

Morphotropy in alkaline uranyl methacrylate complexes



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ABSTRACT

Five uranyl methacrylate complexes with monovalent cations have been synthesized via isothermal room temperature evaporation. The crystal structures of these compounds, $[\text{Li}(\text{H}_2\text{O})_2][\text{UO}_2(\text{macr})_3] \cdot 2\text{Hmacr}$ (**1**, macr denotes the methacrylate anion $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}^-$), $\text{Na}[\text{UO}_2(\text{macr})_3] \cdot \text{H}_2\text{O}$ (**2**), $\text{Rb}[\text{UO}_2(\text{macr})_3]$ (**3**), $\text{Tl}[\text{UO}_2(\text{macr})_3]$ (**4**) and $\text{Cs}[\text{UO}_2(\text{macr})_3]$ (**5**), were determined by single crystal X-ray diffraction. In **1–5**, the main uranyl-containing structural unit is the $[\text{UO}_2(\text{macr})_3]^-$ complex. Variation of the size and nature of the monovalent cations strongly influences the composition and the structure of the compounds. π -interactions between the methacrylate anions, which were previously reported in the crystal structures of $[\text{R}(\text{H}_2\text{O})_6][\text{UO}_2(\text{CH}_2\text{C}(\text{CH}_3)\text{COO})_3]_2 \cdot 8\text{H}_2\text{O}$ ($\text{R} = \text{Mg}$ or Zn), were observed in **1** and **2** as well, and may play an important structure-directing role. The crystals of **3**, **4** and **5** are lacking inversion centers and should exhibit non-linear optical (NLO) properties as well as the previously reported $\text{NH}_4[\text{UO}_2(\text{macr})_3]$ and $\text{K}[\text{UO}_2(\text{macr})_3]$ complexes. The second harmonic generation response of tris(methacrylato)uranylates with monovalent cations (except Tl) has been measured by the powder technique and discussed with respect to previously reported data on the acrylate analogs.

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1. Introduction

The element uranium is one of the most comprehensively studied elements in modern chemistry [1]. Considerable effort has been devoted to research of the actinide elements and particularly uranium because of their use in the nuclear fuel cycle and spent nuclear waste management [2–4]. Apart from its practical applications, there are also important fundamental aspects of uranium chemistry [5]. Uranium can adopt oxidation states from +2 to +6, and the most stable are +4 and +6 [6,7]. The participation of the f-electrons in chemical bonding leads to a variety of coordination geometries. In the solid state, the tetravalent uranium ion has a rather isotropic coordination environment, whereas the U(VI) ion tends to coordinate ligands in an anisotropic way, which is expressed in the formation of the linear UO_2 uranyl cation. The multiple $\text{U}=\text{O}$ bonds in the uranyl cation are much shorter than the equatorial bonds. The uranyl cation can coordinate from 3 to 7 atoms in the equatorial plane and usually adopts a bipyramidal coordination [8–10].

To date, the crystal structures of numerous organic and inorganic uranyl compounds have been studied [11–14]. Some of these compounds exhibit useful properties, such as luminescence and second-harmonic generation [15–19], or the ability to play the role of a polymerization photosensitizer for acrylonitrile, methyl methacrylate, acrylic and methacrylic acids [20,21]. Uranyl-mediated photochemical reactions can also produce peroxide in the presence of daylight, or oxidize cellulose [22,23]. Recent advances in the field of uranium crystal chemistry revealed a great structural diversity of the uranyl compounds. Although the uranyl cation has a rather limited set of first coordination sphere geometries, a great variety of topologies are obtained by exploiting various organic/inorganic ligands, additional metal centers (for example, 3d metals), and the variation of crystallization conditions, such as solvent, temperature, pH, reagent ratio and pressure [24–30]. In most cases the resulting products of a reaction with the uranyl cation can hardly be predicted. However, vast experimental data on uranyl crystal structures combined with modern topological analysis methods expands our ability to rationalize and optimize the synthetic approaches [13]. Due to the well-known affinity of the uranyl cation for carboxylate ligands, both mono- and polycarboxylic acids are often used in the syntheses of new uranyl compounds

