

ELECTRONIC SUPPLEMENTARY INFORMATION

Supramolecular Association of $M^{2+} \cdots \pi$ Induced by Different Electrostatic Properties using Naphthyl Substituted β -Diketonate Complexes (Metal = Cu, Pd, Pt)

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S1. Synthesis of HL^2 and complex **2**

(1) General.

All the chemicals were of reagent grade and used without further purification. Melting points were measured by Yanaco MP-500P. 1H NMR spectra were recorded on a JEOL ECS-400 spectrometer. IR spectra were measured by Shimadzu FTIR-8400S spectrophotometer.

(2) Synthesis and physical properties of HL^2 .

Under Ar atmosphere, freshly distilled 1,1,2,2-tetrachloroethane (50 mL) was added to aluminum(III) chloride (7.54 g, 56.6 mmol), and the mixture was dissolved at 45 °C. A solution of 2-naphthochloride (10.50 g, 55.1 mmol) in 1,1,2,2-tetrachloroethane (50 mL) was added to the solution. Vinyl acetate (5.05 mL, 55.0 mmol) was slowly added dropwise into the solution under 32 °C, and then, the solution was stirred at 35 °C for 18 hours. The reaction mixture was added to 10% HCl aqueous solution under ice-bath, and the solvent was removed by steam distillation. The residue was separated by filtration, extracted by chloroform, and washed by hexane. The product was purified by column chromatography (silica, $CDCl_3$). Pale yellow microcrystals, Yield 14%. mp 152-153 °C. 1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.16 (s, CH, 1H), 7.60 (m, 4H), 8.00 (m, 8H), 8.60 (s, 2H), 17.06 (s, 1H, OH). IR (KBr disk, cm^{-1}): 3055, 1627, 1599, 1583, 1527, 1499, 1429, 1192, 950, 789, 479.

(3) Synthesis and physical properties of **2a**.

A methanol solution (10 mL) of sodium methoxide (118 mg, 2.18 mmol) was slowly added to a THF solution (30 mL) of ligand HL^2 (680 mg, 2.10 mmol), and the mixture was stirred at r.t. for 15 min, and

then $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (179 mg, 1.05 mmol) in MeOH (5 mL) was added to the solution. After stirring for 2 hours, the solution was extracted by CHCl_3 and washed by water, dried by MgSO_4 . The crystal of **2a** was obtained from natural evaporation of the hexane- CH_2Cl_2 solution. Yellowish green prismatic crystals, Yield 88%. mp 300 °C dec. IR (KBr disk, cm^{-1}): 1597, 1591, 1554, 1521, 1498, 1442, 1400, 1342, 1300, 1130, 798.

(4) Synthesis and physical properties of **2b**.

A THF solution (5 mL) of ligand HL^2 (120 mg, 0.37 mmol) was added dropwise into an aqueous solution (15 mL) of potassium tetrachloropalladate (60.8 mg, 0.19 mmol), to give a pale-yellow precipitate in the mixture. Then, 5M NaOH aq. was added into the solution during the colour changing, and the mixture was stirred at r.t. for overnight. After removing the solvent, yellow precipitates were filtered. TLC (silica, CHCl_3) shows a pure product at $R_f = 0.3$. The crystal of **2b** was obtained from natural evaporation of the hexane- CH_2Cl_2 solution. Yellow prismatic crystals, Yield 28%. mp 270 °C dec. ^1H NMR (400MHz, CDCl_3 , TMS): δ 7.16 (s, CH, 2H), 7.58 (t, $J = 7.4$ Hz, 4H), 7.61 (t, $J = 7.4$ Hz, 4H), 7.91 (d, $J = 7.4$ Hz, 4H), 7.96 (d, $J = 8.4$ Hz, 4H), 8.02 (d, $J = 7.4$ Hz, 4H), 8.08 (d, $J = 8.4$ Hz, 4H), 8.60 (s, 4H). IR (KBr disk, cm^{-1}): 1597, 1527, 1504, 1433, 1392, 1344, 1203, 795, 752, 474.

