

调控从非手性双钯（II）和双铂（II）配位组装中心同非手性蒽基吡  
啉配体组装的配位分子角的超分子手性构筑

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**Tuning supramolecular chiral architecture of Molecular Corners  
from achiral dipalladium(II) and diplatinum(II) complexes with  
achiral anthracyl pyrazole ligand**

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**S1. Experimental Section**

All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques. All the organic solvents were distilled from 4 Å molecular sieves under an argon atmosphere. The other chemical and all commercially available reagents were used without any purification. NMR spectra of all compounds were recorded at 400 MHz on a Bruker AIVEN400 spectrometer. Halogenated and aromatic NMR solvents were dried over anhydrous potassium carbonate prior to use. MALDI-TOF analysis were carried out by Bruker Daltonics ultrafleX III spectrometer.

## S2. Procedures

Metal complexer  $[(bpy)_2Pd_2(NO_3)_2](NO_3)_2$ ,  $[(dmbpy)_2Pd_2(NO_3)_2](NO_3)_2$ ,  $[(phen)_2Pd_2(NO_3)_2](NO_3)_2$  and  $[(ppy)_2Pt_2]Cl_2$  were compounded under the reference literature<sup>[1-15]</sup>.

### Synthesis of ligand

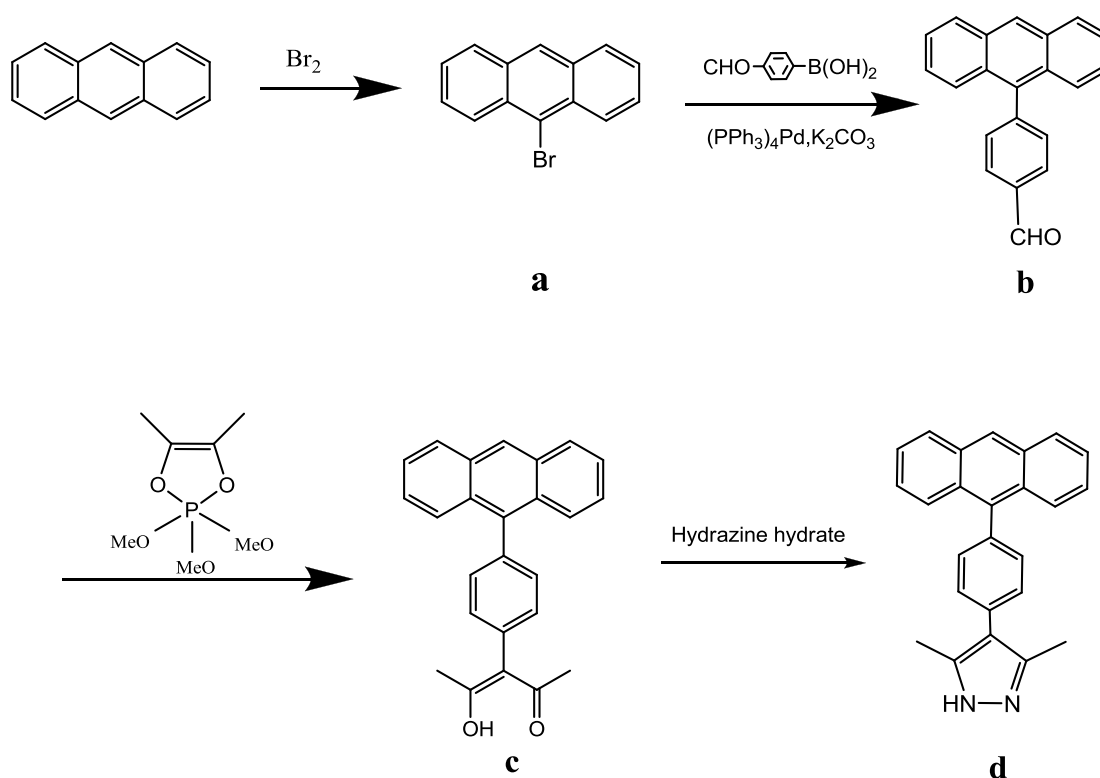


Fig. S1 Synthesis route of 4-(4-(anthracen-9-yl)phenyl)-3,5-dimethyl-1H-pyrazole (L) ligand

### Preparation of 9-bromoanthracene (a):

To a solution of chloroform (120 ml) in 250 ml round bottom flask was added

anthracene (7 g, 40 mmol). Joining bromide (2 ml) by drops in a test tube, then added a small amount of chloroform dilution. Completed all the steps in the ice water bath. The mixture was gradually into a light yellow liquid. Extraction twice with methanol (25 ml), and then continue the reaction for 30 min. Then evaporated in vacuo and dry, we got coarse product 15.7 g. The pure product is obtained by silica gel column for purification, 9-bromoanthracene 4 g.  $^1\text{H-NMR}$  (400MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ , TMS, ppm):  $\delta=8.56$  (s, 1H, anthryl-H), 8.46 (d,  $J=8.0\text{Hz}$ , 4H, anthryl-H), 8.02 (d, 2H, Ar-H), 7.55(t,  $J=4.0\text{Hz}$ , 2H, Ar-H), 7.51(t,  $J=8.0\text{Hz}$ , 4H, anthryl-H).

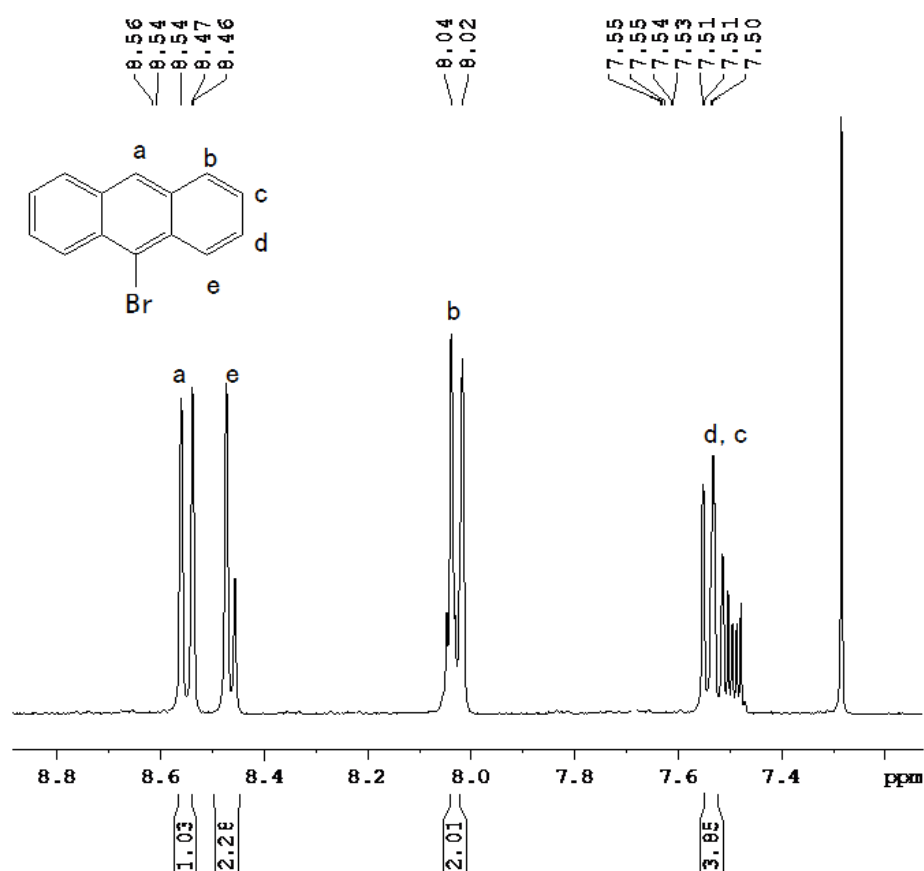


Fig. S2  $^1\text{H}$  NMR spectrum of **a** (400 MHz,  $\text{CD}_3\text{Cl}$ ,  $25^\circ\text{C}$ , TMS).

#### Preparation of 4-(anthracen-9-yl)benzaldehyde (**b**):

9-bromoanthracene (1.0 g, 4mmol), 4-aldehyde benzene boric acid (0.75 g, 5 mmol), four (triphenyl-phosphine) palladium (0.15 g, 0.13 mmol) and potassium carbonate (1.8 g, 13mmol) were added to a mixture of 100 ml DEF and 40 ml water in a round bottom flask under nitrogen environment stirring for 24 h under  $85^\circ\text{C}$ . After the reaction, extraction with water and methylene chloride, dried ( $\text{MgSO}_4$ ), and

evaporated in vacuo to afford 550 mg (Yield : 55%).  $^1\text{H}$ -NMR (400MHz,  $\text{CDCl}_3$ , 25°C, TMS, ppm):  $\delta$ = 10.21 (s, 1H, CHO-H), 8.57 (s, 1H, anthryl-H), 8.11 (d,  $J$ =8.4Hz, 4H, anthryl-H), 7.65 (d,  $J$ =8.4Hz, 2H, Ar-H); 7.53 (t,  $J$ =4.5Hz, 2H, Ar-H); 7.40 (t,  $J$ =4.0Hz, 4H, anthryl-H).