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[13,14]. The growing interest in coordination polymers (and particularly metal–organic frameworks [31]) triggered intense studies on the reactions between the uranyl cation and di- and polycarboxylate acids, which may serve as linker molecules to connect the uranium centers. These ligands are often employed along with the hydrolysis of the uranyl cation under hydrothermal conditions, resulting in a great variety of new uranyl coordination polymers with fascinating structures [22,32–36].

In contrast to the uranyl compounds with polycarboxylate ligands, the synthesis of uranyl monocarboxylates attracts less attention. The reason for this is that the monocarboxylate species cannot be utilized as bridging ligands in coordination polymer design. However, the use of monocarboxylate ligands can turn into a benefit in the study of intermolecular interactions in the crystals of uranyl complexes. For example, one can exploit a monocarboxylate anion as a ligand for an investigation of the intermolecular interactions in the solid state by varying the substituents and their nature in the ligand. Intermolecular interactions have been extensively studied in organic and organometallic chemistry, but a diverse array of supramolecular interactions (i.e. halogen bonding) was employed in the crystal design of actinide compounds only recently [13,32,37]. Besides, uranyl monocarboxylate compounds can exhibit non-linear optical properties, which can be enhanced by introducing unsaturated carboxylate species instead of saturated ones [17]. As well, unsaturated uranyl compounds can undergo solid state dimerization reactions [38], which can be used for uranium immobilization. In this paper we report the synthesis and structural investigation of five novel uranyl methacrylate complexes with monovalent cations.

2. Material and methods

2.1. Caution!

^{238}U is an alpha-particle emitting radionuclide and standard precautions for handling radioactive materials should be followed when working with the quantities used in the syntheses that follow.

2.2. Synthesis

All materials, except UO_3 , were obtained via commercially available sources and used without further purification. UO_3 was obtained by exposing of uranyl nitrate $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in air at a temperature of $350\text{ }^\circ\text{C}$ for 24 h. As methacrylic acid tends to polymerize in the presence of both uranyl cations and UV radiation, all preparations should be carried out in the absence of daylight.

1–5 were obtained by the isothermal room-temperature evaporation of aqueous solutions. The solutions were prepared by dissolving a sample of uranium oxide UO_3 (0.100 g, 0.35 mmol) in an aqueous solution of methacrylic acid in a 1:16 uranium to acid molar ratio. Finely ground samples of Li_2CO_3 (0.026 g, 0.35 mmol), Na_2CO_3 (0.037 g, 0.349 mmol), RbCl (0.085 g, 0.70 mmol), TlCl (0.168 g, 0.70 mmol) or CsCl (0.118 g, 0.70 mmol) for **1–5**, respectively, were added to the solutions so that the monovalent cation to uranium ratio was equal to 2:1. Although TlCl has low solubility in water, the presence of both uranyl cations and methacrylic acid facilitates its dissolution. The resulting yellow transparent solutions were left for slow evaporation at room temperature, approximately $25\text{ }^\circ\text{C}$. Yellow block crystals precipitated in one week and were filtered with a glass filter and dried on air overnight. Several attempts were performed to obtain a pure phase of **4**, but all were unsuccessful. Yields (based on U): 32% (**1**), 29% (**2**), 46% (**3**), 55% (**5**).

