**SUPPORTING INFORMATION**

# Imidazole/Benzimidazole-Modified Cyclotriphosphazenes as Highly Selective Fluorescent Probes for $Cu^{2+}$: Synthesis, Configurational Isomers, and Crystal Structures

Aylin Uslu*, Süreyya Oğuz Tümay, Ahmet Şenocak, Fatma Yuksel, Elif Özcan, Serkan Yeşilot*

Department of Chemistry, Gebze Technical University, Gebze 41400, Kocaeli, Turkey

∗ Corresponding authors. Tel.: +90 262 6053009 and +90 262 6053014

E-mail addresses: aylin@gtu.edu.tr and yesil@gtu.edu.tr

**Compound 2a**

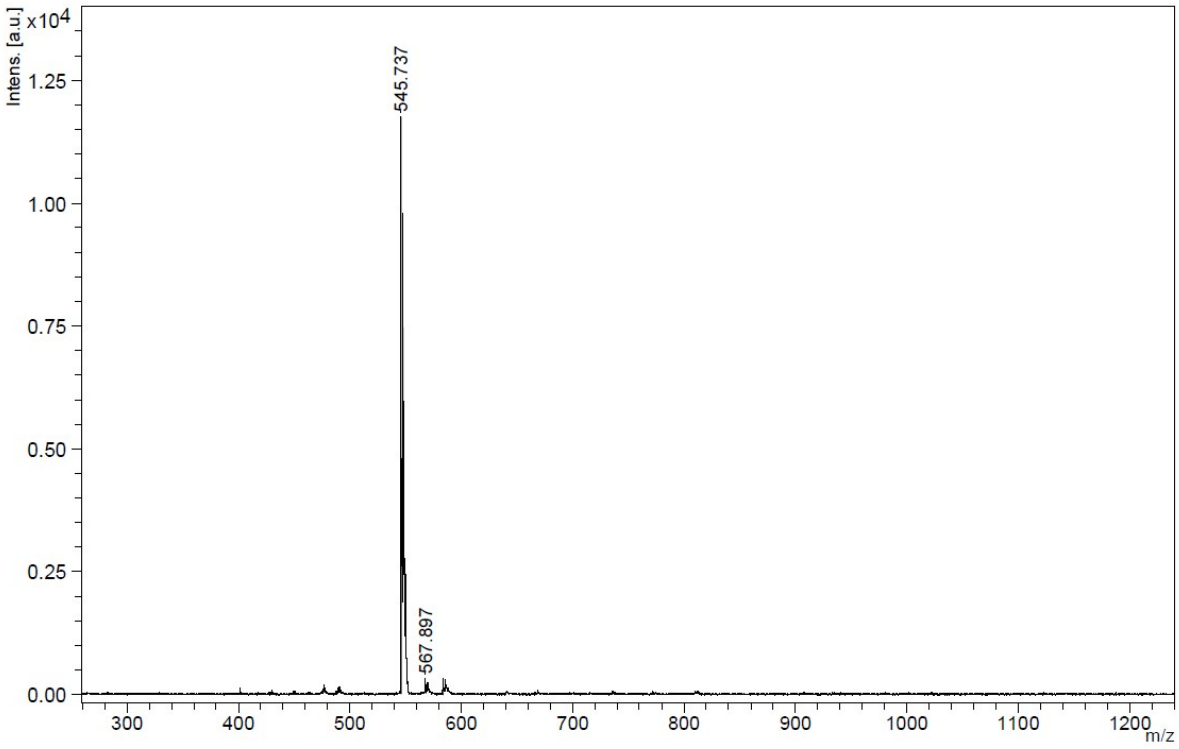


**Figure S1.** MALDI-TOF mass spectrum of compound **2a**

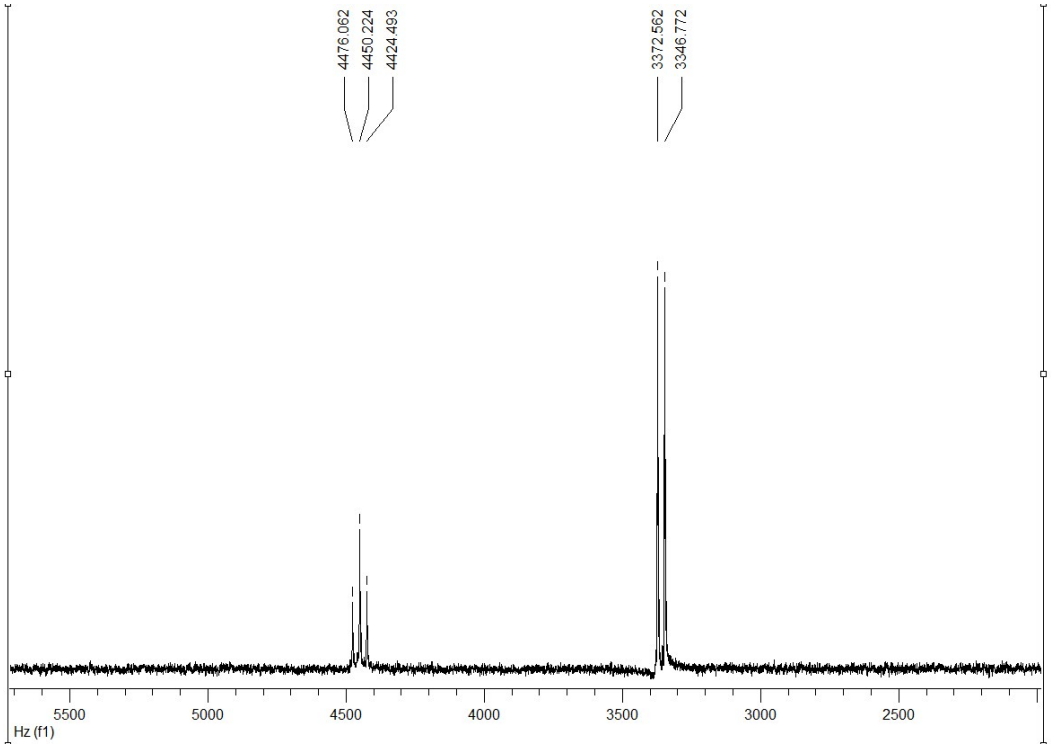

**Figure S2.** The proton decoupled $^{31}P$ NMR spectra of compound **2a** in $CDCl_3$

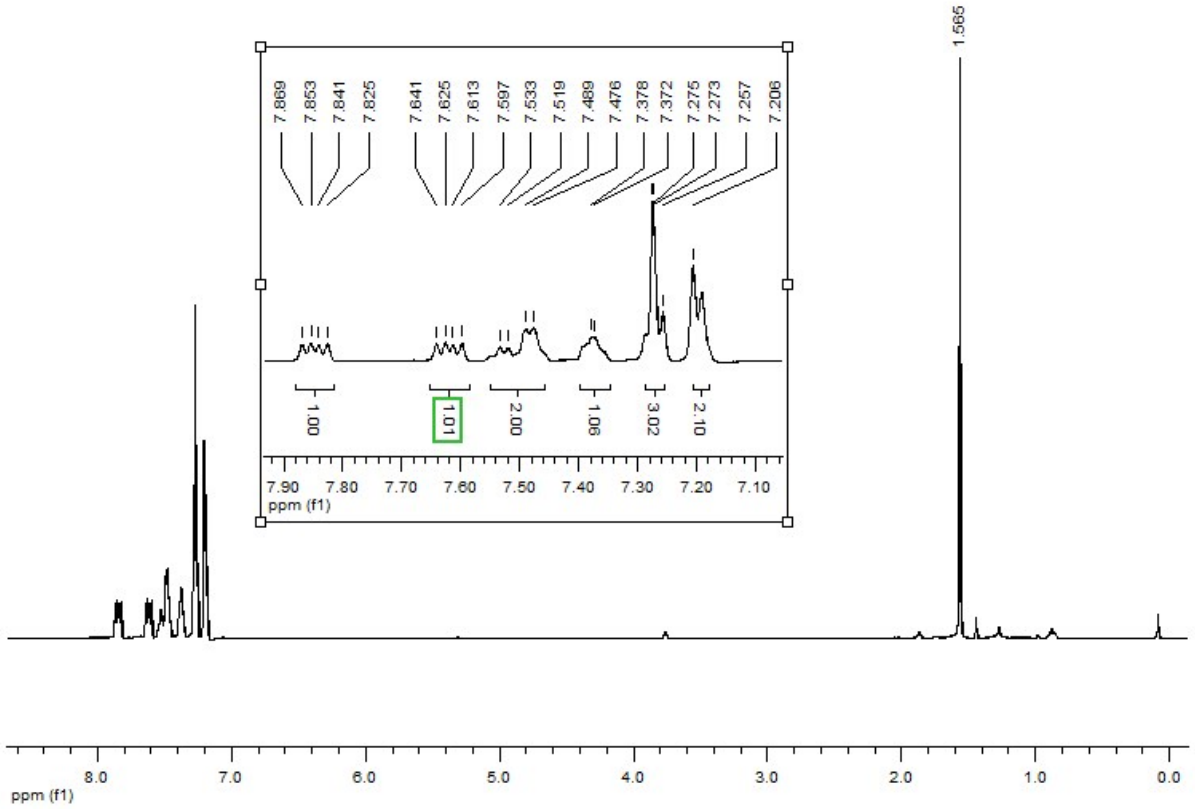


**Figure S3.** The $^{1}H$ NMR spectra of compound **2a** in $CDCl_3$ (1.56 ppm $H_2O$ solvent peak, 7.27 ppm $CDCl_3$ solvent peak)

