reflected in the differences in the chemical shift of the resonances arising from the viologen protons A–D in the ^{1}H NMR spectrum of **10** (Table 2). These differences can be explained from the fact that the porphyrin beads are slightly more shifted towards the central double bond in the *cis* isomer than in the *trans* isomer, which results in downfield shifts for resonances A and B, and upfield shifts for resonances C and D.

Compound **10** was used as a chain transfer agent in the polymerization of cyclooctadiene catalyzed by **2** to synthesize a [3]rotaxane containing a polymeric thread (Scheme 2). Initial studies using 15 equivalents of COD showed that up to 10 units of COD are inserted (Figure 2c). This observation means that [3]rotaxane **10** can successfully be extended to [3]rotaxane **12**. Since **2** is a very active catalyst, chain transfer results in a stepwise increase in mass of *m/z* 54 (Figure 2c).

In conclusion, we have presented a novel procedure to synthesize porphyrin-containing [3]rotaxanes starting from [2]pseudorotaxanes through a self-metathesis reaction using Grubbs' catalyst **3**. These [3]rotaxanes can be extended to [3]rotaxanes containing a polymeric thread by using them as a CTA in the polymerization of COD by **2**. Further studies will be focused on the catalytic epoxidation of the double bonds in the manganese porphyrin derivative of [3]rotaxane **12**, with the intention of mimicking a natural processive enzyme.

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Crown-Shaped Ln Polyoxometalates

Alkali-Metal-Controlled Self-Assembly of Crown-Shaped Ring Complexes of Lanthanide/[α-AsW$_9$O$_{33}$]$^{9-}$: [K$\subset${Eu(H$_2$O)$_2$(α-AsW$_9$O$_{33}$)}$_6$]$^{35-}$ and [Cs$\subset${Eu(H$_2$O)$_2$(α-AsW$_9$O$_{33}$)}$_4$]$^{23-}$[**]

Keisuke Fukaya and Toshihiro Yamase[*]

Polyoxometalates that are formed by self-assembly combine their nanoscopic size with the electronic, magnetic, or optical properties of the metal atoms, which should lead to interesting new materials.[1] The incorporation of the lanthanide ions Ln^{3+} in such polyoxometalates is of interest in supramolecular chemistry because of their luminescent and magnetic properties.[1c,2] With the aim of producing large clusters, much attention has focused on developing Ln^{3+}-incorporated polyoxometalates (polyoxometallolanthanoates), in which the Ln^{3+} ions are used as linkers in the self-assembled structure. Recently it was demonstrated that nano-sized polyoxometallolanthanoates, such as {Pr$_6$Mo$_{120}$},[3] {Eu$_4$Mo$_{128}$},[4] and

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$\{Ce_{16}W_{148}\}$ [5] can be constructed through the coordination of Ln^{3+} ions by the outer oxygen atoms of polyoxometalate ligands. The modular construction of these analogues allows a flexible and rational design, as the architecture and chemical functionality of the polyoxometallolanthanoates can be, in principle, precisely controlled.[6,7] In a continuing project on the development of chelating agents for the Ln^{3+} ions, we have investigated the intramolecular energy transfer between the polyoxometalate ligands and the Ln^{3+} ions.[1c,8] Herein we report how use of the simple ligand, $[\alpha\text{-}AsW_9O_{33}]^{9-}$, leads to a unique supramolecular crown-shaped ring architecture containing Eu^{3+} ions, which is controlled by the alkali-metal ions. These are the first examples of polyoxometallolanthanoates with a crown-shaped ring structure that encapsulates a single alkali-metal cation in the center. Compound **1a** was isolated as the mixed Cs^+/K^+ salt **1** and **2a** as the mixed Cs^+/Na^+ salt **2**.

