Inorganic Chemistry
Communication
pubs.acs.org/IC

Enantiomerically Pure Lanthanide–Organic Polytungstates Exhibiting Two-Photon Absorption Properties

Wei-Wei Ju, Hai-Tao Zhang, Xiao Xu, Yu Zhang, and Yan Xu*

College of Chemistry and Chemical Engineering, State Key Laboratory of Materials-oriented Chemical Engineering, Nanjing Tech University, Nanjing, 210009, People's Republic of China

S *Supporting Information*

ABSTRACT: Two enantiomerically pure polytungstates, $Na_2[(CH_3)_2NH_2]_3\{Na\subset[Ce^{III}(H_2O)(CH_3CH_2OH)(\text{L-}tartH_3)(H_2Si_2W_{19}O_{66})]\}\cdot 3.5H_2O$ (L-**1**) and $[(CH_3)_2NH_2]_7\{Na\subset[Ce^{III}(H_2O)(CH_3CH_2OH)(\text{D-}tartH_3)(Si_2W_{19}O_{66})]\}\cdot 2.5H_2O$ (D-**1**), were successfully synthesized. Structural analysis indicates that chiral tartrate ligands directly connect with novel lacunary $[Si_2W_{19}O_{66}]^{10-}$ polytungstate units. Strong induced optical activity in the polyoxometalate (POM) units is manifested by circular dichroism spectroscopy. Z-scan analysis revealed that L-**1** and D-**1** are the first chiral POM-based complexes that exhibit two-photon absorption properties typical of the third-order nonlinear optical response.

Enantiomerically pure metal oxide cluster materials have received much attention because of their multitudinous potential applications in asymmetric catalysis, molecular recognition, biomedicine, and nonlinear-optical (NLO) response.[1] In this field, Wang et al. have shown a versatile iron chemistry that can isolate various enantiomerically pure ferric chiral polymers ranging from $\{Fe_{28}\}$ wheels to a giant $\{Fe_{168}\}$ cage.[2] Polyoxometalates (POM) as classic early-transition-metal oxide clusters with discrete well-defined structures possess abundant structural diversity and versatile physical and chemical properties.[3] Chiral POM-based compounds, which subtly combine the advantage of POMs with the significance of chirality, have become more and more attractive in recent years.[4] Up to now, about 100 chiral POM-based compounds have been synthesized by the groups of Pope, Yamase, Kortz, Hill, Zubieta, Wei, Cronin, Wang, and Su[5] However, most of these compounds undergo fast racemization in solution or in the solid state. What is more, almost all of the reported enantiomerically pure POM-based compounds are constructed from a transition metal (TM) instead of lanthanide,[6] and most POM anion clusters possess high symmetry and are very difficult to crystallize in non-centrosymmetric space groups. Such problems have seriously impeded the application of enantiomerically pure POM-based compounds in NLO response. Recently, theoretical and experimental studies have shown that chiral POM-based materials possess excellent NLO response, but only a few NLO-active materials contain POM anions, and they are all about the second-order NLO response.[7] Therefore, the hunt for enantiomerically pure POM-based lanthanide–organic compounds with potential third-order NLO applications is one of the most challenging problems in both materials science and synthetic chemistry.

Tartaric acid ($tartH_4$), as a fascinating chiral multifunctional ligand, can act as a chiral source and split agent of chiral syntheses in the pharmaceutical and food industries. Also, it has a relatively small volume and versatile coordination mode, which can coordinate with many metal cations, such as lanthanide ions, to transfer chirality from tartrate to a metal oxide cluster.[8] Among all kinds of POMs, lacunary POMs first seized our attention because (1) they have more terminal oxygen atoms than saturated POMs to bind with metal atoms and (2) dimeric, trimeric, or polymeric lacunary POM anions can construct novel POM anions. In our previous work, we synthesized two compounds containing the unprecedented open Wells–Dawson anion $[Si_2W_{18}O_{66}]^{16-}$, which is constituted by dimerization of $[\alpha\text{-}SiW_9O_{34}]^{10-}$ anions.[9]