## Compound 3a

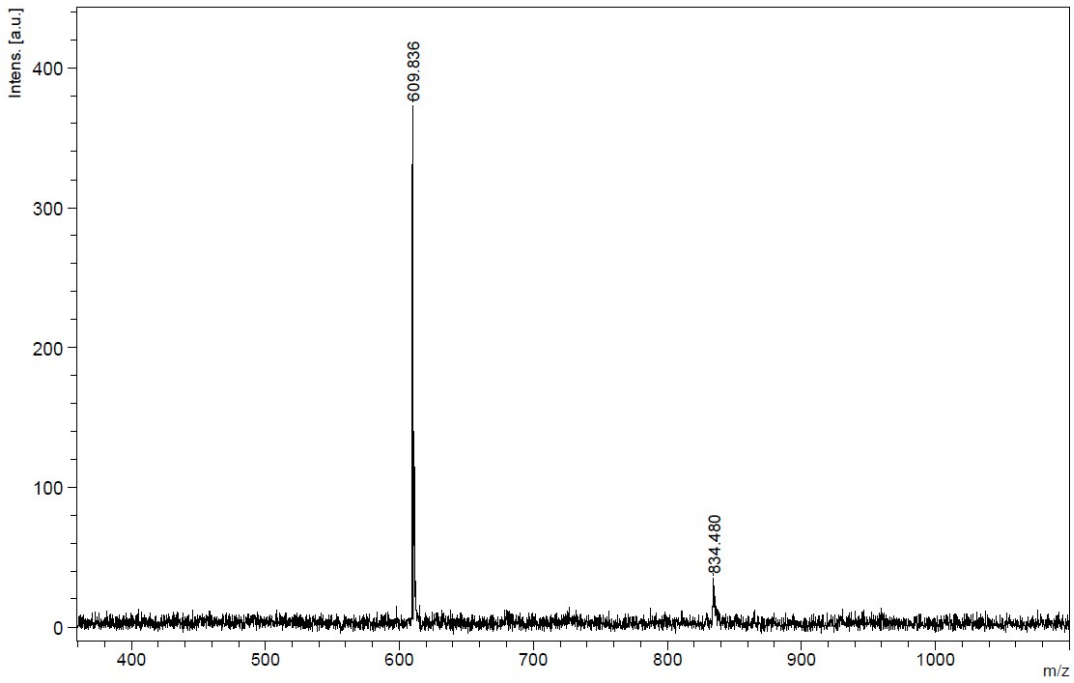

**Figure S4.** MALDI-TOF mass spectrum of compound **3a**

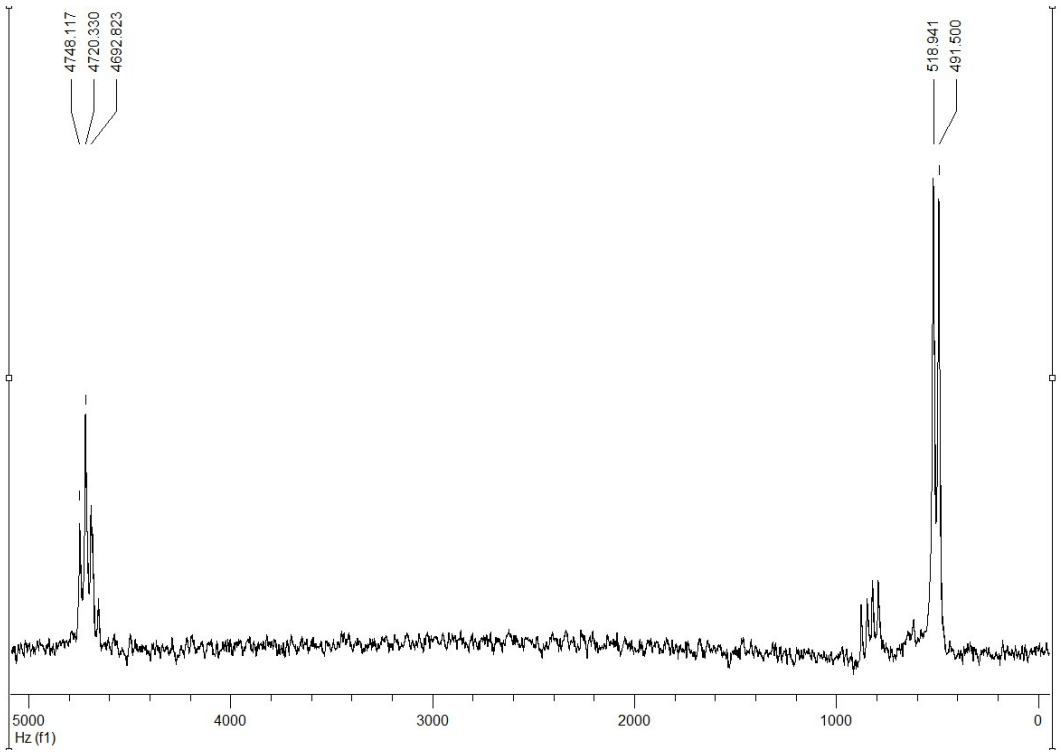


**Figure S5.** The proton decoupled $^{31}P$ NMR spectra of compound **3a** in $CDCl_3$

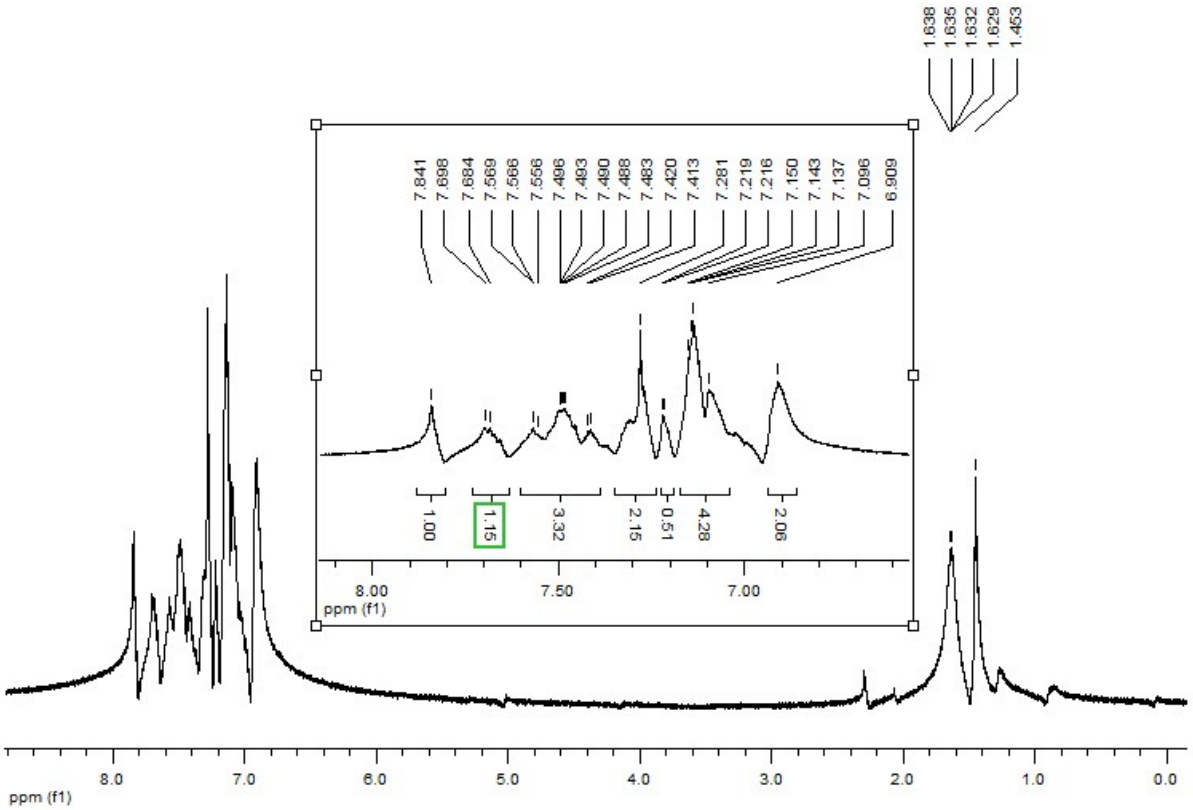


**Figure S6.** The $^{1}H$ NMR spectra of compound **3a** in $CDCl_3$

## Compound 3b

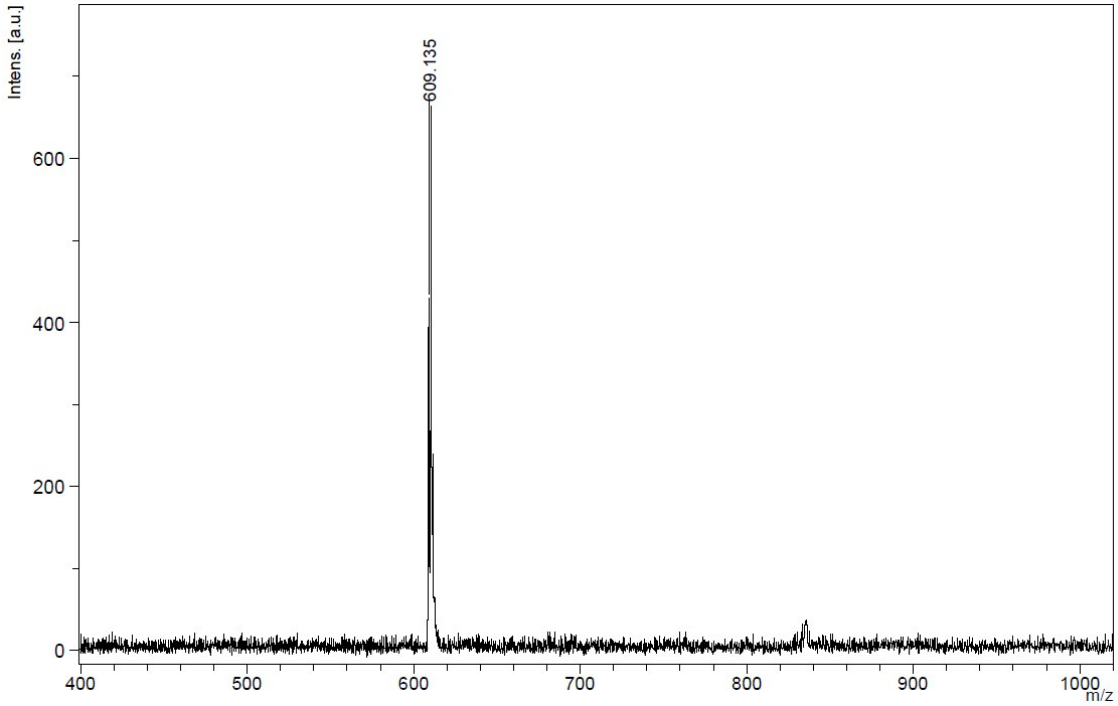


**Figure S7.** MALDI-TOF mass spectrum of compound **3b**

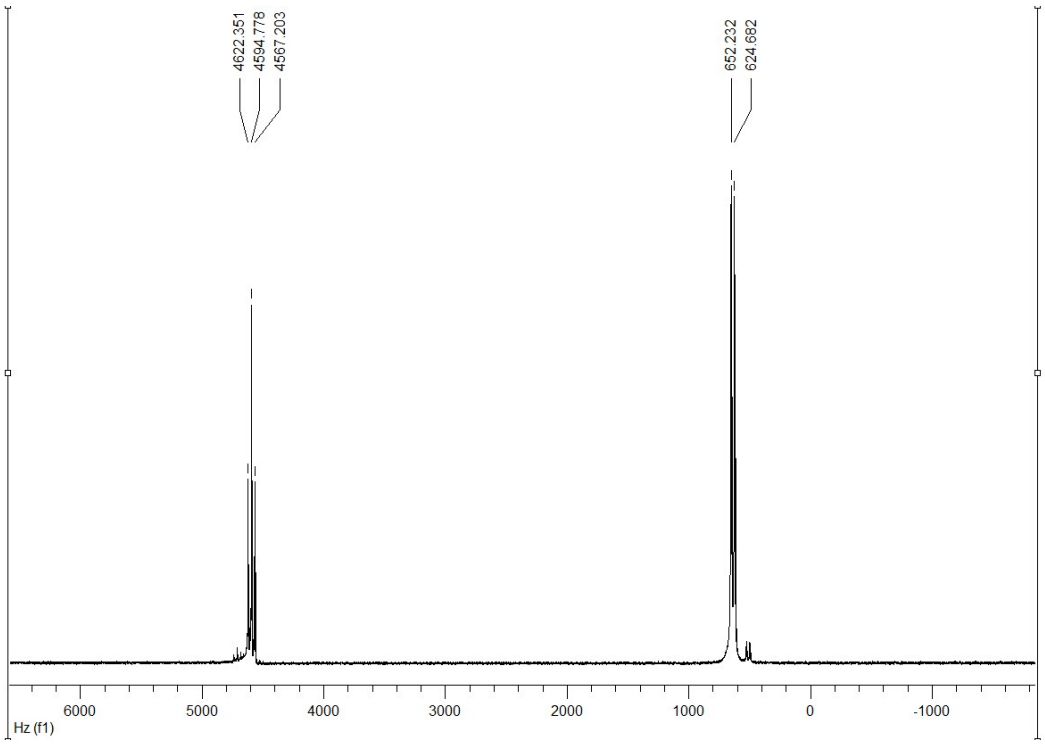

**Figure S8.** The proton decoupled $^{31}P$ NMR spectra of compound **3b** in $CDCl_3$

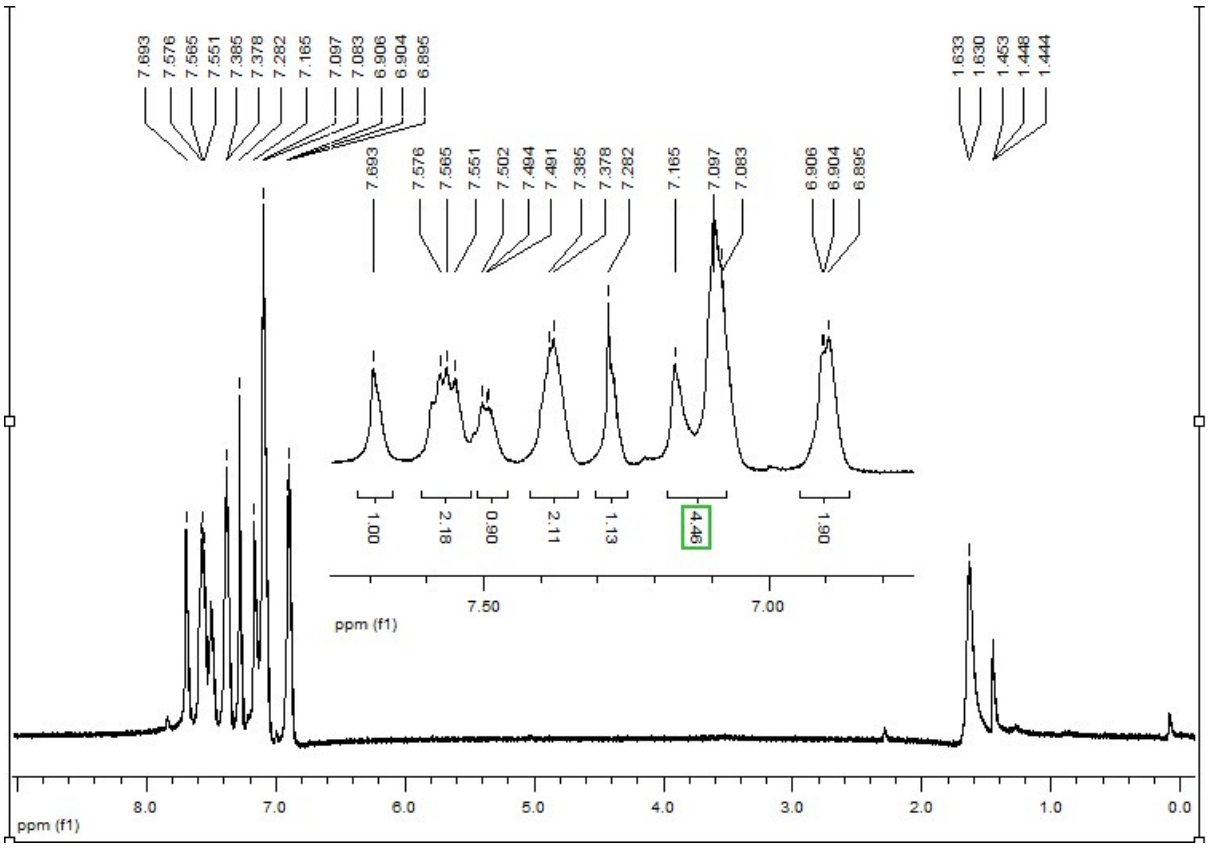


