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A series of novel boat-shaped host-guest complexes were designed and synthesized by the combination of a new calixarene fragments-based tetraphosphine ligand L with group 11 metal salts  $Cu(MeCN)_4ClO_4$ , AgNO<sub>3</sub> in self-assembly process, and by the following anion exchange reactions of complex **1** with sodium *p*-toluenesulfonate, AcONa, PhCO<sub>2</sub>Na and sodium 9-anthrylcarboxylate. The host with a novel boat-shaped cavity are capable of self-adaptive encapsulation of various anions of different sizes through M(I)—O coordinations and CH… $\pi$  interactions between host and guest anion. The DFT calculations confirmed the CH… $\pi$  interaction played a vital role in the self-adaptive phenomenon in complexes **4-6**.

# Introduction

Phosphine ligands, extensively applied in many types of catalytic reactions since the 1970s<sup>1-3</sup> are one of the most important ligands in self-assembly and sensing behaviors of host-guest complexes.<sup>4</sup> Therefore, a wide variety of novel and highly efficient multiphosphine ligands have been designed and synthesized.<sup>5</sup> The multiphosphine ligands as well as their transition-metal complexes also have been explored in self-assembly and sensing behaviors of host-guest complexes for guests anions, cations and neutral molecules<sup>6, 7</sup> through the interactions of intramolecular, such as  $CH\cdots\pi$  interaction,<sup>8-10</sup> weak interaction,<sup>11</sup> hydrogen bond<sup>10</sup> and coordination bond.<sup>12</sup> Additionally, people also have been paying attention to the anion transport by anion exchange in supramolecular medicinal chemistry<sup>13</sup> along with changes of the cavity size.<sup>14</sup> Another attractive feature of host-guest complexes, which usually appears a regular shape, such as those in ring  $\begin{array}{l} {\rm complex,}^{15} {\rm \ in \ cage-like \ complex,}^{16} {\rm \ in \ boat-shaped \ complex,}^{17} {\rm \ in \ boat-shaped \ complex,}^{17} {\rm \ in \ boat-shaped \ cavity \ complex,}^{18-21} {\rm \ and \ in \ capsule-like \ complex,}^{22} \end{array}$ generally can be designed to stabilize the host-guest system and give rise to inclusion complexes.<sup>23</sup>

Recently, a great deal of research effort has been devoted to the study of transition-metal complexes, such as metallacycles and metallocalixarenes.<sup>24, 25</sup> The novel structure complexes are usually

various carbonxylate anions. To the best of our knowledge, there is quite little report of boat-based metal–organic framework constructed from a tetraphosphine ligand in literatures.<sup>17</sup>

# **Results and discussion**

The tetraphosphine ligand **L** was designed and synthesized as shown in Scheme 1. Firstly, the *p*-<sup>t</sup>butylphenol **a** was reacted with BrCH<sub>2</sub>CH<sub>2</sub>Br to form compound **b**,<sup>34</sup> in which the -CH<sub>2</sub>CH<sub>2</sub>- linked the phenoxy-O position. After bromination, the tetrabromide **c** was obtained in high yield. Then, the desired ligand **L** was convenietly prepared from **c**, CIPPh<sub>2</sub> and *n*-BuLi based on a routine arylphosphine synthesis.<sup>35-38</sup> From the structure of the ligand **L**, it can be found that the -CH<sub>2</sub>CH<sub>2</sub>- are linked the two phenoxy-O atom, which constrained the sequence of the two *p*-<sup>t</sup>butylphenol fragments and confirmed the core conformation of the following metallamacrocyles formed by the coordination of tetraphosphine ligand with group 11 metal ions. Thus, the prepared host boat-shaped metallacycles can have a cavity to encapsulate the guest

synthesized by the coordination of functional ligand to transition

metals in mode of multi-site recognition.<sup>26</sup> Our group focused on the syntheses and properties of bis-metallic macrocyclic complexes