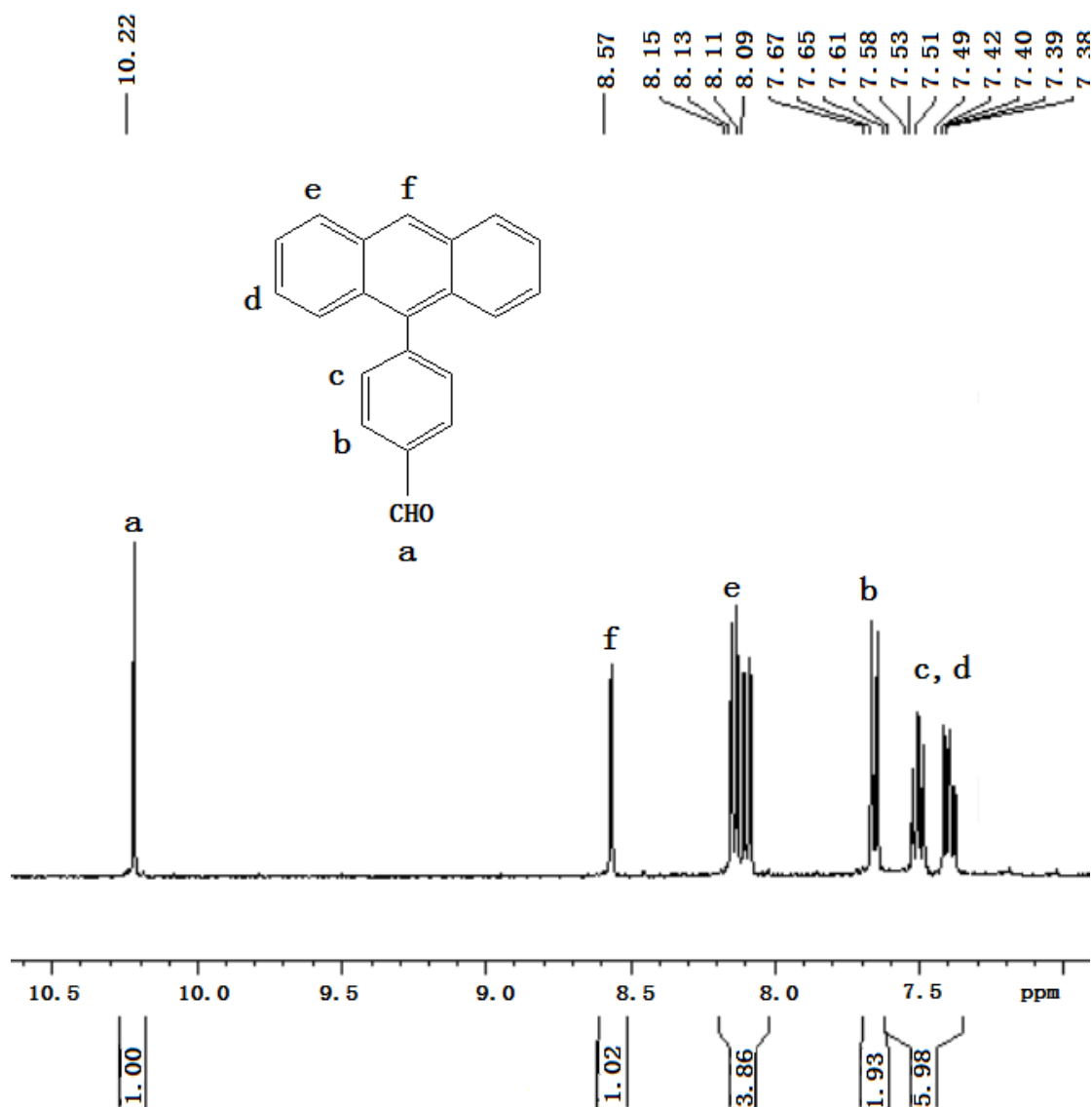


Fig. S3  $^1\text{H}$  NMR spectrum of **b** (400 MHz,  $\text{CD}_3\text{Cl}$ , 25 °C, TMS).

#### Preparation of 4-(4-(anthracen-9-yl)phenyl)-3,5-dimethyl-1H-pyrazole (HL)

4-(anthracen-9-yl)benzaldehyde (300 mg, 10.6 mmol), 2, 3 - butyl ketone 2 - trimethyl phosphite 1:1 adducts 2 ml and 2 ml methylene chloride were added in reaction tube, filled with nitrogen. Stirring for 48 hours at room temperature. After enrichment, added 5ml methanol to reflux for one day. White acicular solid product (Z)-3-(4-(anthracen-9-yl)phenyl)-4-hydroxypent-3-en-2-one (**c**) 60 mg (Yield : 20%)

was got after the suction filter.  $^1\text{H-NMR}$  (400MHz,  $\text{CDCl}_3$ , 25 $^\circ\text{C}$ , TMS, ppm):  $\delta$ =16.01 (s, 1H, OH-H), 8.55 (s, 1H, anthryl-H), 8.04 (m, 4H, anthryl-H), 7.69 (d,  $J$  = 8.4Hz, 4H, anthryl-H), 7.50 (d,  $J$  = 4.0Hz, 4H, Ar-H), 7.43 (d,  $J$  = 4.0Hz, 4H, Ar-H), 2.12 (s, 3H,  $\text{CH}_3$ -H), 1.80 (s, 3H,  $\text{CH}_3$ -H).

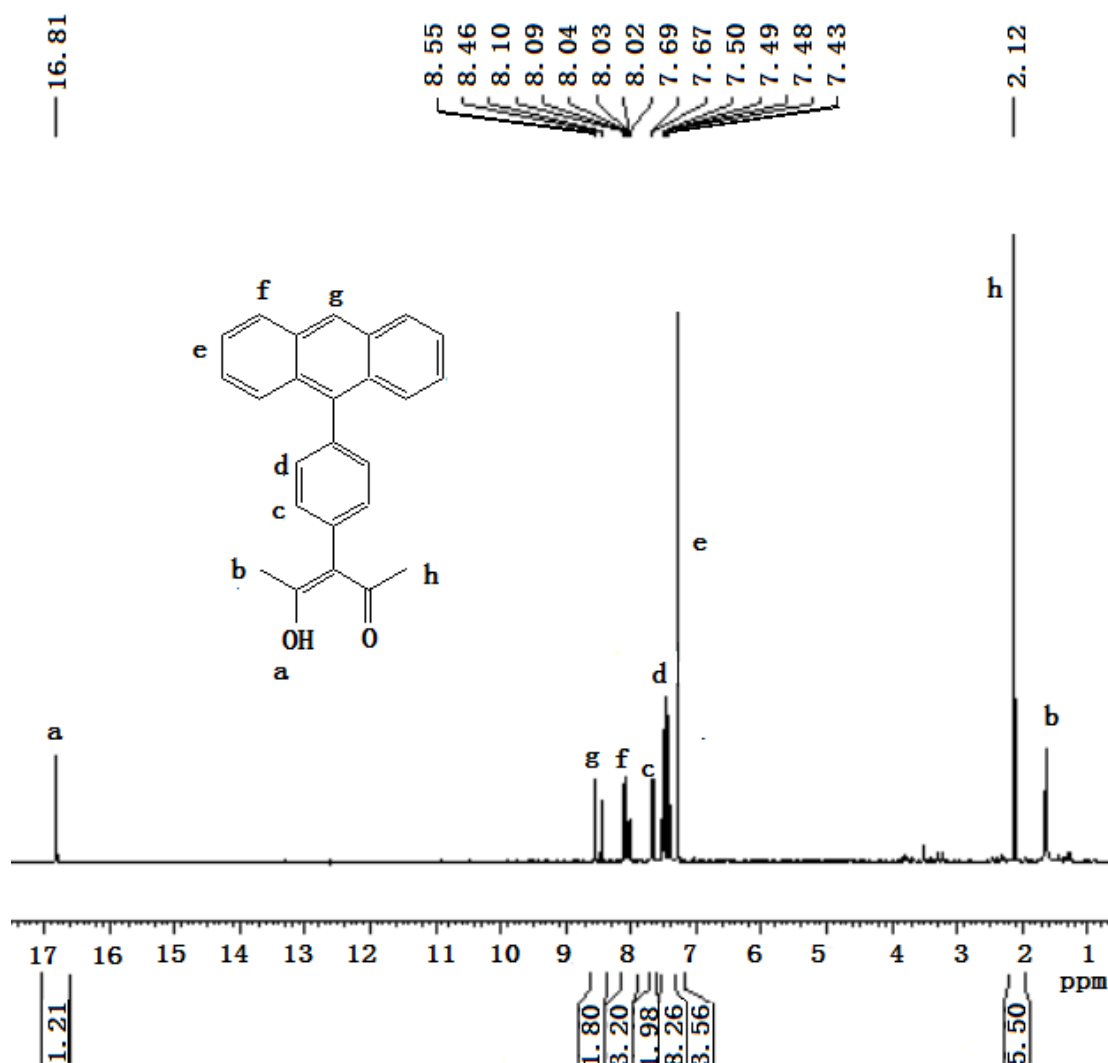


Fig. S4  $^1\text{H}$  NMR spectrum of **c** (400 MHz,  $\text{CD}_3\text{Cl}$ , 25  $^\circ\text{C}$ , TMS)

