

## Electronic Supplementary Information

# Cavity size effect on host-guest property of tiara-like structural $M_n(SR)_{2n}$ nanoclusters probed by NMR spectroscopy

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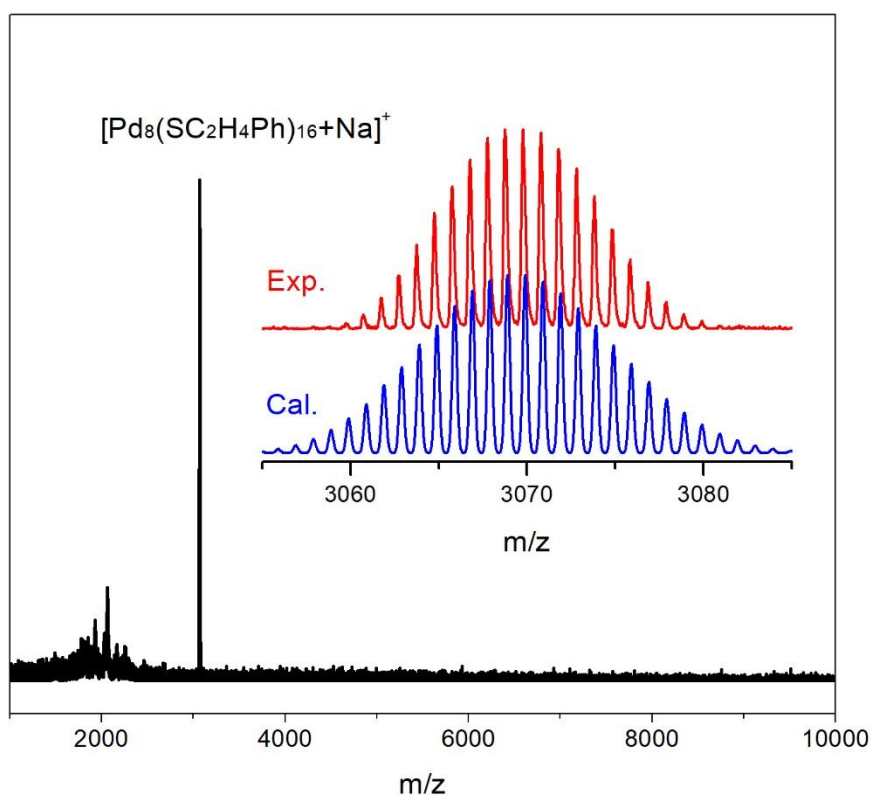
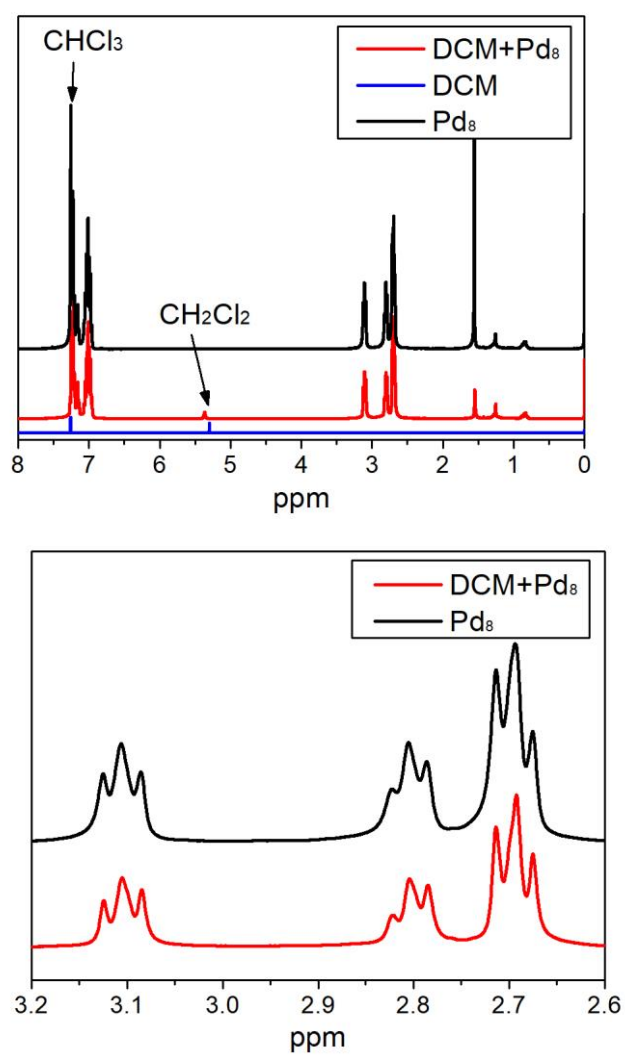


Figure S1 the MALDI-TOF-MS spectrum of  $Pd_8(PET)_{16}$ , inset is the comparison of the experimental (Red) and calculated (Blue) isotope patterns.



