

# Constructing Supramolecular Frameworks Based Imidazolate-Edge-Bridged Metallacalix[3]arenes via Hierarchical Self-Assemblies

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## Supplementary Information (SI)

### Materials

All chemicals and solvents were reagent grade and were purified according to conventional methods.<sup>1</sup> The metal complexes (dmbpy)Pd(NO<sub>3</sub>)<sub>2</sub> and (phen)Pd(NO<sub>3</sub>)<sub>2</sub> were prepared according to literature procedures.<sup>2</sup>

### Instrumentation

<sup>1</sup>H NMR experiment was performed at 400 MHz on a Bruker Avance III HD 400 spectrometer using tetramethylsilane. Elemental analyses (C, H, N, contents) were performed by an Elemental Analyser EA 1108 (Carlo Erba Instruments).

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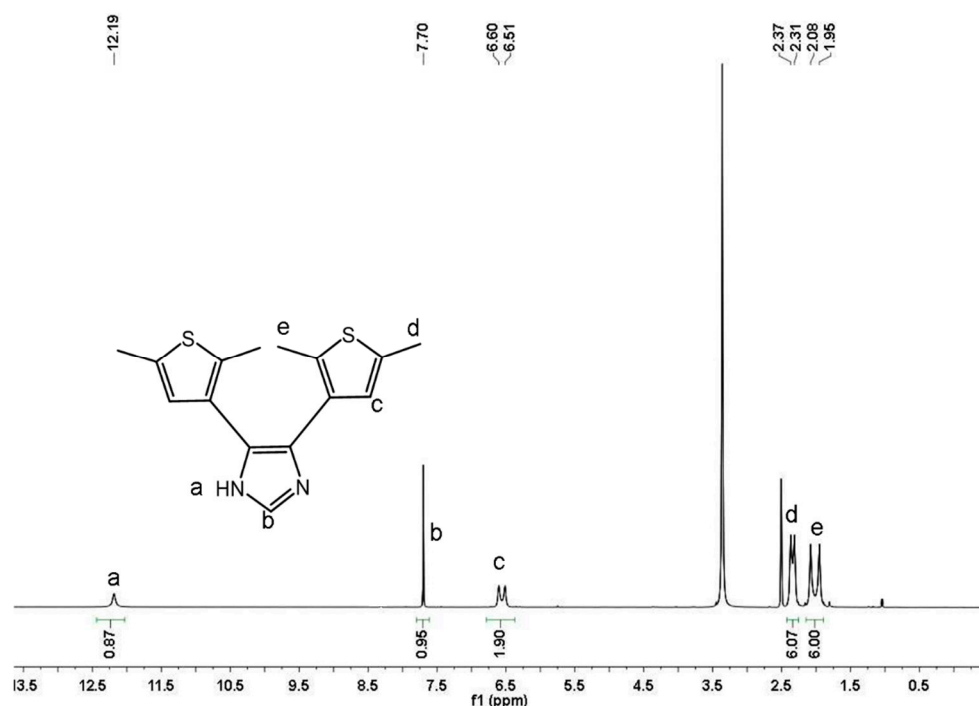
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### 1. NMR spectra and Mass spectrum



**Figure S1.** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of HL.

## 2. Crystal parameters of complexes **1**·3PF<sub>6</sub> and **2**·3NO<sub>3</sub>.

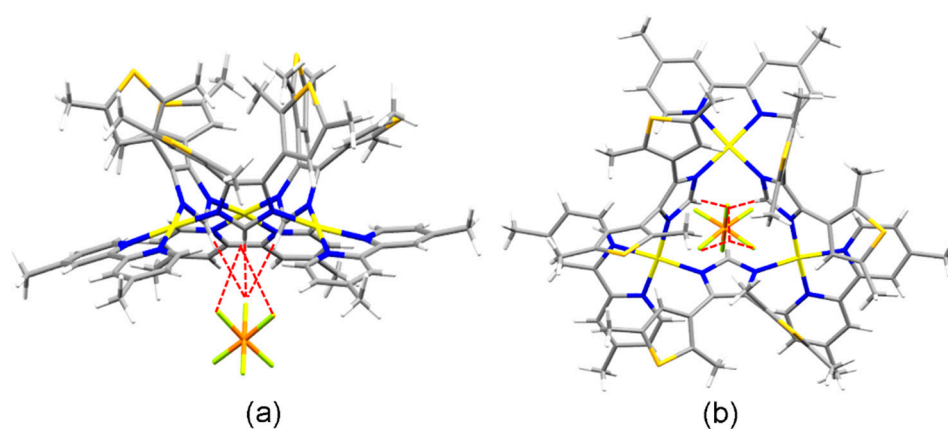
**Table S1.** Selected bond distances (Å) and angles (°) of complex **1**·3PF<sub>6</sub>.