$[K \subset \{Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})\}_6]^{35-}$ **1a**

$Cs_{22}K_{13}[K \subset \{Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})\}_6] \cdot 44\,H_2O$ **1**

$[Cs \subset \{Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})\}_4]^{23-}$ **2a**

$Cs_{16.75}Na_{6.25}[Cs \subset \{Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})\}_4] \cdot 24.5\,H_2O$ **2**

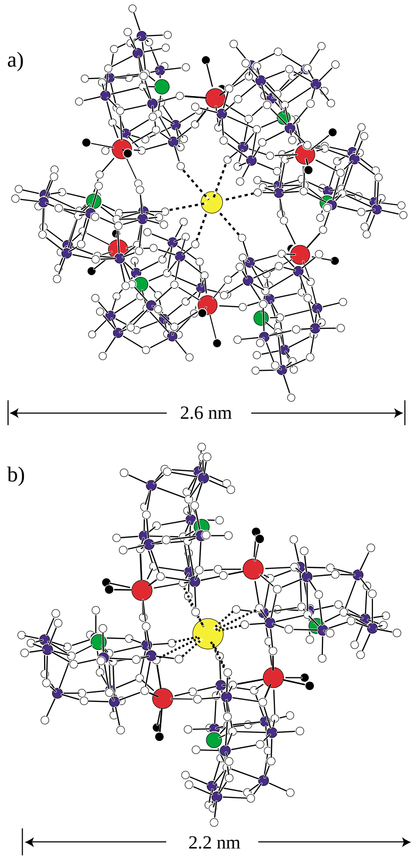

Figure 1. Molecular structures of a) **1a** and b) **2a**: green = As, red = Eu, yellow = K or Cs, blue = W, black = water O, and ○ = O.

Compound **1a** is a cyclic, K^+-ion-encapsulated hexamer of $[Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})]^{6-}$ ions, with idealized S_6 symmetry and a diameter of about 2.6 nm (Figure 1a), and **2a** is Cs^+-ion-encapsulated tetramer of $[Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})]^{6-}$ ions, with idealized C_{4h} symmetry and a diameter of about 2.2 nm (Figure 1b). The arrangement of the six $[\alpha\text{-}AsW_9O_{33}]^{9-}$ ligands in **1a** gives a hexagonal-chair conformation which resembles a watermill propeller, whereas **2a** resembles the vanes of a windmill. The distances between each Eu^{3+} ion of **1a** and **2a** range from 6.5 to 6.6 Å and the ions are located approximately on the As···As axis between $[\alpha\text{-}AsW_9O_{33}]^{9-}$ ligands (9.1 Å between neighboring As atoms; $\sphericalangle$ As···As···As ≈ 90°). Each $[\alpha\text{-}AsW_9O_{33}]^{9-}$ ion is a hexadentate ligand and coordinates to two Eu^{3+} ions through four three-coordinate and two two-coordinate oxygen atoms. The residual coordination sites of the eight-coordinate Eu^{3+} ions are occupied by the oxygen atoms of two water molecules, which together with two two-coordinate oxygen atoms form the least-squares plane of the square-antiprismatic coordination environment (mean distance between neighboring oxygen atoms 2.9 Å); the $W{-}O_{\text{two-coordinate}}$ bond lengths range from 1.74 to 1.82 Å. The angle between the plane (plane 1) described by the four tungsten atoms of the W_4O_4 cavity that coordinates an Eu^{3+} ion, and the plane that is formed by six tungsten atoms that enclose an arsenic center (plane 2) is about 56°(see Figure 2). The mean distance between neighboring oxygen atoms of the W_4O_4 cavity is 2.6 Å. The coordination of each $[\alpha\text{-}AsW_9O_{33}]^{9-}$ ligand to two Eu^{3+} ions is asymmetric and nonequivalent, and results in Eu···As···Eu angles of approximately 90° and asymmetric distances of 5.1 and 4.0–4.1 Å between neighboring Eu and As atoms (for the coordination through the three-coordinate and two-coordinate oxygen atoms, respectively). These factors are instrumental in the construction of the crown-shaped ring. The approximate Eu···Eu···Eu angles among neighboring Eu^{3+} ions in **1a** and **2a** were 120° and 90°, respectively. In **1a** the diameter of the pseudohexagon, that is, the distance between two opposing Eu^{3+} ions, is 13.0 Å, and the central K^+ ion is eight coordinate, being bound by a two-coordinate oxygen atom from each of the six $[\alpha\text{-}AsW_9O_{33}]^{9-}$ ions (K–O 2.9 Å) and two disordered oxygen atoms from apical water molecules (K–O 2.7 Å). As a result, the $[K(H_2O)_2]^+$ ion is bonded to six $[Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})]^{6-}$ units to give an overall hexagonal-bipyramidal geometry (Figure 3a). In **2a** the central Cs^+ ion is 12 coordinate, being bound by two two-coordinate oxygen atoms (mean Cs–O 3.3 Å) and one three-coordinate oxygen atom (mean Cs–O 3.4 Å) from each of the four $[\alpha\text{-}AsW_9O_{33}]^{9-}$ ligands, with no coordinated water molecules. The Cs^+ ion enclosed in the molecular cavity of $[\{Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})\}_4]^{24-}$ is shown in Figure 3b. Interestingly, the molecular cavity of the $[\{Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})\}_4]^{24-}$ ring is too large to accommodate a single K^+ ion. The exchange of one type of Ln^{3+} ion for another demonstrates that the same crown architecture, with almost the same crystal-lattice parameters, could be obtained for other smaller lanthanide ions (across the periodic table until Yb^{3+}). Unfavorable coordination of the four three-coordinate oxygen atoms of the W_4O_4 cavity to large lanthanide ions implies that the high charge density of the Ln^{3+} ion affects the electrostatic interaction of the three-coordinate oxygen atoms in the formation of the crown. It has been established that two