**Figure S2** The <sup>1</sup>H NMR spectra of pure Pd<sub>8</sub>(PET)<sub>16</sub> (the black line), the mixture of CH<sub>2</sub>Cl<sub>2</sub>+Pd<sub>8</sub>(PET)<sub>16</sub> (the red line) and pure CH<sub>2</sub>Cl<sub>2</sub> (the blue line). (Room temperature, CDCl<sub>3</sub> as solvent)

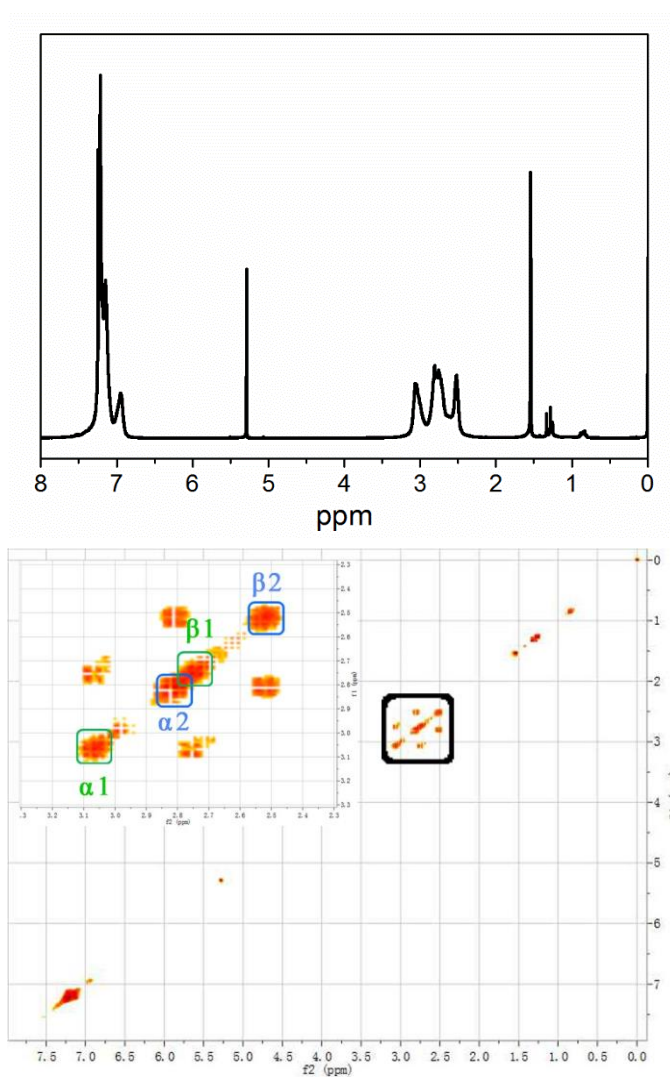


Figure S3  $^1\text{H}$  NMR and COSY spectra of  $\text{Pd}_5(\text{PET})_{10}$ .  $\alpha 1$  and  $\alpha 2$  are two positions of the methylene attached to the S atom,  $\beta 1$  and  $\beta 2$  are two positions of the methylene not attached to the S atom. (Room temperature,  $\text{CDCl}_3$  as solvent)

