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 Two solvent-dependent Al₁₆ nanorings: design, synthesis and nonlinear optical limiting behavior†

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Cyclic compounds are of great interest to chemists for their adjustable organic shells and inorganic cores. Although the abundant bridges provide a bottom-up synthesis approach for the diversity and functionalization of ring compounds, the lack of suitable models still limits us in exploring the influence of bridge types on ring structures. Herein, we demonstrate two Al₁₆ molecular nanorings synthesized via 2 × 8 and 4 × 4 strategies based on the “ligand-induced aggregation and solvent regulation” strategy and discuss the influence of surface bridge flexibility on molecular ring distortion and curvature. Rigid phenol endows **AIOC-135** with unique intramolecular π···π interactions and higher curvature to increase the delocalization and transfer of electrons, resulting in a superior third-order nonlinear optical (NLO) response. This work provides a platform for explaining the relationship between the structure and optical properties of ring compounds at the molecular level.

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Introduction

Macrocyclic molecules have attracted widespread attention due to their unique symmetry, adjustable supramolecular stacking, and central cavity for guest inclusion.^{1–3} Organic–inorganic hybrid macrocycles can be directionally assembled and functionalized, enabling expansion of the applications in specific fields by altering the composition of the organic shell and inorganic metal core.^{4–6} In recent decades, numerous innovative hybrid molecular ring models have emerged, such as the transition metal molecular rings Ti₃₂, Fe₃₆, Zr₇₀, Mn₈₄, Mo₁₅₄ and Mo₁₇₆.^{7–12} Another big family is rare earth molecular rings such as Ln₄₂ (Yb₄₂ and Sm₄₂) bridged by acetoxy, Ce₇₀ with a sulfate linker, and the Gd₁₄₀ ring linked by 80 acetic acid molecules, 40 myo-inositol and 20 CO₃^{2–} anions.^{13–15} Furthermore, heterometallic 3d–4f molecular rings are also the stars of hybrid molecular rings, such as Cr₄Dy₄, Sc₈Gd₈, and Mo₁₂₈Ce₄ with modified delta-chain structures, which are linked *via* benzoates.^{16–18} These macrocyclic molecules exhibit distinct benefits in the optics, magnetism and host–guest chemistry domains.^{19–23} Yang *et al.* reported a {Nd₁₈} molecular ring

exhibiting NIR luminescence sensing of antibiotics.²⁴ Zheng *et al.* synthesized the {Cr₈Dy₈} wheel, which is a single-molecule magnet.²⁵ Sun *et al.* reported the host–guest catalysis and self-assembly of Pd₂L₂ constructed from a pyridine-bonded macrocyclic ligand (L) and Pd²⁺.²⁶ The excellent performance of macrocyclic molecules in these fields encourages us to further develop more cyclic compounds.

Linkers are essential components of cyclic compounds and can be divided into three main groups (Scheme S1†): (a) Chelating entirely by organic linkers with coordination sites such as O_{carboxyl}, OH, S, and N. For example, Zhang *et al.* used *N,N'*-di[1-(2-hydroxyphenyl)-ethylidene]hydrazone ligand and DMF (N) as linkers to synthesize Ni₁₂.²⁷ Milios *et al.* synthesized Co₁₆ by salicylaldehyde bridges.²⁸ Besides, Baca *et al.* constructed a heterometallic ring Fe₆Dy₈ with *N*-butyl diethanolamine isobutyrate and methanol (O_{hydroxyl}).²⁹ Yamamoto *et al.* reported a series of [Pt(μ-SC₈H₁₇)₂]_{*n*} (*n* = 5–13) clusters with the S atom as the connection point.³⁰ (b) Bonding entirely with inorganic bridges. Su *et al.* synthesized [Nb₄₈V₈(OH)₃₀O₁₃₀]^{18–} using μ₂-OH[–] as linkers.³¹ Jacobson *et al.* and Wang *et al.* reported [M₈]^{16–} (M = Cr and Fe) and [Ti₈]^{16–} with μ₂-OH and μ₂-SO₄ bridges.^{32,33} (c) The cooperation between organic connectors and inorganic components constitutes a ring structure. Zhao *et al.* reported on an Ln₇ ring constructed from 1,1'-cyclopropane-dicarboxylic acid and μ₃-OH inorganic linkers (Ln = Gd and Dy).³⁴ Zheng *et al.* synthesized Ti₃₂ constructed from acetic acid and μ_{*n*}-O (*n* = 2 or 3) linkers.³⁵ Christou *et al.* used triethylamine and μ₃-OH to synthesize an Fe₃₆ cluster.¹² Abundant organic/inorganic linkers provide a bottom-up synthesis approach for the diversity of