IR (KBr, cm^{-1}): **1**: 3391 m. [$\nu(\text{H}_2\text{O})$]; 1708 m.; 1661 w. [$\delta(\text{H}_2\text{O})$]; 1637 m. [$\nu(\text{C}=\text{C})$]; 1518 v.s. [$\nu_{\text{as}}(\text{COO})$]; 1459 v.s. [$\nu_{\text{s}}(\text{COO})$]; 1440 v.

s. [$\nu_{\text{s}}(\text{COO})$]; 1376 w. [$\delta(\text{CH}_2)$]; 1240 m. [$\delta(\text{C}-\text{H})$]; 1163 w. [$\delta(\text{CH}_2)$]; 1008 w. [$\delta(\text{CH}_3)$]; 951 m. [$\nu(\text{C}-\text{C})$]; 935 v.s. [$\nu_{\text{as}}(\text{UO}_2)$]; 871 m.; 831 w. [$\nu(\text{C}-\text{C})$]; 624 s. [$\rho(\text{COO})$].

2: 3476 m. [$\nu(\text{H}_2\text{O})$]; 1644 m. [$\nu(\text{C}=\text{C})$]; 1514 v.s. [$\nu_{\text{as}}(\text{COO})$]; 1461 v.s. [$\nu_{\text{s}}(\text{COO})$]; 1442 v.s. [$\nu_{\text{s}}(\text{COO})$]; 1374 m. [$\delta(\text{CH}_2)$]; 1240 m. [$\delta(\text{C}-\text{H})$]; 1006 w. [$\delta(\text{CH}_3)$]; 929 v.s. [$\nu_{\text{as}}(\text{UO}_2)$]; 868 s.; 832 m. [$\nu(\text{C}-\text{C})$]; 622 s. [$\rho(\text{COO})$].

3: 1646 w. [$\nu(\text{C}=\text{C})$]; 1509 v.s. [$\nu_{\text{as}}(\text{COO})$]; 1461 v.s. [$\nu_{\text{s}}(\text{COO})$]; 1439 v.s. [$\nu_{\text{s}}(\text{COO})$]; 1375 w. [$\delta(\text{CH}_2)$]; 1238 m. [$\delta(\text{C}-\text{H})$]; 1007 w. [$\delta(\text{CH}_3)$]; 930 v.s. [$\nu_{\text{as}}(\text{UO}_2)$]; 866 m.; 833 w. [$\nu(\text{C}-\text{C})$]; 620 s. [$\rho(\text{COO})$].

4: 1644 w. [$\nu(\text{C}=\text{C})$]; 1493 v.s. [$\nu_{\text{as}}(\text{COO})$]; 1458 v.s. [$\nu_{\text{s}}(\text{COO})$]; 1436 v.s. [$\nu_{\text{s}}(\text{COO})$]; 1374 w. [$\delta(\text{CH}_2)$]; 1237 m. [$\delta(\text{C}-\text{H})$]; 1007 w. [$\delta(\text{CH}_3)$]; 929 v.s. [$\nu_{\text{as}}(\text{UO}_2)$]; 864 m.; 831 w. [$\nu(\text{C}-\text{C})$]; 620 m. [$\rho(\text{COO})$].

5: 1643 w. [$\nu(\text{C}=\text{C})$]; 1512 v.s. [$\nu_{\text{as}}(\text{COO})$]; 1461 v.s. [$\nu_{\text{s}}(\text{COO})$]; 1439 v.s. [$\nu_{\text{s}}(\text{COO})$]; 1373 w. [$\delta(\text{CH}_2)$]; 1239 m. [$\delta(\text{C}-\text{H})$]; 1006 w. [$\delta(\text{CH}_3)$]; 946 m. [$\nu(\text{C}-\text{C})$]; 928 v.s. [$\nu_{\text{as}}(\text{UO}_2)$]; 865 m.; 833 w. [$\nu(\text{C}-\text{C})$]; 620 s. [$\rho(\text{COO})$].

2.4. Infrared spectroscopy

Infrared spectra were collected for **1–5** as KBr pellets on a Perkin Elmer Spectrum 100 FT-IR spectrometer in the range $400\text{--}4000\text{ cm}^{-1}$. The absorption bands of the spectra were assigned using the literature data [39,40].

