

## <Electronic Supplementary Information>

### **Pseudorotaxane-type *n*-hydrocarbon container. Metallacyclodimer of ionic palladium(II) complexes containing 1,3-bis(4-pyridyl)tetramethyldisiloxane**

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#### **Experimental Section**

##### **Materials and Measurements**

Commercially available chemicals including potassium tetrachloropalladate(II), *N,N,N',N'*-tetramethylethylenediamine (Me<sub>4</sub>en), and silver trifluoromethanesulfonate (Ag(CF<sub>3</sub>SO<sub>3</sub>)) were purchased from Aldrich, and used without further purification. (Me<sub>4</sub>en)PdCl<sub>2</sub><sup>1</sup> and 1,3-bis(4-pyridyl)tetramethyldisiloxane (L)<sup>2</sup> were prepared according to the procedures outlined in the literature.

Infrared spectra were obtained on a Nicolet 380 FT-IR spectrophotometer. <sup>1</sup>H (300 MHz) and <sup>13</sup>C NMR (75 MHz) spectra were recorded on a Varian Mercury Plus 300. Elemental analyses were performed on crystalline samples using a Vario-EL III at Pusan center, KBSI. Thermal analyses were carried out under a dinitrogen atmosphere at a scan rate of 10 °C/min using a Labsys TGA-DSC 1600.

**Synthesis of C<sub>*n*</sub>H<sub>2*n*+2</sub>@[(Me<sub>4</sub>en)Pd(L)]<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>**

(Me<sub>4</sub>en)PdCl<sub>2</sub> (0.1 mmol, 29.3 mg) was suspended in water (10 mL) and stirred for 2 h at room temperature with Silver trifluoromethanesulfonate (0.2 mmol, 51.4 mg). The precipitate of silver chloride was filtered off, the filtrate was evaporated to dryness, after then (Me<sub>4</sub>en)Pd(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> was redissolved in anhydrous acetone (20 mL). To the solution was added a 20 mL acetone solution of L (0.1 mmol, 28 mg). The reaction mixture was refluxed for 4 h. Single crystals suitable for X-ray crystallography were obtained via slow diffusion of alkanes onto the resulting acetone solution.

**C<sub>5</sub>H<sub>12</sub>@[(Me<sub>4</sub>en)Pd(L)]<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>.** Yield: 54% (46 mg). Anal. Calcd (%) for C<sub>49</sub>H<sub>84</sub>N<sub>8</sub>O<sub>14</sub>F<sub>12</sub>S<sub>4</sub>Si<sub>4</sub>Pd<sub>2</sub>: C 34.81; H 5.01; N 6.63; found: C 34.73; H 4.94; N 6.71. IR (KBr pellet, cm<sup>-1</sup>): 1606, 1471, 1423, 1257(s, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>), 1160(m, C–N), 1079(m, CF<sub>3</sub>SO<sub>3</sub>), 1029(s, Si–O), 840, 792(s, Si–O). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, 300 MHz) δ(ppm): 9.34 (d, *J* = 6 Hz, H<sub>α</sub>-pyridyl, 8H), 7.82 (d, *J* = 6 Hz, H<sub>β</sub>-pyridyl, 8H), 3.26 (s, -CH<sub>2</sub>-, 8H), 2.80 (s, -CH<sub>3</sub>, 24H), 1.29 (m, -CH<sub>2</sub>-, 6H), 1.87 (t, *J* = 6 Hz, -CH<sub>3</sub>, 6H), 0.34 (s, -CH<sub>3</sub>, 24H).