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molecular ring types and functionalization. However, exploring the influence of linker types on the ring structures is challenging.

Our group has been dedicated to the isolation of Earth-abundant element related aluminum-based molecular rings and developed the “ligand-induced aggregation and solvent regulation” strategy toward customizing ring compounds.^{36,37} In previous research, we successfully expanded the Al₈ ring to the Al₁₆ ring by tuning the carbon chain length of the flexible primary alcohols and developing the Al₂₀ ring using a rigid phenol linker.^{38,39} As a continuous work, we herein report two rings with the same nuclearity but different degrees of conjugation and study their optical properties. Considering that a ligand with a high degree of conjugation will facilitate photo-related properties, we introduced 2-naphthoic acid (2-NA) instead of the previously used benzoic acid. To investigate the effects of different auxiliary ligands (solvents) on the ring structure, we chose flexible *n*-propanol and rigid phenol (melting point 43 °C). With this in mind, we successfully isolated two Al₁₆ molecular nanorings constructed using a 2-NA ligand but with different auxiliary bridges. The introduction of rigid phenol brings intramolecular π - π interactions, increasing the ring curvature and further influencing the intermolecular stacking, resulting in photoluminescence and nonlinear optical (NLO) changes. This study provides a platform for explaining the structure–function relationship of macrocyclic molecules at the molecular level.

Results and discussion

Synthesis discussion

2-Naphthoic acid (2-NA) plays an essential role in inducing the aggregation of Al³⁺ to form molecular rings, while phenol can be viewed as a solvent and auxiliary bridge like *n*-propanol. A transparent square block crystal [Al₁₆(O^{*n*}Pr)₁₆(μ_2 -OH)₈(2-NA)₂₄] (AIOC-134) was prepared through the one-step self-assembly method by heating Al(O^{*n*}Pr)₃ and 2-naphthoic acid (2-NA) under the regulation of a methylaminoethanol solution and hexamethylenetetramine in a mixture of *n*-propanol, 1,4-dioxane and a DMF solution. When we directly added 6 mL phenol and increased the reaction temperature (100 °C to 120 °C), a light yellow oval shaped block crystal [Al₁₆(phenol)₂₀(μ_2 -OH)₈(2-NA)₂₀] (AIOC-135) was successfully synthesized (Fig. 1). Although AIOC-134 and AIOC-135 are both 16-membered molecular rings, they exhibit different linkage modes (2 × 8 and 4 × 4 strategy).

Aluminum molecular rings supported by flexible *n*-propanol (2 × 8 strategy)

Single-crystal X-ray diffraction (SCXRD) showed the compound AIOC-134 crystallizing in the monoclinic space group *C2/c* with a total diameter of 3.1 nm, a height of about 1.9 nm, and a central hole of 0.5 nm (Fig. 2a and c). The entire molecular ring includes 16 Al³⁺ ions, 24 2-NA ligands, 16 ^{*n*}OPr, and eight bridged hydroxyl connections (Fig. 2a). Each aluminum ion



Fig. 1 “Ligand-induced aggregation and solvent regulation” synthesis of AIOC-134 and AIOC-135.

adopts a six-coordinated octahedral configuration with three carboxylate oxygens (O_{COO}) from three 2-NA ligands, two hydroxyl oxygens from four ^{*n*}OPr ligands and one μ_2 -OH (Fig. S1†), which is similar to the previously reported coordination mode of the Al₁₆ ring bridged by alcohol.³⁸ In AIOC-134, the 2-NA ligand adopts the μ_2 - η^1 : η^1 coordination mode linking two neighbouring Al³⁺ ions to form an edge-sharing [Al₂(^{*n*}OPr)₂(2-NA)₃] (Al₂) dimer (Fig. 2b and S2†). Eight Al₂ dimers are connected with eight μ_2 -OH to form a coronal configuration ring through the vertex sharing mode (2 × 8, Fig. S3†).