Bond Dist.[Å]			
N1-Pd1	2.004(2)	N7-Pd1	1.994(2)
N2-Pd1	2.005(2)	N8-Pd2	2.019(2)
N3-Pd2	2.019(2)	N9-Pd2	2.017(2)
N4-Pd2	2.022(2)	N10-Pd3	2.011(2)
N5-Pd3	2.018(2)	N11-Pd3	2.013(2)
N6-Pd3	2.032(2)	N12-Pd1	2.009(2)
Bond Angel[°]			
C1-N1-Pd1	125.5(2)	C69-N11-Pd3	130.28(19)
C5-N1-Pd1	115.21(19)	C67-N12-Pd1	123.2(2)
C10-N2-Pd1	126.2(2)	C68-N12-Pd1	129.7(2)
C6-N2-Pd1	112.54(19)	N7-Pd1-N2	96.47(10)
C13-N3-Pd2	126.7(2)	N7-Pd1-N1	174.76(11)
C17-N3-Pd2	113.26(19)	N2-Pd1-N1	80.30(10)
C22-N4-Pd2	127.5(2)	N7-Pd1-N12	89.79(10)
C18-N4-Pd2	113.20(18)	N2-Pd1-N12	170.33(10)
C25-N5-Pd3	127.5(2)	N1-Pd1-N12	93.97(10)
C29-N5-Pd3	113.01(19)	N9-Pd2-N3	174.25(11)
C30-N6-Pd3	113.3(2)	N9-Pd2-N8	89.08(10)
C34-N6-Pd3	126.1(2)	N3-Pd2-N8	94.32(10)
C52-N7-Pd1	120.6(2)	N9-Pd2-N4	94.71(9)
C54-N7-Pd1	131.1(2)	N3-Pd2-N4	81.91(10)
C52-N8-Pd2	118.5(2)	N8-Pd2-N4	176.21(10)
C53-N8-Pd2	134.1(2)	N11-Pd3-N10	88.92(10)
C37-N9-Pd2	122.1(2)	N11-Pd3-N5	176.32(11)
C38-N9-Pd2	130.0(2)	N10-Pd3-N5	94.61(10)
C37-N10-Pd3	120.3(2)	N11-Pd3-N6	95.73(10)
C39-N10-Pd3	131.9(2)	N10-Pd3-N6	175.29(10)
C67-N11-Pd3	121.9(2)	N5-Pd3-N6	80.76(10)

**Table S2.** Selected bond distances (Å) and angles (°) of complex **2**·3NO<sub>3</sub>.

Bond Dist.[Å]			
N1-Pd1	2.041(3)	N7-Pd1	1.971(3)
N2-Pd1	2.031(2)	N8-Pd2	1.994(3)
N3-Pd2	2.016(3)	N9-Pd2	1.998(3)
N4-Pd2	2.031(3)	N10-Pd3	2.046(3)
N5-Pd3	2.070(3)	N11-Pd3	2.018(3)
N6-Pd3	2.028(3)	N12-Pd1	2.018(2)
Bond Angel[°]			
C1-N1-Pd1	C1-N1-Pd1	C39-N8-Pd2	135.3(2)
C9-N1-Pd1	C9-N1-Pd1	C52-N9-Pd2	122.7(2)
C8-N2-Pd1	C8-N2-Pd1	C53-N9-Pd2	131.4(2)
C12-N2-Pd1	C12-N2-Pd1	C52-N10-Pd3	122.2(2)
C13-N3-Pd2	C13-N3-Pd2	C54-N10-Pd3	130.1(2)
C17-N3-Pd2	C17-N3-Pd2	C67-N11-Pd3	124.6(2)
C24-N4-Pd2	C24-N4-Pd2	C68-N11-Pd3	128.8(2)
C18-N4-Pd2	C18-N4-Pd2	C67-N12-Pd1	124.3(2)