**C<sub>6</sub>H<sub>14</sub>@[(Me<sub>4</sub>en)Pd(L)]<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>.** Yield: 66% (56 mg). Anal. Calcd (%) for C<sub>50</sub>H<sub>86</sub>N<sub>8</sub>O<sub>14</sub>F<sub>12</sub>S<sub>4</sub>Si<sub>4</sub>Pd<sub>2</sub>: C 35.23; H 5.08; N 6.57; found: C 35.16; H 4.99; N 6.65. IR (KBr pellet, cm<sup>-1</sup>): 1606, 1473, 1423, 1257(s, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>), 1222, 1159(m, C–N), 1079(m, CF<sub>3</sub>SO<sub>3</sub>), 1027(s, Si–O), 840, 792(s, Si–O), 638, 516. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, 300 MHz) δ(ppm): 9.34 (d, *J* = 6 Hz, H<sub>α</sub>-pyridyl, 8H), 7.82 (d, *J* = 6 Hz, H<sub>β</sub>-pyridyl, 8H), 3.26 (s, -CH<sub>2</sub>-, 8H), 2.80 (s, -CH<sub>3</sub>, 24H), 1.27 (m, -CH<sub>2</sub>-, 8H), 1.87 (t, *J* = 6 Hz, -CH<sub>3</sub>, 6H), 0.34 (s, -CH<sub>3</sub>, 24H). MS (FAB): *m/z* = 659.0 ([M–2CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>]<sup>2+</sup>), 1180.1 ([M–L–CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>]<sup>+</sup>), 1468.4 ([M–CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>]<sup>+</sup>).

**C<sub>7</sub>H<sub>16</sub>@[(Me<sub>4</sub>en)Pd(L)]<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>.** Yield: 57% (49 mg). Anal. Calcd (%) for C<sub>50</sub>H<sub>86</sub>N<sub>8</sub>O<sub>14</sub>F<sub>12</sub>S<sub>4</sub>Si<sub>4</sub>Pd<sub>2</sub>: C 35.64; H 5.16; N 6.52; found: C 35.57; H 5.23; N 6.61. IR (KBr pellet, cm<sup>-1</sup>): 1608, 1473, 1425, 1259(s, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>), 1222, 1155(m, C–N), 1081(m, CF<sub>3</sub>SO<sub>3</sub>),

1029(s, Si–O), 842, 800(s, Si–O), 638, 516. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, 300 MHz) δ(ppm): 9.34 (d, *J* = 6 Hz, H<sub>α</sub>-pyridyl, 8H), 7.82 (d, *J* = 6 Hz, H<sub>β</sub>-pyridyl, 8H), 3.26 (s, -CH<sub>2</sub>-, 8H), 2.80 (s, -CH<sub>3</sub>, 24H), 1.27 (m, -CH<sub>2</sub>-, 10H), 1.87 (t, *J* = 6Hz, -CH<sub>3</sub>, 6H), 0.34 (s, -CH<sub>3</sub>, 24H).

### X-Ray Crystallography

All X-ray data were collected on a Bruker SMART automatic diffractometer with a graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and a CCD detector at  $-25 \text{ }^\circ\text{C}$ . Thirty-six frames of two dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the multi-scan method. The structures were solved by the direct method (SHELXS 97) and refined by full-matrix least squares techniques (SHELXL 97). The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined using a riding model. For  $\text{C}_7\text{H}_{16}@[(\text{Me}_4\text{en})\text{Pd}(\text{L})]_2(\text{CF}_3\text{SO}_3)_4$ , the atoms of guest heptane (C23 to C26) have quite large shift/su\_max values and thermal ellipsoids compared to those of metallacyclodimer. Therefore the C23 to C26 were restrained using DFIX and EADP. Crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table S1.

### Referenses

1. V. K. Jain and L. Jain, *Coord. Chem. Rev.*, 2005, **249**, 3075.
2. O.-S. Jung, Y. J. Kim, Y.-A. Lee, S. W. Kang and S. N. Choi, *Crystal Growth Des.*, 2004, **4**, 23.

