Supporting Information

Effect of lanthanide contraction on crystal structures of lanthanide coordination polymers with 2,5-piperazinedione-1,4-diacetic acid

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Materials and methods. All reagents were of commercial origin and were used as received. The hydrothermal syntheses were carried out in polytetrafluoroethylene lined stainless steel containers under autogenous pressure. The C, H, and N microanalyses were carried out with a CE instruments EA 1110 elemental analyzer. The infrared spectrum was recorded on a Nicolet AVATAR FT-IR360 Spectrophotometer with pressed KBr pellets. TGA curve was prepared on a SDT Q600 Thermal Analyzer.

Synthesis of $[La(PODC)_{1.5}(H_2O)]\cdot 2H_2O$ (1). 0.217 g (0.5 mmol) $La(NO_3)_3\cdot 6H_2O$ and 0.115 g (0.5 mmol) 2,5-piperazinedione-1,4-diacetic acid were solved in 10 mL of water. When the pH value of the mixture was adjusted to 4.0~6.0, the cloudy solution was found and subsequently sealed to 18 mL Teflon-lined Parr, heated to 150 ^{o}C for 3 days, then cooled to room temperature at a rate of 2 $^{o}C\cdot h^{-1}$. Needle colourless crystals of **1** were obtained in about 48% yield (based on $La(NO_3)_3$). Anal. Calcd (found) for **1**, $C_{12}H_{18}O_{12}N_3La$ (%): C, 26.90 (27.11); H, 3.36 (3.19); N, 7.84 (7.67). IR (KBr, cm^{-1}): 490(w), 711(m), 956(m), 1197(m), 1283(m), 1341(w), 1392(s), 1427(s), 1481(w), 1590(s), 1563(s), 2848(w), 2918(w), 2996(w).

Synthesis of $[Pr(PODC)_{1.5}(H_2O)]\cdot H_2O$ (2) This compound was prepared using the same procedure as described above for the synthesis of its La(III) cognate, but using 0.218 g (0.5 mmol) $Pr(NO_3)_3\cdot 6H_2O$ in place of $La(NO_3)_3\cdot 6H_2O$. The product was obtained as block-shaped green crystals in about 51% yield (based on $Pr(NO_3)_3$). Anal.

Calcd (found) for **2**, $C_{12}H_{16}O_{11}N_3Pr$ (%): C, 27.74 (27.33); H, 3.08 (2.87); N, 8.09 (7.96). IR (KBr, cm^{-1}): 556(w), 606(w), 718(m), 801(w), 878(w), 960(m), 1042(w), 1191(w), 1290(m), 1337(m), 1381(m), 1403(m), 1501(m), 1633(s), 1680(w), 2966(w), 3032(w).

Synthesis of $[Sm(PODC)_{1.5}(H_2O)]\cdot 4H_2O$ (3) This compound was prepared using the same procedure as described above for the synthesis of its La(III) cognate, but using 0.222 g (0.5 mmol) $Sm(NO_3)_3\cdot 6H_2O$ in place of $La(NO_3)_3\cdot 6H_2O$. The product was obtained as block-shaped light-yellow crystals in about 62% yield (based on $Sm(NO_3)_3$). Anal. Calcd (found) for **3**, $C_{12}H_{22}O_{14}N_3Sm$ (%): C, 24.71 (24.78); H, 3.78 (3.64); N, 7.20 (7.17). IR (KBr, cm^{-1}): 501(w), 719(w), 882(m), 1050(s), 1090(m), 1201(m), 1298(m), 1396(m), 1435(m), 1568(w), 1644(s), 2928(w), 2975(w).

Synthesis of $[Ho(PODC)_{1.5}(H_2O)]\cdot 2H_2O$ (4) This compound was prepared using the same procedure as described above for the synthesis of its La(III) cognate, but using 0.230 g (0.5 mmol) $Ho(NO_3)_3\cdot 6H_2O$ in place of $La(NO_3)_3\cdot 6H_2O$. The product was obtained as block-shaped yellow crystals in about 56% yield (based on $Ho(NO_3)_3$). Anal. Calcd (found) for **4**, $C_{12}H_{18}O_{12}N_3Ho$ (%): C, 25.65 (26.26); H, 3.23 (3.18); N, 7.48 (7.45). IR (KBr, cm^{-1}): 517(w), 575(w), 699(m), 727(w), 960(m), 1190(m), 1291(s), 1341(s), 1396(m), 1485(m), 1583(w), 1645(s), 2945(w), 2984(w).