with the coordination of diphosphines or bis-N-heterocyclic

carbenes containing calixarene fragments to group 11 metal ions.<sup>27-</sup>

<sup>32</sup> In this paper, we would like to report the synthesis and structure

of some novel boat-shaped macrocyclic metal complexes with

cavity to fit organic carboxylate anions on basis of flexible

tetraphosphine ligand. The complexes showed a self-adaptive

ability to the coordinated guest carboxylate anions in the anion

exchange procedure. The cavity of the boat-shaped metal

complexes appeared an interesting self-adaptive phenomenon<sup>33</sup> to

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<sup>&</sup>lt;sup>+</sup> Electronic supplementary information (ESI) available: CCDC 1849188, 1849192-1849194, 1849198, 1858400. NMR spectra, supplementary tables, Geometrical features of crystal structures and optimized structures. See DOI: 10.1039/x0xx00000x

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molecules as the -CH<sub>2</sub>CH<sub>2</sub>- acting as the bottom of the metallocalixarene.



Scheme 1 Three-Step Synthesis of the Tetraphosphine Ligand L

Metal complexes 1-2 were synthesized in good yields by the reactions of the tetraphosphine ligand with 2 equiv of Cu(MeCN)<sub>4</sub>ClO<sub>4</sub> and AgNO<sub>3</sub>, respectively. (Scheme 2).



Fig. 1 Molecular views of the X-ray crystal structures of the Cu(I) complex 1. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms, one perchlorate anion and solvent molecules are omitted for clarity.



Fig. 2 Molecular views of the X-ray crystal structures of the Ag(I) complex 2. Thermal ellipsoids are shown at the 50% probability level. Partial hydrogen atoms and solvent molecules are omitted for clarity.

According to structural feature of complexes 1-2, the derivative complexes 3-6 were synthesized by the anion exchange of 1 with excess of sodium p-toluenesulfonate, sodium acetate, sodium benzoate and sodium 9-anthrylcarboxylate in high yields (Scheme 3), respectively.



Scheme 3 Synthesis of Complexes 3-6

The X-ray crystal structures of complexes 3-6 was shown in Fig. 3-4 and Fig. S23-S24 in the ESI. In complexes 3-6, The coordination geometry of the centre metal Cu(I) ions was analogous to that in complex 1, but with a bidentate organic carboxylate or sulfonate ions instead of the original ClO<sub>4</sub>. The included bidentate ions were

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#### Scheme 2 Synthesis of Complexes 1-2

The flexible tetraphosphine ligand L reacted with group 11 metal ions by self-assembly to form the novel boat-shaped hostguest complexes 1-2 (see Fig. 1-2). In each complex, the two aromatic moieties form the bow and stern, two P-M-P bonds form both sides of the boat, -CH<sub>2</sub>CH<sub>2</sub>- forms the bottom of the boat and guests form sail, respectively. In complex 1, each Cu(I) ions was coordinated with two PPh<sub>2</sub> groups and one oxygen atoms of guest perchlorate ion in planar triangular form. However, in complex 2, each Ag(I) ions was coordinated with two PPh<sub>2</sub> and one NO<sub>3</sub><sup>-</sup> in triangular. Interestingly, the guest is a CHCl<sub>3</sub> solvent molecule, but in disordered form. Hydrogen bond was found between the H atom of CHCl<sub>3</sub> and O atom of nitrate. The dihedral angles of two aromatic moieties that show the size of boat-shaped cavity in complexes 1-2 are 150.3°, 175.4°, respectively. And the boat-shaped cavity endows it with potential application in host-guest self-assembly and recognition. All of these complexes 1-2 have been fully characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>31</sup>P NMR, HRMS and elemental analysis (see details in the ESI).

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*p*-TsO<sup>-</sup>, AcO<sup>-</sup>, PhCO<sub>2</sub><sup>-</sup> and 9-anthrylcarboxylate anion in **3-6**, respectively. The Cu–O bonds in complexes **3-6** are shorter compared with that in complex **1**(see those in Table 1), which showed a stronger coordination of the guest to the metal ions in host. Intramolecular CH···π interactions (see Fig. 3-4, Table 2 and Fig. S24 in the ESI) in complexes **3**, **5**, **6** were found. Additionally, the intermolecular  $\pi$ - $\pi$  interactions between one phenyl of diphenylphosphino group in one molecule and 9-anthryl group of the guest in another molecule of complex **6**(see Fig. 5) was found.