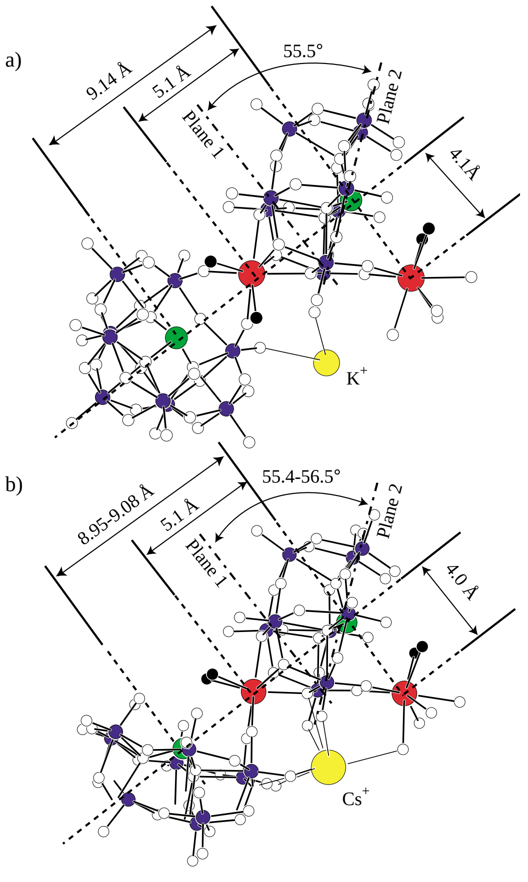

Figure 2. $[Eu(H_2O)_2]^{3+}$ ion coordinated by two hexadentate $[\alpha\text{-}AsW_9O_{33}]^{9-}$ ligands for a) **1a** and b) **2a**: Color code as in Figure 1. Ranges of the bond lengths [Å] and mean values in parentheses for **1a** and **2a**: $Eu{-}O_{\text{three-coordinate}}$ 2.31–2.52 (2.45 for **1a** and 2.43 for **2a**), $Eu{-}O_{\text{two-coordinate}}$ 2.30–2.39 (2.34 for **1a** and 2.36 for **2a**), $Eu{-}O_{\text{water}}$ 2.36–2.55 (2.42 for **1a** and 2.45 for **2a**).