Synthesis of $[Er(PODC)_{1.5}(H_2O)]\cdot 2H_2O$ (5) This compound was prepared using the same procedure as described above for the synthesis of its La(III) cognate, but using 0.231 g (0.5 mmol) $Er(NO_3)_3\cdot 6H_2O$ in place of $La(NO_3)_3\cdot 6H_2O$. The product was obtained as block-shaped pink crystals in about 46% yield (based on $Er(NO_3)_3$). Anal. Calcd (found) for **5**, $C_{12}H_{18}O_{12}N_3Er$ (%): C, 25.55 (25.49); H, 3.19 (3.23); N, 7.45 (7.35). IR (KBr, cm^{-1}): 519(w), 574(w), 695(m), 726(w), 800(w), 959(w), 1154(m), 1189(m), 1286(m), 1341(m), 1380(s), 1450(w), 1485(w), 1648(s), 2927(w), 2983(w).

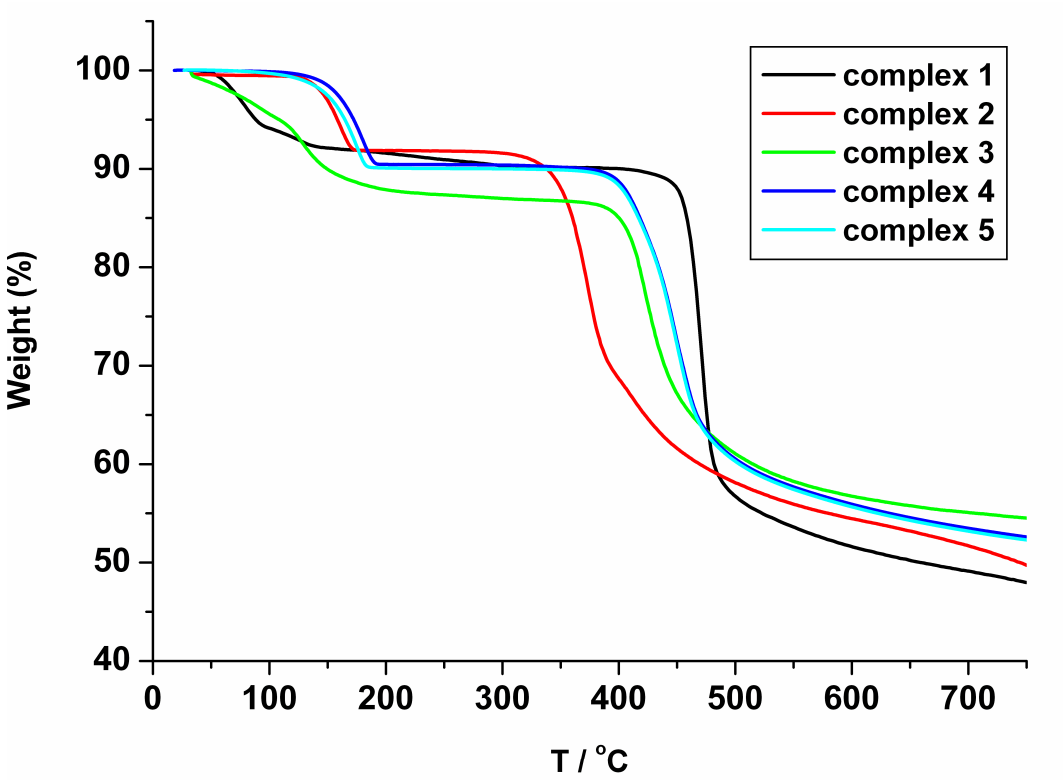

Fig.S1 TGA curves for complexes **1-5** over the temperature range of 25–800 °C.