**Table 1** Characteristic molecular structures of Cu(I) complexes 1 and 3-6

Compou nds	Xª	M-0 <sup><i>b</i></sup> / Å		CH-π <sup>c</sup> D <sub>v</sub> (Å)/D <sub>c</sub> (Å)		θ dihedral angle <sup>d</sup>
1	CIO4 <sup>-</sup>	2.227(3)	2.143(3)			150.3°
3	TsO⁻	2.087(3)	2.098(3)	2.9183/3 .0769	3.2130/3 .1010	144.4°
4	AcO <sup>-</sup>	2.015(5)	2.016(5)			147.9°
5	PhCOO <sup>-</sup>	2.040(4)	2.025(4)	2.9085	3.1380	139.5°
6	AnCOO <sup>-</sup>	1.995(3)	2.003(3)	3.4083/3 .3083	3.5250/3 .4330	133.1°

 $^{\circ}$ Anionic guest.  $^{\circ}$ Cu-O bond length.  $^{\circ}$ D<sub>v</sub> are the perpendicular distances of the H atoms to the arene rings and D<sub>c</sub> are the distances of the H atoms to the centers of the arene rings.  $^{\circ}$ The dihedral angles of –CH<sub>2</sub>CH<sub>2</sub>-bridged two aromatic planes.



**Fig. 3** Molecular views of the X-ray crystal structures of the Cu(I) complex **3**. Thermal ellipsoids are shown at the 50% probability level. Partial hydrogen atoms, one perchlorate anion and solvent molecules are omitted for clarity.



**Fig. 4** Molecular views of the X-ray crystal structures of the Cu(I) complex **6**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms(except that in existed CH··· $\pi$ ), one perchlorate anion, solvent molecules and phenyl are omitted for clarity.

Table 2 CH… $\pi$ Interaction Distance of 3, 5, 6					
	3	5	6		

CH…π <sup>a</sup>	H70/ H74	H22B	H74/ H84
D <sub>v</sub> (Å)	2.9183/3.0769	2.9085	3.4083/3.3083
D <sub>c</sub> (Å)	3.2130/3.1010	3.1380	3.5250/3.4330

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 $^{\it a}D_V$  are the perpendicular distances of the H atoms to the arene rings and  $D_C$  are the distances of the H atoms to the centers of the arene rings.

The cavity size of the hosts in complexes **3-6** can be reflected by the dihedral angles  $\theta$  of the  $-CH_2CH_2$ -bridged two phenyl planes as shown in Table 1. It is noteworthy that the dihedral angles  $\theta$  of two aromatic moieties in complexes **3-6** (144.4°, 147.9°, 139.5° and 133.1° in **3-6**, respectively) are significantly smaller compared to that in complex **1**(150.3°). As shown in Fig. 6, the dihedral angles of two aromatic rings in complexes **4-6** decreased with the addition of the intramolecular CH… $\pi$  interactions between host and guest molecules.



Fig. 5 The  $\pi$ - $\pi$  interaction between complex 6 monomers. The anthryl rings are displayed in ball-and-stick model and the other structure is displayed in wire model.



Fig. 6 The dihedral angles of two aromatic ring planes in complexes 4-6. The CH $\cdots\pi$  interactions in 5-6 are depicted in dashed line.

As can be seen from the above description, the metal-organic framework can encapsulate guests of different size by automatically adjusting its cavity through anions-metal coordination and the host-guest CH… $\pi$  interactions in the process of anion exchange of complex 1, which showed a self-adaptive ability of the metal macrocyclic complex. Complexes **3-6** have also been fully characterized by  $^{1}$ H NMR,  $^{13}$ C NMR,  $^{31}$ P NMR, HRMS and elemental analysis (see details in the ESI).