2.5. X-ray crystallography

Single crystal X-ray diffraction data (φ - and ω - scans) were collected at 100 K on a Bruker KAPPA APEX II diffractometer using $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). Single crystals were mounted on a glass fiber with epoxy glue for the structure determination. The data were collected using a narrow-frame method with the ω -scan mode. Empirical multi-scan absorption corrections were applied with either SADABS (all except **3**) or TWINABS (**3**) software. The structures were solved by direct methods using SHELXS-2014 and then refined anisotropically by full-matrix least-squares refinement on F^2 [41]. Positions of the hydrogen atoms of the methacrylate groups were calculated geometrically and refined in the riding model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}_i)$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}_i)$ for CH_2 and CH_3 groups, where $U_{\text{eq}}(\text{C}_i)$ are the equivalent thermal parameters of the carbon atoms. Disorder of the methacrylate groups in **1** was accounted for by introducing methyl and methylene hydrogen atoms with 0.5 occupancies. The hydrogen atoms of water molecules in **1** and **2** were located from difference Fourier synthesis and refined with the O–H bond lengths restrained to $0.95(2)\text{ \AA}$. A series of crystals of **3** was picked and all of the crystals were found to be non-merohedral twins. Both twin components of **3** were taken into account using HKLF 5 and BASF instructions. Relevant crystallographic data and details of the experimental conditions for all crystals are summarized in Table 1.

2.6. Crystal chemical calculations

All crystal chemical calculations were performed with the TOPOS 4.0 software package [42,43]. The Voronoi-Dirichlet polyhedron (VDP) of an atom is a convex polyhedron whose inner points are closer to the selected atom than to any other atom of this crystal structure. The main VDP characteristics, such as the volume (V_{VDP}), the displacement of the atom from the centroid of its VDP (D_{A}), were calculated using the Dirichlet program. Coordination sequences of MUO_6 metal–oxygen frameworks in **3–5** were calculated with the ADS program.

The analysis of the interchain interactions in **2** was performed with the method of molecular VDP [43–45]. This method serves

Table 1
Crystallographic data for **1–5**.^a

Chemical formula	[Li(H ₂ O) ₂][UO ₂ (macr) ₃]·2Hmacr (1)	Na[UO ₂ (macr) ₃]·H ₂ O (2)	Rb[UO ₂ (macr) ₃] (3)	Tl[UO ₂ (macr) ₃] (4)	Cs[UO ₂ (macr) ₃] (5)
Formula weight	740.42	566.28	610.74	729.64	658.18
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	trigonal
Space group	C2/c	P2 ₁ /n	P2 ₁	P2 ₁	R3
Z	4	8	4	4	12
a (Å)	9.8061(2)	8.63240(10)	11.9192(3)	11.9030(3)	17.5961(2)
b (Å)	12.7995(3)	33.0471(6)	11.8775(3)	11.8478(3)	17.5961(2)
c (Å)	21.7984(4)	12.7440(2)	11.9654(3)	11.9614(3)	19.7831(4)
β (°)	90.1670(10)	103.2780(10)	94.856(2)	95.1270(10)	90.00
V (Å ³)	2735.97(10)	3538.36(10)	1687.86(7)	1680.10(7)	5304.66(16)
ρ _{calcd.} (g cm ⁻³)	1.798	2.126	2.403	2.885	2.472
μ, (mm ⁻¹)	5.995	9.238	12.515	19.239	11.240
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Color	yellow				
Crystal dimension (mm)	0.40 × 0.34 × 0.28	0.34 × 0.18 × 0.12	0.36 × 0.32 × 0.20	0.40 × 0.28 × 0.20	0.26 × 0.20 × 0.16
Reflections/Unique	20648/3976	35573/7982	18189/18189	59526/13747	20842/5337
Goodness of fit	1.236	1.070	1.018	1.061	0.836
R ₁ [I > 2σ(I)]	0.0325	0.0458	0.0375	0.0207	0.0235
wR ₂ (all data)	0.0756	0.0982	0.0847	0.0391	0.0447
Flack	–	–	0.017(5)	0.016(3)	0.021(3)