**Figure S9.** The $^{1}H$ NMR spectra of compound **3b** in $CDCl_3$

## Compound 4a

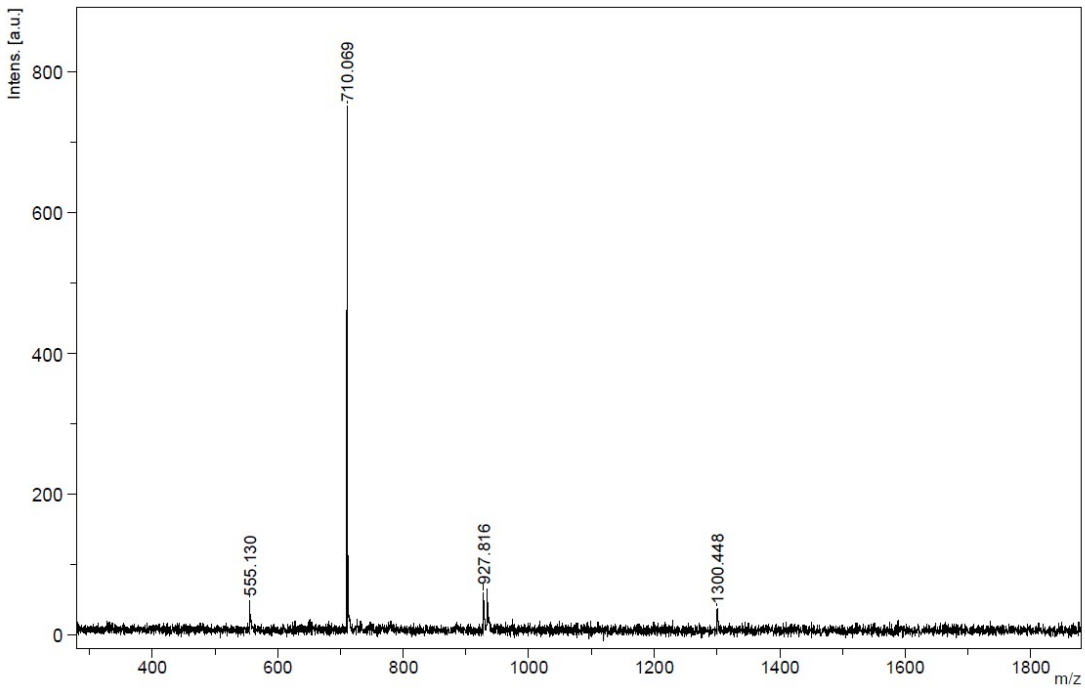


**Figure S10.** MALDI-TOF mass spectrum of compound **4a**

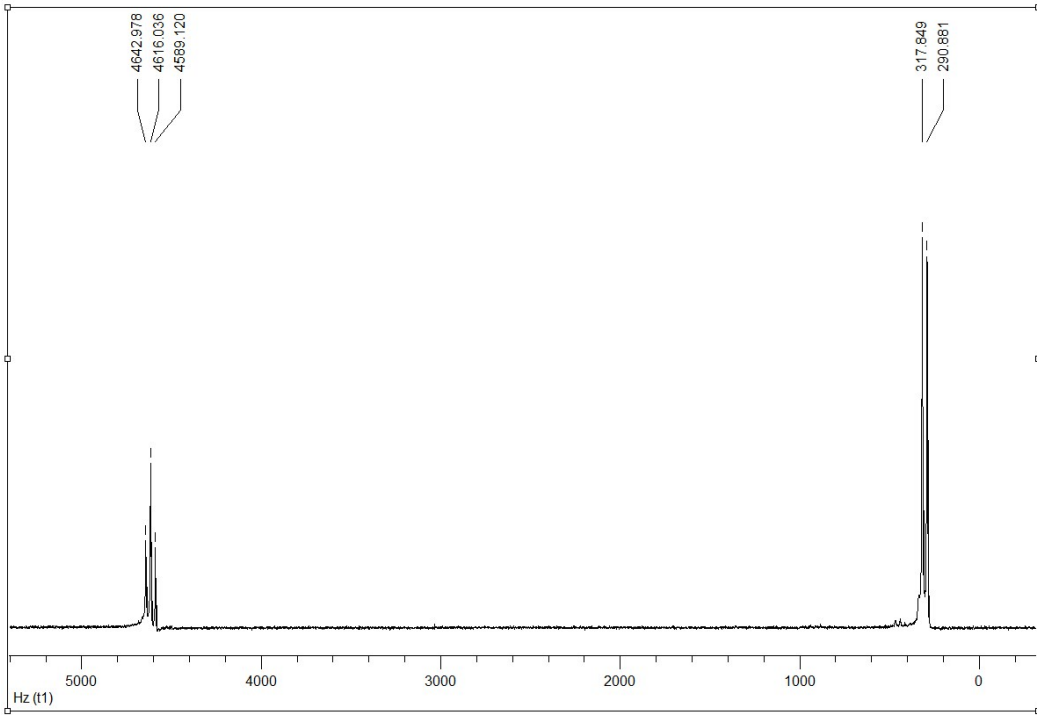


**Figure S11.** The proton decoupled $^{31}P$ NMR spectra of compound **4a** in $CDCl_3$

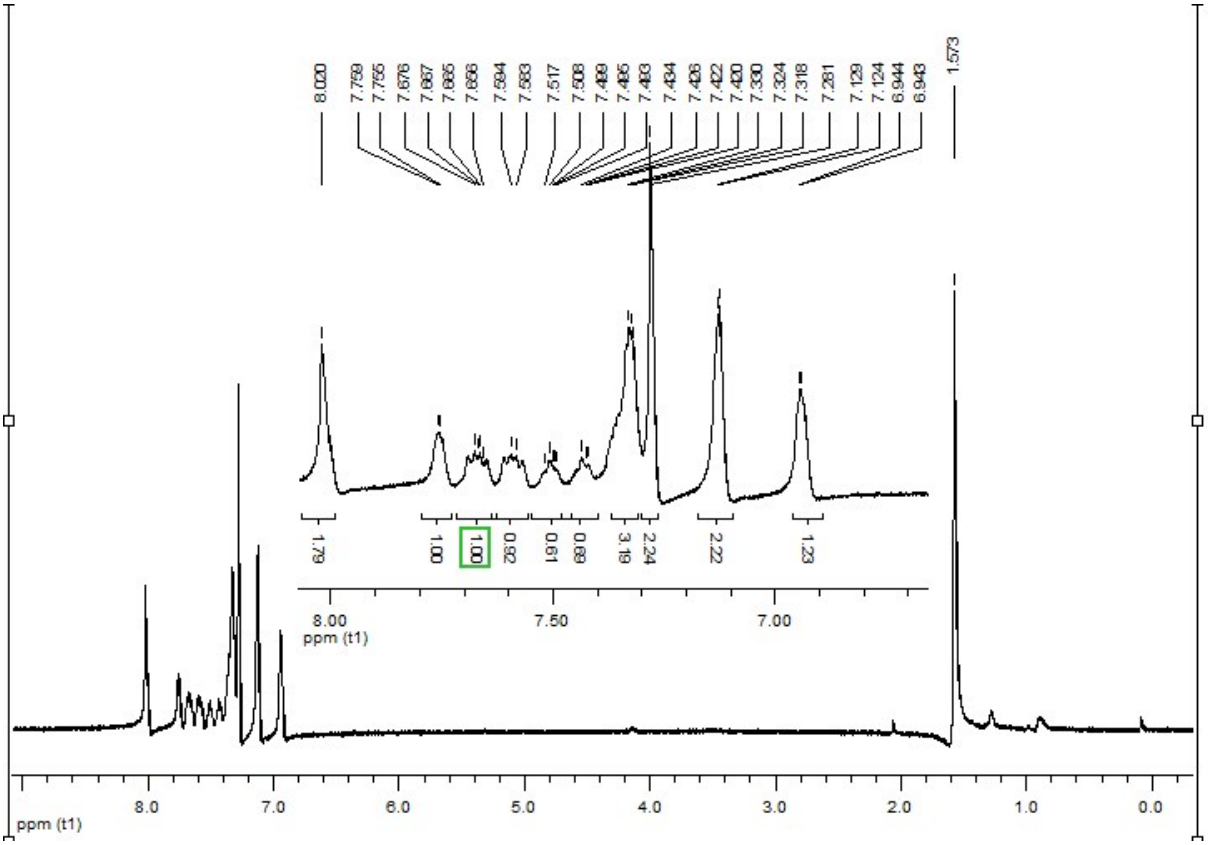


**Figure S12.** The $^{1}H$ NMR spectra of compound **4a** in $CDCl_3$

## Compound 4b

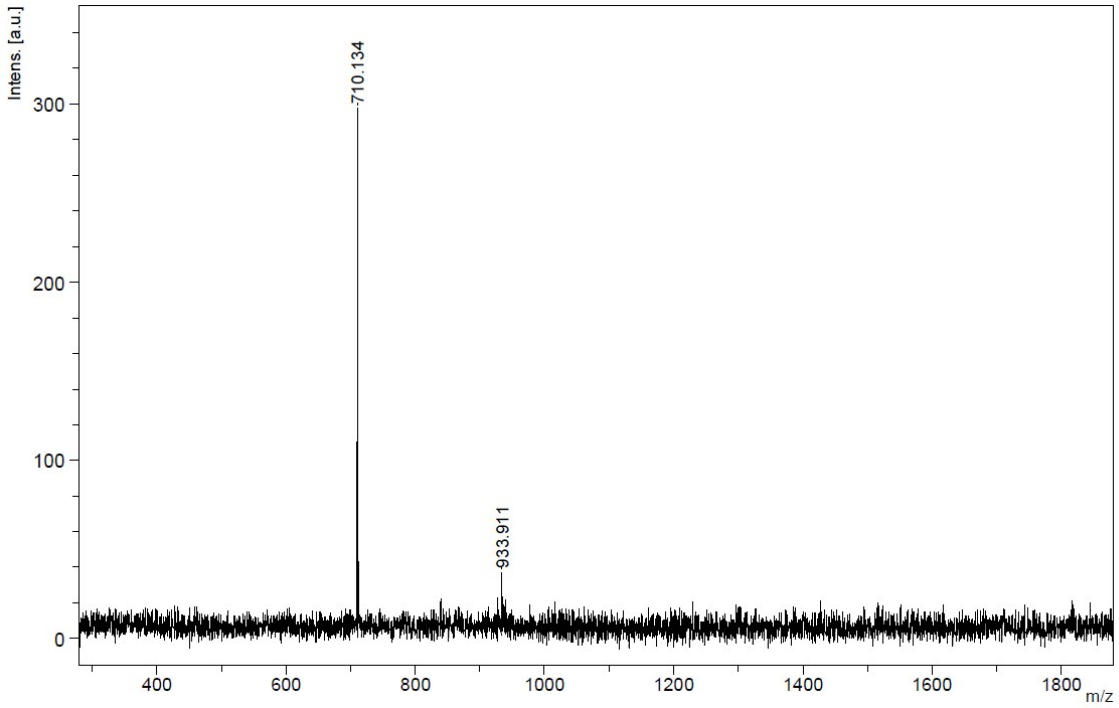


**Figure S13.** MALDI-TOF mass spectrum of compound **4b**

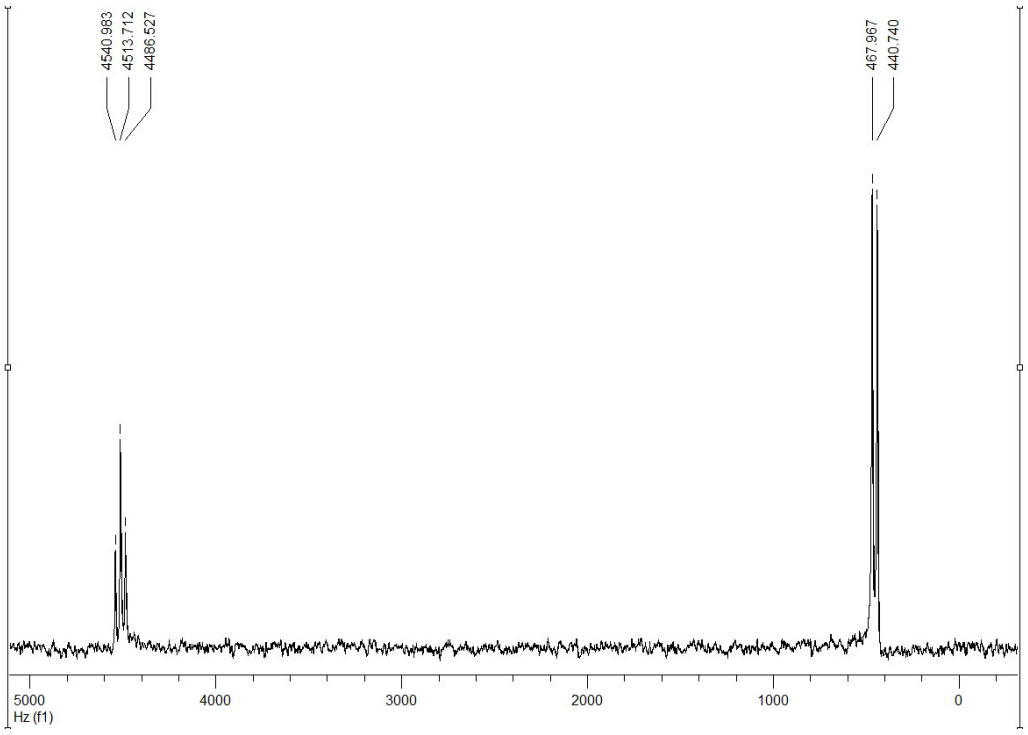

**Figure S14.** The proton decoupled $^{31}P$ NMR spectra of compound **4b** in $CDCl_3$

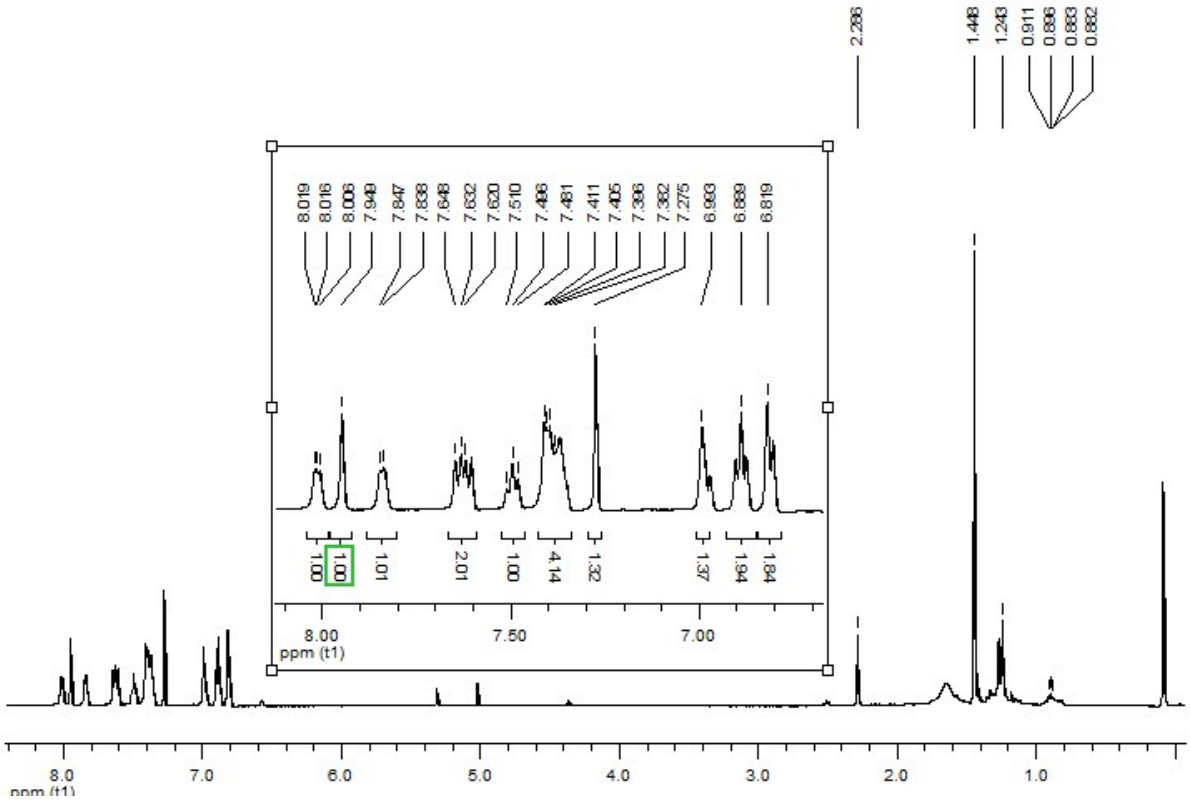


