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large alkali-metal templated Na_2Co_{24} and KCo_{24} Clusters.[10] Although we (amongst other groups) have successfully used different calix[4]arenes and organic linkers as co-ligands to prepare a large number of high-nuclearity transition metal compounds, there is only one Ho_{12} metallawheel with the number of lanthanide ions higher than 10 for calix[4]arene-based lanthanide compounds so far. As we know, the recent increasing interest in lanthanide chemistry is focused on the synthesis of polynuclear lanthanide clusters originating from the following two reasons: distinct magnetic behaviors[11] and interesting luminescent properties.[12] Especially for the complexes of Nd^{III}, Er^{III} and Yb^{III}, the near-infrared (NIR) emission around 900-1600 nm, can apply in optical amplification, telecommunication networks, bioassays and luminescent probes.[13] As an extension of our research work on calixarene-phosphate/phosphonate system, we have tried to introduce lanthanide metal salts to prepare high-nuclearity clusters. Fortunately, we have successfully prepared three high-nuclearity neodymium clusters, namely, $[Nd_{10}(BSC4A)_4(MePO_3)_4(Cl)_2(OH)_4(H_2O)_2(DMF)_8(MeOH)_2]\cdot 3DMF\cdot 7CH_3OH$ (**1**), $[Nd_{11}(BSC4A)_3(PhPO_3)_6(Cl)_2(OH)_6(DMF)_{12}]Cl\cdot 7DMF\cdot 2CH_3OH$ (**2**) and $[Nd_{19}(BSC4A)_5(PhPO_3)_5(CO_3)_6(HCOO)_7(OH)_8(H_2O)_7(DMF)_{12}]\cdot 11DMF\cdot 14CH_3OH$ (**3**). Herein, the syntheses, structures, luminescent and magnetic properties of compounds **1-3** are presented and discussed.

Experimental Section

General Procedures. The H_4BSC4A ligand was prepared as previously reported,[14] while other starting chemicals were commercially available and used as received without further purification. Elemental analysis was performed with a German Elementary Varil EL III analyzer. Infrared (IR) spectra were recorded in the range 4000–400 cm^{-1} with a Magna 750 FT-IR spectrometer using KBr pellets. The NIR photoluminescent measurement was measured at room temperature with an Edinburgh FL-FS90 TCSPC system. Variable temperature magnetic susceptibility measurements were measured on a Quantum Design PPMS-9T and MPMS-XL magnetometer in the range of 2−300 K.

Preparation of compound 1

A mixture of H_4BSC4A (43 mg, 0.05 mmol), $NdCl_3\cdot 6H_2O$ (100 mg, 0.28 mmol), $MePO_3H_2$ (5 mg, 0.05 mmol) in a mixed solvent of 2 mL CH_3OH and 2 mL DMF was sealed in a 25 mL Teflon-lined bomb at 120 °C for 72 h. With a cooling rate of 4 °C h^{-1} to room temperature, colorless block-shaped crystals of **1** in 52% yield based on H_4BSC4A ligand were isolated by filtration, washed with DMF/CH_3OH (1:1, v/v) and air dried. Elemental analysis calcd (%) for **1**: C, 38.61; H, 4.80; N, 2.37; found: C, 38.07; H, 4.61; N, 2.25. IR (KBr disk, v / cm^{-1}): 3408 (m), 2959 (s), 2871 (s), 1660 (s), 1606 (s), 1495 (s), 1482 (s), 1389 (w), 1362 (m), 1268 (s), 1216 (w), 1159 (m), 1133 (s), 1082 (s), 992 (m), 908 (w), 843 (w), 791 (s), 752 (m), 733 (w), 674 (w), 646 (m), 603 (m), 554 (s), 482(w).