**Table S1** Crystal data and structure refinements for  $C_nH_{2n+2}@[(Me_4en)Pd(L)]_2(CF_3SO_3)_4$

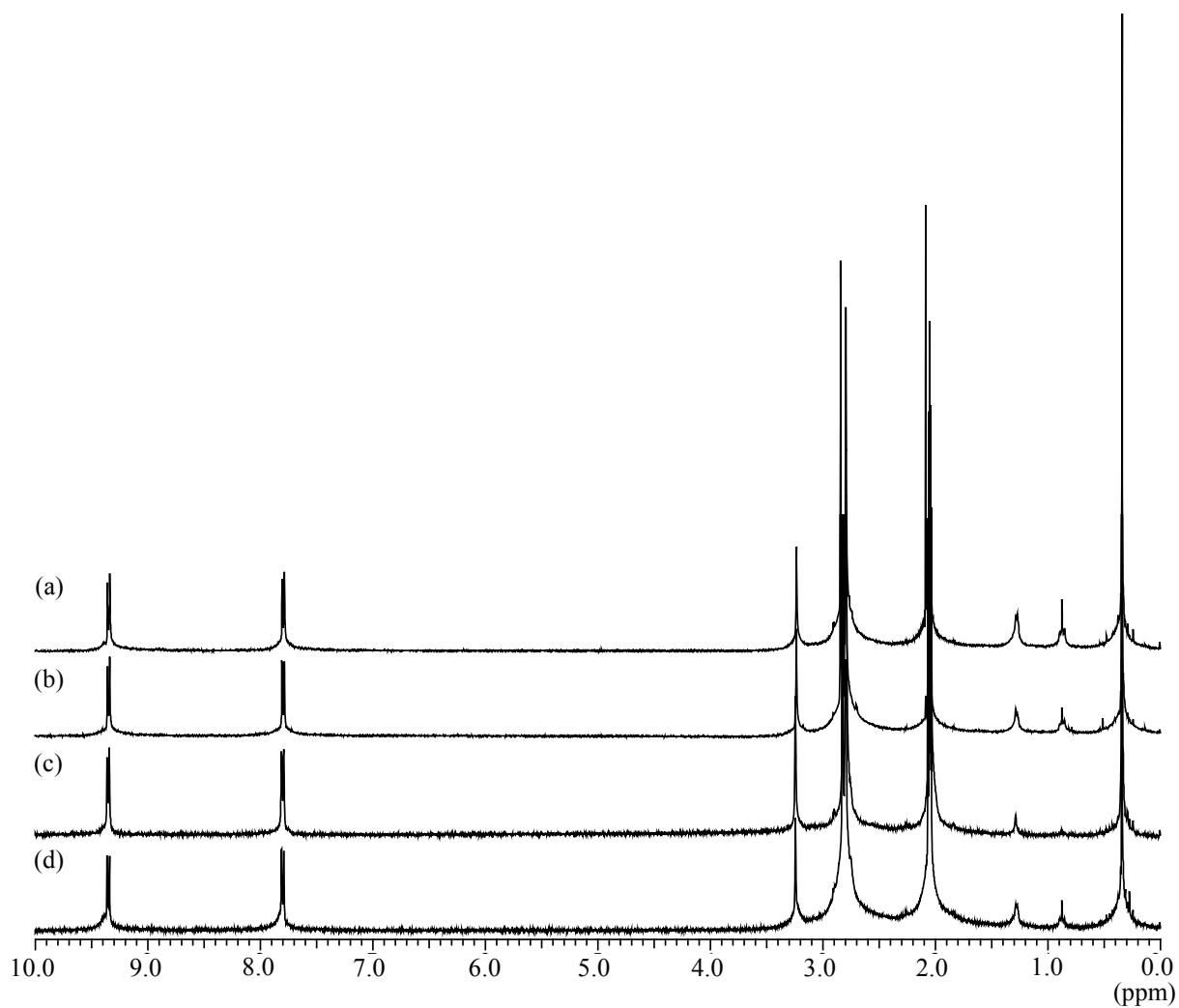
	$C_5H_{12}@$ [[ $(Me_4en)Pd(L)$ ] $_2(CF_3SO_3)_4$ ]	$C_6H_{14}@[(Me_4en)Pd(L)]_2(C$ $F_3SO_3)_4$	$C_7H_{16}@$ [[ $(Me_4en)Pd(L)$ ] $_2(CF_3SO_3)_4$ ]
Formula	$C_{49}H_{86}F_{12}N_8O_{14}Pd_2S_4Si_4$	$C_{50}H_{86}F_{12}N_8O_{14}Pd_2S_4Si_4$	$C_{51}H_{87}F_{12}N_8O_{14}Pd_2S_4Si_4$
$M_w$ [gmol <sup>-1</sup> ]	1692.66	1704.67	1713.65
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
$a$ [Å]	10.0638(2)	10.0994(2)	10.0959(2)
$b$ [Å]	13.5769(2)	13.5934(2)	13.5504(2)
$c$ [Å]	13.6782(2)	13.6673(3)	13.6869(2)
$\alpha$ [°]	96.8630(1)	96.2680(1)	95.8110(1)
$\beta$ [°]	98.9950(1)	99.3650(1)	98.5510(1)
$\gamma$ [°]	90.9640(1)	91.0070(1)	91.1020(1)
$V$ [Å <sup>3</sup> ]	1831.51(5)	1839.05(6)	1840.97(5)
$Z$	1	1	1
$\mu$ [mm <sup>-1</sup> ]	0.761	0.758	0.758
GOF on $F^2$	1.065	1.026	1.015
$R_1$ [ $I > 2\sigma(I)$ ] <sup>a</sup>	0.0578	0.0368	0.0770
$wR_2$ (all data) <sup>b</sup>	0.1186	0.0975	0.1716