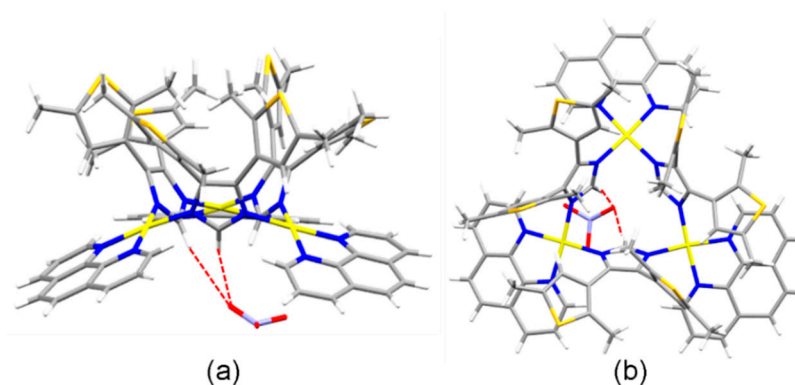
C25-N5-Pd3	129.0(2)	C69-N12-Pd1	131.5(2)
C29-N5-Pd3	109.6(2)	N7-Pd1-N12	88.58(11)
C36-N6-Pd3	129.9(2)	N7-Pd1-N2	96.14(11)
C30-N6-Pd3	111.7(2)	N12-Pd1-N2	173.39(10)
C37-N7-Pd1	128.0(2)	N7-Pd1-N1	177.02(10)
C38-N7-Pd1	126.5(2)	N12-Pd1-N1	94.39(10)
C37-N8-Pd2	120.0(2)	N2-Pd1-N1	80.93(11)
N8-Pd2-N9	89.31(11)	N11-Pd3-N6	93.88(11)
N8-Pd2-N3	95.43(11)	N11-Pd3-N10	89.33(11)
N9-Pd2-N3	173.72(11)	N6-Pd3-N10	175.56(10)
N8-Pd2-N4	176.84(10)	N11-Pd3-N5	173.91(10)
N9-Pd2-N4	93.74(10)	N6-Pd3-N5	83.38(11)
N3-Pd2-N4	81.47(11)	N10-Pd3-N5	93.71(11)



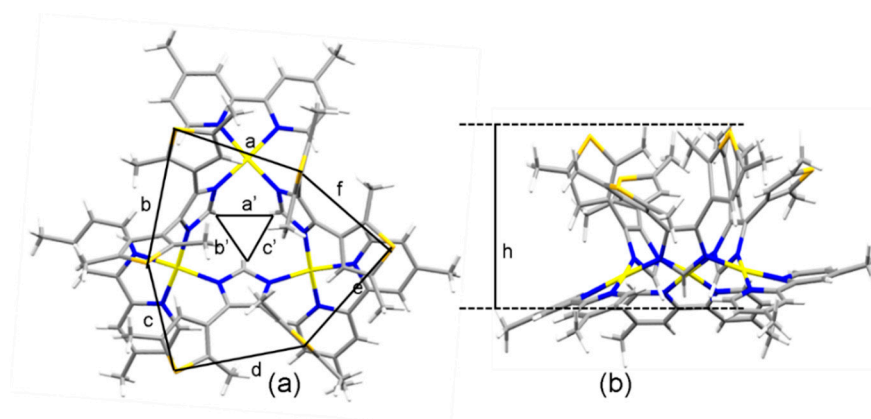
**Figure S2.** (a) Top view and (b) side view of the basket-shape structure of  $1 \cdot 3\text{PF}_6$ .