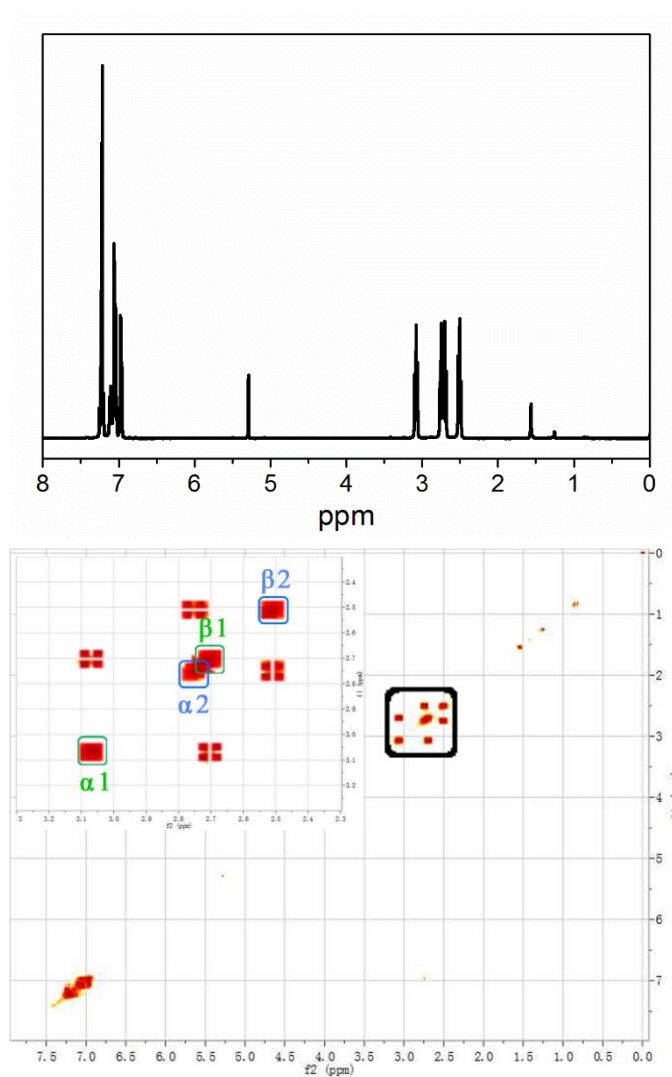


Figure S4  $^1\text{H}$  NMR and COSY spectra of  $\text{Pd}_6(\text{PET})_{12}$ .  $\alpha 1$  and  $\alpha 2$  are two positions of the methylene attached to the S atom,  $\beta 1$  and  $\beta 2$  are two positions of the methylene not attached to the S atom. (Room temperature,  $\text{CDCl}_3$  as solvent)

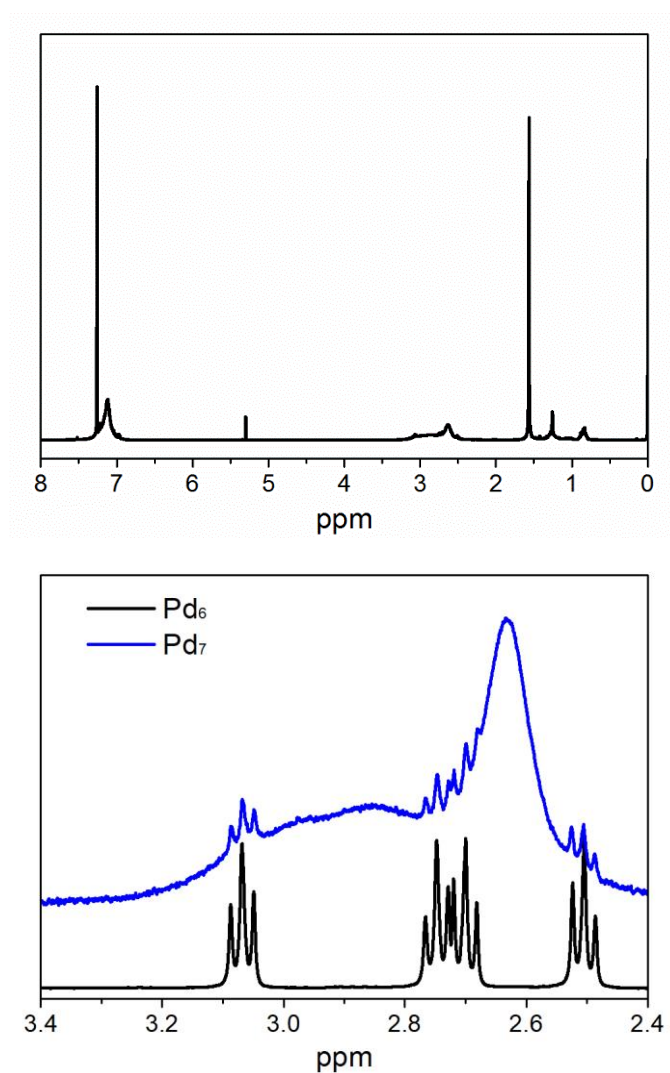


Figure S5 <sup>1</sup>H NMR spectrum of Pd<sub>7</sub>(PET)<sub>14</sub> and the comparison of the <sup>1</sup>H NMR spectra of Pd<sub>7</sub>(PET)<sub>14</sub> and Pd<sub>6</sub>(PET)<sub>12</sub> in the aliphatic region. (Room temperature, CDCl<sub>3</sub> as solvent) The sample were purified by TLC for five times, but it is difficult to remove the Pd<sub>6</sub>(PET)<sub>12</sub> impurity at all. The peaks of Pd<sub>6</sub>(PET)<sub>12</sub> impurity are obvious in <sup>1</sup>H NMR, but very weak peak is found in the MALDI-TOF-MS.

