. Recently, Wade et al. synthesized and characterized a dinuclear stibine–palladium complex  $[(o\text{-}(\text{Ph}_2\text{P})\text{C}_6\text{H}_4)_3\text{SbPdCl}]^+$  with high selectivity and visual recognition for  $\text{F}^-$  anion.<sup>1</sup> Although the colorimetric fluoride sensing properties have been investigated by X-ray diffraction, NMR spectroscopy, and UV/vis spectra, there are several important questions: What is the origin of high selectivity for  $\text{F}^-$  anion? What role does the transition-metal play in sensing  $\text{F}^-$  anion? What is the sensing mechanism that really controls the observed color change process? With these questions, we will present systematic DFT calculations on a series of selected and designed heterodinuclear main-group/transition-metal complexes  $[(o\text{-}(\text{Ph}_2\text{P})\text{C}_6\text{H}_4)_3\text{M}^1\text{M}^2\text{Cl}]^+$  ( $\text{M}^1 = \text{As}, \text{Sb}, \text{Bi}$ ;  $\text{M}^2 = \text{Pd}$  and  $\text{Pt}$ ); see Figure 1.

#### [Computational methods]

All calculations were performed with the Gaussian09 program package at the DFT level in both gas phase and dichloromethane solvent, where the PBE0 hybrid functional was used throughout. The nature of each stationary point was verified by harmonic vibrational frequency calculation. Two kinds of basis set system were employed here. In basis set I (BS-I), (541/541/211/1) and (21/21/1) basis sets were employed with Los Alamos ECPs for transition metals (Pd and Pt) and main group heavy atoms (As, Sb and Bi), respectively. For C, H, O atoms, 6-31G(d) were employed, and 6-31+G(d) were used for P and halogen (F, Cl, Br) atoms. All of the TDDFT calculations were carried out with a larger basis set system (BS-II). In BS-II, (5311/5311/211/1) basis set was employed for Pd and Pt with the same Los Alamos ECPs, while aug-cc-pVTZ was used for main group atoms (As, Sb, Bi) with relativistic ECPs. cc-pVDZ basis sets were used for C, H, and O atoms, and aug-cc-pVDZ basis sets were employed for P and halogen atoms.

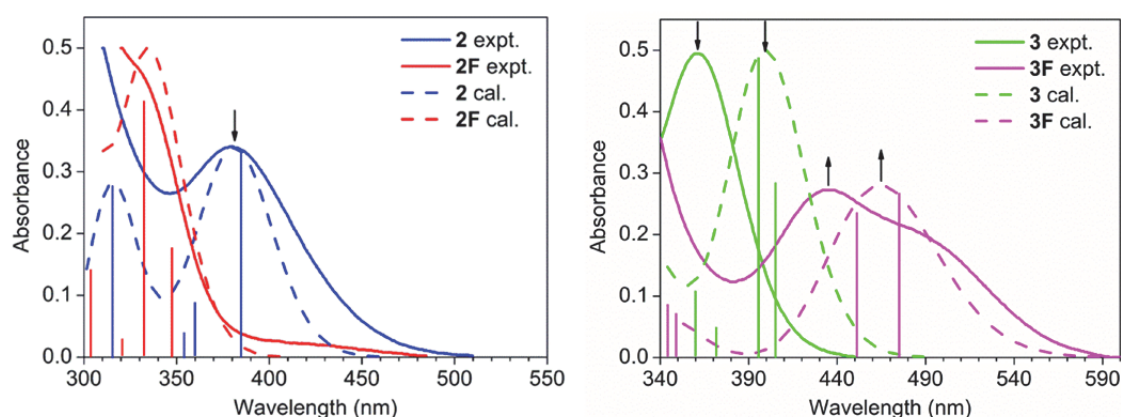
#### [Results and Discussion]

In complexes **2** and **3**, the Pd center takes a four-coordinate planar structure, in which the three-coordinate Sb center interacts with the Pd center. In the fluoride ion-capturing process, the Sb center changes to a five-coordinate system, indicating that the Sb takes hypervalent electronic structure (**2F** and **3F** in Figure 1). In addition, the Pd center of **3F** becomes five-coordinate



**Figure 1.** Optimized structures and selected geometric parameters of **2**, **2F**, **3** and **3F** calculated at PCM( $\text{CH}_2\text{Cl}_2$ )/PBE0/BS-I level (bond lengths and angles in angstroms and degrees, respectively). Hydrogen atoms are omitted for clarity.