(5) Synthesis and physical properties of **2c**.

2.5 M NaOH aq. (2 mL) was added dropwise into a THF solution (20 mL) of ligand HL^2 (328 mg, 1.0 mmol), and the solution was added into an aqueous solution of 25 mM $[\text{Pt}(\text{H}_2\text{O})_4](\text{ClO}_4)_2$ at 90 °C under a rate of 3-4 drops per sec. to give black precipitates in the mixture. Then, 1M NaOH aq. was added into the solution during the color changing, and the mixture was stirred at 90 °C for 44 h. After removing the solvent, black precipitates were filtered. The residue was extracted by CH_2Cl_2 and dried by MgSO_4 to yield orange and brown solids as crude products. This red-orange solid was dissolved in CH_2Cl_2 and it was natural evaporated to give crystal **2c**. Orange prismatic crystals, Yield 24%. mp 280 °C dec. ^1H NMR (400MHz, CDCl_3 , TMS): δ 7.17 (s, CH, 2H), 7.58 (t, $J = 7.2$ Hz, 4H), 7.61 (t, $J = 7.2$ Hz, 4H), 7.91 (d, $J = 7.2$ Hz, 4H), 7.96 (d, $J = 8.8$ Hz, 4H), 8.02 (d, $J = 7.2$ Hz, 4H), 8.08 (d, $J = 8.8$ Hz, 4H), 8.60 (s, 4H). IR (KBr disk, cm^{-1}): 1521, 1504, 1460, 1429, 1386, 1342, 1203, 798, 744, 479.

S2. Crystal data and structures of HL² and complex 2.

The crystal data were shown in Table S1.

Table S1. Crystal data of HL² and complex 2.

	HL ²	2a	2b	2c
Chemical formula	C ₂₃ H ₁₆ O ₂	C ₄₆ H ₃₀ CuO ₄	C ₄₆ H ₃₀ PdO ₄	C ₄₆ H ₃₀ PtO ₄
Description, color	plate, pale yellow	prismatic, green	prismatic, yellow	prismatic, orange
Crystal size	0.257x0.157x0.024	0.130x0.065x0.047	0.128x0.124x0.045	0.067x0.044x0.028
Formula weight	324.36	710.24	753.10	841.79
<i>T</i> [K]	100	100	100	200
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	<i>Pna</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	7.2918(5)	13.093(7)	35.924(6)	15.8989(17)
<i>b</i> [Å]	5.9870(4)	5.920(4)	6.0389(11)	6.0142(6)
<i>c</i> [Å]	36.209(2)	21.808(12)	16.287(3)	17.7912(19)
α [°]	90	90	90	90
β [°]	90	102.070(11)	109.919(5)	97.217(5)
γ [°]	90	90	90	90
<i>V</i> [Å ³]	1580.74(18)	1653.0(16)	3321.9(10)	1687.7(3)
<i>Z</i>	4	2	4	2
<i>D</i> _c [g cm ⁻³]	1.363	1.427	1.506	1.656
<i>F</i> (000)	680	734	1536	832
<i>R</i> _{int}	0.0571	0.1166	0.1259	0.1606
Reflections measured	18478	20850	17498	21540
Reflections independent	2795	2901	2927	2980
GOF	1.130	1.078	1.046	1.032
<i>R</i> [(<i>I</i>) > 2σ(<i>I</i>)]	0.0741	0.0452	0.0453	0.0458
<i>wR</i> (<i>F</i> _o ²)	0.2197	0.1048	0.1095	0.0912
CCDC No.	1984649	1984650	1984651	1984652

a) Molecular structure of HL²:

In the crystal (Figure S1), whole molecule HL² was observed as asymmetric unit. H atoms attached to C atoms were refined as riding on their idealized positions, with C-H = 0.95 Å for aromatic atoms.