Since the lanthanide-based compounds exhibit excellent photoluminescent and magnetic properties,[10] introduction of lanthanide cations into the POM-based complexes may induce new functionalities. However, the oxophilic lanthanide cations usually possess high reactivity with oxygen-enriched POM anions, which always result in precipitate rather than crystallization.[11] As a result, there are only a few chiral POM-based compounds constructed from lanthanide ions.[12]

Here, using the lanthanide tartrate coordination centers and lacunary Keggin POM ions as building blocks, two enantiomerically pure polytungstates, $Na_2[(CH_3)_2NH_2]_3\{Na\subset[Ce^{III}(H_2O)(CH_3CH_2OH)(\text{L-}tartH_3)(H_2Si_2W_{19}O_{66})]\}\cdot 3.5H_2O$ (L-**1**) and $[(CH_3)_2NH_2]_7\{Na\subset[Ce^{III}(H_2O)(CH_3CH_2OH)(\text{D-}tartH_3)(Si_2W_{19}O_{66})]\}\cdot 2.5H_2O$ (D-**1**), were successfully synthesized. The POM anion $[Si_2W_{19}O_{66}]^{10-}$ is reported for the first time. Z-scan analysis of L-**1** and D-**1** revealed that they are the first chiral POM-based complexes that exhibit two-photon absorption (2PA) properties typical of the third-order NLO response.

Single-crystal X-ray diffraction analyses revealed that compounds L-**1** and D-**1** are enantiomers and their crystal system, space group, unit-cell dimensions, related bond distances, and bond angles are only slightly different. So, only the structure of L-**1** will be discussed in detail. Compound L-**1** crystallizes in the chiral monoclinic space group $P2_1$. The asymmetric unit of L-**1** consists of one $[Si_2W_{19}O_{66}]^{10-}$ unit, one cerium(III) cation, one ethanol ligand, one L-$tartH_3$ ligand, three sodium ions, three protonated dimethylamines, and some water molecules (Figure S1 in the Supporting Information, SI). The structure of L-**1**

Received: January 22, 2014
Published: March 24, 2014

exhibits a novel polytungstate anion assembled from $[Si_2W_{19}O_{66}]^{10-}$ inorganic clusters and cerium tartrate coordination centers (Figure 1). The $[Si_2W_{19}O_{66}]^{10-}$ cluster is an unprecedented cluster constructed from one $W^{VI}O_6$ (W14) octahedron possibly from decomposition of $[\alpha\text{-}SiW_9O_{34}]^{10-}$ in the acidic condition and the open Wells−Dawson $[Si_2W_{18}O_{66}]^{16-}$ anion, which is dimerized by two trilacunary $[\alpha\text{-}SiW_9O_{34}]^{10-}$ subunits (Figure S3 in the SI). The two $[\alpha\text{-}SiW_9O_{34}]^{10-}$ subunits are linked by two communal oxygen atoms, which come from two adjacent and edge-sharing tungsten atoms. The W14 center and $[Si_2W_{18}O_{66}]^{16-}$ anion are further linked by three communal oxygen atoms (O7 from one $[\alpha\text{-}SiW_9O_{34}]^{10-}$ unit and O16 and O25 from another $[\alpha\text{-}SiW_9O_{34}]^{10-}$) to form an unprecedented $[Si_2W_{19}O_{66}]^{10-}$ anion cluster. Compared with Hill's polyanion, which exhibits a dimeric structure by sharing one oxygen atom, composed of $[\alpha\text{-}SiW_9O_{34}]^{10-}$ and $[\alpha\text{-}SiW_{10}O_{37}]^{10-}$ units, linked by a Co_4 cluster,[13] the polyanions of the title compounds are made up of two $[\alpha\text{-}SiW_9O_{34}]^{10-}$ and one WO_6 center through the sharing of five terminal oxygen atoms, while in L-**1**, one L-tartH_3 ligand is bonded to the $[Si_2W_{19}O_{66}]^{10-}$ anion, and chirality transfers to a nanosized polyanion to generate an interesting chiral polyanion of $[Ce(H_2O)(CH_3CH_2OH)(L/D\text{-tart}H_3)(Si_2W_{19}O_{66})]^{8-}$. Compared with the first examples of optically active dendritic POM systems,[14] in this work, there is a rare-earth ion connected with POM.