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## **Computational details**

All density functional theory (DFT)<sup>39</sup> calculations have been accomplished using B3LYP method<sup>40</sup> embedded in Gaussian16<sup>41</sup> program. The initial structures were taken from XRD structures and then optimized in geometry using mixed basis set. The LANL2DZ basis set<sup>42</sup> was adopted for Cu and 6-31G(d)<sup>43</sup> for other elements. Vibrational analysis on these optimized structures were systematically carried out in order to avoid any imaginary vibrational mode and determine the entropic contributions to the free energies. Moreover, the electrolyte solvent (trichloromethane) was taken into account for the solvation free energy calculations using the steered molecular dynamics (SMD) solvation model.

In addition, the dispersion contributions have been considered during all the calculations using the D3 code of Grimme and collaborators.<sup>44</sup> All the results with D3 correction have been compared with those without dispersion corrections to emphasize the intramolecular interaction.

We decided to further investigate the self-adaptive phenomenon revealed by complexes **4**, **5** and **6** using density functional theory calculations. Geometry optimization both with and without D3 dispersion corrections were carried out. Among the optimized geometries without D3, complex **4** showed good consistency with the experimental one, while complexes **5** and **6** exhibited differences (see the dihedral angle in Table 1 and Table 3). Among the optimized geometries with D3, the dihedral angles of the hosts in complexes **4**, **5** and **6** all represented a good consistency with the experimental ones (see Table 1 and Table 3), which indicate that the CH… $\pi$  interaction between host and guest plays a vital role in the geometry of the complexes.<sup>8</sup>

 Table 3 Details of calculation(with D3) data collection for complexes

 4-6

	θ dihedral angle	Gibbs free Energy(a.u.)	Interaction Energy(a.u.)	Interaction Energy(kJ/mol)
host		-4614.6069		
complex 4	142.8°	-4843.2623	-0.1010	-265.13
guest 4		-228.5543		
complex 5	140.7°	-5034.9757	-0.1088	-285.55
guest 5		-420.2600		
complex 6	130.2°	-5342.2087	-0.1549	-406.57
guest 6		-727.4469		

The interaction energies between hosts and guests of complexes **4**, **5** and **6** are listed in Table 3 The interaction energy is defined as:

$$\mathbf{E}_i = \mathbf{E}_{hg} - \mathbf{E}_h - \mathbf{E}_g,$$

where  $E_i$  represents the interaction energy,  $E_h$  represents the energy of the host,  $E_g$  represents the energy of the guest and  $E_{hg}$  represents the energy of the complex, respectively. An observation can be concluded from Table 3 that the larger the interaction energy is, the smaller the dihedral angle is, which is in consistency with the results of the experiments. Until now, the essence of the self-adaptive phenomenon is revealed to be the interaction between the host and the guest. By common sense, larger guest introduces larger steric hindrance, which should enlarge the dihedral angle of the host. However, in the cases of complex **4**, **5** and **6**, the larger guests correspond to stronger interactions towards the host, thus decrease the dihedral angle instead.

Though the calculated dihedral angles are satisfactory in term of reasonable error in calculation, some structural differences still exist between the calculational and experimental geometries of complex **4**, **5**(see Fig. S27 in the ESI) and **6**. For instance, guest **6** leans to one side in the calculated structure(see Fig. S26c in the ESI), while it keeps vertical in the experimental crystal structure. These differences are possibly due to the intermolecular interactions (like the  $\pi$ - $\pi$  stacking) between complex monomers in their crystal structures(see Fig. S).

## Conclusions

In summary, we have successfully synthesized the novel tetraphosphine ligand and its host-guest complexes with novel boat-shaped cavities via a directed self-assembly process. These complexes were fully characterized, including by X-ray crystallography analysis. Complexes **1-2** showed a self-assembly synthetic method of host-guest complexes by coordinate bonds, or weak interactions between ligand, metal ions and guest anions. However, complexes **3-6** showed a self-adaptive anion exchange by coordinate bonds, CH···π interactions and  $\pi$ -π interactions between host and guest molecules, which showed the potential application in supramolecular medicinal chemistry. Using dispersion-corrected density functional theory, the computed geometrical parameters are in good agreement with those in experiments. The theoretical results can be anticipated to be useful in terms of self-assembly and sensing behaviors of host-guest complexes for some anionic guests.