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR_2 = (\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2)^{1/2}$$

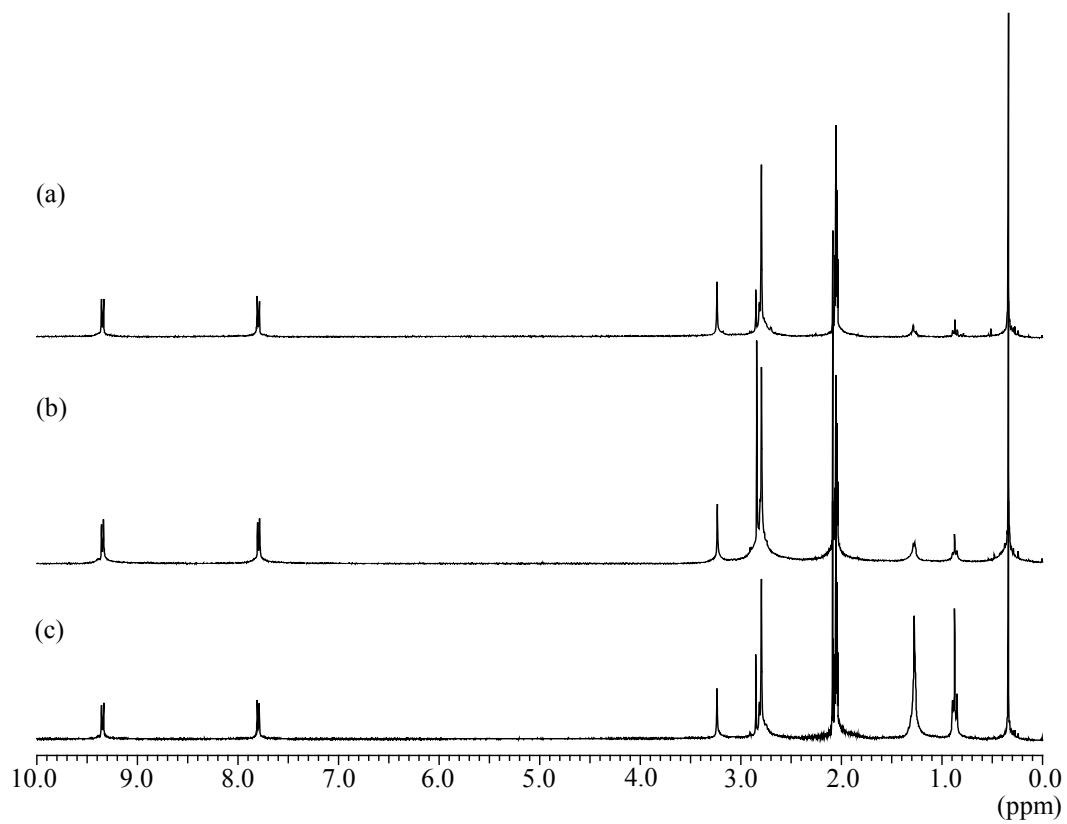
**Table S2** Relevant bond lengths [Å] and angles [°] for  $C_nH_{2n+2}@[(Me_4en)Pd(L)]_2(CF_3SO_3)_4$