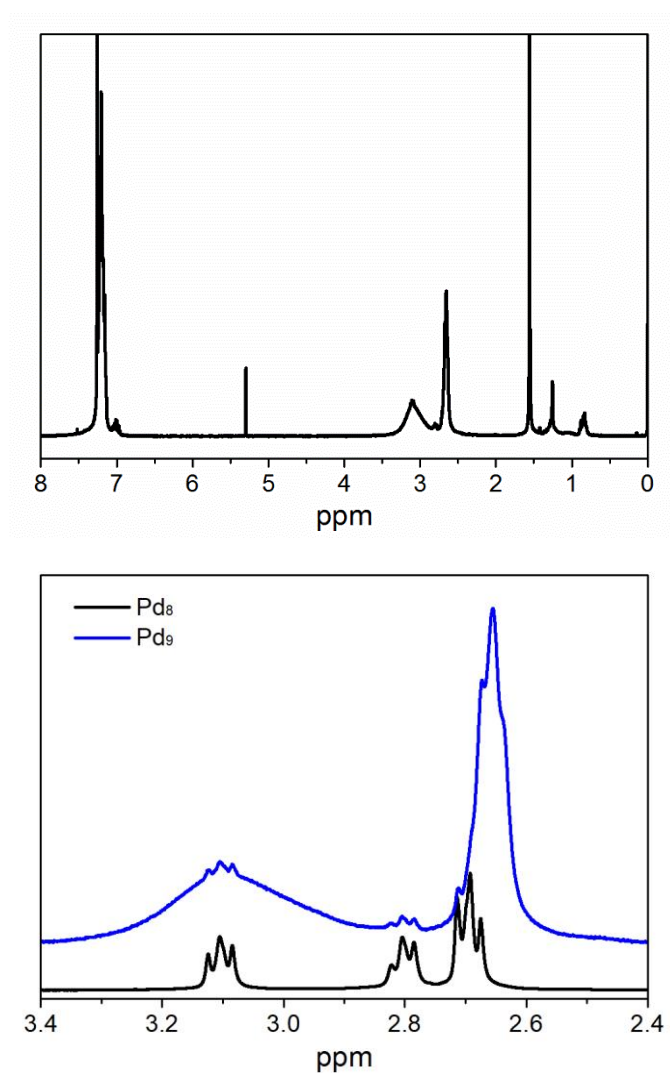


Figure S6 <sup>1</sup>H NMR spectrum of Pd<sub>9</sub>(PET)<sub>18</sub> and the comparison of the <sup>1</sup>H NMR spectra of Pd<sub>9</sub>(PET)<sub>18</sub> and Pd<sub>8</sub>(PET)<sub>16</sub> in the aliphatic region. (Room temperature, CDCl<sub>3</sub> as solvent) The sample is purified by TLC for 5 times, there are still several weak peaks of Pd<sub>8</sub>(PET)<sub>16</sub> appeared in the <sup>1</sup>H NMR.