## Experimental

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques, unless stated otherwise. All solvents were distilled from appropriate drying agents under argon before using. <sup>31</sup>P, <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV400 spectrometer. HRMS were carried out on Agilent 6520 Q-TOF mass spectrometers. Chemical shifts, d, are reported in ppm relative to the internal standard TMS. *J* values are given in Hz. Elemental analyses were measured using a Perkin-Elmer 2400C Elemental Analyzer.

#### Synthesis of Compound b.

The 4-tert-butylphenol (0.2mol) and potassium hydroxide (0.2 mol) were dissolved in 60 ml of alcohol and 25 g of ethylene bromide added. The mixture was refluxed overnight. The solutions were then cooled, filtered and the potassium bromide washed out with water. The resultant solid was washed out with alcohol. Yield: 6.8 g (21%). Mp: 86-87 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.34 (dd, 4H, J = 8.7, 1.1 Hz, Ar-H), 6.92 (dd, 4H, J = 8.8, 1.2 Hz, Ar-H), 4.33 (d, 4H, J = 0.9 Hz, OCH<sub>2</sub>), 1.33 (d, 18H, J = 1.4 Hz, *t*-Bu). 13C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  156.36, 143.70, 126.23, 114.13, 66.48, 34.06, 31.51.

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#### Synthesis of Compound c.

The 1,2-bis(4-tert-butylphenoxy)ethane 0.95g (2.91 mmol) was dissolved in 20 ml of CHCl<sub>3</sub>/AcOH(1:1), and the solution was cooled to 0°C. Bromine (2.05g 12.80 mmol) was added dropwise into the stirred reaction mixture. After the reaction was completed as checked by TLC, Saturated NaOH(ag) was added to the solution to remove the HBr. The aqueous solution was extracted with dichloromethane, the organic phase was washed with saturated aqueous NaCl solution and dried over MgSO<sub>4</sub>, and the solvent was removed under reduced pressure. 1,2-bis(2,6-dibromo-4-tertbutylphenoxy)ethane was obtained. Yield: 1.76 g (95%). Mp: 113-115 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.49 (s, 4H, Ar-H), 4.45 (s, 4H, OCH<sub>2</sub>), 1.29 (s, 18H, t-Bu). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 150.78, 149.96, 129.85, 117.73, 71.61, 34.56, 31.13. HR-MS(ESI) calcd for  $C_{22}H_{26}Br_4O_2Na^+$  (M + Na<sup>+</sup>) 664.8523, found 664.8521. Elemental analysis calcd (%) for C<sub>22</sub>H<sub>26</sub>Br<sub>4</sub>O<sub>2</sub> C 41.16, H 4.08; found C 41.39, H 3.96.

#### Synthesis of Ligand L.

To a stirred THF (120 mL) of 1,2-bis(2,6-dibromo-4-tertbutylphenoxy)ethane (3.21 g, 5 mmol) at -78 °C was added 8 mL (20 mmol) of *n*-butyl lithium solution (2.5 M in hexane). The reaction mixture was stirred for 2 h at -78 °C, then a solution of 3.68 mL (20 mmol) of CIPPh2 in THF (20 mL) was added. The reaction mixture was left to stir overnight and slowly warmed up to room temperature. The solvent was removed under reduced pressure, and 50 mL dichloromethane was added. The organic phase was washed with aqueous NaCl solution and dried over MgSO<sub>4</sub>, and the solvent was removed under reduced pressure. After recrystallization from dichloromethane and methyl alcohol. L was obtained. Yield: 2.05 g (39%). Mp: 261-263 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.26 (dd, 40H, J = 9.1, 4.2 Hz, PPh-H), 6.71 (d, 4H, J = 3.0 Hz, Ar-H), 4.33 (s, 4H, OCH<sub>2</sub>), 0.89 (s, 18H, *t*-Bu). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 161.80, 146.61, 137.19, 134.16-133.63, 132.12, 130.36, 128.30, 72.26, 34.44, 31.02.  $^{31}\text{P}$  NMR (162 MHz, CDCl\_3):  $\delta$  -16.54 (s). HR-MS(ESI) calcd for  $C_{70}H_{67}O_2P_4^+$  (M + H<sup>+</sup>) 1063.4086, found 1063.4077.