Aluminum molecular rings supported by rigid phenol (4 × 4 strategy)

When we replace the flexible *n*-propanol connector with rigid phenol, the Al₁₆ crown-core is transformed into a twisted saddle-core (AIOC-135). AIOC-135 crystallizes in the tetragonal space group *P4₂/n* with a slightly smaller diameter (2.7 nm), a central hole of 0.4 nm and a height of about 2.3 nm (Fig. 2e and g). AIOC-135 consists of 16 Al³⁺ ions, 20 NA⁻ ligands, 20 phenols and eight bridged hydroxyl groups (Fig. 2e). As shown in Fig. S1,† all Al³⁺ ions in this Al₄ tetramer have a distorted octahedral geometry: for Al₁, the coordination oxygen comes from two O_{COO} and four phenols; for Al₂, the coordination comes from two O_{COO}, three phenols, and one μ_2 -OH; and for Al₃, the coordination comes from three O_{COO}, one phenol, and two μ_2 -OH. Four 2-NA ligands adopt the same mode bridging bidentate μ_2 -linking four neighbouring Al³⁺ ions to construct an edge-sharing [Al₄(phenol)₅(2-NA)₅] tetramer (Fig. 2f and S2†). Four independent μ_2 -OH connect two adjacent Al₄ tetramers to form a saddle-shaped Al₁₆ ring (4 × 4, Fig. S3†) with a bigger bending degree.

Ring curvature discussion

We tried to introduce rigid ligands with larger sizes to adjust the structural curvature, such as benzyl alcohol, 1-naphthol and 2-naphthol. Unfortunately, no related compounds were





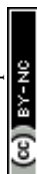
Fig. 2 Structure of AIOC-134 and AIOC-135. (a) The space-filling view of AIOC-134 (total diameter of 3.1 nm and central hole of about 0.5 nm); (b) the ball-and-stick view of the 2×8 ring of AIOC-134 (Al_2 connected with μ_2 -OH); (c) the side view of the corona-shaped ring of AIOC-134 (presenting the intramolecular hydrogen bond interactions); (d) nanotube stacking diagram of AIOC-134; (e) the space-filling view of AIOC-135 (total diameter of 2.7 nm and central hole of about 0.4 nm); (f) the ball-and-stick view of the 4×4 ring of AIOC-135 (Al_4 connected with μ_2 -OH); (g) the side view of the corona-shaped ring of AIOC-135 (presenting the intramolecular hydrogen bond interactions and $\pi \cdots \pi$ interaction); (h) nanotube stacking diagram of AIOC-135; and (i) curvature changes of the aluminum molecular ring; currently AIOC-135 has the largest curvature aluminum molecular ring. Color code: Al, green; O, red; C, black; H, grey; $\pi \cdots \pi$ interaction, blue dashed line in (g); and intramolecular hydrogen bonds, orange dashed lines in (c) and (g).

isolated, which may be attributed to their larger steric hindrance. The degree of curvature of the AIOC-134 (crown-type) is caused by significant intramolecular hydrogen bond interactions ($\text{C-H} \cdots \text{O}$, 2.691 Å to 3.288 Å) (Fig. 2c and Table S3†). Compared to AIOC-134 and previous aluminum molecular rings, AIOC-135 exhibits the most significant curvature and a rare saddle structure (Fig. 2i).^{38–44} In solvent systems containing conjugated ligands, phenols with stronger polarity can easily interact with them *via* $\pi \cdots \pi$ interaction, thereby distorting the Al_{16} nucleus. This is also the reason why the amount of the linker phenol (20) is greater than that of *n*-propanol (16). Besides, the saddle-shaped conformation provides stronger supramolecular interactions within AIOC-135, manifested in strong hydrogen bonding interactions ($\text{C-H} \cdots \text{O}$, 2.722–2.831 Å, Table S4†) and intramolecular $\pi \cdots \pi$ stacking interactions between phenols (4.549–4.562 Å, Fig. S4†). The two factors combine to cause the large curvature of AIOC-135. In both structures, all nanorings are connected to adjacent molecular rings by rich $\pi \cdots \pi$ interactions (4.129–4.869 Å, Fig. S4 and Table S5†) to form a dense array of supramolecular nanotubes. The Al–O bond lengths of two Al_{16} rings fell within the range