	$C_5H_{12}@[(Me_4en)Pd(L)]_2(CF_3SO_3)_4$	$C_6H_{14}@[(Me_4en)Pd(L)]_2(CF_3SO_3)_4$	$C_7H_{16}@[(Me_4en)Pd(L)]_2(CF_3SO_3)_4$
Pd(1)···Pd(1) <sup>#</sup> [Å]	11.995(4)	12.062(2)	12.188(7)
O(1)···O(1) <sup>#</sup> [Å]	8.238(4)	8.158(4)	7.903(8)
Pd(1)···N(1) [Å]	2.039(3)	2.030(3)	2.032(6)
Pd(1)···N(2) <sup>#</sup> [Å]	2.023(3)	2.041(2)	2.032(6)
N(1)···Pd(1)···N(2) <sup>#</sup> [°]	87.3(1)	87.0(9)	86.9(2)
Pd(1)···N(3) [Å]	2.065(3)	2.065(3)	2.065(6)
Pd(1)···N(4) [Å]	2.069(3)	2.066(3)	2.072(6)
N(3)···Pd(1)···N(4) <sup>#</sup> [°]	86.3(1)	86.1(1)	86.1(2)
Pd(1)···X [Å]	3.048(3)	3.081(2)	3.082(6)
	3.404(4)	3.398(3)	3.405(6)

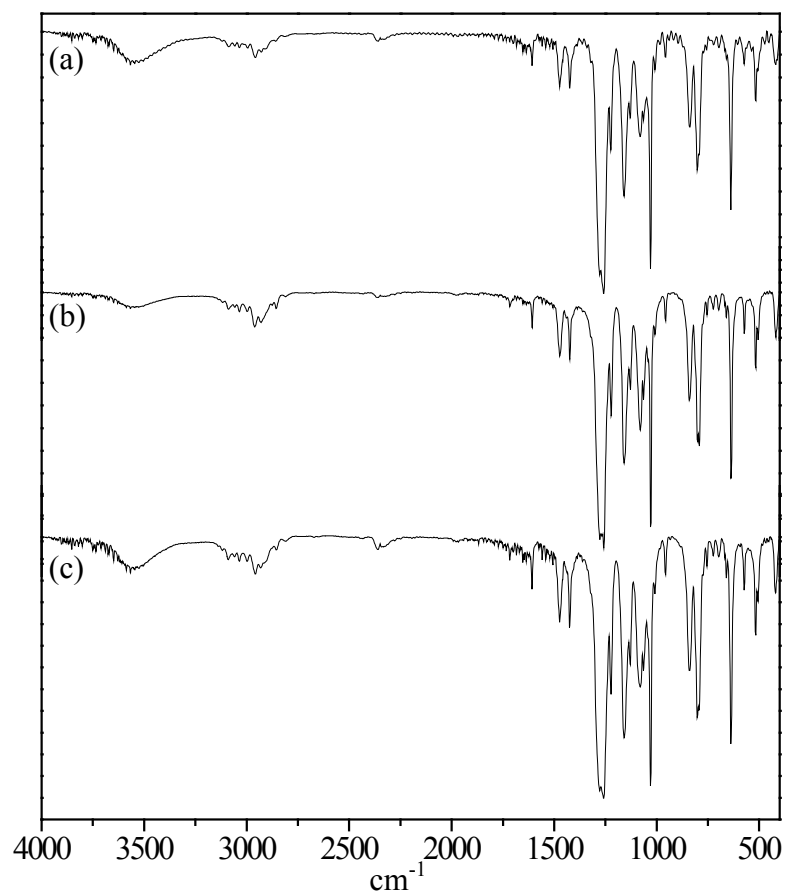
# -x+1,-y+1,-z+1



**Fig. S1** <sup>1</sup>H NMR spectra in acetone-*d*<sub>6</sub> of C<sub>6</sub>H<sub>14</sub>@[(Me<sub>4</sub>en)Pd(L)]<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>.  
C<sub>6</sub>H<sub>14</sub>@[(Me<sub>4</sub>en)Pd(L)]<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub> before (a) and after dryness in vacuo at 50 °C for 5 h (b),  
at 80 °C for 5h (c) and on exposure to *n*-hexane for 3 h (d).