#### Specified C-H...Anion hydrogen bonds present in complex $1 \cdot 3\text{PF}_6$

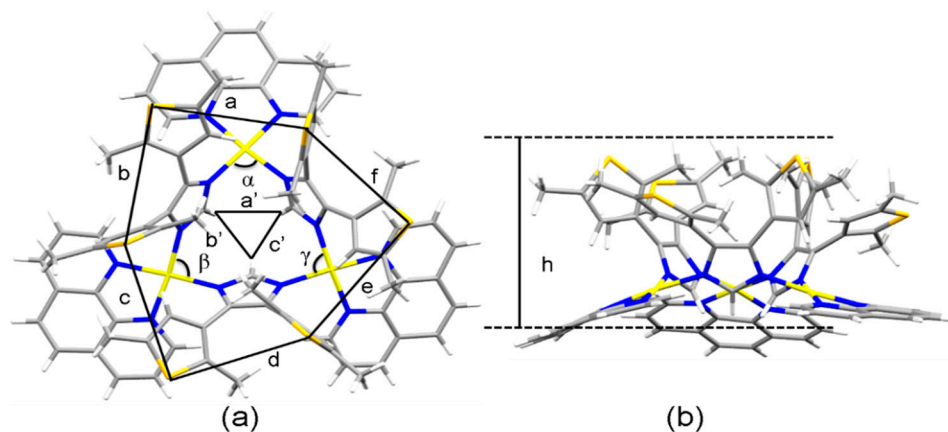
In the structure of  $1 \cdot 3\text{PF}_6$ , the distances of the C-H...F hydrogen bond between hexafluorophosphate anion and basket-shaped cation are 3.10–3.46 Å, separately. Based on these distances, the C-H...F hydrogen bond belongs to the weak hydrogen bond. Therefore, the steady basket-shaped structure is stabilized with the hydrogen bonding interaction accompanied by an internal charge assistance interaction. The same phenomenon was existed in the structure of  $2 \cdot 3\text{NO}_3$ .



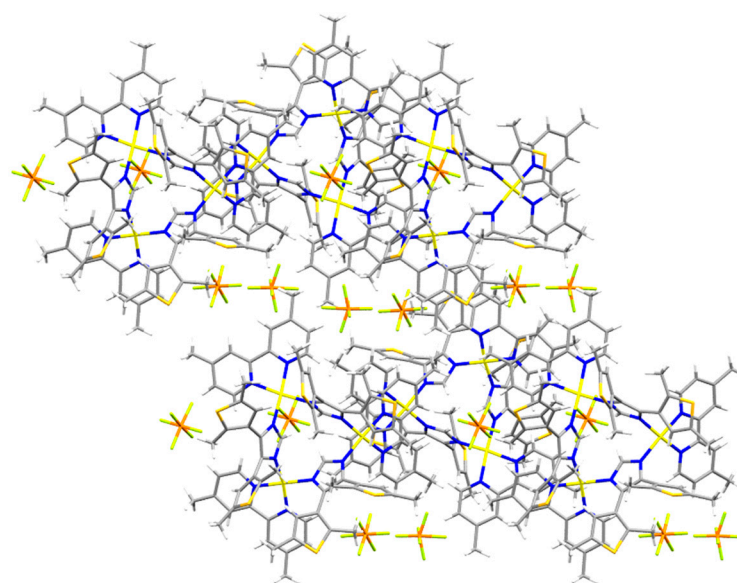
**Figure S3.** Top view (a) and side view (b) of the basket-shape structure of  $2 \cdot 3\text{NO}_3$ .



**Figure S4.** (a) Top view and (b) side view of the basket-shaped structure of **1·3PF<sub>6</sub>**. Important parameters for the cavity are: selected distances [Å]:  $a'=2.228$ ,  $b'=2.133$ ,  $c'=2.374$ ,  $a=5.920$ ,  $b=5.974$ ,  $c=5.985$ ,  $d=6.202$ ,  $e=5.976$ ,  $f=6.189$ ,  $h=6.113$ ; selected angles:  $\alpha=90.83^\circ$ ,  $\beta=90.64^\circ$ ,  $\gamma=88.91^\circ$ .



**Figure S5.** (a) Top view and (b) side view of the basket-shaped structure of **2·3NO<sub>3</sub>**. Important parameters for the cavity are: selected distances [Å]:  $a'=2.317$ ,  $b'=2.473$ ,  $c'=2.482$ ,  $a=6.108$ ,  $b=6.523$ ,  $c=5.955$ ,  $d=5.957$ ,  $e=6.179$ ,  $f=5.788$ ,  $h=6.633$ ; selected angles:  $\alpha=89.30^\circ$ ,  $\beta=89.33^\circ$ ,  $\gamma=88.58^\circ$ .