**c** (170 mg, tendency for 0.47), 0.5 ml hydrazine hydrate and anhydrous ethanol 12 ml were added to a 25 ml round bottom flask and the mixture was heated under 80  $^\circ\text{C}$ . Reflux for 24 h, white powder (**HL**) 105 mg (Yield: 63%) was collected by filtration.  $^1\text{H-NMR}$  (400MHz,  $\text{DMSO}-d_6$ , 25  $^\circ\text{C}$ , TMS, ppm):  $\delta$ = 12.41 (s, 1H, Pz-H), 8.69 (s, 1H, anthryl-H), 8.16 (d,  $J$ =6.9Hz, 4H, anthryl-H), 7.66 (d,  $J$ =6.9Hz, 4H, anthryl-H), 7.55 (t,  $J$ =5.6Hz, 4H, anthryl-H), 7.46 (s, 4H, Ar-H), 2.51 (s, 3H,  $\text{CH}_3$ -H), 2.50 (s, 3H,  $\text{CH}_3$ -H).

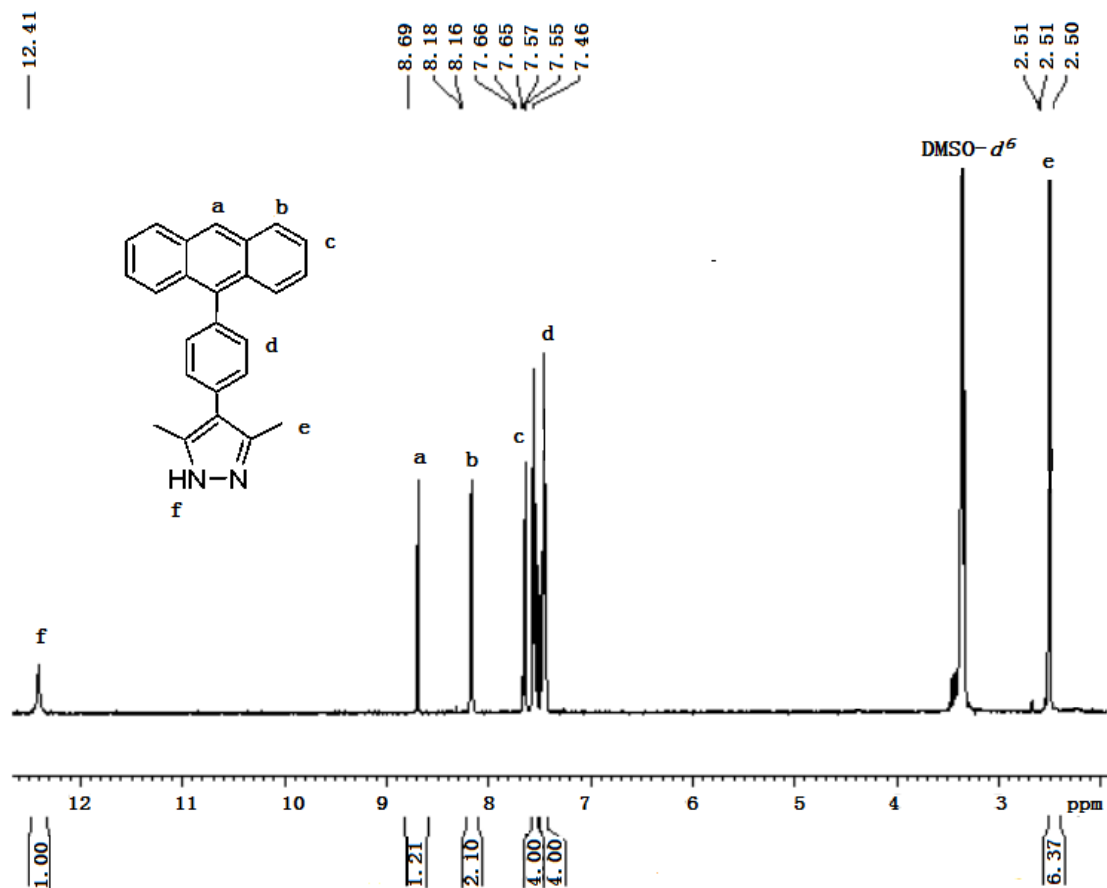


Fig. S5  $^1\text{H}$  NMR spectrum of **HL** (400 MHz,  $\text{DMSO-}d^6$ , 25  $^\circ\text{C}$ , TMS)

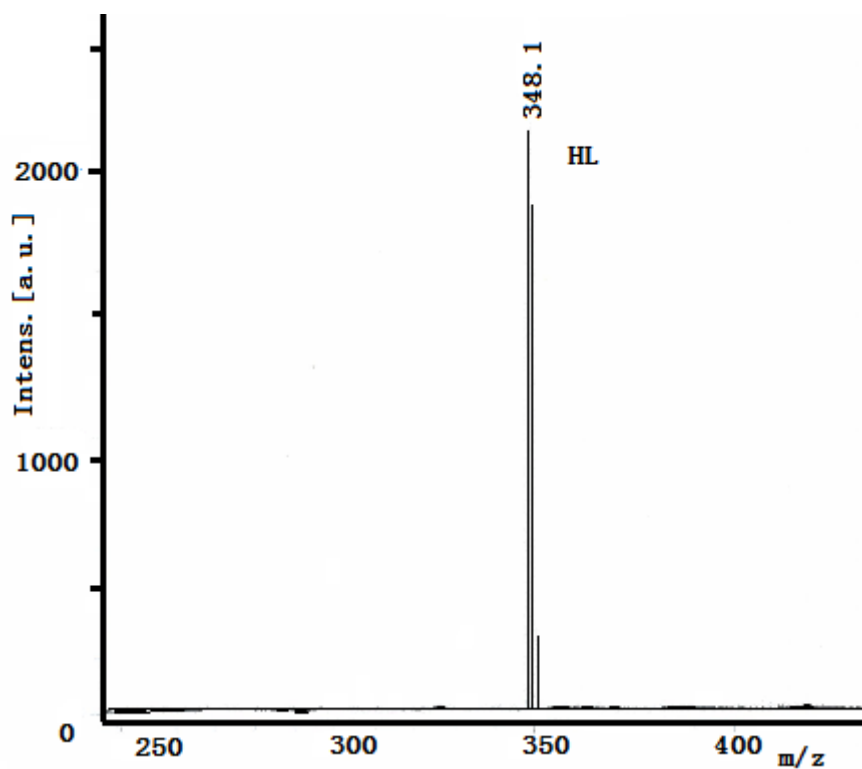


Fig. S6 MALDI-TOF spectra of **HL** in  $\text{CHCl}_3$ .

## S2. Procedures

Here are characterization of  $\mathbf{1} \cdot 2\text{PF}_6^-$ ,  $\mathbf{2} \cdot 2\text{PF}_6^-$ ,  $\mathbf{3} \cdot 2\text{PF}_6^-$  and **4** below:

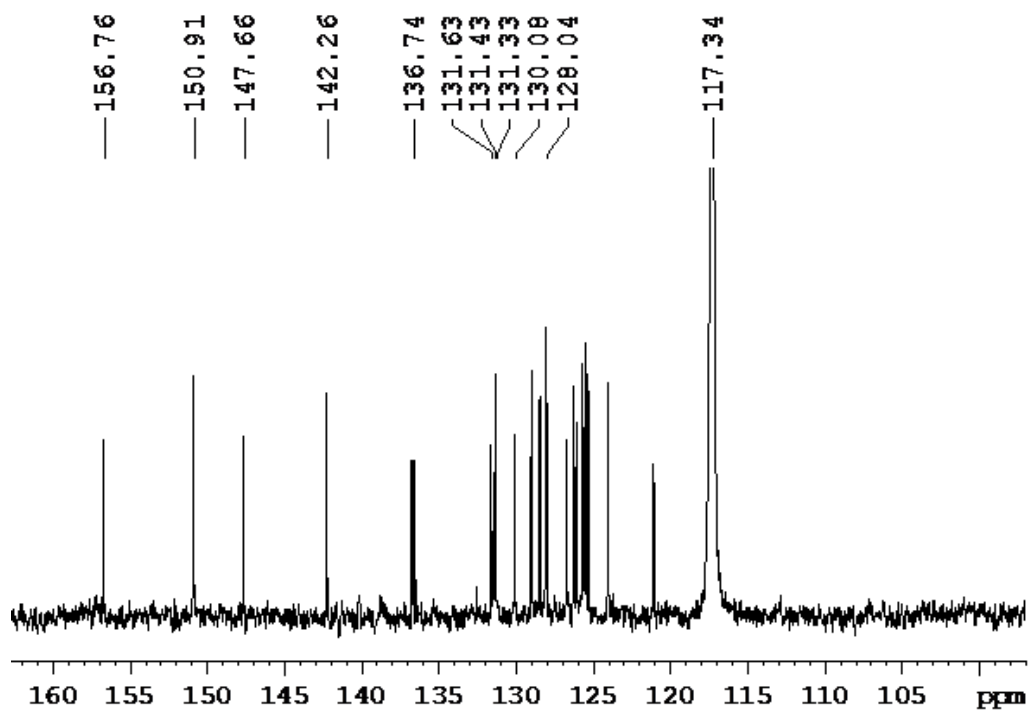


Fig. S7  $^{13}\text{C}$  NMR spectrum of  $\mathbf{1} \cdot 2\text{PF}_6^-$  (400 MHz,  $\text{CD}_3\text{CN}$ , 25 °C, TMS)