#### Complex 1.

Under an atmosphere of argon and in the absence of light, to a dichloromethane (20 ml) solution of L (106 mg, 0.10 mmol) was added Cu(CH<sub>3</sub>CN)<sub>4</sub>ClO<sub>4</sub> (74 mg, 0.20 mmol) at room temperature. The mixture was allowed to stir for 30 min. After filtration of any insoluble materials, the solution was evaporated, and the resultant solid was recrystallized from trichloromethane and diethyl ether, affording the complex  $[(Cu_2L)(ClO_4)]ClO_4$  as a white powder. Yield: 98 mg (71%). Mp: 271-273 °C. Anal. Calc. for C<sub>70</sub>H<sub>66</sub>Cl<sub>2</sub>Cu<sub>2</sub>O<sub>10</sub>P<sub>4</sub>: C, 60.52; H, 4.79. Found: C, 60.29; H, 5.00%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.49 (m, 40H, J = 19.4, 13.1, 7.6 Hz, PPh-H), 7.02 (s, 4H, Ar-H), 3.96 (s, 4H, OCH<sub>2</sub>), 0.93 (s, 18H, t-Bu). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 160.77, 149.09, 134.91, 134.24-133.35, 133.36-133.35, 131.55, 131.20, 129.93, 129.79-129.73, 129.48, 128.77, 123.75, 123.43, 71.99, 34.77, 31.09-30.56. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ -12.72 (s). HR-MS(ESI) calcd for  $C_{70}H_{66}Cu_2O_2P_4^{2+}$  (M – 2ClO<sub>4</sub><sup>-</sup>) 594.1297, found 594.1296.

Complex 2.

Under an atmosphere of argon and in the absence of light, to a dichloromethane (20 ml) solution of  $\boldsymbol{L}$  (106 mg, 0.10 mmol) was added a dichloromethane (10 ml) solution of AgNO<sub>3</sub> (34 mg, 0.20 mmol) at room temperature. The mixture was allowed to stir for 30 min. After filtration of any insoluble materials, the solution was evaporated, and the resultant solid was recrystallized from trichloromethane and diethyl ether, affording the complex [Ag<sub>2</sub>L(NO<sub>3</sub>)<sub>2</sub>(CHCl<sub>3</sub>)] as a white powder. Yield: 123 mg (88%). Mp: 191-193 °C. Anal. Calc. for  $C_{70}H_{66}Ag_2N_2O_8P_4$ · $H_2O$ ·0.5CHCl<sub>3</sub>: C, 57.19; H, 4.66, N, 1.89. Found: C, 56.91; H, 4.27, N, 2.10%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.51-7.33 (m, 40H, PPh-H), 6.87 (s, 4H, Ar-H), 3.73 (s, 4H, OCH<sub>2</sub>), 0.85 (s, 18H, *t*-Bu). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 159.99, 147.78, 134.89, 133.82, 131.57-131.31, 131.57-129.94, 129.26, 124.37, 72.19, 34.59, 30.74.  $^{31}$ P NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  -3.95 (dd, J = 515.5, 36.7 Hz). HR-MS(ESI) calcd for  $C_{70}H_{66}Ag_2O_2P_4^{2+}$  (M – 2NO<sub>3</sub>) ) 639.1056, found 639.1050.