Preparation of compound 2

A mixture of H_4BSC4A (85 mg, 0.1 mmol), $NdCl_3\cdot 6H_2O$ (150 mg, 0.4 mmol), $PhPO_3H_2$ (32 mg, 0.2 mmol) in a mixed solvent of 5 mL CH_3OH and 5 mL DMF was sealed in a 25 mL Teflon-lined bomb at 120 °C for 72 h. With a cooling rate of 4 °C h^{-1} to room temperature, colorless block-shaped crystals of **2** in 48% yield based on H_4BSC4A ligand were isolated by filtration, washed with DMF / CH_3OH (1:1, v / v) and air dried. Elemental analysis calcd (%) for **2**: C, 38.43; H, 4.64; N, 3.96; found: C, 39.01; H, 4.63; N, 3.88. IR (KBr disk, v / cm^{-1}): 3410 (m), 2960 (s), 2871 (s), 1660 (s), 1606 (s), 1495 (s), 1482 (s), 1389 (w), 1362 (m), 1268 (s), 1216 (w), 1159 (m), 1133 (s), 1082 (s), 992 (m), 908 (w), 843 (w), 791 (s), 753 (m), 733 (w), 674 (w), 646 (m), 603 (m), 554 (s), 482(w).

Preparation of compound 3

A mixture of H_4BSC4A (85 mg, 0.1 mmol), $NdCl_3\cdot 6H_2O$ (150 mg, 0.4 mmol), $PhPO_3H_2$ (16 mg, 0.1 mmol) in a mixed solvent of 5 mL CH_3OH and 5 mL DMF was sealed in a 25 mL Teflon-lined bomb at 120 °C for 72 h, then cooled slowly at 4 °C h^{-1} to room temperature. Slow concentration of the filtrate at room temperature for several days and then colorless block-shaped crystals of **3** in 45% yield based on H_4BSC4A ligand were isolated by filtration, washed with DMF/CH_3OH (1:1, v / v) and air dried. Elemental analysis calcd (%) for **3**: C, 36.21; H, 4.58; N, 2.98; found: C, 35.89; H, 4.43; N, 2.82. IR (KBr disk, v / cm^{-1}): 3435 (m), 2958 (s), 2871 (s), 1660 (s), 1606 (s), 1495 (s), 1479 (s), 1440 (s), 1394 (s), 1360 (m), 1267 (s), 1219 (w), 1134 (s), 1080 (s), 1027 (w), 979 (m), 905 (w), 744 (m), 856 (w), 836 (m), 796 (m), 756 (m), 735 (w), 677 (w), 640 (m), 602 (m), 554 (s), 522 (m), 491 (w), 462(w).

Single-Crystal X-ray Diffraction

Crystal data for compounds **1-3** were performed on a SuperNova diffractometer equipped with a copper micro-focus X-ray sources Cu-Kα (λ = 1.5406 Å) and an Atlas CCD detector at 100 K. Data were corrected for absorption using the *CrystalClear* program.[15] Structure solution by direct methods and full-matrix least-squares refinement on F^2 were solved by using *SHELXTL*-97 program package.[16] All the non-hydrogen atoms were refined anisotropically except several badly disordered carbon atoms of *tert*-butyl groups. Organic hydrogen atoms of the ligands were placed in calculated positions and refined isotropically with fixed thermal factors. Because of the weak crystal diffractions, disorder of the *tert*-butyl groups and some highly disordered MeOH and DMF molecules of crystallization in void spaces of the compounds, the crystal structures were treated by the "SQUEEZE" method, a part of the PLATON package of crystallographic software, which had dramatically improved the agreement indices.[17] Moreover, the aforementioned disorder solvent molecules were directly added into the molecular formulas. Crystallographic Data and Structure Refinement for compounds **1-3** were summarized in Table S1 in the ESI. CCDC-1445821 (**1**), CCDC-1445822 (**2**) and CCDC-1445823 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/conts/retrieving.html.

Results and Discussion

Synthesis and Structures

Hydro(solvo)thermal techniques, which may promote some interest inorganic and organic ligands generated *in situ*, have been employed to prepare high-nuclearity coordination compounds in recent years. In addition, both H_4BSC4A and phosphonate ligands with several available oxygen atoms have been proved to be excellent multidentate ligands to construct polymetallic compounds due to their various anionic forms and rich coordination fashions. Considering the abovementioned two aspects, we use H_4BSC4A and phosphonate ligands as co-ligands to react with neodymium chloride at 120 °C in a mixed DMF and CH_3OH solvent, which has resulted in three high-nuclearity coordination compounds with different architectures ranging from an oval-shaped Nd_{10} cluster (**1**), to a rugby-like Nd_{11} nanocage (**2**), to a large irregular Nd_{19} cluster (**3**). As we expect, the H_4BSC4A and phosphonate ligands in all three structures use their donor oxygen atoms to coordinate neodymium ions and show four and three kinds of coordination modes, respectively. In addition, the extended structure of compounds **1**-**3** are assembled by the stacking of Nd_{10}, Nd_{11} and Nd_{19} entities, respectively, which further construct into skewed bilayer array *via* weak interactions such as van der Waals, $\pi\cdots\pi$ and hydrogen-bonding interactions (Figure S1-S3, in the ESI). It should be noted that DMF played an important role in the syntheses of Nd_{19} cluster, because it serves as the source of $HCOO^-$ and CO_3^{2-} anions. Specifically, $HCOO^-$ anions could be generated through the decarbonylation of DMF under the solvothermal conditions. Furthermore, with the aid of water molecules, partial $HCOO^-$ anions would be slowly oxidized to CO_3^{2-} anions at the high temperatures under basic conditions.[18] Certainly, another source of CO_3^{2-} anion may be the atmospheric CO_2 due to the slow concentration exposed directly to air.[19]