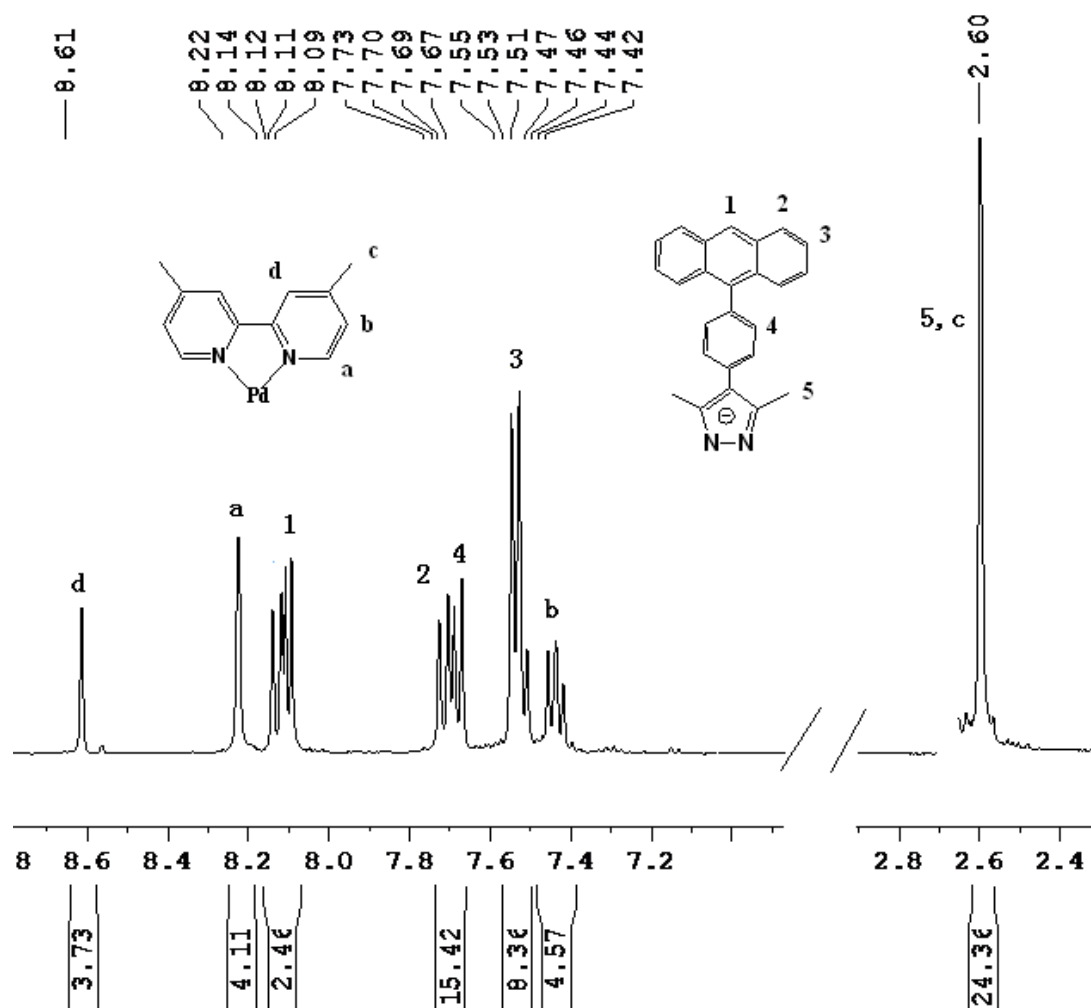


Fig. S8  $^1\text{H}$  NMR spectrum of  $2 \cdot 2\text{PF}_6^-$  (400 MHz,  $\text{CD}_3\text{CN}$ , 25  $^\circ\text{C}$ , TMS).

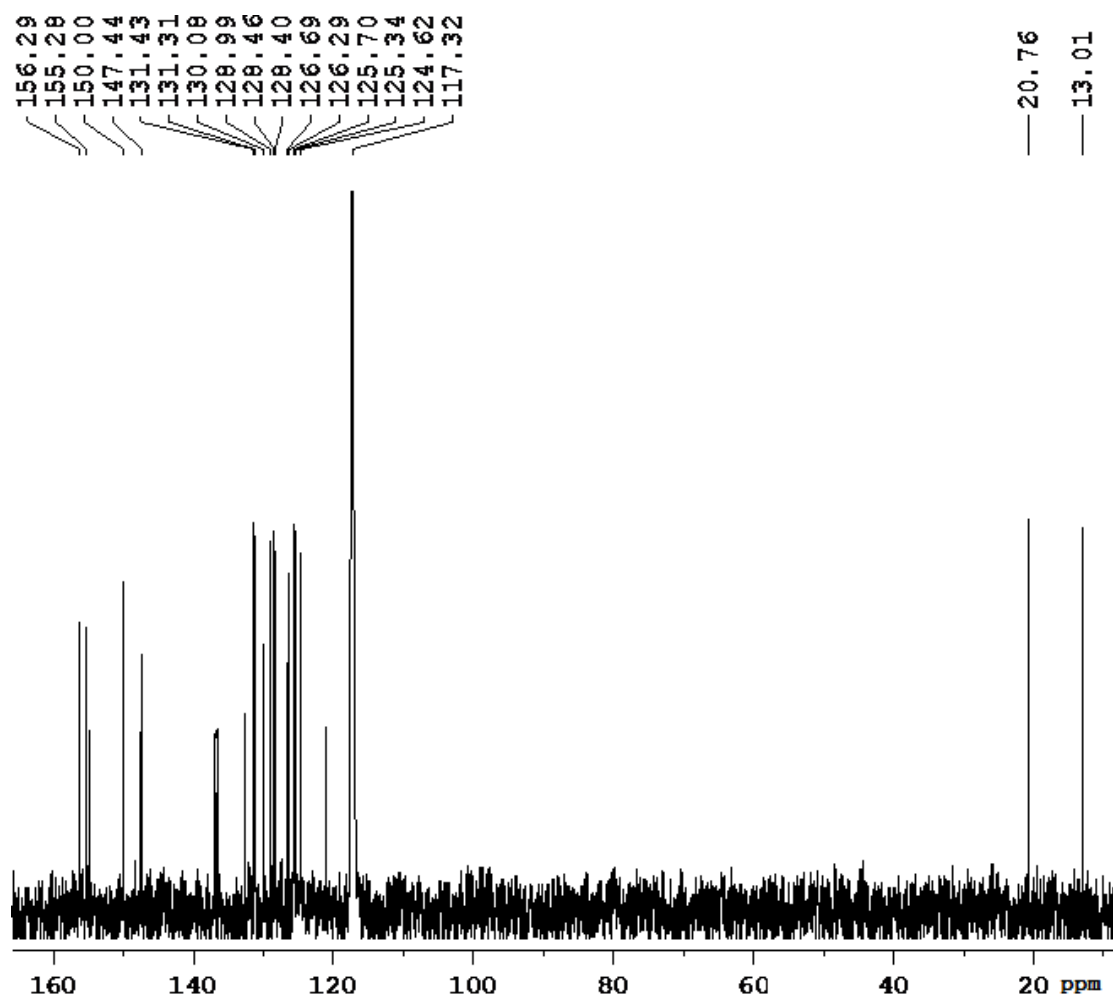


Fig. S9  $^{13}\text{C}$  NMR spectrum of  $2 \cdot 2\text{PF}_6^-$  (400 MHz,  $\text{CD}_3\text{CN}$ , 25  $^\circ\text{C}$ , TMS)