#### Complex 3.

Under an atmosphere of argon, to a dichloromethane (20 ml) solution of [(Cu<sub>2</sub>L)(ClO<sub>4</sub>)]ClO<sub>4</sub> (139 mg, 0.10 mmol) was added sodium p-toluenesulfonate (70 mg, 0.40 mmol) at room temperature. The mixture was allowed to reflux for 12 h. After filtration of any insoluble materials, the solution was evaporated, and the resultant solid was recrystallized from trichloromethane and *n*-hexane, affording the complex [(Cu<sub>2</sub>L)(OTs)]ClO<sub>4</sub> as a white powder. Yield: 124 mg (85%). Mp: 260-263 °C. Anal. Calc. for  $C_{70}H_{66}Cl_2Cu_2O_{10}P_4$ ·0.5H<sub>2</sub>O: C, 62.92; H, 5.07 Found: C, 62.89; H, 5.15%. <sup>1</sup>H NMR (400 MHz, DMSO) δ 7.60-7.36 (m, 40H, L-PPh-H; 2H, Tos-Ar-H), 7.09 (d, 2H, J = 7.8 Hz, Tos-Ar-H), 6.52 (s, 4H, L-Ar-H), 4.41 (s, 4H, OCH<sub>2</sub>), 2.27 (s, 3H, Tos-t-Bu), 0.64 (s, 18H, L-t-Bu). <sup>13</sup>C NMR (101 MHz, DMSO) δ 137.44, 133.57, 132.82, 131.86, 130.46, 128.64, 127.91, 125.37, 123.41, 72.60, 33.62, 30.12, 20.67. <sup>31</sup>P NMR (162 MHz, DMSO)  $\delta$  -9.80 (s). HR-MS(ESI) calcd for C<sub>70</sub>H<sub>66</sub>Cu<sub>2</sub>O<sub>2</sub>P<sub>4</sub><sup>2+</sup> (M – 2ClO<sub>4</sub>) 594.1297, found 594.1296.

#### Complex 4.

Under an atmosphere of argon, to a dichloromethane (20 ml) solution of  $[(Cu_2L)(ClO_4)]ClO_4$  (139 mg, 0.10 mmol) was added sodium acetate (33 mg, 0.40 mmol) at room temperature. The mixture was allowed to reflux for 12 h. After filtration of any insoluble materials, the solution was evaporated, and the resultant solid was recrystallized from trichloromethane and *n*-hexane, affording the complex  $[(Cu_2L)(OAc)]ClO_4$  as a white powder. Yield: 134 mg (92%). Anal. Calc. for  $C_{72}H_{69}ClCu_2O_8P_4$ : C, 64.12; H, 5.16 Found: C, 64.30; H, 5.24%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.89-7.27 (m, 40H, PPh-H), 6.92 (s, 4H, Ar-H), 3.87 (s, 4H, OCH<sub>2</sub>), 1.78 (s, 3H, CCH<sub>3</sub>), 0.89 (s, 18H, *t*-Bu). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  177.81, 160.87, 148.31, 134.08, 133.16, 130.90, 129.28, 124.59, 71.64, 34.62, 30.82, 25.34. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  -14.28 (s). HR-MS(ESI) calcd for  $C_{70}H_{66}Cu_2O_2P_4^{2+}$  (M – 2ClO<sub>4</sub><sup>-</sup>) 594.1297, found 594.1302.

#### Complex 5.

Under an atmosphere of argon, to a dichloromethane (20 ml) solution of  $[(Cu_2L)(ClO_4)]ClO_4$  (139 mg, 0.10 mmol) was added sodium benzoate (70 mg, 0.40 mmol) at room temperature. The mixture was allowed to reflux for 12 h. After filtration of any insoluble materials, the solution was evaporated, and the resultant