Crystal Structure of 1

Single-crystal X-ray analysis reveals that compound **1** crystallizes in the monoclinic system with space group $P2_1$/n. Compound **1** contains an oval-shaped cluster core involving 10 Nd^{III} ions constructed from four BSC4A^{4-} ligands, four $MePO_3^{2-}$ ligands as well as other bridging anions (Figure 1a), which lies about an inversion center. Each BSC4A^{4-} ligand takes pinched cone conformation and bridges three Nd^{III} ions to form a Nd_3-BSC4A subunit, where the ligand acts as a tetradentate chelating ligand ions through a phenoxo oxygen atom and a sulfonyl oxygen atom for one Nd^{III} ion through four low-rim phenoxo oxygen atoms, and also acts as a bisbidentate chelating ligand for other two Nd^{III} respectively (Figure 1b). With a closer inspection, the latter two Nd^{III} ions are shared by the neighboring BSC4A^{4-} ligands and nine-coordinated in triangular dodecahedron geometries calculated by SHAPE program[20] with the five remaining coordination sites to be bonded by one ligated DMF molecule and four oxygen atoms from two $MePO_3^{2-}$ ligands; while the former Nd^{III} ion is eight-coordinated in a biaugmented trigonal prism geometry and the four remaining coordination sites are occupied by one μ_3-OH, one DMF molecule and two oxygen atoms from two $MePO_3^{2-}$ ligands. Each nearby Nd_3-BSC4A subunit is linked together by sharing one Nd^{III} ion to constitute an large 16-membered wheel with -[Nd-O]- repeating unit, which is similar to the reported Ln_8 wheels linked by eight AcO^- anions. However, this oval-shaped Nd_{10} cluster core involves two kinds of linking components and is linked by four $MePO_3^{2-}$ ligands and two NdO_7Cl groups. All the $MePO_3^{2-}$ ligands in this structure coordinate to five Nd^{III} ions with $[5.2_{12}2_{34}2_{45}]$ coordination mode according to Harris notation.[21] Moreover, the longest and shortest diameters for the oval-shaped Nd_{10} cluster core were estimated to be 10.996 Å for Nd5···Nd5A and 8.713 Å for Nd2···Nd2A, respectively.