**Figure S6.** Packing X-ray structure of **1·3PF<sub>6</sub>**.

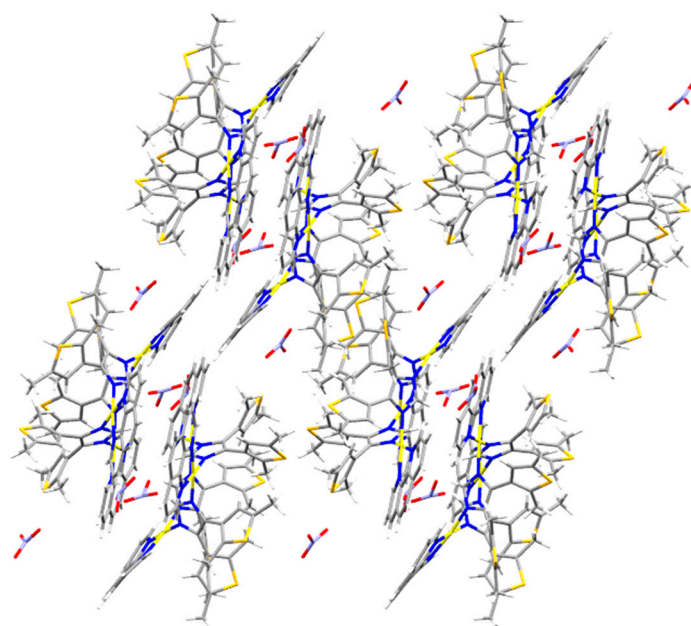


Figure S7. Packing X-ray structure of  $2 \cdot 3\text{NO}_3$ .

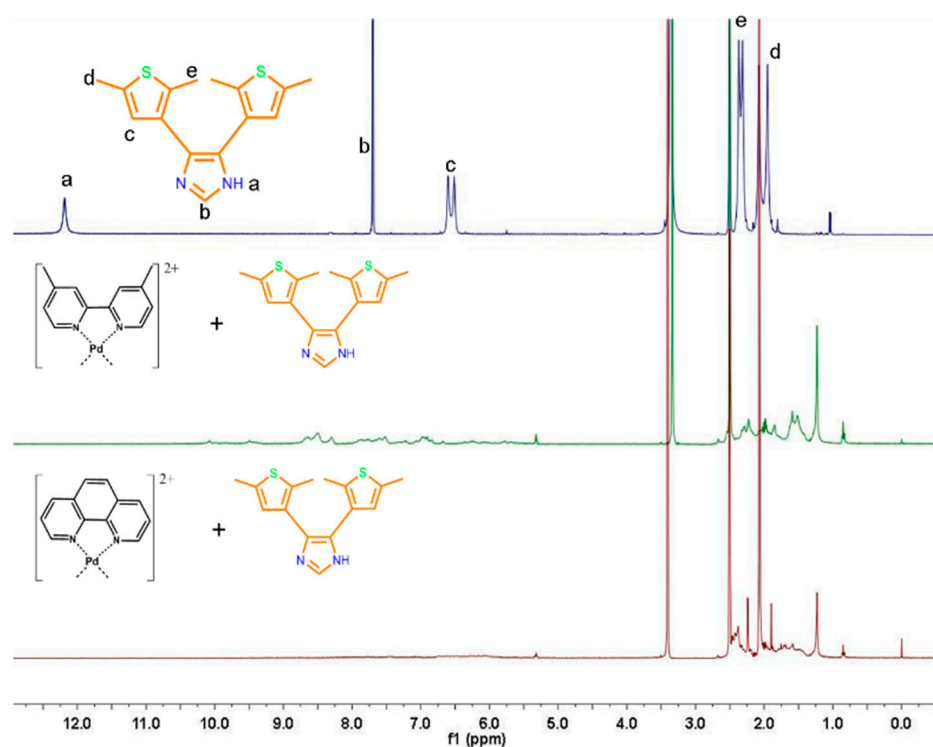


Figure S8.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) spectra of HL,  $1 \cdot 3\text{NO}_3$  and  $2 \cdot 3\text{NO}_3$ .

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