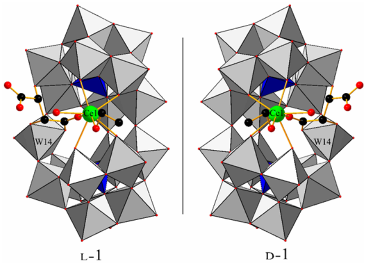

Figure 1. Combination ball-and-stick/polyhedral representations of L-**1** and D-**1** with the tungsten oxide and phosphorus oxide frameworks in polyhedral notations and the others in ball-and-stick notations: gray spheres, W; blue, P; green, Ce; black, C; red, O; yellow, Na. For clarity, all of the hydrogen atoms, sodium ions, and protonated dimethylamines are omitted.

The angle between the lacunary POM subunits of L-**1** is about 42.648(17)°, which is different from the previously reported 41°. Similarly, the W−O−W angles in the connecting position are 151.394(834)° and 152.068(770)°, also different from the formerly reported 147−148°. These differences indicate that insertion of one tungsten(VI) and cerium tartrate coordination center decreases the open angle of $[Si_2W_{18}O_{66}]^{16-}$ anions. The bond lengths of W−O and Si−O in the $[Si_2W_{19}O_{66}]^{10-}$ cluster vary from 1.660(15) to 2.364(14) Å and from 1.586(15) to 1.671(13) Å, respectively. All of these bond distances are consistent with those reported in open Wells−Dawson structural compounds.[15]

There is only one crystallographically independent cerium(III) center (Figure 1). Ce1 is seven-coordinated with a distorted pentagonal-bipyramid coordination geometry formed by one oxygen atom from a water molecule, one hydroxyl oxygen atom from an ethanol molecule, one carboxylate oxygen atom from a tartarate ligand, and four terminal oxygen atoms from lacunary $[Si_2W_{19}O_{66}]^{10-}$ POM. Also, the only tartarate ligand acts as a hexadentate chelating ligand ($\mu_4\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{:}\eta^1$) linked to two tungsten centers, one cerium center, and one sodium center (Scheme S1 in the SI). On the basis of this coordination mode, there is one sodium ion wrapped in the polyanion of L-**1** (Figure S4 in the SI). Every sodium center is six-coordinated defined by two carboxyl oxygen atoms from a tartaric acid molecule and four terminal oxygen atoms from the $[Si_2W_{19}O_{66}]^{10-}$ polyanion (Figure S4 in the SI).

Different from the reported chiral POM-based compounds containing rare-earth metal ions,[12b,c] the polyanion of L-**1** is made up of chiral POM-based lanthanide−organic polytungstate. The lanthanide−organic center is introduced for the first time to the chiral POM-based anions. In L-**1**, one tartaric acid molecule is coordinated with one cerium(III) ion to form a cerium tartrate coordination center, which is inserted into the $[Si_2W_{19}O_{66}]^{10-}$ open anion and forms the chiral POM-based cerium tartrate polytungstate. At the same time, chiral tartrate ligands directly connect with novel lacunary $[Si_2W_{19}O_{66}]^{10-}$ polytungstate units and chirality transfer from the chiral ligand to polytungstate units. Furthermore, the chiral POM-based polyanions of L-**1** are connected together through hydrogen-bonding interactions to form a supermolecular structure (Figure S6 in the SI).