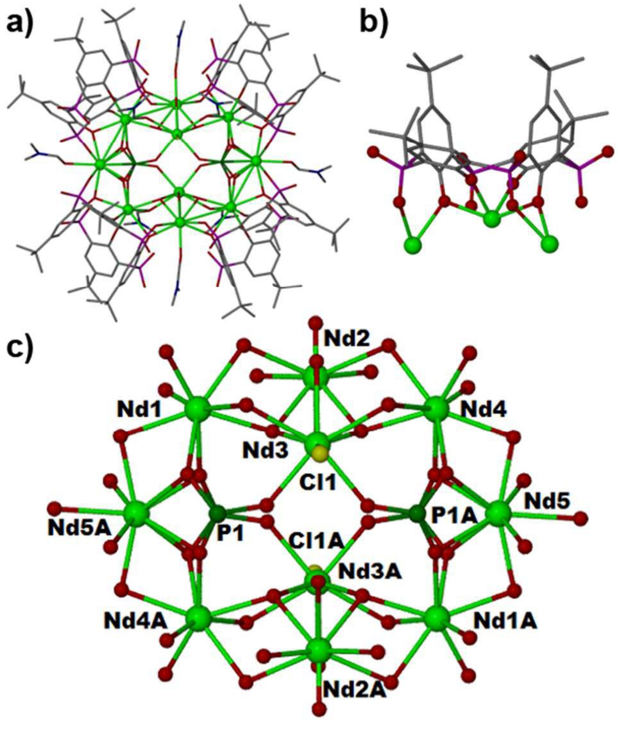


Figure 1. (a) Molecular structure of compound **1**. Hydrogen atoms and isolated solvent molecules are omitted for clarity. (b) Schematic diagram of the chelation mode of the BSC4A^{4-} ligands in **1**. (c) The oval-shaped Nd_{10} core within compound **1**. Symmetry code: (A) 2-x,1-y,1-z.

Crystal Structure of 2

Compound **2** crystallizes in an orthorhombic cell with the space group $P2_1$/n. The metallic core of **2**, capped by three BSC4A^{4-} ligands, six $PhPO_3^{2-}$ ligands and six μ_3-hydroxide anions, describes a novel rugby-like Nd_{11} core housing two μ_4-Cl anions (Figure 2a). Different to the BSC4A^{4-} ligands in compound **1**, three BSC4A^{4-} ligands in this structure are in cone conformation and coordinate to four Nd^{III} ions to generate Nd_4-BSC4A subunits. We just take one Nd_4-BSC4A subunit as an example to describe, because they are structurally analogous and show similarity in their coordination environments. We note that the BSC4A^{4-} ligand acts as a bidentate chelating ligand for one Nd^{III} ion through one phenoxo oxygen and one sulfonyl oxygen, a bistridentate chelating ligand for two Nd^{III} ions through two phenoxo oxygen atoms and a sulfonyl oxygen atom and also acts as monodentate chelating ligand for one Nd^{III} ion through a sulfonyl oxygen atom (Figure 2b). We note that the 11 crystallographically independent Nd^{III} ions have four kinds of coordination environments: (i) Nd1 and Nd11 are seven-coordinated in capped octahedron geometries with a μ_4-Cl, three oxygen atoms from three $PhPO_3^{2-}$ ligands, and three ligated DMF molecules; (ii) Nd2-Nd4 and Nd8-Nd10 are nine-coordinated and spherical capped square antiprism in geometry with a μ_4-Cl, two μ_3-OH, two oxygen atoms from two $PhPO_3^{2-}$ ligands, and one phenoxo oxygen atom and two sulfonyl oxygen atoms from two BSC4A^{4-} ligands; (iii) Nd6 is eight-coordinated in a square antiprism geometry with two μ_3-OH, two oxygen atoms from two $PhPO_3^{2-}$ ligands, two ligated DMF molecules, and two sulfonyl oxygen atoms from two BSC4A^{4-} ligands; (iv) Nd5 and Nd7 are nine-coordinated in spherical tricapped trigonal prism geometries with one phenoxo oxygen atom from BSC4A^{4-} ligands, and with the same to those in Nd5 for the eight remaining coordination sites. The nearby Nd$_4$-BSC4A subunits are connected by sharing one Nd^{III} ion and two PhPO$_3^{2-}$ ligands to form the body of the rugby, whose vertexes are further capped by two Nd^{III} ions (Nd1 and Nd11) respectively. Moreover, the height and diameter for the rugby-like Nd$_{11}$ core are estimated to be 9.677 Å (the Nd1$\cdots$Nd11 distance) and 8.656 Å, respectively.

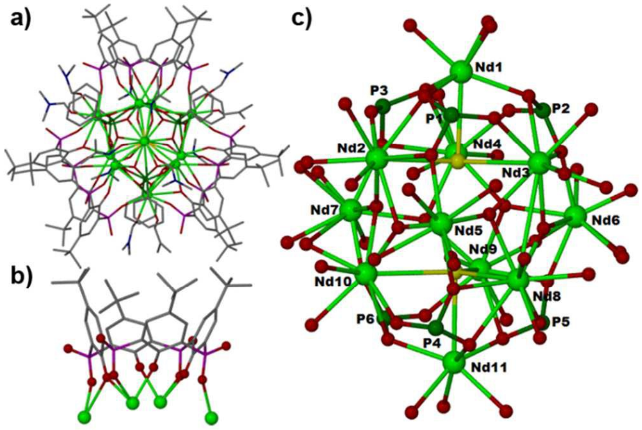


Figure 2. (a) Molecular structure of compound **2**. Hydrogen atoms and isolated solvent molecules are omitted for clarity. (b) Schematic diagram of the chelation mode of the BSC4A^{4-} ligands in **2**. (c) The rugby-like Nd$_{11}$ core within compound **2**.