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solid was recrystallized from trichloromethane and *n*-hexane, affording the complex [(Cu<sub>2</sub>L)(PhCO<sub>2</sub>)]ClO<sub>4</sub> as a white powder. Yield: 134 mg (92%). Mp: 190-193 °C. Anal. Calc. for C<sub>70</sub>H<sub>66</sub>Cl<sub>2</sub>Cu<sub>2</sub>O<sub>10</sub>P<sub>4</sub>·2H<sub>2</sub>O: C, 63.92; H, 5.22 Found: C, 64.08; H, 5.40%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 (d, 2H, *J* = 7.1 Hz, PhCO<sub>2</sub>-Ar-*H*), 7.64-7.30 (m, 40H, L-PPh-*H*; 3H, PhCO<sub>2</sub>-Ar-*H*), 6.89 (d, 4H, *J* = 4.1 Hz, L-Ar-*H*), 3.99 (s, 4H, OCH<sub>2</sub>), 0.85 (s, 18H, *t*-Bu). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.00, 161.34, 148.32, 134.34, 134.33-134.30, 133.61, 131.68-131.61, 131.51, 130.86, 130.22-130.19, 129.27, 128.06, 124.66, 71.88, 34.59, 30.78. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  -14.46 (s). HR-MS(ESI) calcd for C<sub>70</sub>H<sub>66</sub>Cu<sub>2</sub>O<sub>2</sub>P<sub>4</sub><sup>2+</sup> (M – 2ClO<sub>4</sub><sup>-</sup>) 594.1297, found 594.1298.

#### Complex 6.

Under an atmosphere of argon, to a dichloromethane (20 ml) solution of [(Cu<sub>2</sub>L)(ClO<sub>4</sub>)]ClO<sub>4</sub> (139 mg, 0.10 mmol) was added sodium 9-anthraconate (98 mg, 0.40 mmol) at room temperature. The mixture was allowed to reflux for 12 h. After filtration of any insoluble materials, the solution was evaporated, and the resultant solid was recrystallized from trichloromethane and n-hexane, affording the complex  $[(Cu_2L)(AnCO_3)]ClO_4$  as a white powder. Yield: 121 mg (80%). Anal. Calc. for  $C_{85}H_{75}ClCu_2O_8P_4$ : C, 67.57; H, 5.00 Found: C, 67.29; H, 5.27%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.46 (s, 1H, AnCO<sub>3</sub>-H), 8.03 (d, 2H, J = 8.5 Hz, AnCO<sub>3</sub>-H), 7.54 (t, 6H; 6H, J = 7.2 Hz, AnCO<sub>3</sub>-H; L-PPh-H), 7.37 (dt, J = 14.8, 19H, 9.7 Hz, L-PPh-H), 7.29-7.21 (m, 3H, L-PPh-H; 2H, CDCl<sub>3</sub>), 7.09 (d, 2H, J = 8.6 Hz, L-PPh-H), 7.05-6.93 (m, 10H, L-PPh-H; 2H, L-Ar-H), 6.64 (t, 2H, J = 7.5 Hz, L-Ar-H), 4.14 (s, 4H, OCH<sub>2</sub>), 1.01 (s, 18H, t-Bu). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.09, 161.84-161.25, 148.40, 134.63, 133.85, 133.27, 131.59, 130.95, 130.66, 129.99, 129.63, 128.89, 128.30, 126.27, 125.62, 125.39-124.55, 72.11, 34.72, 31.03. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  -14.43 (s). HR-MS(ESI) calcd for C<sub>70</sub>H<sub>66</sub>Cu<sub>2</sub>O<sub>2</sub>P<sub>4</sub><sup>2+</sup>(M - 2ClO<sub>4</sub><sup>-</sup>) 594.1297, found 594.1309, calcd for C15H9O2 (AnCOO) 221.0608, found 221.0601.

#### Crystallography.

Colorless single crystals of complexes **1-2** suitable for X-ray diffraction were obtained by diffusion of ether into a CHCl<sub>3</sub> solution of the compound. Colorless single crystals of complexes **3-6** suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a CHCl<sub>3</sub> solution of the compound. Data collections were carried out on a Rigaku Saturn 724 CCD for **1-2** or Rigaku Saturn 70 for the remaining compounds diffractometer equipped with a rotating anode system at 113(2) K or 293(2) K by using graphite-monochromated Mo K $\alpha$  radiation ( $\omega$ -2 $\theta$  scans,  $\lambda$  = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least squares. Calculations were performed by using the SHELXL<sup>45</sup> program system. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations.

# **Conflicts of interest**

There are no conflicts to declare.

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