**Figure S15.** The $^{1}H$ NMR spectra of compound **4b** in $CDCl_3$

## Crystal Structure Analysis

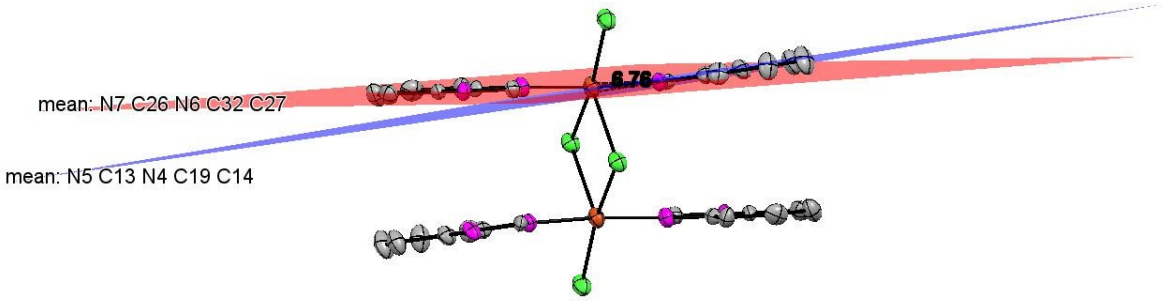


**Fig S16**. The orientation of imidazole rings in compound **5** (Viewing only complex moiety)

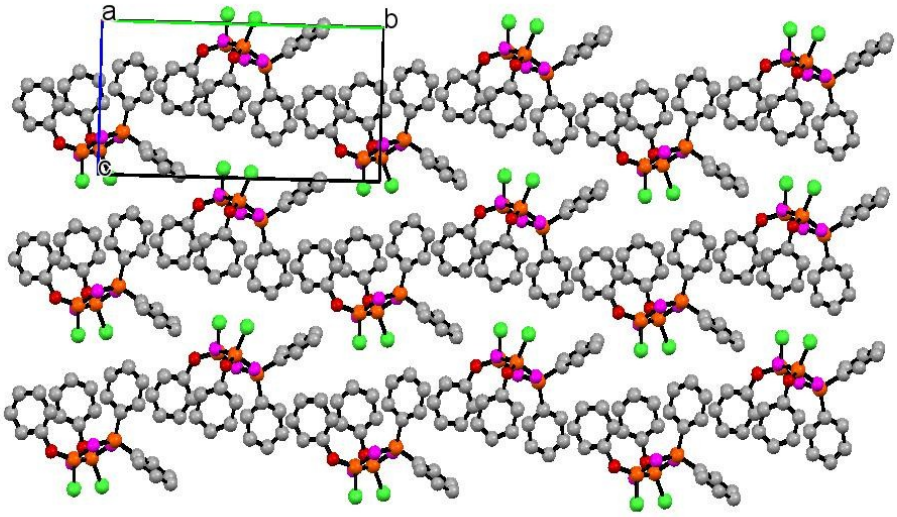


**Fig. S17** View of crystal packing of compound **2a**.

**Table S1.** Selected inter-molecular interactions for compound **2a**

| D-H···A | D-H | H···A | D···A | DHA | Symmetry code |
|---|---|---|---|---|---|
| C8-H8···N3 (intra) | 0.95 | 2.62 | 3.028(4) | 106 | |
| C9-H9···N2 | 0.95 | 2.50 | 3.413(5) | 161 | 1-x,1/2+y,-z |
| C4-H4···Cg3[1] | 0.95 | 2.77 | 3.648(4) | 154 | x,y,1+z |
| C6-H6···Cg5[2] | 0.95 | 2.89 | 3.679(3) | 141 | x,y,z |
| C14-H14···Cg5[2] | 0.95 | 2.74 | 3.444(3) | 132 | 1+x,y,z |