of 1.837–1.943 Å (Table S2†), comparable with those reported in the literature.^{38,40,45} The conjugated system is instrumental in exploring the application of the two compounds in optics.

Characterization

The experimental PXRD peaks of AIOC-134 and AIOC-135 match well with the simulated peaks based on their space groups and cell parameters obtained using Berrar–Baldinozzi refinement. Negligible difference curves (R_{wp} and R_{p} values less than 5%) demonstrate the high purity of synthesized crystals (Fig. 3a and b). The energy dispersive spectroscopy (EDS) (Fig. S5 and S6†) and Fourier transform infrared spectroscopy (FT-IR) demonstrate the introduction of ligands (Fig. S7 and S8†). The vibration at 3054 cm^{-1} (AIOC-134) and the vibration at 3058 cm^{-1} (AIOC-135) are assigned to the C–H vibration of the aromatic ring. The absorption band of 3618 cm^{-1} (AIOC-135) is attributed to the $\nu(\text{O-H})$ stretching on phenol; the bands at 1550 cm^{-1} (AIOC-134) and 1556 cm^{-1} (AIOC-135) can be ascribed to $-\text{CO}_2^-$ asymmetric stretching. The bond valence sum (BVS) calculation shows that all Al ions have a +3 oxidation state (Tables S6 and S7†). The contact angle test



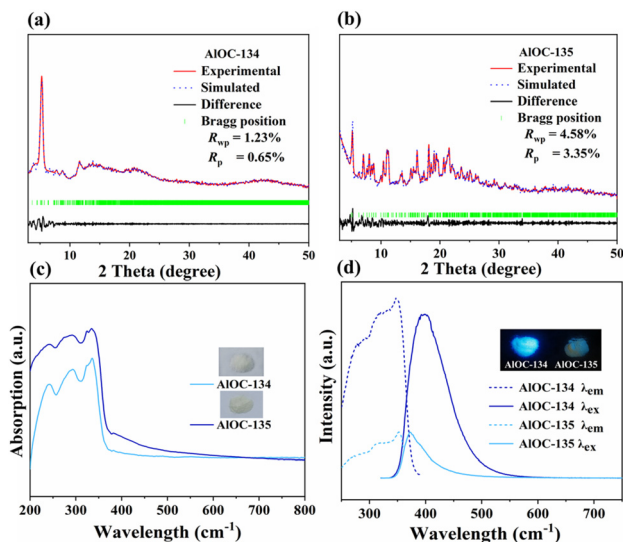


Fig. 3 (a) Simulated PXRD patterns (blue) and experimental PXRD patterns (red) of AIOC-134. (b) Simulated PXRD patterns (blue) and experimental PXRD patterns (red) of AIOC-135. (c) UV-vis diffuse reflectance spectra of AIOC-134 and AIOC-135 (insets are solid-state crystal samples). (d) Room-temperature photoluminescence spectra of AIOC-134 and AIOC-135 (inset is solid-state crystal samples under 365 nm UV light; λ_{em} is measured at an excitation wavelength of λ_{ex} = 300 nm).

reflects their excellent hydrophobicity and stability (Fig. S9[†]). Their thermal stability was evaluated by thermogravimetric analysis (TGA) (Fig. S10 and S11[†]). The solvent and air stability of the compounds are demonstrated by PXRD under different conditions, single crystal diffraction patterns and crystal pictures (Fig. 1 and S12–S14[†]). The excellent stability limited the dissolution of the compound in the organic solvent, which prevented further solution stability studies such as mass spectrometry.