threefold symmetric $[\alpha\text{-}AsW_9O_{33}]^{9-}$ ligands can sandwich three transition-metal (TM) ions with TM···TM distances of 4.7–5.5 Å.[9] In these complexes the TM ions are coordinated through two two-coordinate oxygen atoms bonded to two of the six equatorial W atoms of the $[\alpha\text{-}XW_9O_{33}]^{9-}$ ligand (X = As, Sb, Bi) which results in an approximate D_{3h} symmetry. The coordination of the $[\alpha\text{-}AsW_9O_{33}]^{9-}$ ligands to metal ions through two two-coordinate oxygen atoms was also observed for Ln^{3+}-ion complexes, such as $\{Ce_{16}W_{148}\}$,[5] **3**,[7a] **4**,[10a] and **5**.[10b] The coordination of the $[\alpha\text{-}XW_9O_{33}]^{9-}$ ligand to the Ln^{3+} ion through the four three-coordinate oxygen atoms of the W_4O_4 cavity has been recently shown for **6** [6] where one of two square-antiprismatic LnO_8 coordination sites consists of four three-coordinate oxygen atoms of the $[\alpha\text{-}SbW_9O_{33}]^{9-}$ ligand and four two-coordinate oxygen atoms from $[W_5O_{18}]^{6-}$ (and the other site consists of six two-coordinate oxygen atoms from the $[W_5O_{18}]^{6-}$, and $[\alpha\text{-}SbW_9O_{33}]^{9-}$ ligands, and two water molecules). Interestingly, the coordination of three three-coordinate oxygen atoms to an Ln^{3+} ion has been shown for the highly negative charged $[Nb_6O_{19}]^{8-}$ ligand in **7**, where each Ln^{3+} ion has an approximately bicapped-trigonal-prismatical coordination environment, and is coordinated by three three-coordinate O atoms (mean O···O 2.7 Å) of the Nb_3O_3 cavity for the equatorially positioned $[Nb_6O_{19}]^{8-}$ ligand, one two-coordinate oxygen atom from an adjacent equatorially positioned Nb_6O_{19} ligand, an oxygen atom from a water molecule, two oxygen atoms shared by two Eu and Al atoms, and one oxygen atom shared by three Eu atoms in the central $\{Ln_3O(OH)_3(H_2O)_3\}_2$ core.[11]

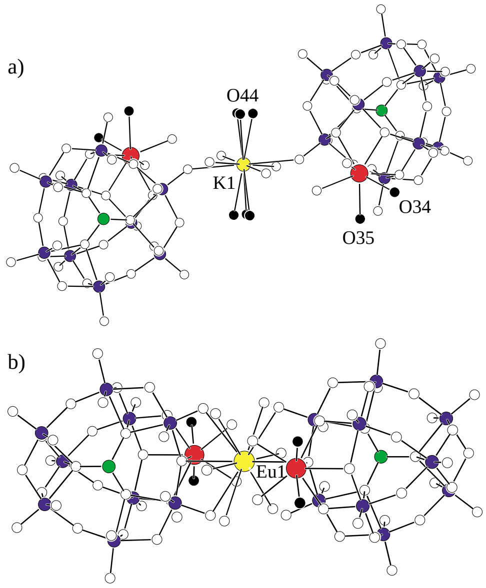

Figure 3. The coordination environment of a central alkali-metal a) **1a** b) **1b**: Color codes as in Figure 1. Apical O44 atoms in **1a** are related by C_3 symmetry in the interatomic O···O distances of 0.87(8) Å fixed at 1/3 occupancy . $K{-}O_{\text{hexagonal}}$; 2.92 Å, $K{-}O_{\text{apical}}$; 2.68 Å. $Cs{-}O_{\text{three-coordinate}}$; 3.31–3.45 Å (mean, 3.40 Å), $Cs{-}O_{\text{two-coordinate}}$; 3.11–3.44 Å (mean, 3.26 Å).