Crystal Structure of 3

Compound **3** crystallizes in the triclinic system with space group *P*-1, and contains a large irregular cluster involving 19 Nd^{III} ions constructed from five BSC4A^{4-} ligands, five PhPO$_3^{2-}$ ligands and other bridging anions (Figures 3b and 3c). This Nd$_{19}$ cluster can be regarded as a larger Nd$_{16}$ cluster (Nd4-Nd19) attach to a smaller Nd$_3$ cluster (Nd1-Nd3). There are four pinched-conic Nd$_3$-BSC4A subunits (Figure 3a) in the former Nd$_{16}$ cluster, in which four BSC4A^{4-} ligands all act as tetradentate and bisbidentate chelating ligand. The coordination modes of the BSC4A^{4-} ligands are much different in **1** and **3** by comparison. In **1**, two coordinated sulfonyl oxygen atoms are from two neighbor sulfonyl groups, but in **3** they are from two opposite sulfonyl groups (Figure S4, in the ESI). Then, these four Nd$_3$-BSC4A subunits are further linked by five Nd^{III} ions, four PhPO$_3^{2-}$ ligands and other bridging anions (including OH$^-$, HCOO$^-$ and CO$_3^{2-}$ anions) to form the larger Nd$_{16}$ cluster. Different from the abovementioned BSC4A^{4-} ligands, the ligand in the latter Nd$_3$ cluster is in cone conformation and coordinates to two Nd^{III} ions (Nd1 and Nd2) through a sulfonyl oxygen atom and two phenoxo oxygen atoms to comprise one Nd$_2$-BSC4A subunit (Figure 3b). By sharing one neodymium ion (Nd3) through one PhPO$_3^{2-}$ ligands, two hydroxide anions and two HCOO$^-$ anions, this Nd$_2$-BSC4A subunit cluster is attached to the above Nd$_{16}$ cluster to make up an irregular Nd$_{19}$ cluster.

In **3**, these 19 crystallographically independent Nd^{III} ions are all coordinated by oxygen atoms and have four kinds of coordination modes. Specially, (1) Nd1, Nd8 and Nd14 are eight-coordinated in triangular dodecahedron geometries; (2) Nd2, Nd5, Nd12 and Nd19 are also eight-coordinated but in square antiprism geometries; (3) Nd3, Nd4, Nd9, Nd13 and Nd18 are nine-coordinated and in spherical capped square antiprism geometry; (4) Nd6, Nd7, Nd10, Nd11 and Nd15-Nd17 are also nine-coordinated but in muffin geometries. It should be noted that five PhPO$_3^{2-}$ ligands have three different binding modes: (i) one ligand coordinates in a [3.111] manner; (ii) one binds in a $[4.2_{12}2_{23}1_{4}]$ fashion; (iii) while the remaining three adopt the $[4.2_{12}2_{23}2_{34}]$ modes (Scheme 2). Except the X-ray crystal data, the abovementioned CO$_3^{2-}$ and HCOO$^-$ anions generated *in situ* have also been confirmed by IR analyses. Absorption peaks on 856 and 796 cm^{-1} can be separately indexed to face and out-face deformation vibration absorption of CO$_3^{2-}$ anions, while strong peak of 1440 cm^{-1} can be referred to asymmetric stretching vibration absorption of CO$_3^{2-}$.[22] In addition, the band around 640 and 1394 cm^{-1} can be referred to the δ_{O-H} and C=O vibration of HCOO$^-$, respectively.[23] Both of the CO$_3^{2-}$ and HCOO$^-$ anions take three kinds of coordination modes. For six CO$_3^{2-}$ anions, (i) one anion coordinates in a [6.222] manner; (ii) two adopt the $[5.2_{12}2_{34}2_{45}]$ modes; (iii) three binds in a $[6.2_{123}2_{34}2_{56}]$ fashion. For seven HCOO$^-$ anions, (i) one anion coordinate in a [2.11] manner; (iii) three adopt the [3.12] modes; (ii) three take the