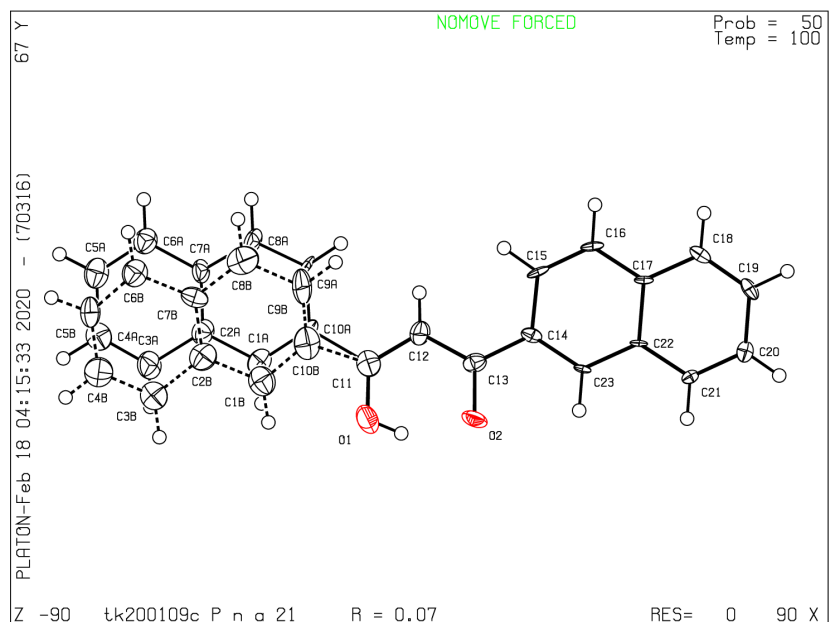


Figure S1. The molecular structure of HL² drawing by PLATON in checkCIF.

b) Molecular structure of 2a:

In the crystal (Figure S2), one half of the complex was observed as asymmetric unit. The whole complex was comprised as one Cu(II) ions, two ligands L². H atoms attached to C atoms were refined as riding on their idealized positions, with C-H = 0.95 Å for aromatic atoms.

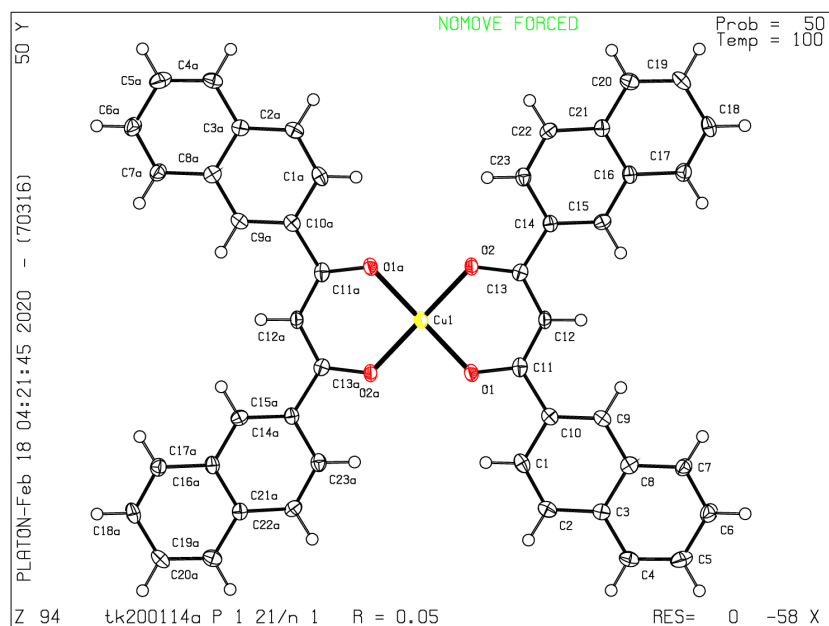


Figure S2. The molecular structure of 2a drawing by PLATON in checkCIF.

c) Molecular structure of **2b**:

In the crystal (Figure S3), one half of the complex was observed as asymmetric unit. The whole complex was comprised as one Pd(II) ions, two ligands L^2 . H atoms attached to C atoms were refined as riding on their idealized positions, with C-H = 0.95 Å for aromatic atoms.