$[Ce(Ce_2OH)(H_2O)_{10}(WO_2)_4(\alpha\text{-}AsW_9O_{33})_4]^{20-}$ **3**

$[\{Eu(H_2O)\}_3(\alpha\text{-}SbW_9O_{33})(W_5O_{18})_3]^{18-}$ **4**

$[Ce_3(CO_3)(\alpha\text{-}SbW_9O_{33})(W_5O_{18})_3]^{20-}$ **5**

$[(W_5O_{18})Ln(\alpha\text{-}SbW_9O_{33})Ln(H_2O)_2(W_5O_{18})]^{12-}$
(Ln = Eu, Dy, Er) **6**

$[\{Ln_3O(OH)_3(H_2O)_3\}_2Al_2(Nb_6O_{19})_5]^{26-}$ (Ln = Eu, Er, Lu) **7**

The fact that **1** and **2** were also obtained by mixing solutions containing $[\alpha\text{-}AsW_9O_{33}]^{9-}$ and Eu^{3+} ions with an aqueous solution containing alkali-metal ions at approximately 80 °C reveals that the $[Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})]^{6-}$ ion is the simple building unit for the crown-shaped ring structure. In the absence of any alkali-metal cations other than Na^+, no crown-shaped ring structure was formed, which suggests that the structure is stabilized by Cs^+ ions,[12] since the crystallization of **1a** was possible by treatment of a solution containing ligand, KCl, and Ln^{3+} with an aqueous solution containing Cs^+ ions. The structures of **1a** and **2a** originate from the approximately 90° Eu···As···Eu angle of the hexadentate $[\alpha\text{-}AsW_9O_{33}]^{9-}$ ligands coordinated to the $[Eu(H_2O)_2]^{3+}$ ions through the four three-coordinate and the two two-coordinate oxygen atoms which leads to the asymmetric position of the Eu^{3+} ion (Eu···As separations of 5.1 and 4.0–4.1 Å) on the almost linear As···Eu···As axis of the crown-shaped ring. The formation of the crown-shaped ring results from the cyclic polymerization of the $[Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})]^{6-}$ units which is governed by the radius of the encapsulated alkali-metal cation. Such an L-shaped $[Ln(H_2O)_2(\alpha\text{-}AsW_9O_{33})]^{6-}$ building unit provides an elegant approach to allow the development of the crown-shaped ring $[\{Ln(H_2O)_2(\alpha\text{-}AsW_9O_{33})\}_n]^{6n-}$ (n is an even number ≥ 8), which could encapsulate a large cation (such as $C_{60}{}^+$ or $C_{70}{}^+$ ion with the radius larger than Cs^+) which may form extended structures.

Experimental Section

1: A solution of $Na_2WO_4{\cdot}2H_2O$ (19.8 g, 60 mmol) and $NaAsO_2$ (0.87 g, 6.7 mmol) in water (60 mL) was heated at approximately 80 °C, thereafter acidified with 6 M HCl (20 mL, 120 mmol), and a solution of $Eu(NO_3)_3{\cdot}4H_2O$ (2.23 g, 5.0 mmol) in water (10 mL) was added. The solution pH was adjusted to 7–8 by the addition of KOH (8.0 g) in water (40 mL). The resulting cloudy solution was warmed again to approximately 80 °C and stirred for 30 min, then solid KCl (10 g) was added to precipitate the white product (21.8g), which was isolated by filtration. Recrystallization of the crude product (1.0 g) from a solution of CsCl (0.2 g) in water (40 mL) gave colorless hexagonal columnar crystals of **1**, which were isolated after the solution was left to stand at room temperature overnight. Yield: 0.18 g (18 % based on W). Elemental analysis (%) calcd: Cs 15.44, K 2.89, Eu 4.81, W 52.43, As 2.37; found: Cs 15.42, K 2.97, Eu 4.68, W 50.17, As 2.37. IR (KBr disk) metal–oxygen stretches at $\tilde{\nu} = 939$ (m), 883 (s), 795 (s), 715 cm^{-1} (s). For details of the synthesis of **2**, see Supporting Information.