The polyanions of D-**1** are the same as those of L-**1** except that L-tartaric acids are replaced by D-tartaric acids and their countercations are also different. In compound L-**1**, their countercations are three Na^+ ions, three protonated dimethylamines, and two H^+ ions, while in D-**1**, they turn into one Na^+ and seven protonated dimethylamines.

The chiroptical activities and stabilities of both enantiomeric compounds L-**1** and D-**1** are manifested by circular dichroism (CD) spectroscopy. The profiles of the solid-state CD spectra and liquid CD spectra of L-**1** and D-**1** are mirror images of one another and demonstrate that the nanosized polytungstates of L-**1** and D-**1** are enantiomers (Figures 2 and S9 in the SI). It is known to all that the spectrum of the L-tartH_4 molecule only shows a single negative Cotton effect at about 214 nm, and in the long-wavelength spectral region, L-tartH_4 is almost CD-silent above 240 nm. In contrast, the CD spectrum of L-**1** exhibits strong Cotton effects up to 350 nm, the spectral region characteristic of the oxygen-to-tungsten charge-transfer bands of the lacunary polyoxoanions.[16] These results clearly indicate that the induced CD (ICD) in the lacunary POM clusters, owing to the chirality transfer from the small chiral tartH_4 ligands to the much larger POM anion clusters, leads to a lowering of the symmetry of the polyoxoanions. The CD spectra of enantiomeric compounds L-**1** and D-**1** are unchanged with time (Figures S11 and S12 in the SI), indicating that both of them are stable and there is no racemization of the enantiomeric complex in aqueous solutions.

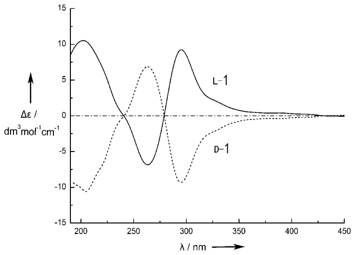

Figure 2. CD spectra of L-**1** and D-**1** in aqueous solutions.

The third-order NLO responses, 2PA cross sections (δ) of L-**1** and D-**1**, were obtained by the open-aperture Z-scan technique. The samples were dissolved in water at a concentration of 3.2×10^{-4} mol/L for D-**1** (1.36×10^{-3} mol/L for L-**1**) and determined under a laser wavelength of 740 nm. Figures 3 and S13 in the SI show the typical Z-scan measurements of D-**1** and L-**1**. The filled squares represent the experimental data, and the solid line is the theoretical simulated curve (for computing method, see in the SI). The nonlinear absorption coefficient and 2PA cross section are calculated as 0.00279 cm/GW and 392 GM (1 GM = 10^{-50} $cm^4 \cdot s$/photon) for D-**1** (0.01369 cm/GW and 389 GM for L-**1**), respectively. The δ values are very close to Sun's value (448 GM),[17] which is a moderately strong 2PA ($\delta > 100$) upon near-IR spectrum excitation. They are the first chiral POM-based complexes to exhibit 2PA properties typical of the third-order NLO response.

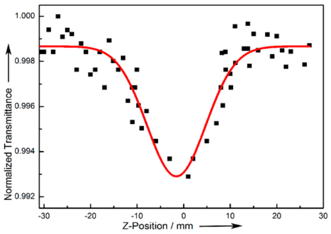

Figure 3. Z-scan data for D-**1** in aqueous solution, obtained under an open-aperture configuration. The dots are the experimental data, and the solid curve is the theoretical fit.

In conclusion, two stable enantiomers of POM-based lanthanide–organic compounds have been successfully synthesized. They represent the first example of $[Si_2W_{19}O_{66}]^{10-}$ polytungstate and the first enantiomers of POM-based lanthanide–organic compounds. The solid-state and liquid CD spectra of L-**1** and D-**1** reveal significantly induced optical activity in the lacunary POM clusters. It is believed that chirality transfer from a chiral tartrate ligand to much larger POM units occurs. In addition, Z-scan analysis of L-**1** and D-**1** revealed that they are the first chiral POM-based complexes to exhibit 2PA properties. The successful synthesis of both compounds may open up possibilities for the design of new chiral POM-based materials by introducing various organic ligands.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files in CIF format, experimental section, additional structural figures, and physical characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yanxu@njtech.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Natural Science Foundation of Jiangsu Province, China (Grant BK2012823), and the Project of Priority Academic Program Development of Jiangsu Higher Education Institutions.