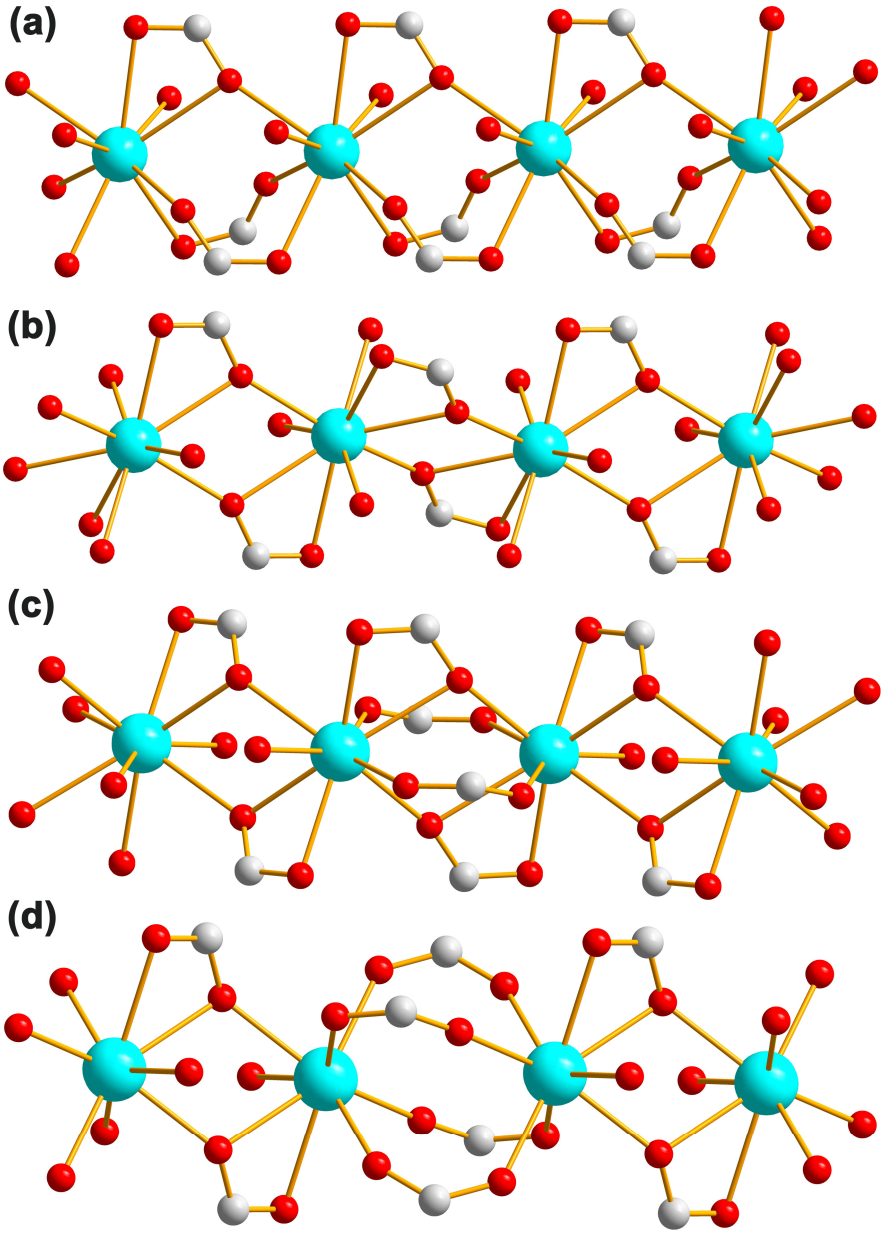

Fig.S2 Ball and stick view of (a) the $\{La\text{-}(COO)_3\}_n$ chain in **1**; (b) $\{Pr\text{-}(COO)_2\}_n$ chain in **2**; (c) $\{Sm\text{-}(COO)_4\text{-}Sm\text{-}(COO)_2\}_n$ chain in **3** and (d) $\{Ln\text{-}(COO)_4\text{-}Ln(COO)_2\}_n$ (Ln = Ho, for **4** and Ln = Er for **5**) in **4** and **5**.