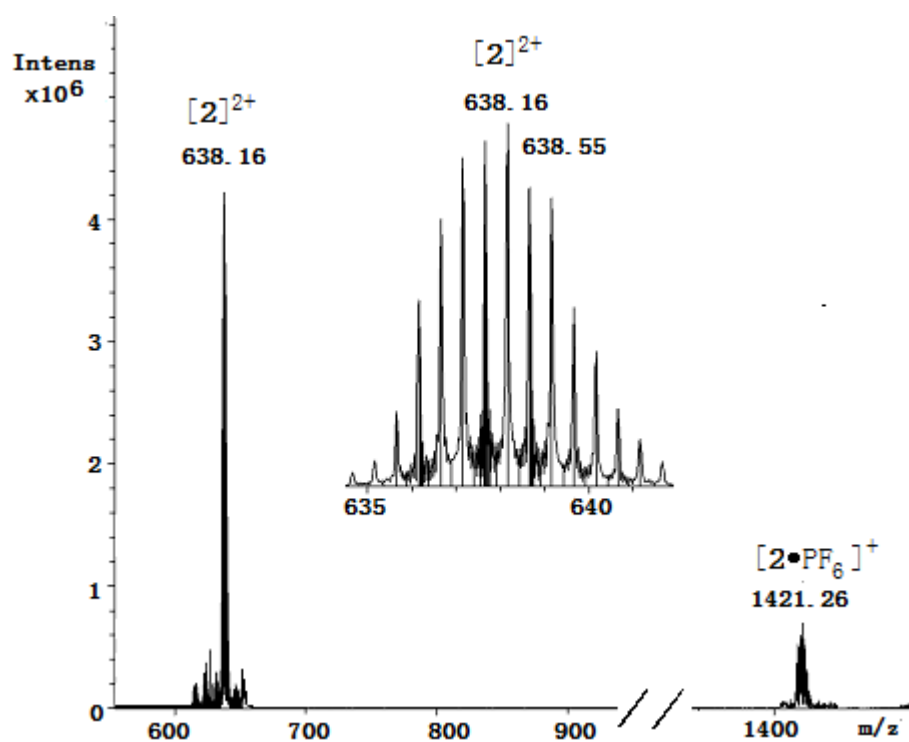


Fig. S12 ESI-MS spectra of **2** PF<sub>6</sub><sup>-</sup> in acetonitrile; the inset shows the isotopic

distribution of the species 1421.25 for [2]<sup>2+</sup>.

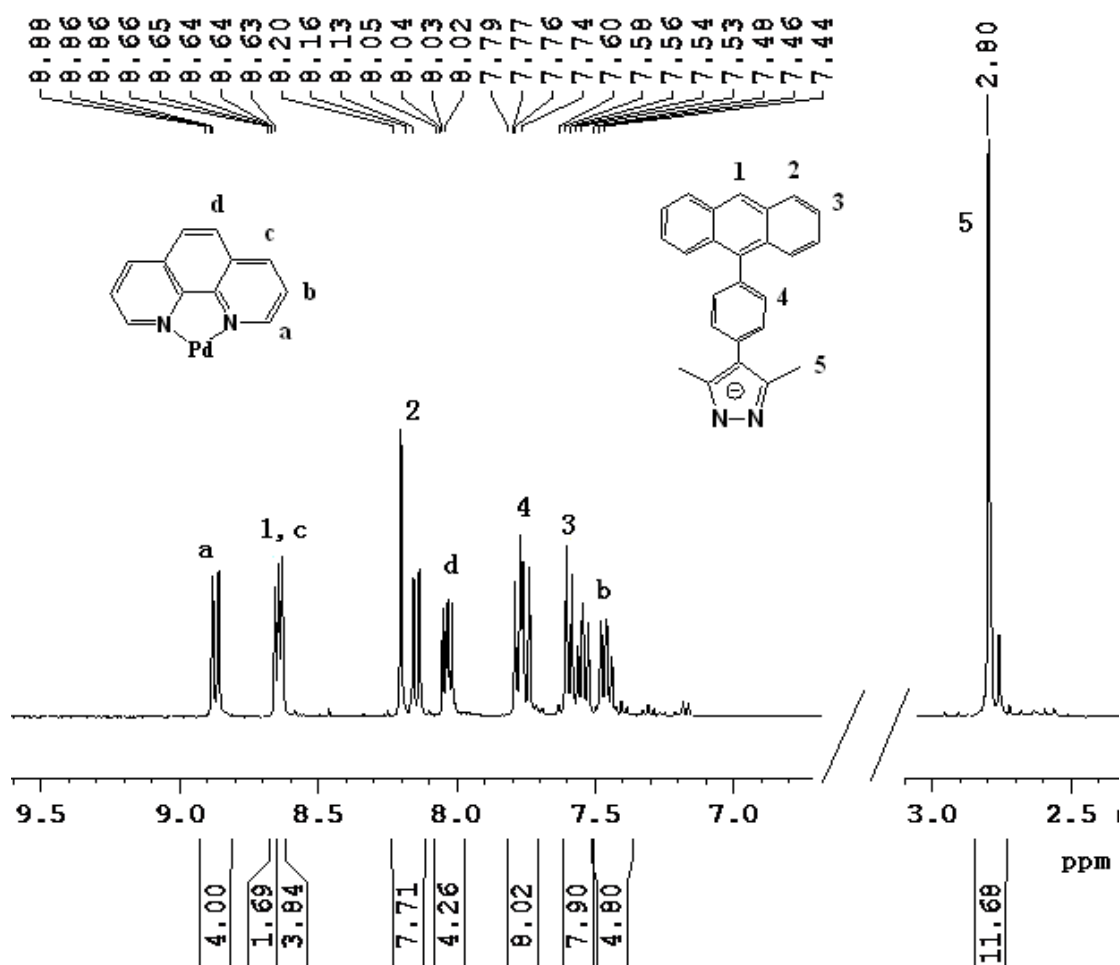


Fig. S10 <sup>1</sup>H NMR spectrum of **3** 2PF<sub>6</sub><sup>-</sup> (400 MHz, CD<sub>3</sub>CN, 25 °C, TMS)

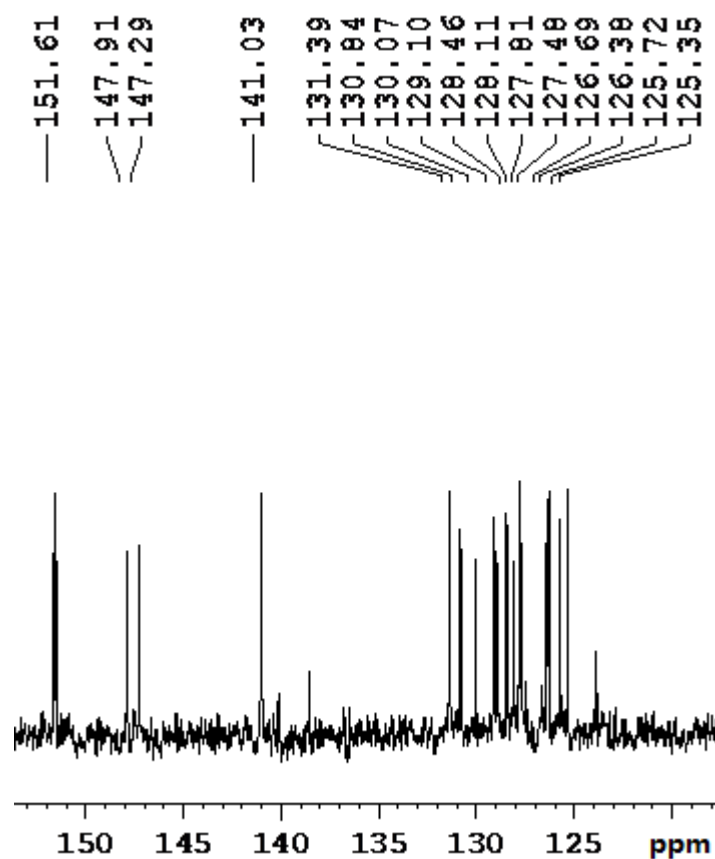


Fig. S11  $^{13}\text{C}$  NMR spectrum of  $3\ 2\text{PF}_6^-$  (400 MHz,  $\text{CD}_3\text{CN}$ , 25  $^\circ\text{C}$ , TMS)

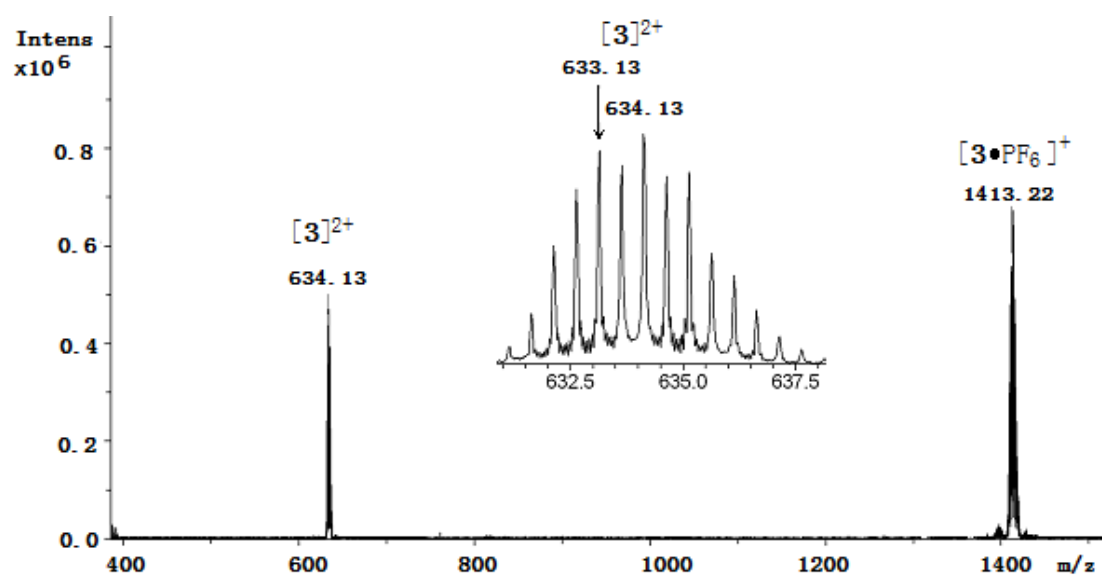


Fig. S12 ESI-MS spectra of  $3\ 2\text{PF}_6^-$  in acetonitrile; the inset shows the isotopic distribution of

the species 633.12 for  $[3]^{2+}$ .