Luminescence properties

The large π -conjugated systems and abundant supramolecular forces encouraged us to investigate their optical properties. We first explored the light absorption properties of AIOCs by measuring the UV-vis diffuse reflectance spectra. As shown in Fig. 3c, the results show that the absorption spectra of both AIOC-134 and AIOC-135 exhibit broad profiles ranging from 250 nm to 450 nm (Fig. S15 and S16[†]), which are similar to the absorption bands of 2-NA ligands (Fig. S17[†]). Subsequently, the fluorescence properties of the solid-state samples were measured at room temperature. As shown in Fig. 3d and S18,[†] the maximum emission peaks show a red shift (28 nm for AIOC-134, 3 nm for AIOC-135) at the same excitation wavelength (300 nm). Besides, AIOC-134 has a longer lifetime and higher quantum yield (9.76 ns, 17.87%) than AIOC-135 (2.57 ns, 7.85%) (Fig. S19 and S20[†]). The comparative emission spectra show that the luminescence of the nanoring can be attributed to the coordination of the 2-NA ligand with inorganic aluminum atoms.⁴⁶ The difference in

their emission intensity may be related to the quantity of the 2-NA ligands (24 in AIOC-134 vs. 20 in AIOC-135) (Fig. 3d).

Third-order nonlinear optical (NLO) properties

Third-order nonlinear optics has shown potential applications in fields such as laser protection and optical switches.^{47,48} The large conjugated system of Al₁₆ rings encouraged us to combine crystalline materials with third-order NLO properties. The hydrophobic shell of the ring makes it less soluble and dispersible in solvents. Thus, we chose polydimethylsiloxane (PDMS, one chemically inert material with transmittance and excellent flexibility) as a solid dispersion substrate and made flexible AIOCs@PDMS films (30 mm in diameter).^{49,50} All sample films had similar thicknesses and high linear transmittance (inset pictures in Fig. 4a). Open aperture (OA) Z-scan measurements were performed on solid samples under a nanosecond laser at 532 nm and a pulse energy at 80 μ J (Fig. 4a). As shown in Fig. 4b, the Z-scan curves of AIOC-134 and AIOC-135 display typical reverse saturation absorption (RSA) responses. The minimum normalised transmittance (T_{min}) values at the focal point were 0.84 and 0.79 for AIOC-134 and AIOC-135, respectively. Such responses were reproducible and presented consistent T_{min} values, showing that the prepared samples featured excellent chemical and physical stability (Fig. S21 and S22[†]). According to eqn (4) and (5), the light

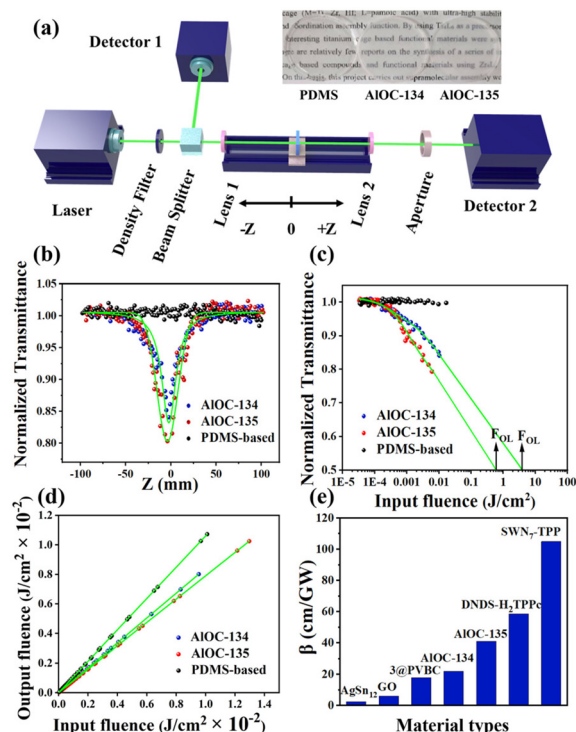


Fig. 4 (a) Schematic representation of the Z-scan setup (inset is a picture of the PDMS substrate and AIOCs@PDMS under natural light); (b) the OA Z-scan curves of input laser pulse energy 80 μ J of AIOCs@PDMS; (c) the plots of normalized transmittance versus input fluence; (d) curves of output fluence versus input fluence; and (e) the plots of comparisons of the nonlinear absorption coefficients.



was used to perform an analysis of the contact angles of all the powder samples.