^a macr = methacrylate anion CH₂=C(CH₃)COO⁻.

as a tool for analysis of intermolecular interactions in crystal structures using characteristics of molecular VDPs. A molecular VDP comprises all the atomic VDPs of a molecular, chain or layer unit. This method usually employs the following set of descriptors: S_{ij} and δ_{AZ} show the area of an A/Z contact in the absolute and partial (expressed as the percentage of the total intermolecular surface area) units, where A and Z are the chemical sorts of atoms sharing a common VDP face; k_{ij} – the overall amount of A/Z contacts per formula unit; d_{\min} and d_{\max} – minimum and maximum intermolecular distances between A and Z atoms. The overall molecular VDP interchain surface area was normalized to the single formula unit of compound **2**.

2.7. Second harmonic generation measurements

Non-centrosymmetric compounds (except the Tl-containing one, which was not obtained in the form of a pure phase) were shown to be non-centersymmetric by second harmonic generation (SHG) measurements with the method described in [46]. A YAG:Nd laser ($\lambda = 1.064 \mu\text{m}$) was used as the source of the radiation, with a repetition rate of 10–15 impulses per second and a duration of impulses of about 10–12 ns. The registration of doubled frequency radiation ($I_{2\omega}$) in the backward direction was performed using the powder crystalline samples of the studied compounds and compared with the intensity of radiation generated by a sample of α -quartz with a particle size of about $3 \mu\text{m}$ ($I_{2\omega}$ /SiO₂).

3. Results and discussion

In all the compounds under consideration, the uranyl cations coordinate three methacrylate anions to form typical tricarboxylate [UO₂(macr)₃]⁻ complexes [14]. The uranium atoms are 8-coordinated with a hexagonal bipyramidal environment. The axial and equatorial U–O bond lengths are in the ranges 1.739(6)–1.775(6) and 2.422(6)–2.491(9) Å, respectively. The volumes of the Voronoi-Dirichlet polyhedra of the U atoms span a range from 9.23 to 9.42 Å³ and agree well with the average 9.3(4) Å³ found for U^{VI}O_n VDPs [8].

3.1. [Li(H₂O)₂][UO₂(macr)₃]·2Hmacr (Hmacr = methacrylic acid) (1)

Compound **1** crystallizes in the monoclinic space group C2/c. The crystal structure of **1** is built from electroneutral molecular

{[Li(H₂O)₂][UO₂(macr)₃]} units (Fig. 1), which have a twofold rotational symmetry, and methacrylic acid molecules. In the {[Li(H₂O)₂][UO₂(macr)₃]} unit, the Li atom is bound to two carboxylate O atoms from two adjacent methacrylate anions and two water molecules to complete its tetrahedral environment. The Li–O bond lengths and OLiO angles are in the ranges 1.913(6)–1.922(6) Å and 87.8(4)–119.86(16)°, respectively. It is noteworthy that the methacrylate anions in the [UO₂(macr)₃]⁻ complexes are mostly flat and disordered so that the C–CH₃ and C=CH₂ fragments cannot be distinguished unambiguously by the interatomic C–C distances, which are in a rather narrow range from 1.391(7) to 1.414(8) Å. This kind of disorder is observed in the crystal structures of the previously reported compounds CH₂C(CH₃)COOLi and [R(H₂O)₆][UO₂(macr)₃]₂ (R = Mg and Zn) as well [47,48].