| C4-H4···Cg2[3] | 0.95 | 2.73 | 3.490(4) | 137 | 1-x,-1/2+y,1-z |
| [1]Cg3:C7C8C9C10C11C12<br>[2]Cg5:C19C20C21C22C23C24<br>[3]Cg2:C1C2C3C4C5C6 | | | | | |

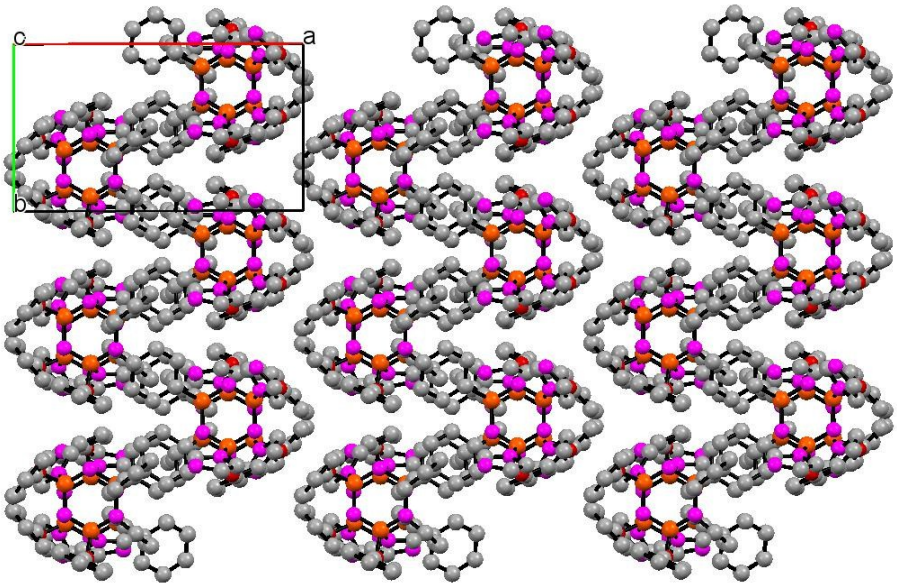


**Fig. S18** View of crystal packing of compound **3a**.

**Table S2.** Selected inter-molecular interactions for compound **3a**

| **D-H···A** | **D-H** | **H···A** | **D···A** | **DHA** | **Symmetry code** |
|---|---|---|---|---|---|
| C15-H15···Cg1[1] | 0.95 | 2.76 | 3.700(7) | 169 | -x,1/2+y,1/2-z |
| C12-H12···Cg7[2] | 0.95 | 2.98 | 3.750(6) | 139 | x,y,z |
| C18-H18···Cg7[2] | 0.95 | 2.92 | 3.686(6) | 139 | x,-1+y,z |
| [1]Cg1:N4C19N5C20C21<br>[2]Cg7:C22C23C24C25C26C27 | | | | | |