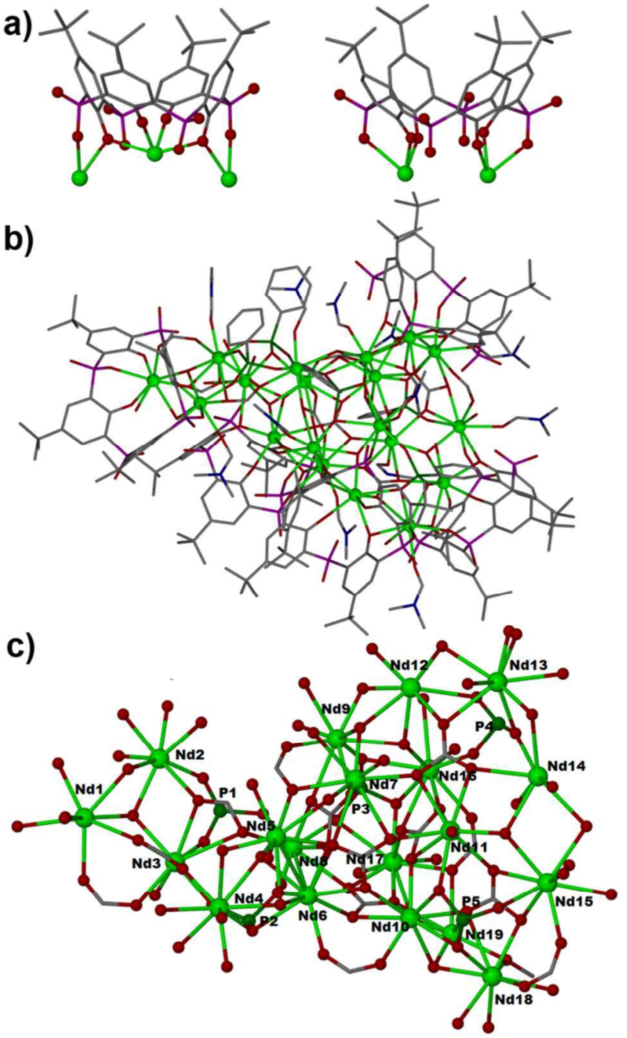
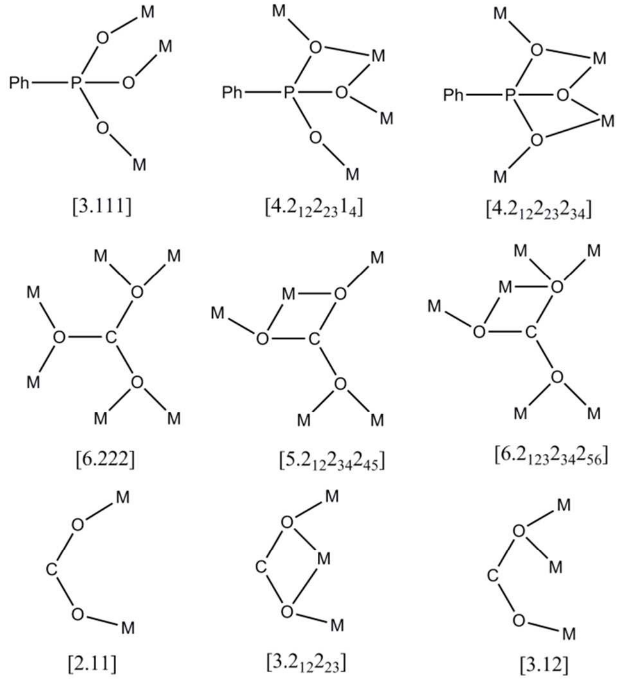


Figure 3. (a) Schematic diagrams of the chelation modes of the BSC4A^{4-} ligands in **3**. (b) Molecular structure of compound **3**. The hydrogen atoms and isolated solvent molecules are omitted for clarity. (c) The irregular Nd$_{19}$ core within compound **3**.

$[3.2_{12}2_{23}]$ fashions (Scheme 2). As we know, compounds **2** and **3** give the first two examples of lanthanide compounds with odd number of metal atoms based on H_4BSC4A, which are totally different from the reported compounds with even number of metal atoms containing 2, 4, 8 and 12 lanthanide centers.[24] Moreover, compound **3** also represents the highest-nuclearity lanthanide cluster based on H_4BSC4A ligand so far.