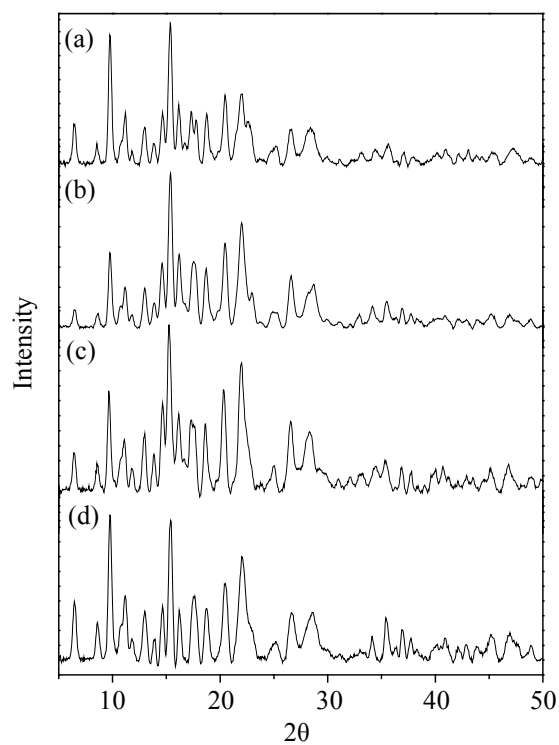


**Fig. S2**  $^1\text{H}$  NMR spectra in acetone- $d_6$  of  $\text{C}_n\text{H}_{2n+2}@[(\text{Me}_4\text{en})\text{Pd}(\text{L})]_2(\text{CF}_3\text{SO}_3)_4$  ( $n = 5$  (a), 6 (b), 7 (c)).