trigonal-bipyramidal structure by one more coordination of phosphine P<sub>3</sub>. Complex **3** presents a strong capturing ability for F<sup>-</sup> anion;  $\Delta E = -15.5$  kcal mol<sup>-1</sup>, where  $\Delta E$  represents the potential energy change by the F<sup>-</sup>-adduct formation (Table 1). It is noted that this kind of hetero-dinuclear compound possesses higher selectivity for F<sup>-</sup> anion than such other anions as Cl<sup>-</sup>, Br<sup>-</sup>, CN<sup>-</sup>, and SCN<sup>-</sup> (Table 1). Cooperation between the intramolecular acid-base interaction (M<sup>1</sup>⋯P<sub>3</sub>) and coordination interaction (M<sup>2</sup>⋯P<sub>3</sub>) controls the change of coordination structure at the M<sup>2</sup> center, which plays a crucial role in the colorimetric response for F<sup>-</sup> anion (Figure 2). For instance, the conversion of **2** to **2F** decreases the absorption band around 380 nm but provides a new peak around 330 nm, as experimentally observed<sup>1</sup> (Figure 2). The conversion of **3** to **3F** quenches the absorption band around 400 nm, but provides a new absorption peak around 475 nm. This is assigned as Pd-based ligand-field transition (LFT:  $d_{xy} \rightarrow d_{z^2}$  and  $d_{x^2-y^2} \rightarrow d_{z^2}$ ); in our calculations, these two excitations occur at nearly the same energy. It is noted that a five-coordinate **3F** induces intense LFT, which is important for hyperchromic effect. Besides, the introduction of heavy-main-group element Bi causes bathochromic shift in the absorption spectra, while the replacement by late-transition-metal Pt makes the spectra blue shift.



**Figure 2.** Comparison of experimental and calculated absorption spectra of systems **2** and **3** upon binding F<sup>-</sup> anion by PCM(CH<sub>2</sub>Cl<sub>2</sub>)/TD-PBE0/BS-II level. Experimental data see ref. 1.

We tried to understand theoretically the sensing performance of such complexes for hydrated fluoride at different extents [F<sup>-</sup>⋯(H<sub>2</sub>O)<sub>n</sub>]<sup>-</sup> (n = 1-3) instead of a naked F<sup>-</sup> anion. In the presence [NMe<sub>4</sub>]<sup>+</sup> and the phenyl ligands around F<sup>-</sup> anion, the maximum number of water molecules interacting with F<sup>-</sup> anion is 2. The strong interaction between water molecules and F<sup>-</sup> anion makes the F<sup>-</sup> anion-capturing process of **3** gradually difficult. However, the F<sup>-</sup> adduct formation is exothermic, indicating that **3** also possesses good ability for F<sup>-</sup>-capturing from aqueous solution. The presence of two water molecules leads to the formation of four-coordinate complex without P<sub>3</sub> coordination, which makes colorimetric sensing of **3** for hydrated fluoride become not obvious.

**Table 1.** Proposed anionic capturing reactions and the reaction energies ( $\Delta E$ , in kcal mol<sup>-1</sup>) calculated at PCM/PBE0/BS-II/PCM/PBE0/BS-I level (CH<sub>2</sub>Cl<sub>2</sub> as solvent).

	M <sup>1</sup>	M <sup>2</sup>	reaction	( $\Delta E$ )
(1)	Sb	Pd	[ <b>3</b> ]BMe <sub>4</sub> + [NMe <sub>4</sub> ]F → <b>3F</b> + [NMe <sub>4</sub> ]BMe <sub>4</sub>	-15.5
(2)	Sb	Pd	[ <b>3</b> ]BMe <sub>4</sub> + [NMe <sub>4</sub> ]F → <b>3F</b> <sup>a</sup> + [NMe <sub>4</sub> ]BMe <sub>4</sub>	-13.8
(3)	Sb	Pd	[ <b>3</b> ]BMe <sub>4</sub> + [NMe <sub>4</sub> ]Cl → <b>3Cl</b> <sup>a</sup> + [NMe <sub>4</sub> ]BMe <sub>4</sub>	6.0
(4)	Sb	Pd	[ <b>3</b> ]BMe <sub>4</sub> + [NMe <sub>4</sub> ]Br → <b>3Br</b> <sup>a</sup> + [NMe <sub>4</sub> ]BMe <sub>4</sub>	4.3
(5)	Sb	Pd	[ <b>3</b> ]BMe <sub>4</sub> + [NMe <sub>4</sub> ]CN → <b>3CN</b> <sup>a</sup> + [NMe <sub>4</sub> ]BMe <sub>4</sub>	-9.9
(6)	Sb	Pd	[ <b>3</b> ]BMe <sub>4</sub> + [NMe <sub>4</sub> ]SCN → <b>3SCN</b> <sup>a</sup> + [NMe <sub>4</sub> ]BMe <sub>4</sub>	3.1
(7)	Sb	Pd	[ <b>3</b> ]BMe <sub>4</sub> + [NMe <sub>4</sub> ]F·H <sub>2</sub> O → <b>3F·H<sub>2</sub>O</b> + [NMe <sub>4</sub> ]BMe <sub>4</sub>	-14.0
(8)	Sb	Pd	[ <b>3</b> ]BMe <sub>4</sub> + [NMe <sub>4</sub> ]F·2H <sub>2</sub> O → <b>3F·2H<sub>2</sub>O</b> <sup>a</sup> + [NMe <sub>4</sub> ]BMe <sub>4</sub>	-11.5
(9)	Sb	Pd	[ <b>3</b> ]BMe <sub>4</sub> + [NMe <sub>4</sub> ]F·3H <sub>2</sub> O → <b>3F·3H<sub>2</sub>O</b> <sup>a</sup> + [NMe <sub>4</sub> ]BMe <sub>4</sub>	-11.6

<sup>a</sup> Four-coordinate structure around Pd.

#### [Reference]

1. Wade, C. R., Ke, I.-S., Gabbai, F. P. *Angew. Chem. Int. Ed.* **2012**, *51*, 478–481.