Compounds **1** and **2** were also obtained by the reaction between the $[\alpha\text{-}AsW_9O_{33}]^{9-}$ ligand and the Ln^{3+} ion in an aqueous solution containing alkali-metal cations: For **1**, solid KCl (1.0 g, 13.4 mmol) was added to a solution of $Na_9(\alpha\text{-}AsW_9O_{33}){\cdot}19.5H_2O$ (1.4 g, 0.50 mmol)[13] and $Eu(NO_3)_3{\cdot}6H_2O$ (0.22 g, 0.50 mmol) in water (55 mL) at pH 6.2. The solution was warmed to approximately 80 °C for 30 min then cooled to room temperature to yield a white precipitate. After isolation of the crude product by filtration (1.5 g), a portion (1.0 g) was recrystallized from a solution of CsCl (0.2 g, 1.2 mmol) in water (30 mL) with a yield of 0.46 g.

Data for the single crystal X-ray studies of **1** and **2** were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer with a graphite monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) at −130° and −100 °C, respectively. Lorentz polarization effects and numerical absorption corrections (by using the program Numabs and Shape, T. Higashi, *Program for Absorption Correction*, Rigaku Corporation, Tokyo, **1999**) were applied to the intensity data, and H atoms were not indicated in the calculation. Na, K, and Cs atoms (except for disordered atoms) and As, Eu, and W atoms were refined anisotropically, and all the O atoms and the disordered atoms were refined isotropically.

For **1** a total of 53693 reflections (ω scan and $2\theta_{max} = 54.9°$) was collected of which 11261 unique reflections ($R_{int} = 0.11$) were used. Crystal data: $M_r = 19045.31$, Space group $P\bar{3}$ (No. 147), $a = 23.560(1)$, $c = 15.370(1)$ Å, $Z = 1$, $V = 7388.6(6)$ Å^3, $\rho = 4.26$ g cm^{-3}, $\mu = 258.3$ cm^{-1}, $F(000) = 8192$. Crystal size $= 0.20 \times 0.15 \times 0.15$ mm. Transmission factors of 0.03–0.40. The structure was solved by a direct method (SIR92) and refined based on 5521 observed reflections with $I > 3\sigma(I)$ and 330 parameters to $R_1 = 0.066$ (refined against $|F|$) and $R_w = 0.170$ (refined against $|F^2|$). The highest residual electron density was 6.0 e Å^{-3}. All calculations were performed using the teXsan software package (teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation **1998–1999**). The site occupancies of two Cs atoms (Cs4 and Cs5) and one K (K3) were fixed at 1/3, since distances between these atoms related by the C_3 symmetry are very short (< 3.0 and < 2.8 Å for Cs^+ and K^+, respectively), which may be brought about the disorder of these atoms. Similarly, the occupancy of O44 (apical coordination to K1) was also fixed at 1/3 because of the short distance (0.87(8) Å) between C_3-symmetric atoms. Furthermore, two water O atoms O42 and O43 were fixed at an occupancy of 1/2 because of their large thermal displacement parameters and short interatomic distance (2.4(1) Å), and the site occupancy of K4 was fixed at 5/6 to balance the charge of the molecule, which suggests the formula of **1** given.[14] A total of 22 Cs^+ (Cs1–Cs5) and 13 K^+ (K2–K4) counter cations are in the lattice coordinated by 5–14 oxygen atoms belonging to anion and lattice water molecules with Cs–O and K–O bond lengths of < 3.7 and < 3.2 Å, respectively. For details of **2**, see Supporting Information

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[12] Preliminary results showed that Na^+ ions in the absence of other alkali-metal cations formed the hamburger-type sandwiched

$[Yb_2(H_2O)_5(\alpha\text{-}AsW_9O_{33})_2]^{12-}$ ion, where the Yb^{3+} ion is seven-coordinate, being bound by two two-coordinate O atoms from each $[\alpha\text{-}AsW_9O_{33}]^{9-}$ ligand and five (including one Yb–O–Yb bridging) water molecules. Single-crystal X-ray analysis is in progress. For $Na_{12}[Yb_2(H_2O)_6(\alpha\text{-}AsW_9O_{33})_2]\cdot m\,H_2O$ IR (KBr disk): $\tilde{\nu} = 938$ (m), 887 (s), 788 (m), 724 cm^{-1} (s).