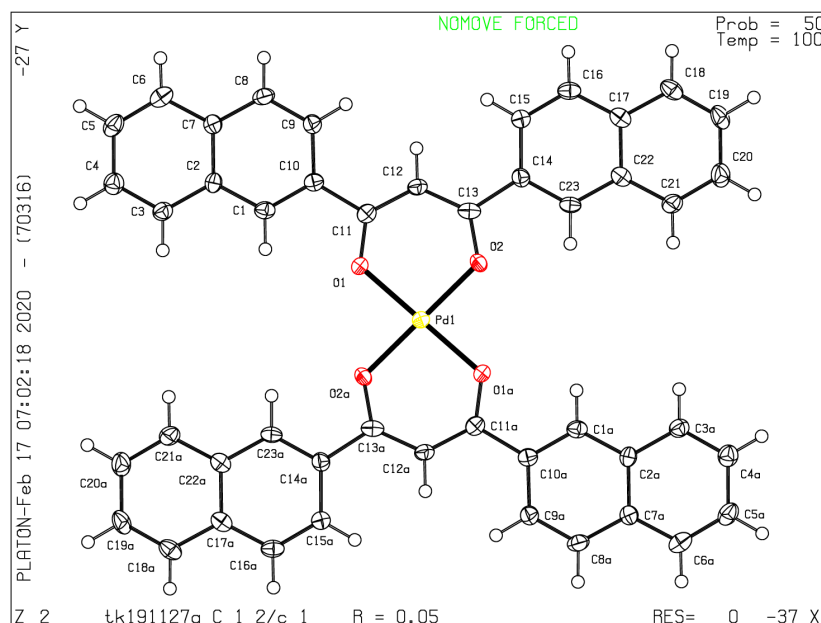


Figure S3. The molecular structure of **2b** drawing by PLATON in checkCIF.

d) Molecular structure of **2c**:

In the crystal (Figure S4), one half of the complex was observed as asymmetric unit. The whole complex was comprised as one Pt(II) ions, two ligands L^2 . H atoms attached to C atoms were refined as riding on their idealized positions, with C-H = 0.95 Å for aromatic atoms.

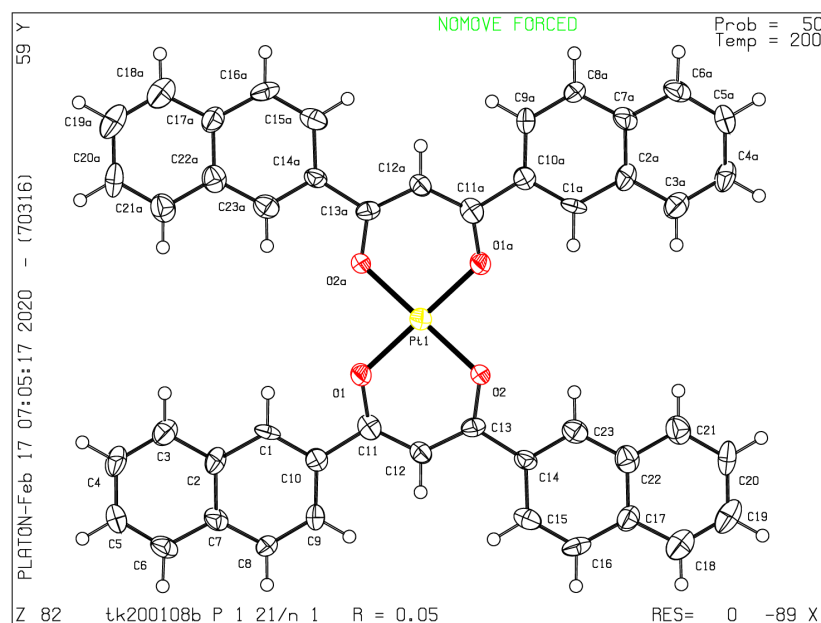


Figure S4. The molecular structure of **2c** drawing by PLATON in checkCIF.