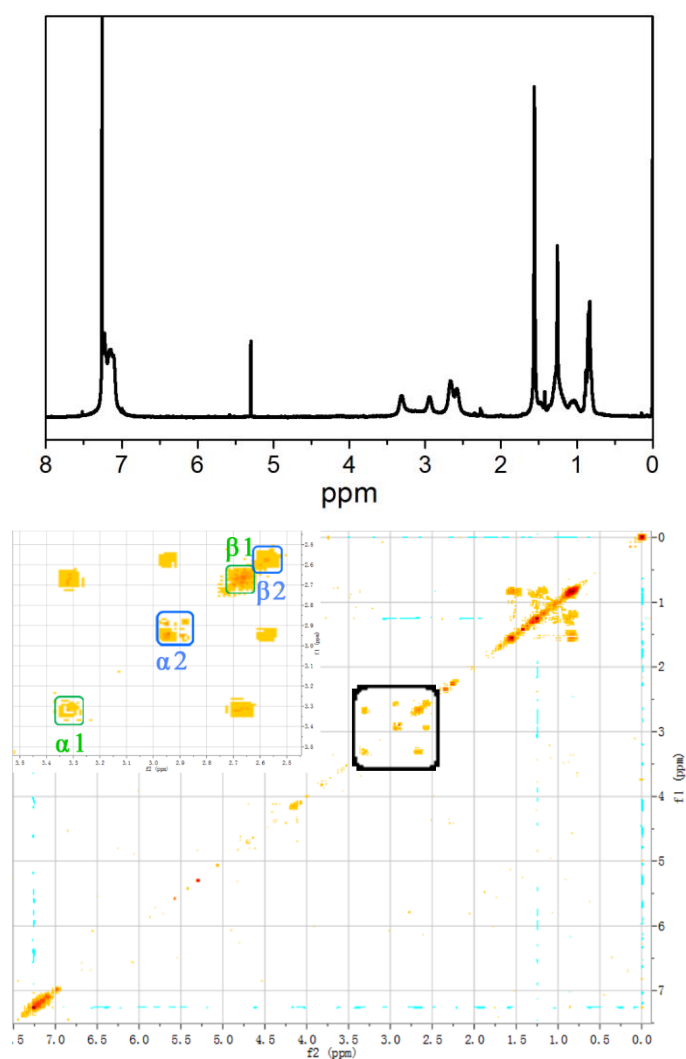


Figure S7  $^1\text{H}$  NMR and COSY spectra of  $\text{Pd}_{10}(\text{PET})_{20}$ .  $\alpha 1$  and  $\alpha 2$  are two positions of the methylene attached to the S atom,  $\beta 1$  and  $\beta 2$  are two positions of the methylene not attached to the S atom. (Room temperature,  $\text{CDCl}_3$  as solvent)

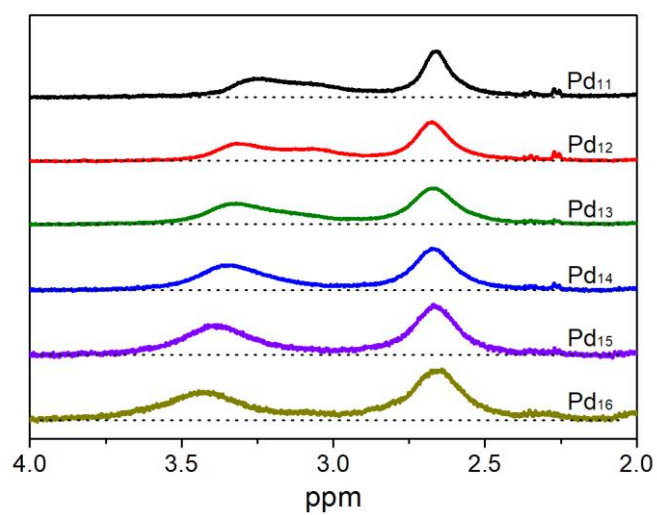
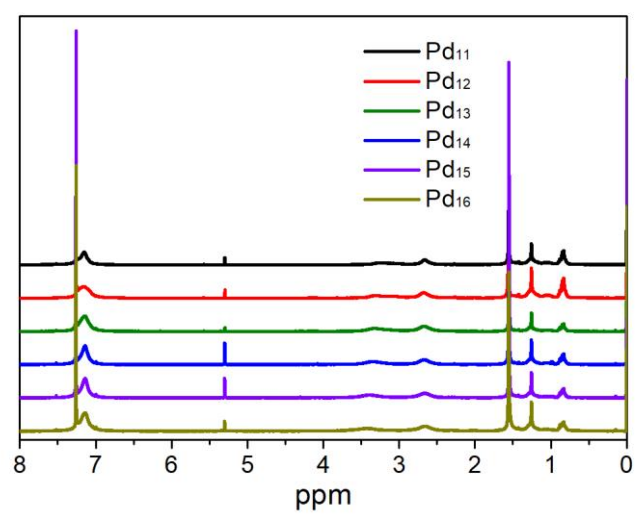


Figure S8  $^1\text{H}$  NMR spectra of  $\text{Pd}_n(\text{PET})_{2n}$  ( $11 \leq n \leq 16$ ) in the range of 0~8 and 2~4.