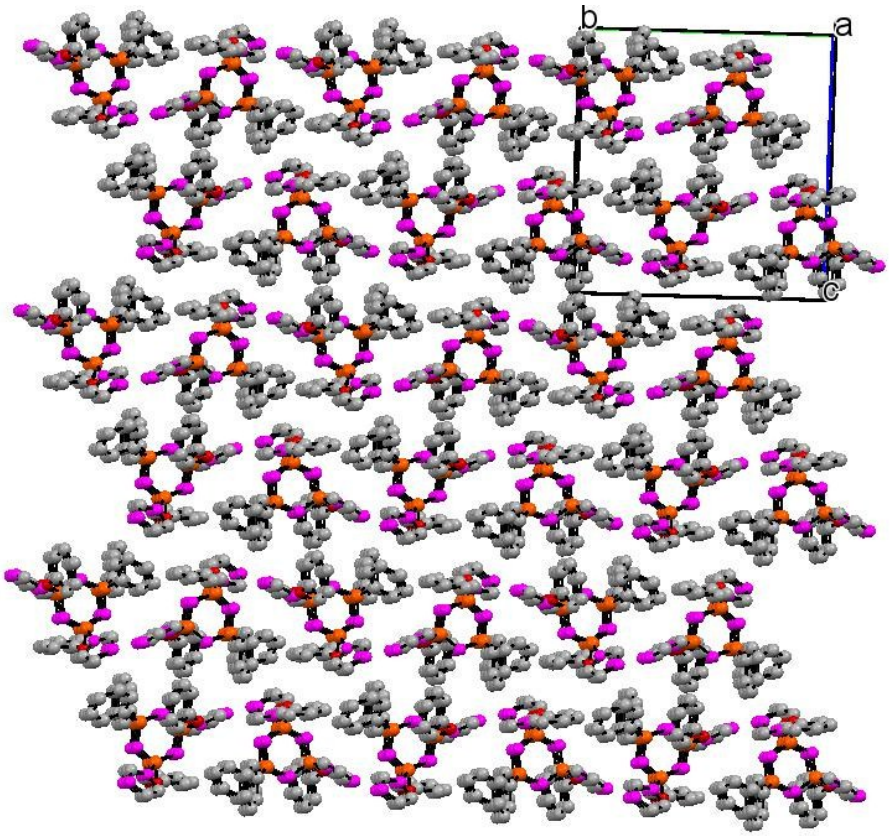


**Fig. S19** View of crystal packing of compound **3b**.

**Table S3.** Selected inter-molecular interactions for compound **3b**

| **D-H···A** | **D-H** | **H···A** | **D···A** | **DHA** | **Symmetry code** |
|---|---|---|---|---|---|
| C15-H15···Cg1[1] | 0.95 | 2.85 | 3.562(3) | 132 | x,y,z |
| C24-H24···Cg4[2] | 0.95 | 2.76 | 3.625(2) | 151 | 3/2-x,1/2+y,1/2-z |
| C29-H29···Cg5[3] | 0.95 | 2.73 | 3.490(4) | 137 | -1/2+x,1/2-y,-1/2+z |
| C21-H21···Cg7[4] | 0.95 | 2.98 | 3.698(2) | 134 | x,y,z |
| [1]Cg1:N4C19N5C20C21<br>[2]Cg4:C1C2C3C4C5C6<br>[3]Cg5:C7C8C9C10C11C12<br>[4]Cg7:C22C23C24C25C26C27 | | | | | |

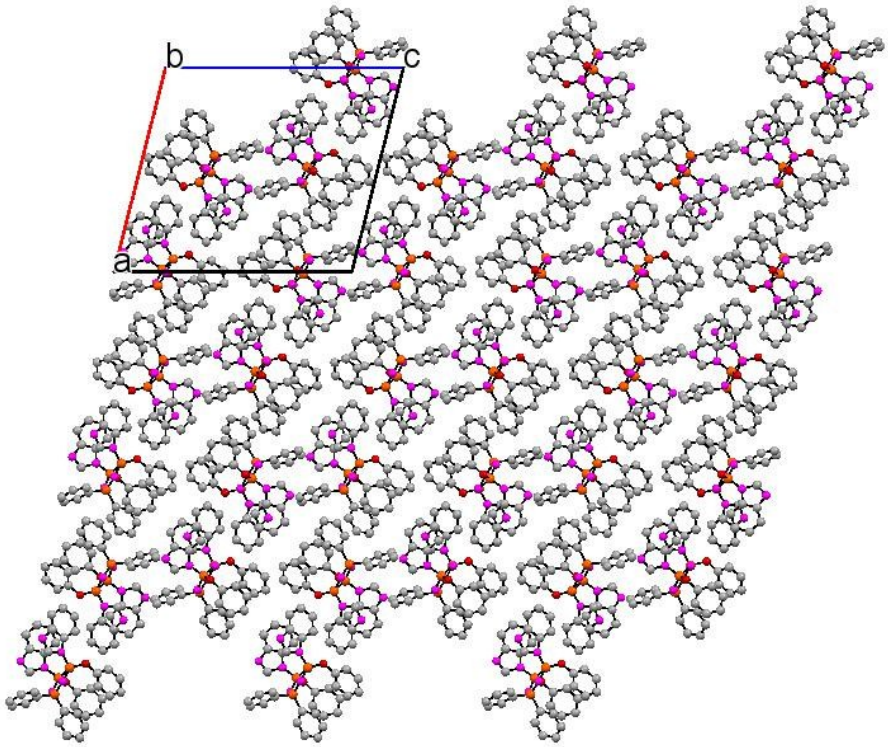


**Fig. S20** View of crystal packing of compound **4a**.

**Table S4.** Selected inter-molecular interactions for compound **4a**

| **D-H···A** | **D-H** | **H···A** | **D···A** | **DHA** | **Symmetry code** |
|---|---|---|---|---|---|
| C2-H2···Cg7[1] | 0.95 | 2.90 | 3.677(4) | 140 | x,y,z |
| [1]Cg7:C20C21C22C23C24C25 | | | | | |

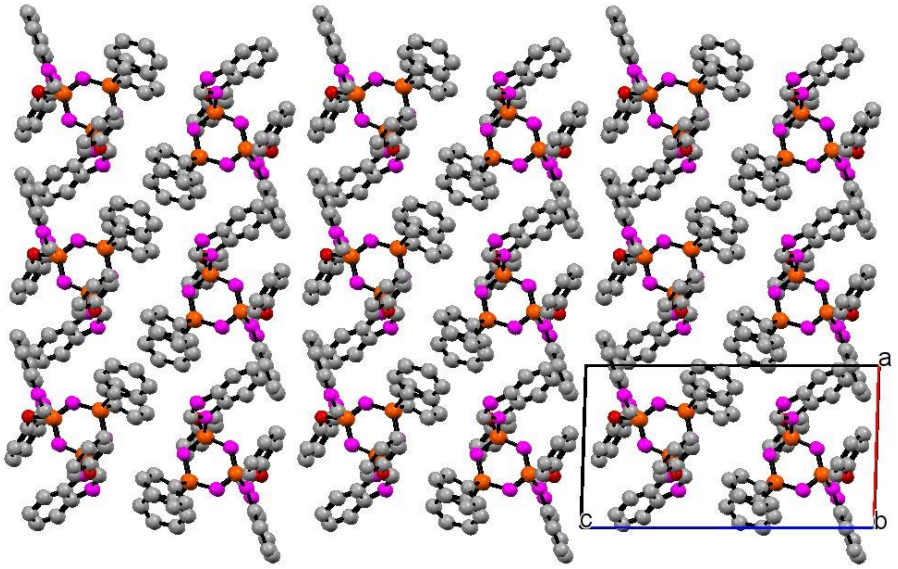


**Fig. S21** View of crystal packing of compound **4b**.

**Table S5.** Selected inter-molecular interactions for compound **4b**

| **D-H···A** | **D-H** | **H···A** | **D···A** | **DHA** | **Symmetry code** |
|---|---|---|---|---|---|
| C4-H4···Cg5[1] | 0.95 | 2.55 | 3.383(2) | 146 | 2-x,1-y,1-z |
| C30-H30···Cg6[4] | 0.95 | 2.75 | 3.547(2) | 143 | 1-x,1-y,2-z |
| C16-H16···Cg7[3] | 0.95 | 2.79 | 3.571(2) | 140 | 2-x,1-y,2-z |
| C13-H13···Cg9[2] | 0.95 | 2.96 | 3.806(2) | 150 | x,y,z |
| [1]Cg5:C7C8C9C10C11C12<br>[2]Cg6:C14C15C16C17C18C19<br>[3]Cg7:C20C21C22C23C24C25<br>[4]Cg9:C33C34C35C36C37C38 | | | | | |