S3. Packing structures of 2.

a) Packing structure of 2a:

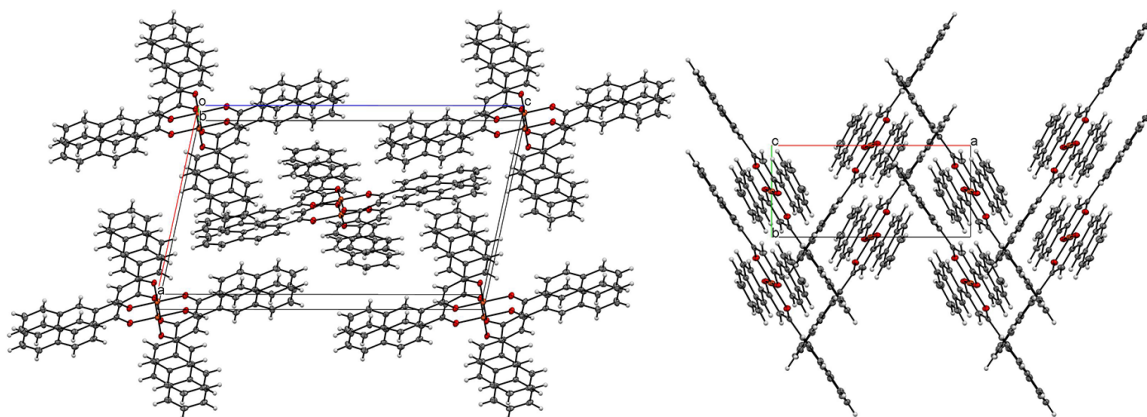


Figure S5. The packing structure of 2a drawing by Mercury.

b) Packing structure of 2b:

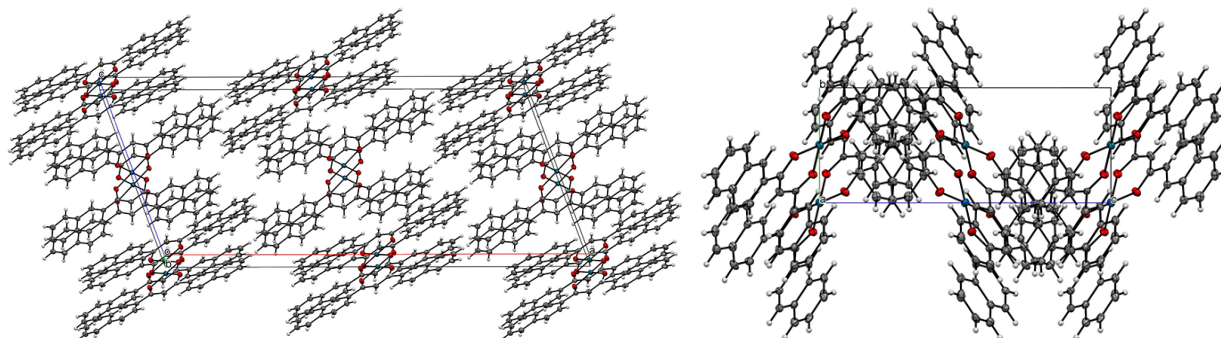


Figure S6. The packing structure of 2b drawing by Mercury.

c) Packing structure of 2c:

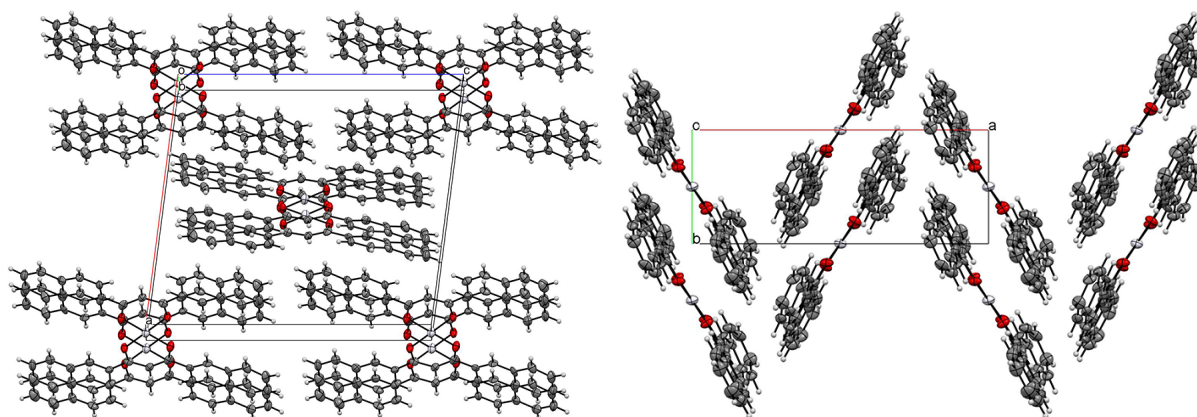


Figure S7. The packing structure of 2c drawing by Mercury.

S4. Remarkable intermolecular interactions of 2.

a) Metal $\cdots\pi$ and CH $\cdots\pi$ interactions of 2a:

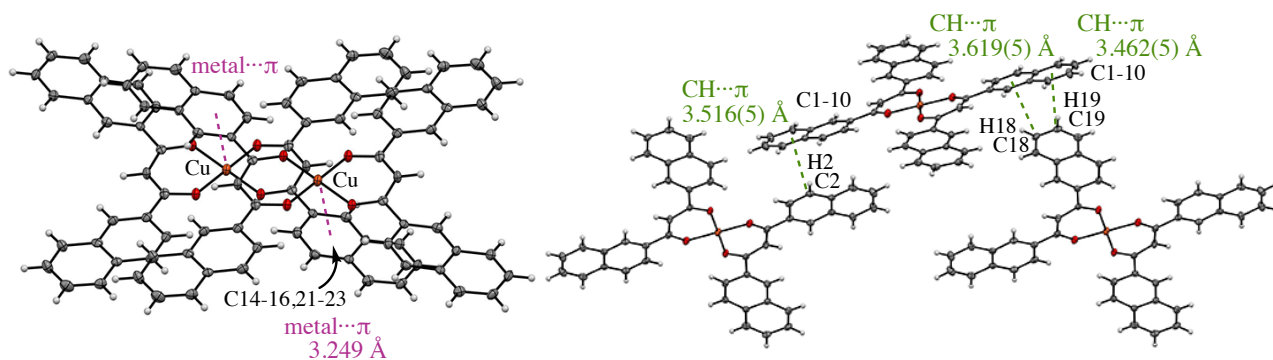


Figure S8. Parts of packing structure of 2a drawing by Mercury.

b) Metal $\cdots\pi$ and CH $\cdots\pi$ interactions of 2b:

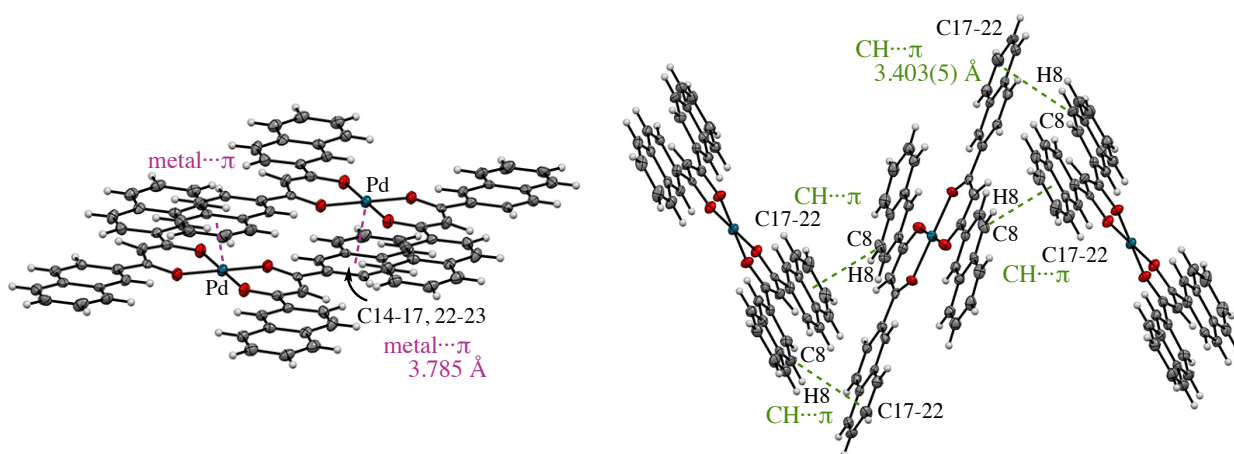


Figure S9. Parts of packing structure of 2b drawing by Mercury.

c) Metal $\cdots\pi$ and CH $\cdots\pi$ interactions of 2c:

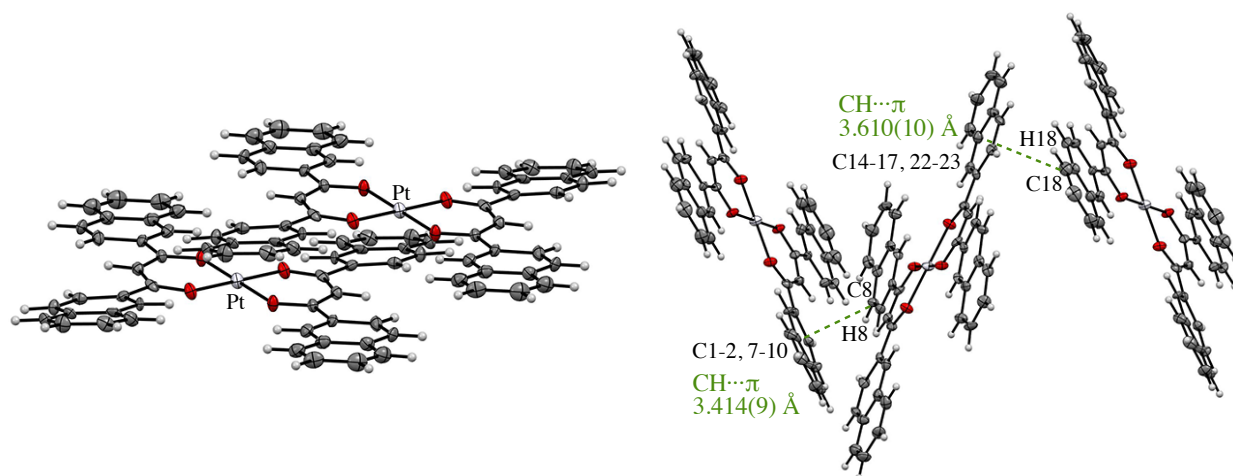


Figure S10. Parts of packing structure of 2c drawing by Mercury.

S5. DFT calculations of 1 and 2.

DFT calculation was performed by Spartan'18 and used ω B97X-D and 6-31G* as a functional and basis set, respectively. The structures of **1a** and **1b** were used by the previously reported CIF data [CCDC1441959 for **1a**¹⁾ and CCDC1229561 for **1b**²⁾].

