**Tailor-made Synthesis of Multilayered Trimetallocyclophanes via Transannula Interactions**

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**Abstract**

Synthesis and operation of a nano-demension 24 × 24 × 15 Å3 “left and right ball-joint-type host-guest system” via one π∙∙∙π interaction and three NH∙∙∙O=C hydrogen-bonds along with the combined helicity are described. The system consists of unprecedented conglomerate aggregates of two distinct helical metallacyclophanes, chiral isomer (*P*)-[Pd3X6(L1)2]@(*M*)-[Pd3X6(L1)(L2)] and its enantiomer (*M*)-[Pd3X6(L1)2]@(*P*)- [Pd3X6(L1)(L2**)**]are described. Successive reactions afford desirable four-layered metallacyclophanes via tailor-made procedure. Synthesis and operation of a nano-demension size multilayered metallacyclophane system via one π∙∙∙π interaction along with the combined helicity are described. A synthetic strategy of generation of new molecular species utilizing a provision of nature has been reported: nano-dimensional (23(2) × 21(1) × 16(1) Å3) hetero four-layered trimetalla-cyclophanes via the proof-of-concept experiments that utilize a suitable combination of π∙∙∙π interactions between the central aromatic rings, tailor-made short/long spacer tridentate donors, and the combined helicity are constructed. The unprecedented four-layered metallacyclophane system’s behavior offers a landmark in the development of new molecular system.

*****Scheme 1.*** Construction of hetero four-layered tripalladium(II)cyclophanes through consecutive, substitution, and direct reactions.

**LLA**

**LLE**

**LLA**

**LSA**

***40***

***41***

***42***

***43***

+ **2 LLE**

**2 LSA**

+ **2 LLA**

**2 LSA**

+ **3 LLA**

**1 LSA**

**≡** [**Pd2+**]**(NO3)2**

**2 LLE**

**2 LLA**

**3 LLA**

**LSA**

**≡** [**PdCl2**]

**AgNO3**

**AgCl**

**≡**

**≡**

**≡**

 **LSA**

 **LLE**

 **LLA****