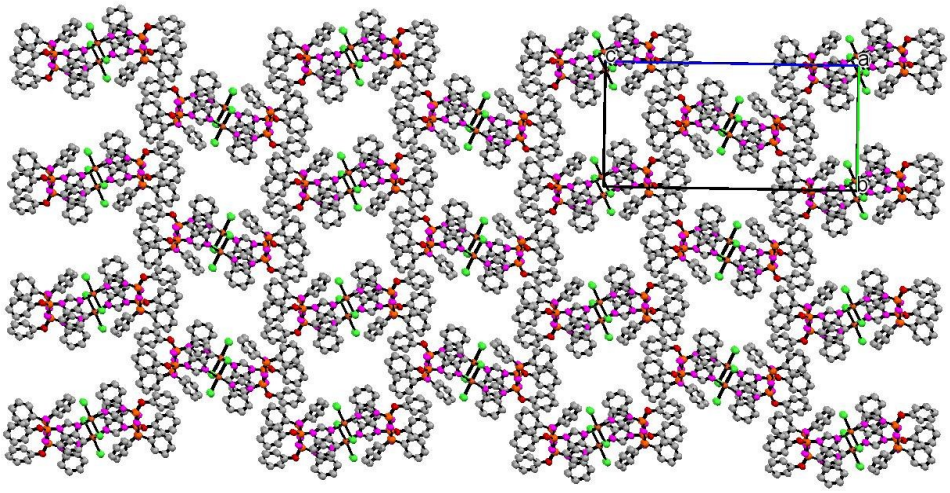

**Fig. S22** View of crystal packing of compound **5**.

**Table S6.** Selected inter-molecular interactions for compound **5**

| **D-H···A** | **D-H** | **H···A** | **D···A** | **Dihedral angle** | **DHA** | **Symmetry code** |
|---|---|---|---|---|---|---|
| Cg2[1]··· Cg3[2] | | | 3.746(3) | 6.8(3) | | x,y,z |
| Cg2[1]··· Cg4[3] | | | 3.746(3) | 6.8(3) | | 1-x,-y,-z |
| Cg3[2]··· Cg8[4] | | | 4.420(3) | 6.2(3) | | x,y,z |
| Cg8[4]··· Cg10[5] | | | 3.932(3) | 4.7(2) | | 1-x,-y,-z |
| C3-H3···Cg3[2] | 0.95 | 2.92 | 3.643(6) | | 134 | 1+x,y,z |
| C3-H3···Cg4[3] | 0.95 | 2.92 | 3.643(6) | | 134 | 2-x,-y,-z |
| | [1]Cg2:N4C13N5C14C19<br>[2]Cg3:N6C32C27#N7#C26#<br>[3]Cg4:N7C26N6#C32#C27<br>[4]Cg8:C14C15C16C17C18C19<br>[5]Cg10:C27C28C29C30C31#C32#<br>symmetry code (#): −x+1, −y, −z | | | | | |