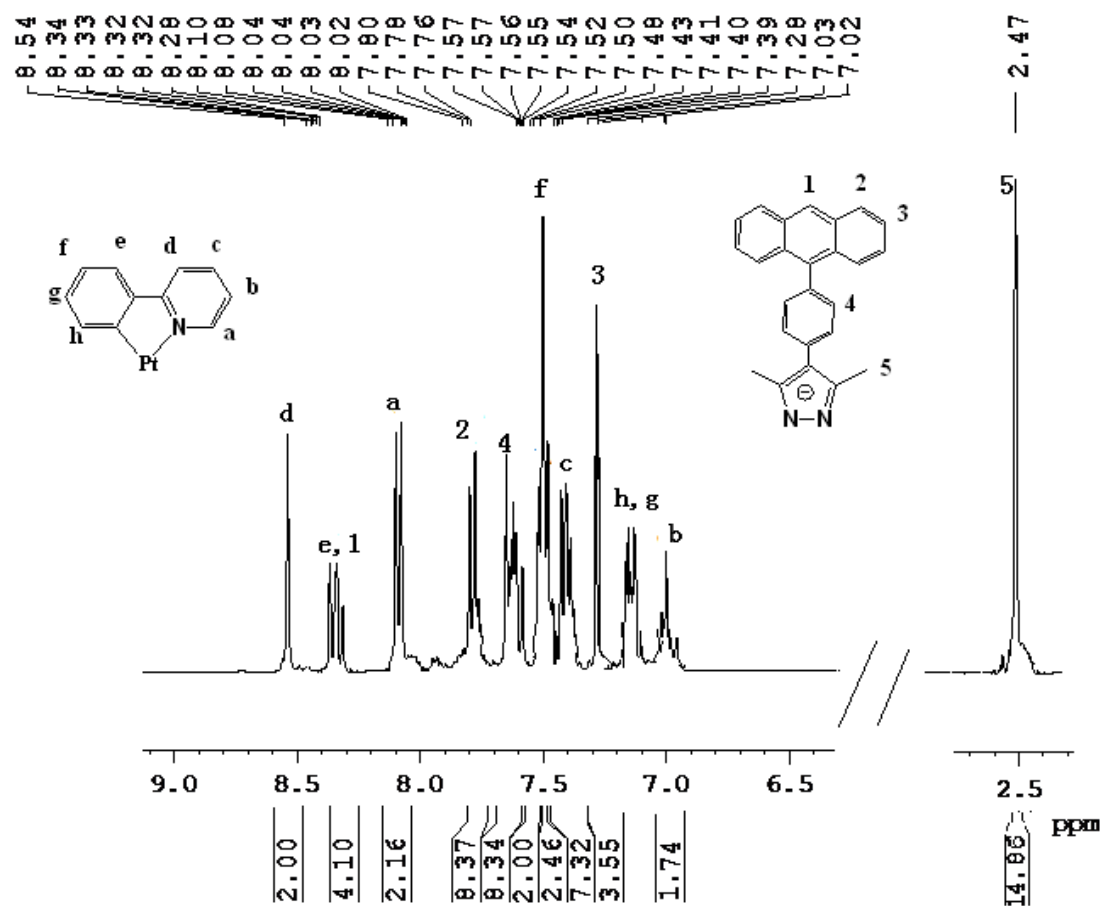


Fig. S13 <sup>1</sup>H NMR spectrum of 4 (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS)

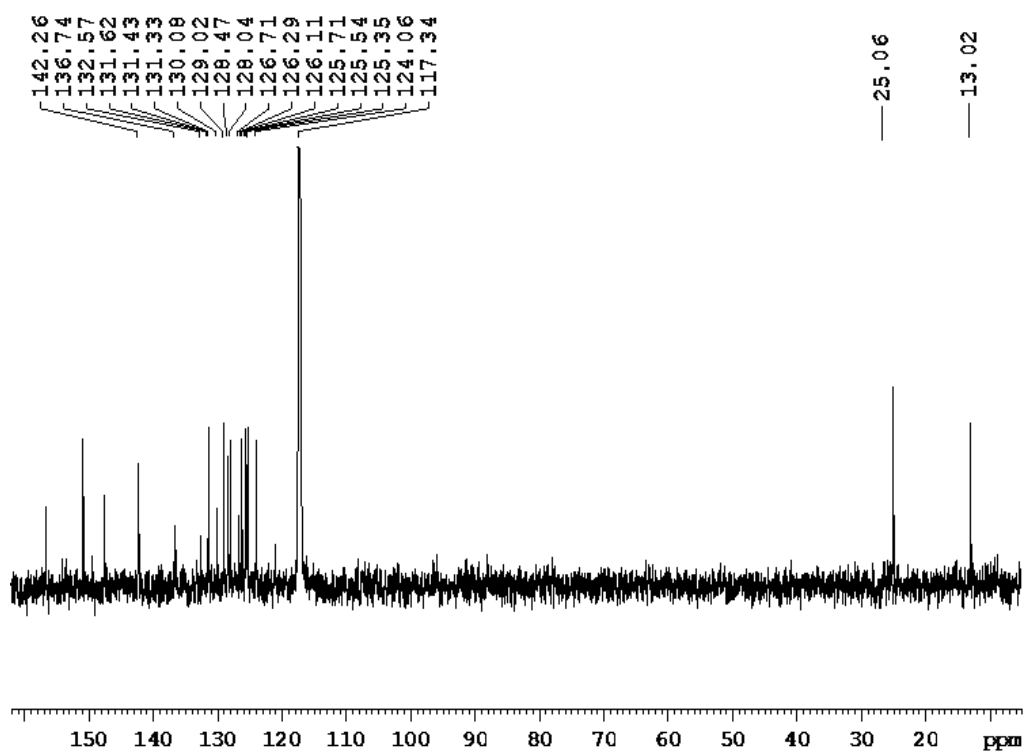


Fig. S14  $^{13}\text{C}$  NMR spectrum of **4** (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ , TMS)

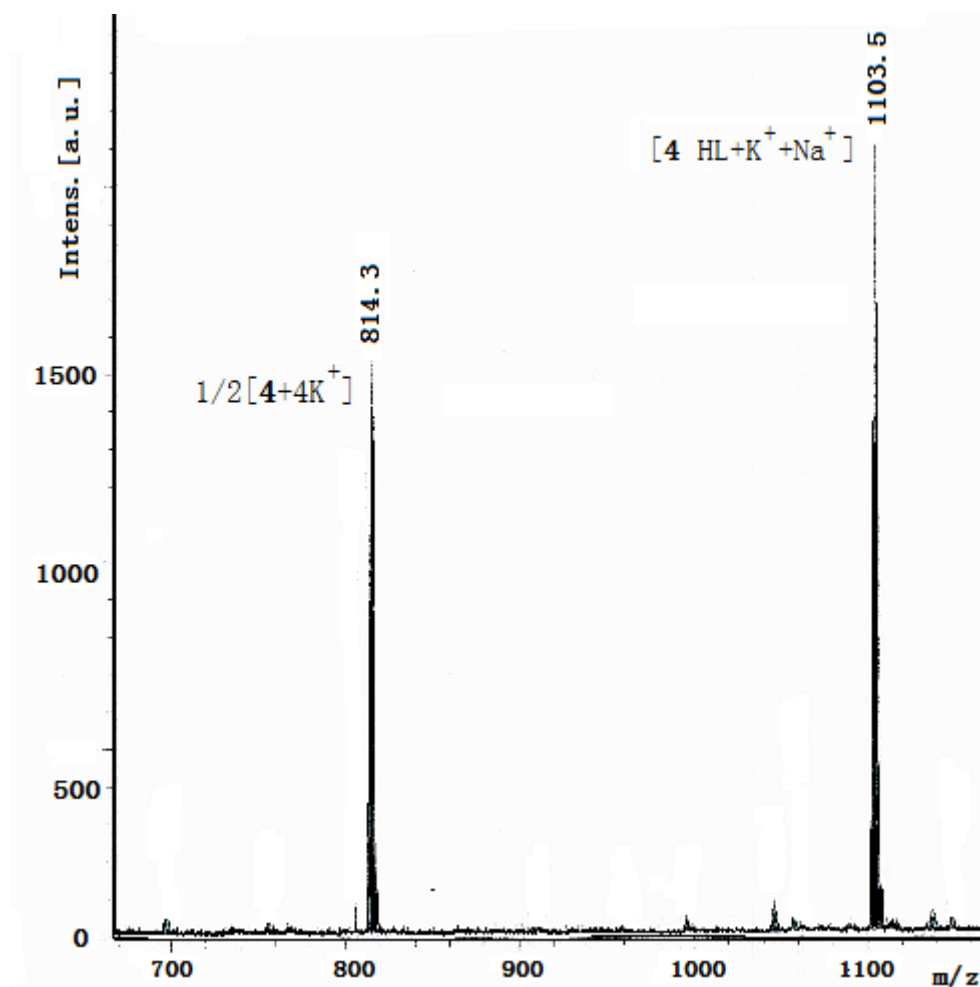


Fig. S15 MALDI-TOF spectra of **4** in  $\text{CHCl}_3$ ; 814.3 and 1103.5 for  $[\mathbf{4}\text{-HL}+\text{Na}^++\text{K}^+]$  and  $1/2[\mathbf{4}+2\text{K}^+]$ .