■ REFERENCES

(1) (a) Tourne, C. M.; Tourne, G. F.; Zonnevijlle, F. *J. Chem. Soc., Dalton Trans.* **1991**, 143. (b) Compain, J. D.; Mialane, P.; Dolbecq, A.; Marrot, J.; Proust, A.; Nakatani, K.; Yu, P.; Sécheresse, F. *Inorg. Chem.* **2009**, *48*, 6222.

(2) (a) Zhang, Z. M.; Li, Y. G.; Yao, S.; Wang, E. B.; Wang, Y. H.; Clérac, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 1581. (b) Zhang, Z. M.; Yao, S.; Li, Y. G.; Clérac, R.; Lu, Y.; Su, Z. M.; Wang, E. B. *J. Am. Chem. Soc.* **2009**, *131*, 14600.

(3) (a) Drewes, D.; Limanski, E. M.; Krebs, B. *Dalton Trans.* **2004**, *14*, 2087. (b) Burkholder, E.; Zubieta, J. *Chem. Commun.* **2001**, *20*, 2056.

(4) Judd, D. A.; Nettles, J. H.; Nevins, N.; Snyder, J. P.; Liotta, D. C.; Tang, J.; Ermolieff, J.; Schinazi, R. F.; Hill, C. L. *J. Am. Chem. Soc.* **2001**, *123*, 886.

(5) (a) Xin, F. B.; Pope, M. T. *J. Am. Chem. Soc.* **1996**, *118*, 7731. (b) Kortz, U.; Savelieff, M. G.; Ghali, F. Y. A.; Khalil, L. M.; Maalouf, S. A.; Sinno, D. I. *Angew. Chem., Int. Ed.* **2002**, *41*, 4070. (c) Inoue, M.; Yamase, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3055. (d) Hou, Y.; Fang, X. K.; Hill, C. L. *Chem.—Eur. J.* **2007**, *13*, 9442. (e) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J.; O'Connor, C. J. *Science* **1993**, 1596. (f) Zhang, J.; Hao, J.; Wei, Y. G.; Xiao, F. P.; Yin, P. C.; Wang, L. S. *J. Am. Chem. Soc.* **2010**, *132*, 14–15. (g) Xiao, F. P.; Hao, J.; Zhang, J.; Lv, C. L.; Yin, P. C.; Wang, L. S.; Wei, Y. G. *J. Am. Chem. Soc.* **2010**, *132*, 5956–5957. (h) Streb, C.; Long, D. L.; Cronin, L. *Chem. Commun.* **2007**, 471. (i) Tan, H. Q.; Li, Y. G.; Zhang, Z. M.; Qin, C.; Wang, X. L.; Wang, E. B.; Su, Z. M. *J. Am. Chem. Soc.* **2007**, *129*, 10066.

(6) (a) Lan, Y. Q.; Li, S. L.; Su, Z. M.; Shao, K. Z.; Ma, J. F.; Wang, X. L.; Wang, E. B. *Chem. Commun.* **2008**, 58. (b) An, H. Y.; Wang, E. B.; Xiao, D. R.; Li, Y. G.; Su, Z. M.; Xu, L. *Angew. Chem., Int. Ed.* **2006**, *45*, 904. (c) Naruke, H.; Iijima, J.; Sanji, T. *Inorg. Chem.* **2011**, *50*, 7535.