Scheme 2. Observed bonding modes of the phosphonate ligands, formate and carbonate anions.

NIR Luminescent Properties

The NIR spectra of compounds **1**-**3** in the solid state recorded at room temperature are shown in Figure 4. Upon excitation at 375 nm, the emission spectra of all title compounds exhibit three characteristic bands of Nd^{III} ion centered at λ = 889, 1063, and 1327 nm, which are assigned to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$, and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ transitions of Nd^{III} ion, respectively.[25] The most intense band is at 1063 nm which is similar to the other reported calixarene-supported neodymium compounds.[26]

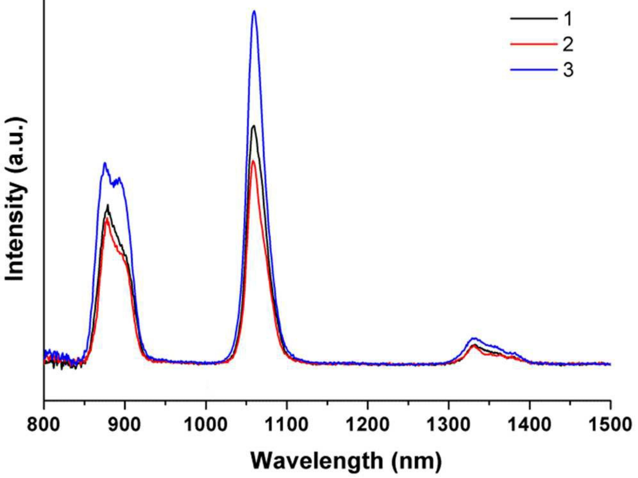


Figure 4. The NIR luminescent spectra of compounds **1**-**3** in the solid state at room temperature.

Magnetic Properties

The direct-current temperature dependence of magnetic susceptibilities are collected in the temperature range of 2 to 300 K on the polycrystalline sample of compounds **1**-**3** under an applied field of 1000 Oe (Figure 5). The $\chi_m T$ products at room temperature are 15.92, 16.92 and 28.59 cm^3 K mol^{-1} for **1**-**3**, which are close to the expected values of 10 (16.00 cm^3 K mol^{-1}), 11 (17.60 cm^3 K mol^{-1}) and 19 (30.40 cm^3 K mol^{-1}) uncoupled Nd^{III} ($^4I_{9/2}$, S = 3/2, L = 6, g = 8/11) ions respectively.[27] Upon the temperature cooling, the $\chi_m T$ curves for **1** and **2** decrease gradually from room temperature to around 100 K and then decreases more rapidly to 5.79 and 7.43 cm^3 K mol^{-1} K at 2 K. While the $\chi_m T$ curve for **3** decreases gradually until reaching the minimum value of 15.80 cm^3 K mol^{-1}at 6.5 K and then increases to 17.11 cm^3 K mol^{-1} K at 2 K. The increases of $\chi_m T$ value at low temperature are suggestive of ferrimagnetic or weak ferromagnetic interactions between the Nd^{III} spin carriers.

For all three compounds, the χ_m^{-1} vs. T data from 100 K to 300 K can be fitted by Curie–Weiss law ($1/\chi_m = T/C - \theta/C$) to give C = 16.05 cm^3 K mol^{-1} and θ = -50.82 K for **1**, C = 17.26 cm^3 K mol^{-1} and θ = -38.58 K for **2**, and C = 29.03 cm^3 K mol^{-1} and θ = -43.33 K = for **3** (Figure S5, in the ESI). The negative θ values together with the decrease of the $\chi_m T$ values upon reduction of the temperature may be ascribed to either antiferromagnetic interactions between the spin carriers or the progressive depopulation of the Stark sublevels of Nd^{III} ions, which is known to be derived from the splitting of the free ion ground state by the crystal field.