### S3. X-ray crystallography, circular dichroism spectroscopy and fluorescence excitation spectra of complex $\mathbf{1}\cdot 2\text{PF}_6^-$ , $2\cdot 2\text{PF}_6^-$ and $3\cdot 2\text{PF}_6^-$

Table S1 Bond angle and bond distances (Å) in the crystal structure of  $\mathbf{1}\cdot 2\text{PF}_6^-$

| bond distances of $\mathbf{1}\cdot 2\text{PF}_6$ |          |           |          |
|--------------------------------------------------|----------|-----------|----------|
| Pd1-N2                                           | 2.003(6) | Pd2-N1    | 2.007(6) |
| Pd1-N4                                           | 1.998(7) | Pd2-N3    | 2.007(6) |
| bond angle of $\mathbf{1}\cdot 2\text{PF}_6$     |          |           |          |
| N2-Pd1-N4                                        | 84.6(3)  | N7-Pd2-N1 | 95.8(3)  |
| N2-Pd1-N5                                        | 96.8(3)  | N7-Pd2-N3 | 176.7(3) |
| N4-Pd1-N5                                        | 174.9(3) | N1-Pd2-N3 | 86.0(2)  |
| N2-Pd1-N6                                        | 177.1(3) | N7-Pd2-N8 | 81.2(3)  |
| N4-Pd1-N6                                        | 97.5(3)  | N1-Pd2-N8 | 175.4(3) |

|           |         |           |         |
|-----------|---------|-----------|---------|
| N5-Pd1-N6 | 81.0(3) | N3-Pd2-N8 | 96.8(3) |
|-----------|---------|-----------|---------|

**Table S2 Bond angle and bond distances (Å) in the crystal structure of  $2 \cdot 2\text{PF}_6^-$**

| bond distances of $2 \cdot 2\text{PF}_6^-$ |            |             |            |
|--------------------------------------------|------------|-------------|------------|
| Pd2-N1                                     | 3.2031(5)  | Pd3-N9      | 2.019(3)   |
| Pd1-N1                                     | 2.039(4)   | Pd2-N6      | 1.993(3)   |
| bond angle of $2 \cdot 2\text{PF}_6^-$     |            |             |            |
| N5-Pd1-N8                                  | 84.48(14)  | N6 Pd2 N4   | 175.30(15) |
| N8-Pd1-N2                                  | 98.03(14)  | N4 Pd2 N7   | 98.78(14)  |
| N2-Pd1-N1                                  | 79.93(16)  | N7 Pd2 N3   | 175.06(14) |
| N8-Pd1-Pd2                                 | 62.69(10)  | N13 Pd3 N9  | 95.11(15)  |
| N2-Pd1-Pd2                                 | 118.54(10) | N13 Pd3 N10 | 176.16(15) |
| N5-Pd1-N2                                  | 177.41(14) | N13 Pd3 N16 | 84.63(15)  |

**Table S3 Bond angle and bond distances (Å) in the crystal structure of  $3 \cdot 2\text{PF}_6^-$**

| bond distances of $3 \cdot 2\text{PF}_6^-$ |          |           |          |
|--------------------------------------------|----------|-----------|----------|
| Pd1-N3                                     | 2.071(7) | Pd2-N1    | 2.000(8) |
| Pd1-N4                                     | 2.075(7) | Pd2-N2    | 1.993(8) |
| bond angle of $3 \cdot 2\text{PF}_6^-$     |          |           |          |
| N8-Pd1-N6                                  | 82.2(3)  | N5-Pd2-N7 | 87.5(3)  |
| N8-Pd1-N3                                  | 100.2(3) | N5-Pd2-N2 | 165.7(3) |
| N6-Pd1-N3                                  | 177.5(3) | N7-Pd2-N2 | 92.0(3)  |
| N8-Pd1-N4                                  | 177.1(3) | N5-Pd2-N1 | 96.5(3)  |
| N6-Pd1-N4                                  | 99.1(3)  | N7-Pd2-N1 | 175.2(3) |
| N3-Pd1-N4                                  | 78.6(3)  | N2-Pd2-N1 | 83.5(3)  |

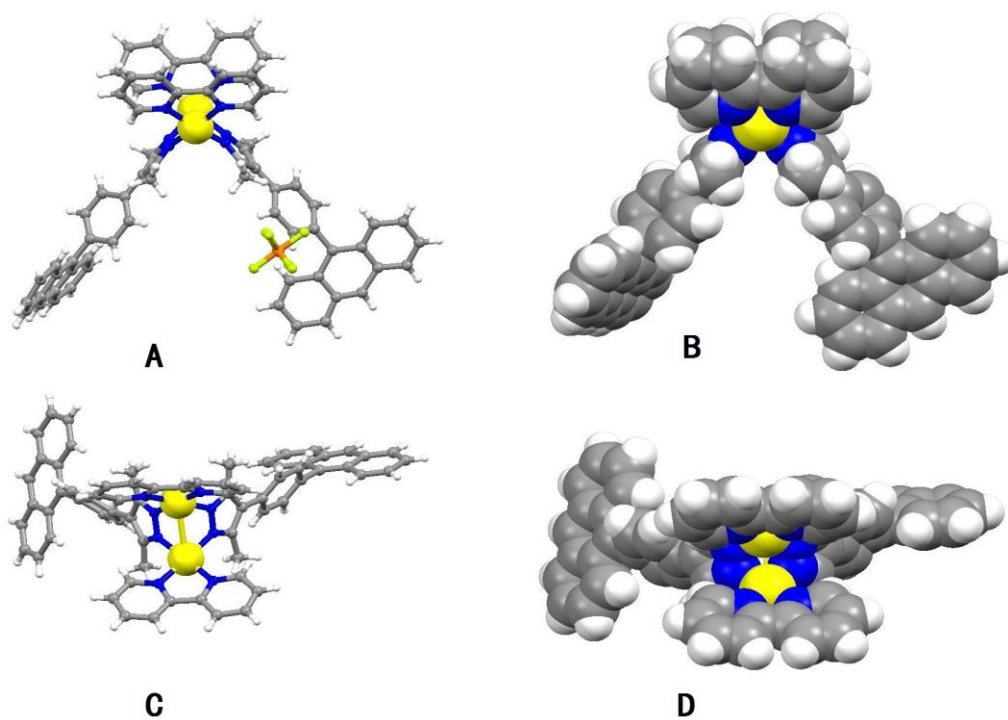


Fig. S16 The coordination mode and corners structure of  $1 \cdot 2\text{PF}_6^-$  drawn in the ball and stick mode. All solvents and counter anions were omitted for clarity.