(7) (a) Guan, W.; Yang, G. C.; Yan, L. K.; Su, Z. M. *Eur. J. Inorg. Chem.* **2006**, 4179. (b) Zhang, X. M.; Shan, B. Z.; Duan, C. Y.; You, X. Z. *Chem. Commun.* **1997**, 1131. (c) Xie, Y. M.; Zhang, Q. S.; Zhao, Z. G.; Wu, X. Y.; Chen, S. C.; Lu, C. Z. *Inorg. Chem.* **2008**, *47*, 8086.

(8) (a) Fang, X. K.; Anderson, T. M.; Hill, C. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 3540. (b) Fang, X. K.; Anderson, T. M.; Hou, Y.; Hill, C. L. *Chem. Commun.* **2005**, *40*, 5044.

(9) (a) Leclerc-Laronze, N.; Marrot, J.; Hervé, G. *Inorg. Chem.* **2005**, *44*, 1275. (b) Leclerc-Laronze, N.; Marrot, J.; Hervé, G. *Chem. Commun.* **2003**, 2360. (c) Leclerc-Laronze, N.; Haouas, M.; Marrot, J.; Taulelle, F.; Hervé, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 139.

(10) (a) Sabbatini, N.; Guardigi, M.; Bolletta, F.; Manet, I.; Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1501. (b) Yang, X. P.; Jones, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 7686. (c) Xia, J.; Zhao, B.; Wang, H. S.; Shi, W.; Ma, Y.; Song, H. B.; Cheng, P.; Liao, D. Z.; Yan, S. P. *Inorg. Chem.* **2007**, *46*, 3450. (d) Dupré, N.; Rémy, P.; Micoine, K.; Boglio, C.; Thorimbert, S.; Lacôte, E.; Hasenknopf, B.; Malacria, M. *Chem.—Eur. J.* **2010**, *16*, 7256.

(11) Shang, S. S.; Zhao, J. W.; Chen, L. J.; Li, Y. Y.; Zhang, J. L.; Li, Y. Z.; Niu, J. Y. *J. Solid State Chem.* **2012**, *196*, 29.

(12) (a) Peacock, R. D.; Weakley, T. J. R. *J. Am. Chem. Soc.* **1971**, 1836. (b) Naruke, H.; Iijima, J.; Sanji, T. *Inorg. Chem.* **2011**, *50*, 7535. (c) Chen, W. L.; Li, Y. G.; Wang, Y. H.; Wang, E. B. *Eur. J. Inorg. Chem.* **2007**, 2216.

(13) Zhu, G. B.; Geletii, Y. V.; Kögerler, P.; Schilder, H.; Song, J.; Lense, S. R.; Zhao, C. C.; Hardcastle, K. I.; Musaev, D. G.; Hill, C. L. *Dalton Trans.* **2012**, *41*, 2084.

(14) Jahier, C.; Cantuel, M.; McClenaghan, N. D.; Buffeteau, T.; Cavagnat, D.; Agbossou, F.; Carraro, M.; Bonchio, M.; Nlate, S. *Chem.—Eur. J.* **2009**, *15*, 8703–8708.

(15) (a) Leclerc-Laronze, N.; Marrot, J.; Hervé, G. *Inorg. Chem.* **2005**, *44*, 1275. (b) Wang, X. L.; Wang, Y. F.; Liu, G. C.; Tian, A. X.; Zhang, J. W.; Lin, H. Y. *Dalton Trans.* **2011**, *40*, 9299.

(16) Tézé, A.; Canny, J.; Gurban, L.; Thouvenot, R.; Hervé, G. *Inorg. Chem.* **1996**, *35*, 1001.

(17) (a) Ji, Z. Q.; Li, Y. J.; Pritchett, T. M.; Makarov, N. S.; Haley, J. E.; Li, Z. J.; Drobizhev, M.; Rebane, A.; Sun, W. F. *Chem.—Eur. J.* **2011**, *17*, 2479–2491. (b) Sun, W. F.; Zhang, B. G.; Li, Y. J.; Pritchett, T. M.; Li, Z. J.; Haley, J. E. *Chem. Mater.* **2010**, *22*, 6384–6392.