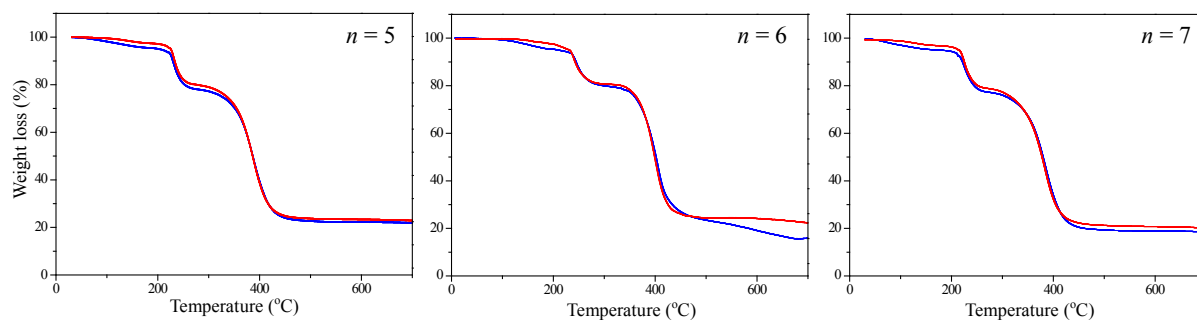


**Fig. S3** IR spectra of  $C_nH_{2n+2}@[(Me_4en)Pd(L)]_2(CF_3SO_3)_4$  ( $n = 5$  (a), 6 (b), 7 (c)).

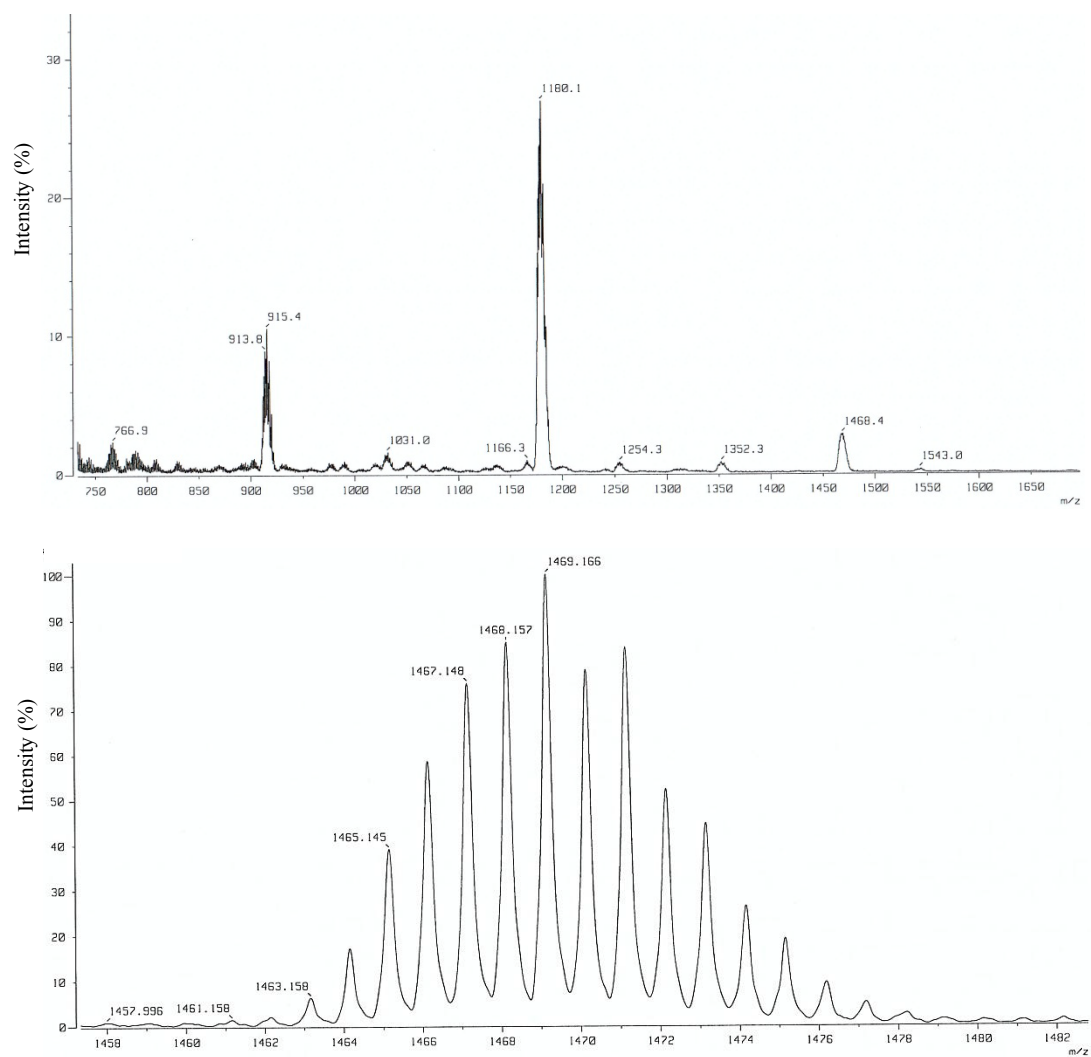




**Fig. S4** Powder XRD data of  $C_nH_{2n+2}@[(Me_4en)Pd(L)]_2(CF_3SO_3)_4$  ( $n = 5$  (a), 6 (b), 7 (c)) and guest-removed  $[(Me_4en)Pd(L)]_2(CF_3SO_3)_4$  (d).



**Fig. S5** TGA curves of  $C_nH_{2n+2}@[(Me_4en)Pd(L)]_2(CF_3SO_3)_4$  (blue) and  $[(Me_4en)Pd(L)]_2(CF_3SO_3)_4$  (red).



**Fig. S6** FAB-mass data of  $C_6H_{14}@[(Me_4en)Pd(L)]_2(CF_3SO_3)_4$ .