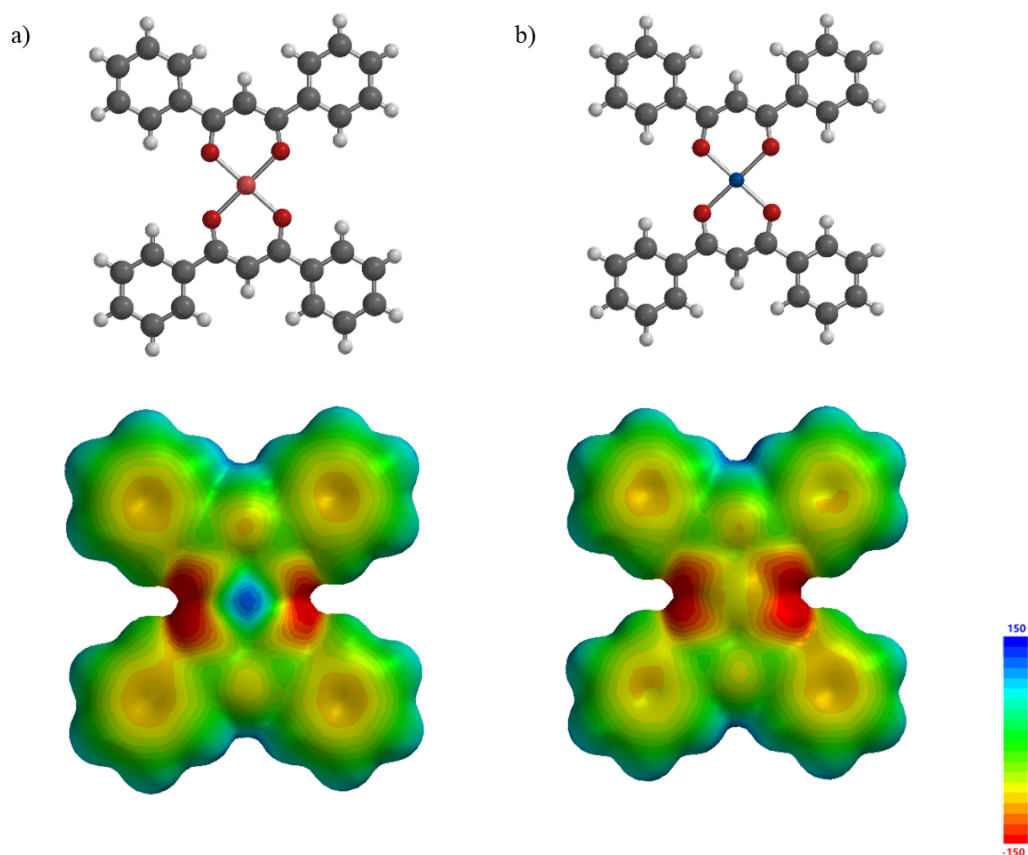


Figure S11. The energy potential maps of a) **1a** and b) **2a**: the color of potential is shown between -150 kJ mol^{-1} (red) to $+150 \text{ kJ mol}^{-1}$ (blue).

Table S2. The remarkable values of electrostatic potential (kJ mol^{-1}) in the complexes **1** and **2**.

	1a	1b	2a	2b	2c
maximum	+116.71	+112.23	+122.84	+103.00	+104.11
minimum	-199.12	-184.77	-194.23	-186.62	-177.20
π center	-75 ~ -85	-75 ~ -85	-70 ~ -80	-70 ~ -80	-70 ~ -80
metal	+116.71	-73	+122.84	-75	-113.9

1) S. Layek, S. Kumari, Anuradha, B. Agrahari, R. Ganguly, D. D. Pathak, *Inorg. Chim. Acta*, 2016, **453**, 735.

2) E. A. Shugam, L. M. Shkol'nikova, A. N. Knyazeva, *Zh. Strukt. Khim. (J. Struct. Chem.)*, 1968, **9**, 222.