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Supporting Information for:

# Lanthanide Salen "Square Prism" and Wrapped Exolanthanide Salen "Double Decker"

## Yu-Bo Shu and Wei-Sheng Liu\*

Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization of Gansu Province and State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, China. E-mail: liuws@lzu.edu.cn

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#### **Experimental details**

All reagents were commercially available and were used without further purification. The H<sub>2</sub>L ligand was synthesized by reaction of ethylenediamine (0.1202 g, 2 mmol) with 4-(diethylamino)salicyladehyde (0.773 g, 4 mmol) in ethanol (30 mL) under reflux for 6 hours. Infrared spectra were recorded on a Nicolet FT-170SX instrument using KBr discs in the 400–4000 cm<sup>-1</sup> region. Powder X-Ray diffraction (PXRD) patterns were collected with a PANalytical X'Pert Pro Diffractometer operated at 40 kV and 40 mA with Cu *Ka* radiation (step size: 0.0167113°, step time: 10.16 s). Elemental analyses were performed using an Elementar Analysenesysteme GmbH varioEL cube instrument. Inductively coupled plasma-atomic emission spectroscopies (ICP-AES) analyses were carried out on an IRIS Advantage ER/S spectrophotometer. Thermal analyses were recorded on a Shimadzu UV-2550 UV-Visible Spectrophotometer at room temperature. Steady-state excitation and emission spectra were recorded on FLS920 of Edinburgh Instrument at room temperature.











Figure S4 Coordination geometries of Er(III) in 1 (a) and 2 (b).



**Figure S5** Intermolecular  $\pi$ - $\pi$  stacking (3.699 and 3.726 Å), van der Waals repulsion (3.528 Å), and van der Waals attraction (5.158 Å) in **1**.



Figure S6 The 1-D array of "double decker" cations in 2.