Fluorescence spectroscopy measurement

Photoluminescence spectra (PL) and luminescence decay curves were performed on an Edinburgh FLS1000 fluorescence spectrometer at room temperature. All test samples were solid crystalline particles (5 mg). Emission wavelength, quantum yield and fluorescence lifetime were all measured at maximum excitation.

Preparation of AIOCs@PDMS samples

Sylgard 184 (Dow Corning) is a kit product consisting of liquid A and B components, including basic components and a curing agent. PDMS samples were fabricated using Sylgard 184 (Dow Corning) by thoroughly mixing ten parts base with one part curing agent. The fully ground AIOC samples were added to the PDMS mixture and stirred for 3 h to form AIOC dispersed PDMS suspension. Then the mixed suspension was added to a round mould, and the template was placed in a vacuum oven at 60 °C for six hours to obtain transparent and flexible AIOCs@PDMS films. The thickness of the films was measured using a digital caliper (MNT951101 manufactured by Shanghai Minette).

Third-order NLO measurement

The NLO properties of the samples were evaluated using the open-aperture (OA) Z-scan technique. The excitation light source was an Nd:YAG laser with a repetition rate of 10 Hz. The laser pulses (period, 8.5 ns; wavelength, 532 nm) were split into two beams with a mirror. The pulse energies at the front and back of the samples were monitored using energy detectors D1 and D2. All of the measurements were conducted at room temperature. The measured Z-scan curves were fitted using the following expressions:

$$T(Z, S = 1) = \frac{1}{\sqrt{\pi(Z, 0)}} \int_{-\infty}^{\infty} \ln[1 + q_0(Z, 0)e^{-r^2}] dr \quad (1)$$

$$q_0(Z, 0) = \beta I_0 L_{\text{eff}} \quad (2)$$

$$L_{\text{eff}} = \frac{1 - e^{-\alpha l}}{\alpha} \quad (3)$$

$$F_{\text{in}}(z) = \frac{4E_{\text{in}} \sqrt{\ln 2}}{\pi^2 \omega(z)^2} \quad (4)$$

$$\omega(z) = \frac{\omega_0}{\left[1 + \left(\frac{z}{z_0}\right)^2\right]^{\frac{1}{2}}} \quad (5)$$

$$\text{Im}\chi^{(3)} = \frac{\lambda \epsilon_0 c^2 n_0^2}{4\pi^2} \beta \quad (6)$$

$$\text{FOM} = \left| \frac{\text{Im}\chi^{(3)}}{\alpha} \right| \quad (7)$$

where T is the normalized transmittance, β is the nonlinear absorption coefficient, I_0 is the peak on-axis irradiance of the

laser beam at the focus, L_{eff} is the effective thickness of the sample, α is the linear absorption coefficient at the laser wavelength ($\alpha = \ln(\frac{1}{T})/d$), z is the Z-scan displacement, ϵ_0 is the permittivity of vacuum ($8.85 \times 10^{-12} \text{ F m}^{-1}$), c is the speed of light and l denotes the thickness of the glass cell.

Data availability

The datasets supporting this article have been uploaded as part of the ESI.† CCDC reference numbers 2289659 (AIOC-134) and 2289660 (AIOC-135) contain the X-ray crystallographic data.†

Author contributions

All authors contributed extensively to the work presented in this paper. J. Zhang and W.-H. Fang conceived the research project. S.-T. Wang and X. Qi performed the synthesis, characterization, fluorescence property analysis and third-order NLO properties analysis. R.-Q. Chen assisted with the data collection and analysis. W.-H. Fang, X. Qi and S.-T. Wang wrote the manuscript and the ESI with input from the other authors.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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