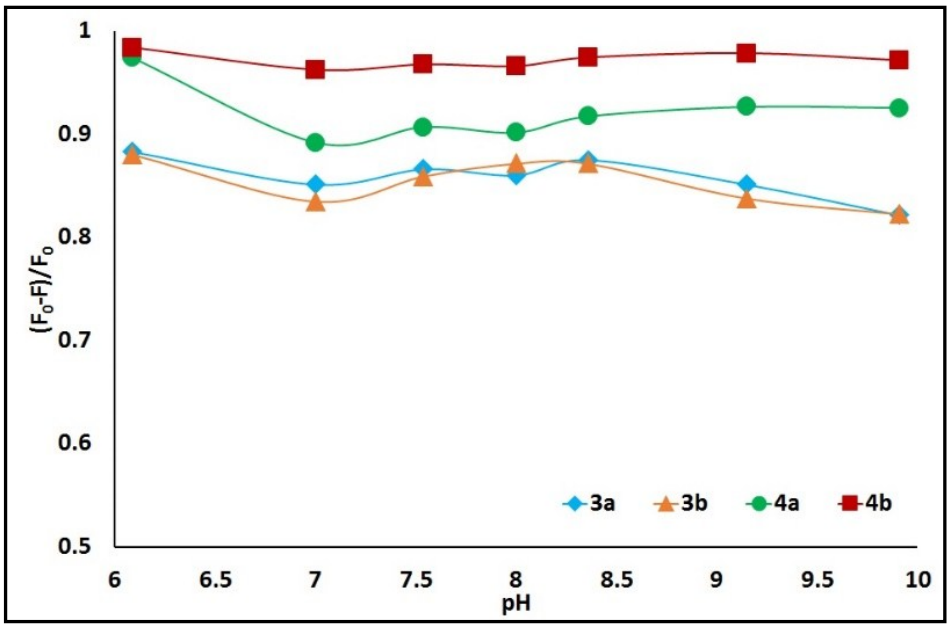


**Fig. S23**

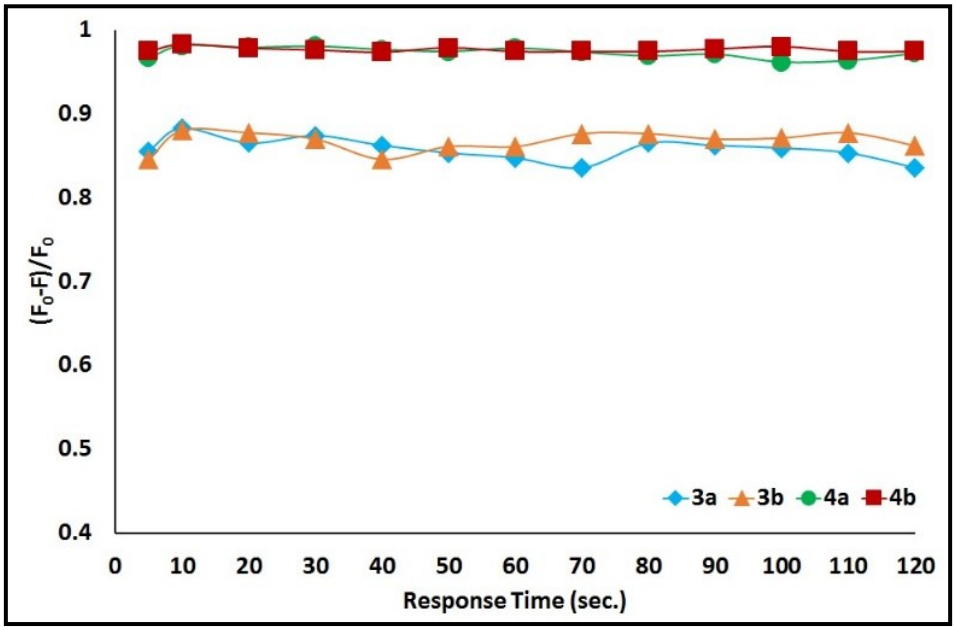


**Fig. S24**

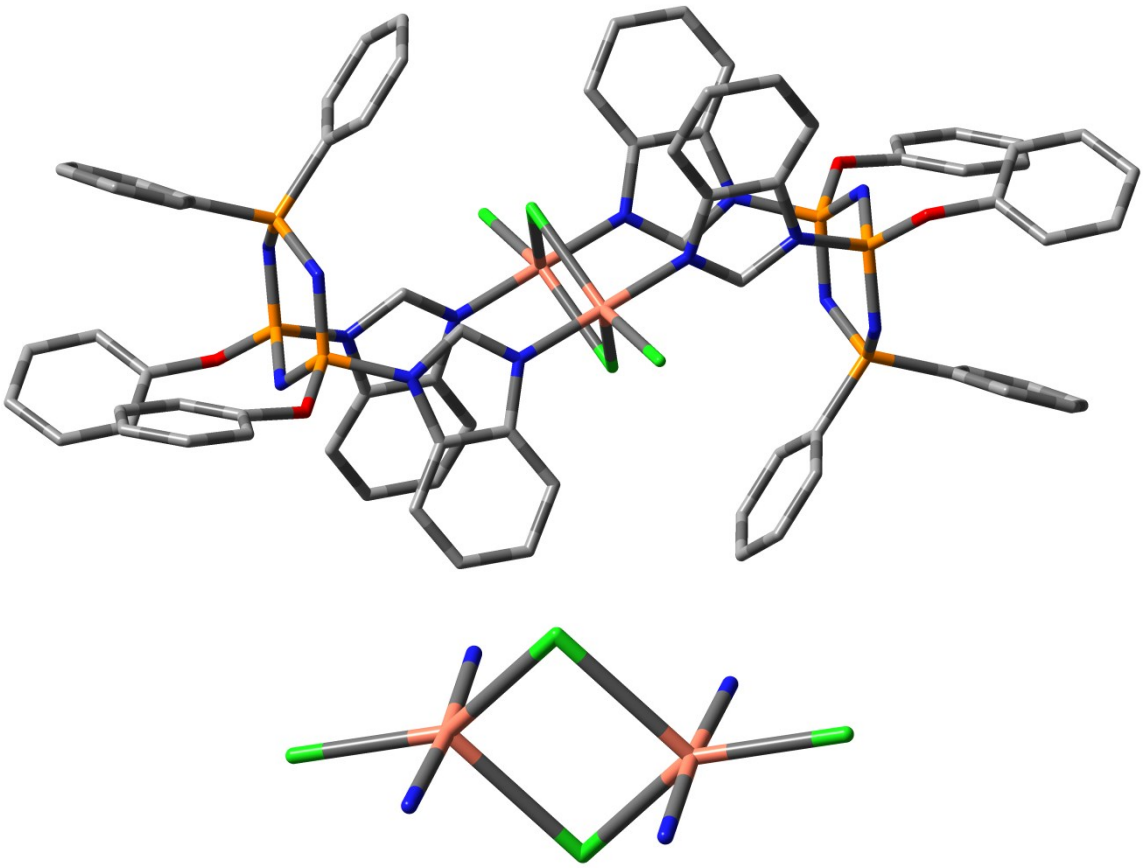

**Figure S25.** Optimized structure of compound **5**

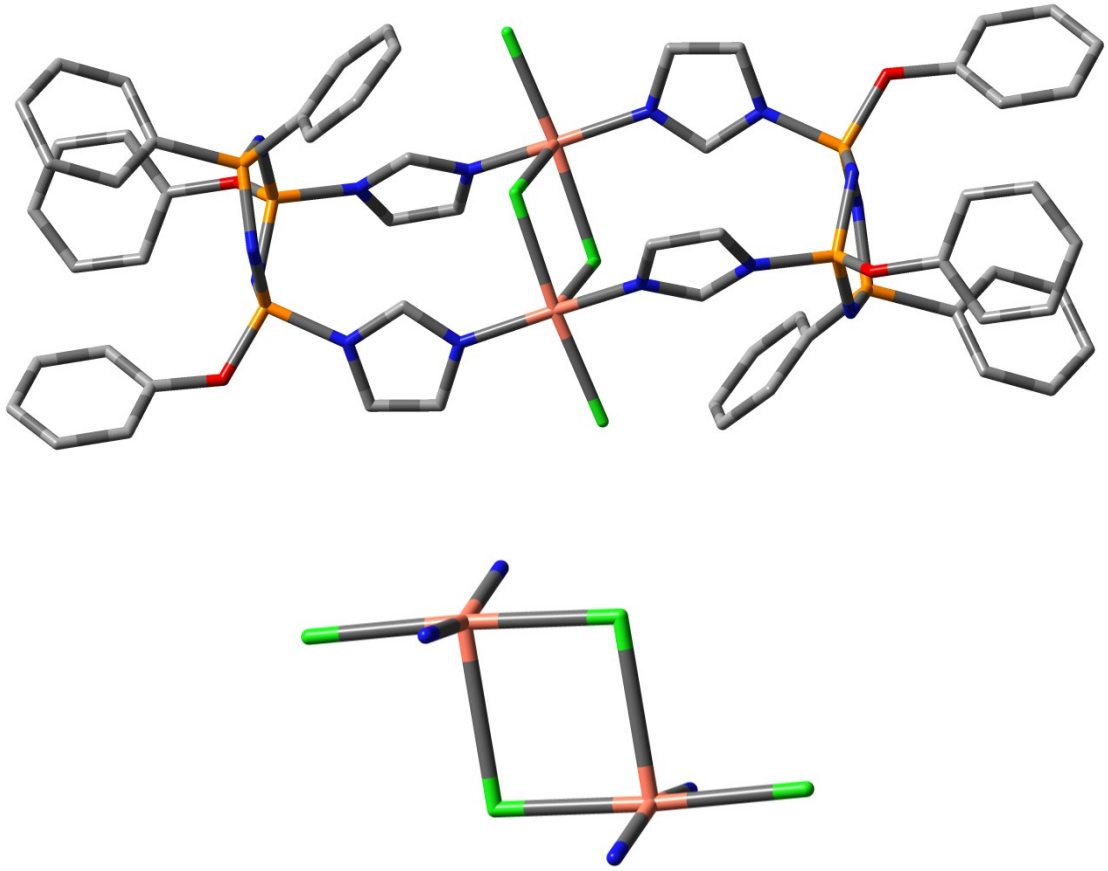

**Figure S26.** Optimized structure of compound **3a** with Cu(II).

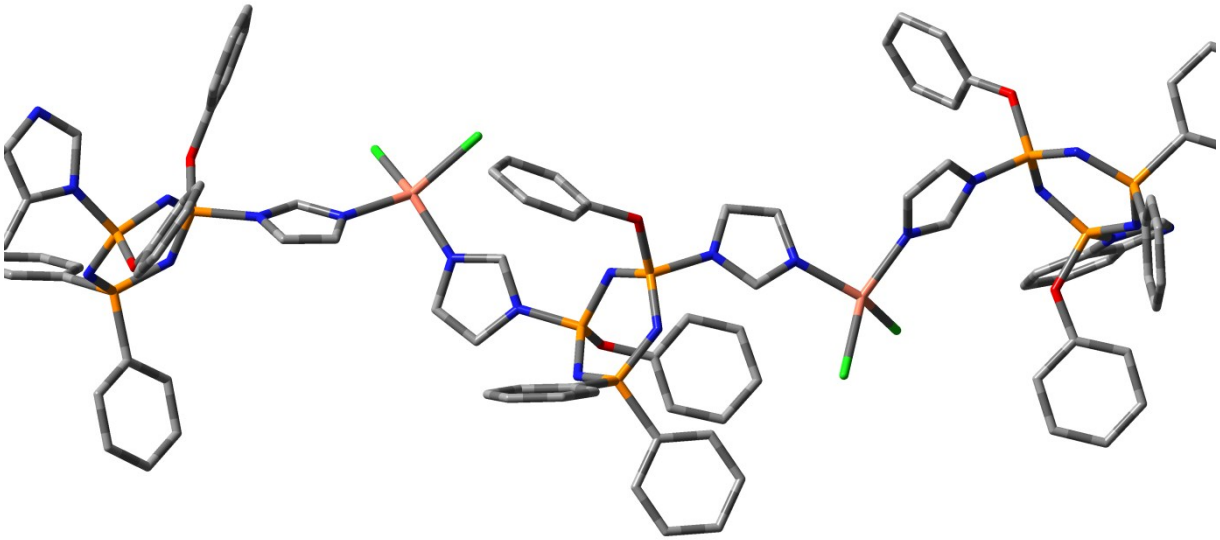

**Figure S27.** Optimized structure of compound **3b** with Cu(II).

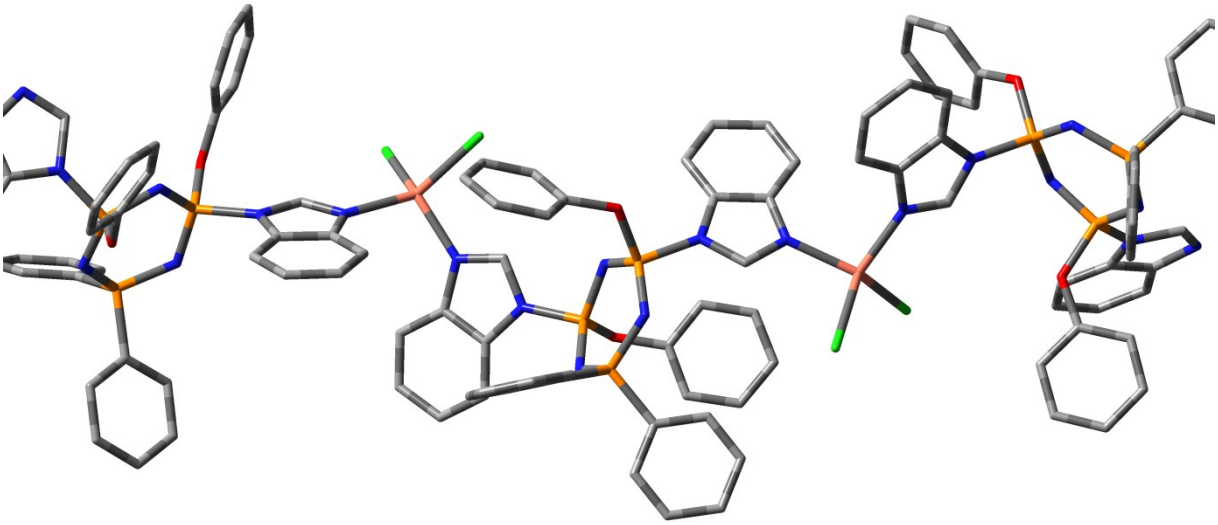

**Figure S28.** Optimized structure of compound **4b** with Cu(II).

**Table S7.** The data obtained from DFT calculations.

| | | B3LYP/LanL2DZ | Experimental |
|---|---|---|---|
| **5** | **Cu1-N5** | 1.977 | 1.990(4) |
| | **Cu1-N7** | 1.980 | 2.004(4) |
| | **Cu1-Cl1** | 2.418 | 2.3037(14) |
| | **Cu1-Cl2** | 2.593 | 2.3102(12) |
| | **Cu1-Cl2#** | 2.723 | 2.6426(14) |
| | **Cu1-Cu1#** | 3.686 | 3.5187(9) |
| **3a** with Cu(II) | **Cu1-N5** | 2.006 | |
| | **Cu1-N7** | 1.993 | |
| | **Cu1-Cl1** | 2.430 | |
| | **Cu1-Cl2** | 2.495 | |
| | **Cu1-Cl2#** | 2.868 | |
| | **Cu1-Cu1#** | 3.941 | |
| **3b** with Cu(II) | **Cu-N1** | 2.034 | |
| | **Cu-N2** | 2.056 | |
| | **Cu-Cl1** | 2.335 | |
| | **Cu-Cl2** | 2.313 | |
| **4b** with Cu(II) | **Cu-N1** | 2.040 | |
| | **Cu-N2** | 2.064 | |
| | **Cu-Cl1** | 2.313 | |
| | **Cu-Cl2** | 2.338 | |

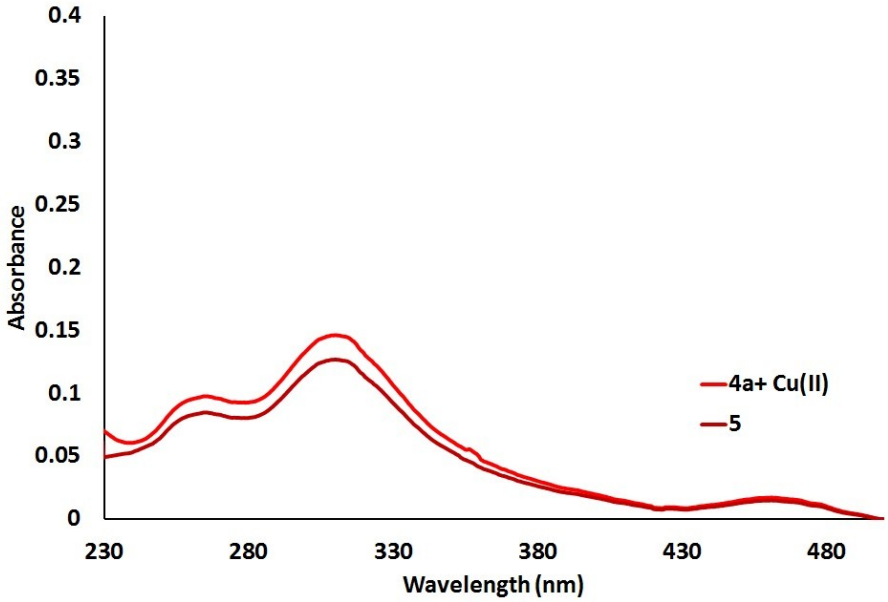


**Figure S29.** Absorption spectra of 10 μM compound **4a** + 1eqv. $Cu^{2+}$ and compound **5** in ACN.