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[14] The existence of a broad asymmetric peak (at 579.4 and 580.3 nm with approximately 1:4 intensity ratio) for the $^5D_0 \rightarrow {}^7F_0$ transition in the 77 K photoluminescence spectrum (under the exposure to the 396 nm light corresponding to the $^7F_0 \rightarrow {}^5L_6$ transition) of solid **1** indicated the existence of at least two different sites (with approximate occupancy ratio of 1:4) for the Eu^{3+} luminescence. This supports the disorder (with 5/6 occupancy) for the K4 atom which is coordinated by water O atoms (O34 and O35) for $[Eu(H_2O)_2]^{3+}$, since the $^5D_0 \rightarrow {}^7F_0$ transition at about 580 nm cannot be split by any crystal field, see Supporting Information.

[15] Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-391197 **1** and CSD-391198 **2**.

Conducting Polymers

Facile Solid-State Synthesis of Highly Conducting Poly(ethylenedioxythiophene)[**]

Hong Meng, Dmitrii F. Perepichka, and Fred Wudl[*]

Conducting polymers continue to be a rapidly expanding, significant research area, attracting scientists from different disciplines.[1–3] Though synthesis has had a major role, a large effort has been focused on materials processing in organic electronics. Thin-film organic electronic devices such as light-emitting diodes, field effect transistors, solar cells, high-storage capacitors, and various other types of semiconductor devices have been widely investigated.[4–6] Efforts have also been directed toward developing new processing techniques and exploring new materials with a higher degree of molecular order.[2,7] However, the existence of very few single-crystalline polymers and the defects associated with the usual synthetic methods constitute a serious problem for the in-depth investigation of molecular order in conducting polymers.[8]

In general, it is not possible to obtain well-defined polymer structures unless the conducting polymers can be synthesized by endogenous polymerization routes, that is, without addition of initiators or catalysts. A possible solution for this problem lies in the solid-state polymerization of a structurally pre-organized crystalline monomer. The idea of solid-state polymerization of a suitable monomer in a well-ordered crystalline state was already realized in the 1960s and 1970s with polydiacetylenes and $(SN)_x$.[9–11] However, there were no reports on the solid-state synthesis of the most widely investigated conducting polymers—the polythiophenes. The importance of this goal is emphasized by the high potential of polythiophenes for industrial applications, as compared to other conducting polymers.[12] For example, the synthesis of poly(3,4-ethylenedioxythiophene), one of the most successful conducting polymers used in industry, is still confined to chemical or electrochemical oxidation of monomer solutions.[13] As a consequence, defect sites and a relatively low degree of intermolecular order limit the number of possible applications.

On the other hand, solid-state polymerization could give rise to a nearly defect-free, highly ordered or even "single-crystalline" conjugated polymer. With this in mind, while our discovery fall short of the mark regarding high degree of order, we report the first solid-state synthesis of conducting PEDOT by facile polymerization of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) in the solid state.

The monomer DBEDOT[14] is a white, crystalline solid, melting at 96 °C and very soluble in all common organic solvents. Its solutions in solvents such as tetrahydrofuran, hexane, xylene, chloroform, ethanol, acetone, dimethylformamide, 1,4-dioxane, and 1,2-dichlorobenzene are very stable, even on heating to reflux. However, prolonged storage of DBEDOT in the solid state at room temperature results in transformation of the sample to blue-black "crystals" or "fibers" with metallic luster, while retaining the morphology of the starting material (Figure 1). To our surprise, the blue-

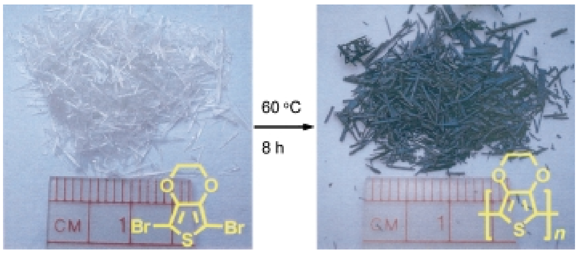

Figure 1. Photographs of crystals of DBEDOT (left) and PEDOT (right), formed on heating the crystals of the monomer at 60 °C for 8 h.

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