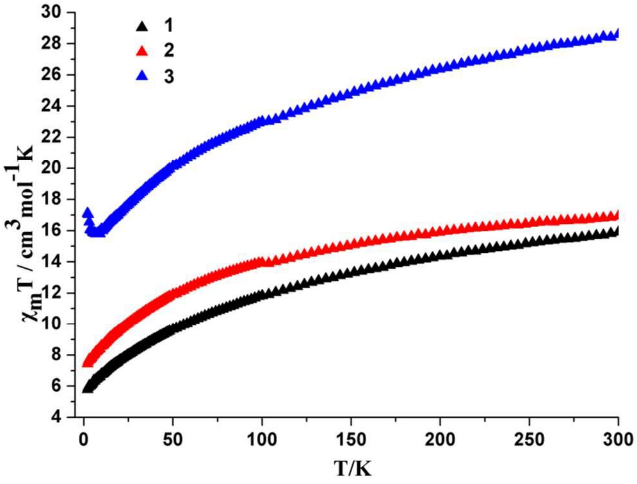


Figure 5. Temperature dependence of $\chi_m T$ for compounds **1**-**3** measured in a 1000 Oe field.

Conclusion

In conclusion, three high-nuclearity neodymium compounds have been prepared and characterized based on H_4BSC4A and phosphonate ligands in this paper. When $MePO_3H_2$ was utilized as co-ligand, an oval-shaped Nd_{10} cluster (**1**) was synthesized. Employment of different content of $PhPO_3H_2$ ligand in the same reaction condition has resulted in two different architectures: a rugby-like Nd_{11} nanocage (**2**) and a large irregular Nd_{19} cluster (**3**). To the best of our knowledge, compound **3** represents the highest nuclearity neodymium compound based on H_4BSC4A ligand so far. The photoluminescent analyses reveal that all three compounds show the characteristic emissions of Nd^{3+} ion at the NIR region. Magnetic measurements suggest the presence of dominant antiferromagnetic interactions (in 100-300 K) between the Nd^{III} centers and/or depopulation of the Stark sublevels of the Nd^{III} ions. Our future studies will focus on pure polynuclear lanthanide based on calixarene by using other multidentate oxygen-donor molecules as co-ligands.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [X-ray crystallographic data in CIF format, χ_m^{-1} vs. T data and other additional pictuires for compounds **1**-**3**]. See DOI: 10.1039/b000000x/

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Table of Contents Synopsis

Syntheses, structures, luminescent and magnetic properties of three high-nuclearity neodymium compounds based on mixed sulfonylcalix[4]arene-phosphonate ligands

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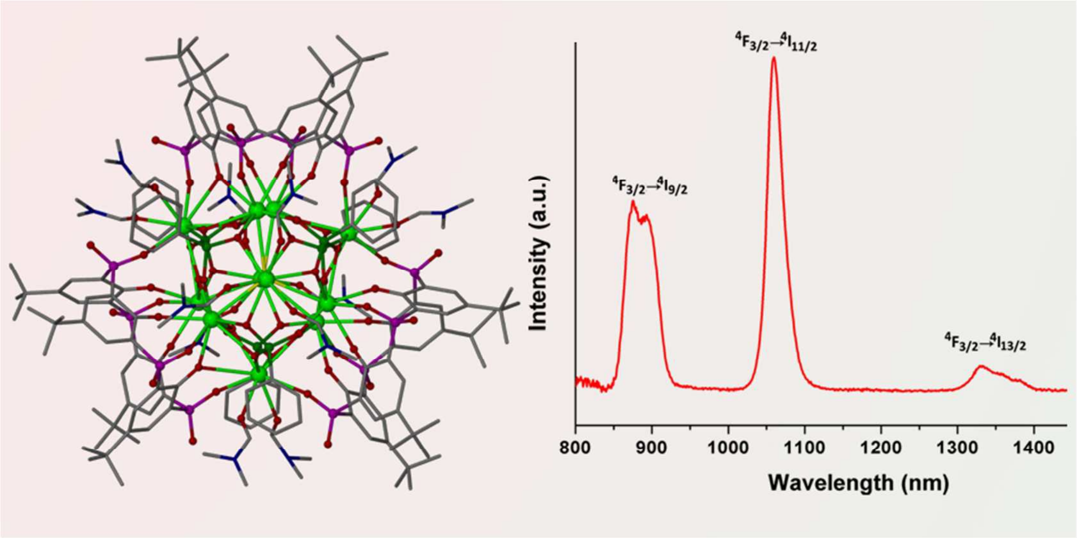

Solvethermal reactions of *p-tert*-butylsulfonylcalix[4]arene (H_4BSC4A), phosphonic acid and neodymium chloride have resulted in three novel high-nuclearity neodymium coordination compounds.