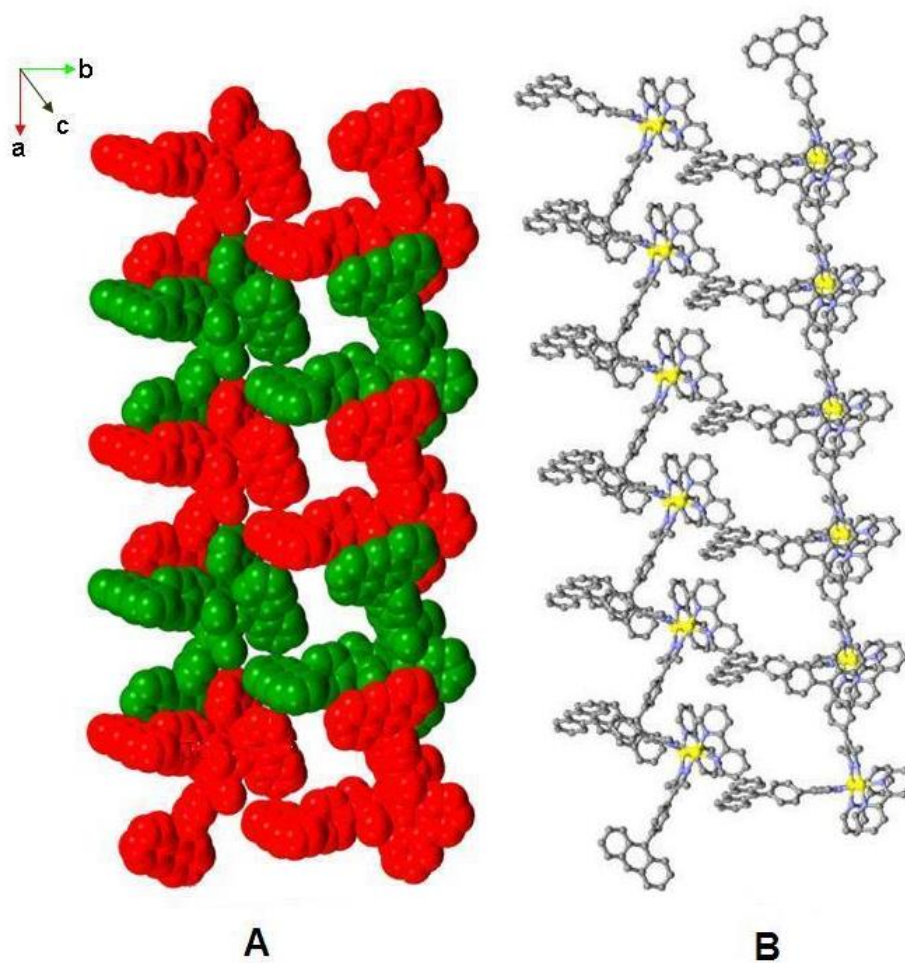


Fig. S17 The one-dimensional crystallization structure of  $1 \cdot 2\text{PF}_6^-$  drawn in the spacefilling (A) and ball and stick mode (B).

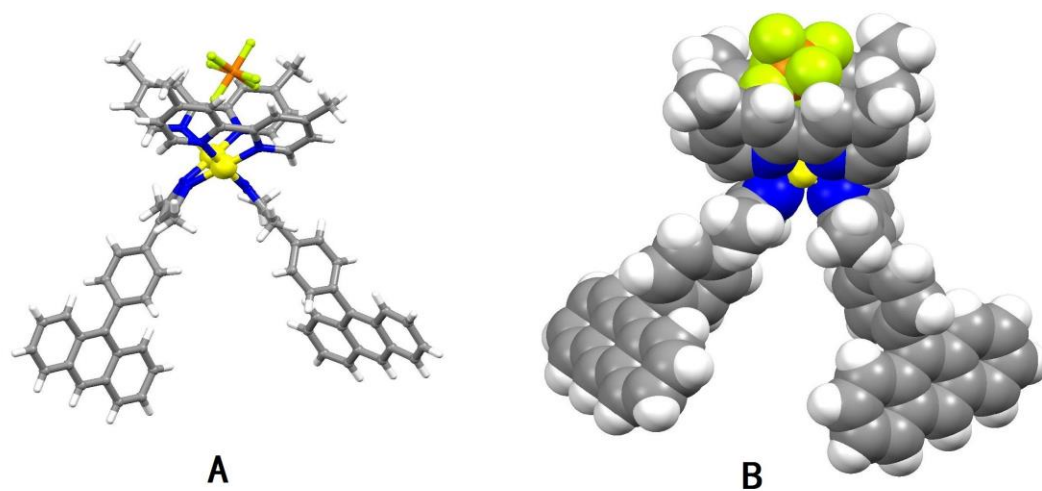


Fig. S18 The coordination mode and corners structure of  $2 \cdot 2\text{PF}_6^-$  drawn in the ball and stick mode.

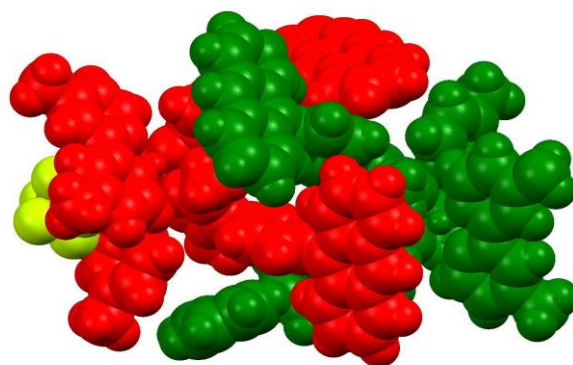


Fig. S19 The dimer structure of  $2 \cdot 2\text{PF}_6^-$  drawn in the spacefilling mode.

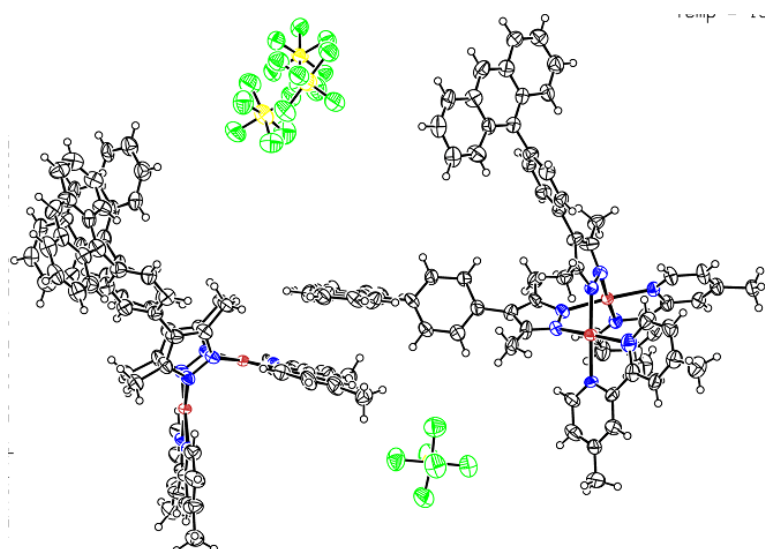


Fig. S20 The crystal structure of metal-organic corner  $2 \cdot 2\text{PF}_6^-$ .

## Circular dichroism spectroscopy

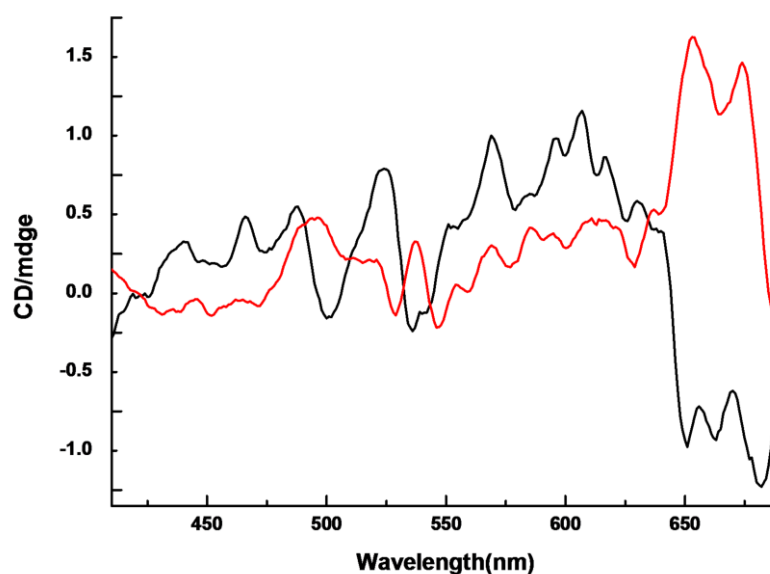


Fig. S21 Solid-state CD spectra of a single crystal of  $3 \cdot 2\text{PF}_6^-$  in its two enantiomeric forms measured by the Nujol mull method.

## Fluorescence excitation spectra

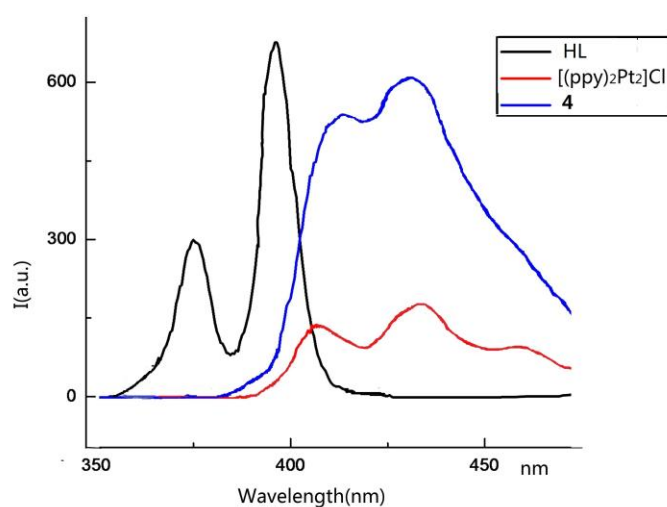


Fig. S22 Fluorescent spectra of **HL**,  $[(\text{ppy})_2\text{Pt}_2]\text{Cl}_2$  and **4**

## S4 References

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