Of the six carboxylate O atoms comprised in the [UO₂(macr)₃]⁻ complex only two are coordinated by the Li atoms, whereas the remaining four are involved in hydrogen bonding with either water molecules from an adjacent {[Li(H₂O)₂][UO₂(macr)₃]} complex or methacrylic acid molecules. It is noteworthy that the {[Li(H₂O)₂][UO₂(macr)₃]} unit contains four donors and four acceptors of hydrogen bonds and, therefore, does not require other kinds of molecules to fulfill its full hydrogen bonding potential. Nevertheless, there are outer sphere methacrylic acid molecules that have both a hydrogen bond donor and an acceptor sites. The methacrylic acid molecules serve as a hydrogen bond bridge by linking neighboring {[Li(H₂O)₂][UO₂(macr)₃]} complexes (Fig. 2). The hydrogen bonds connect the complexes into layers perpendicular to the c axis. The underlying net of the layers corresponds to the square planar net, whose nodes are associated with {[Li(H₂O)₂][UO₂(macr)₃]} units. The methacrylic acid molecules decorate the net with 2-c nodes, which offer an additional edge to each pair of linked nodes.

In our recent work we have noticed that a parallel orientation of the methacrylate anions in the crystal structures of [R(H₂O)₆][UO₂(macr)₃]₂ (R = Mg and Zn) is preferred and may play a subtle structure-directing role [48]. Although these two compounds and **1** share a common uranyl structural unit, with only slight geometrical variations, the nature of the outer sphere cation implies significant differences in their structures. However, the structure of **1** contains methacrylate anions with a parallel mutual orientation as well. Taking into account the twofold symmetry of the {[Li(H₂O)₂][UO₂(macr)₃]} unit (and the [UO₂(macr)₃]⁻ complex thereof), there are two unique methacrylate anions in the [UO₂(macr)₃]⁻ complex. One of them has C₂ symmetry and is

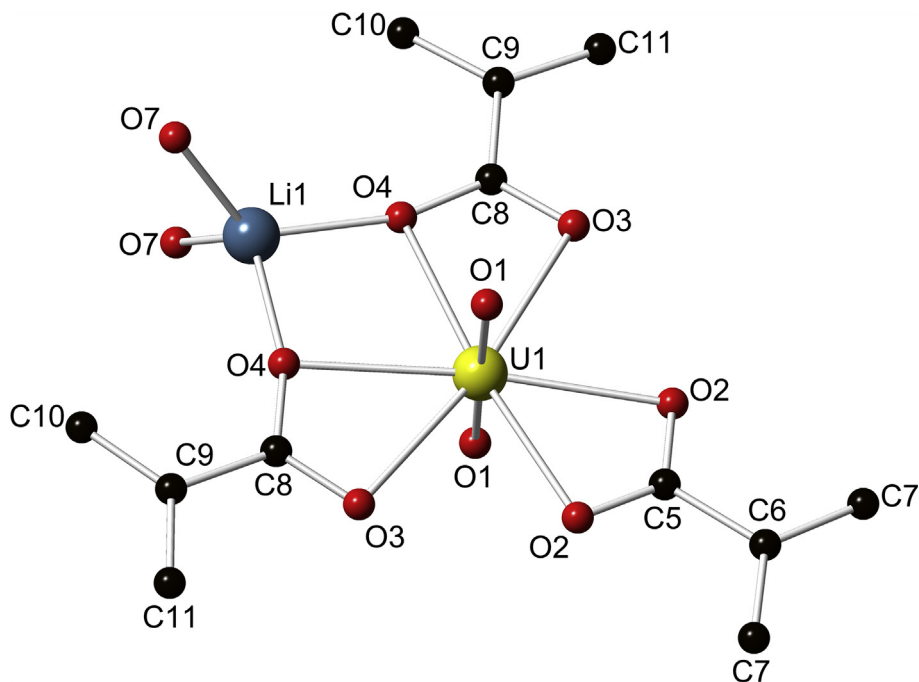


Fig. 1. A view of the $\{[Li(H_2O)_2][UO_2(macr)_3]\}$ unit and numeration scheme in the structure of $[Li(H_2O)_2][UO_2(macr)_3] \cdot 2Hmacr$ (1). Hydrogen atoms are omitted for clarity.

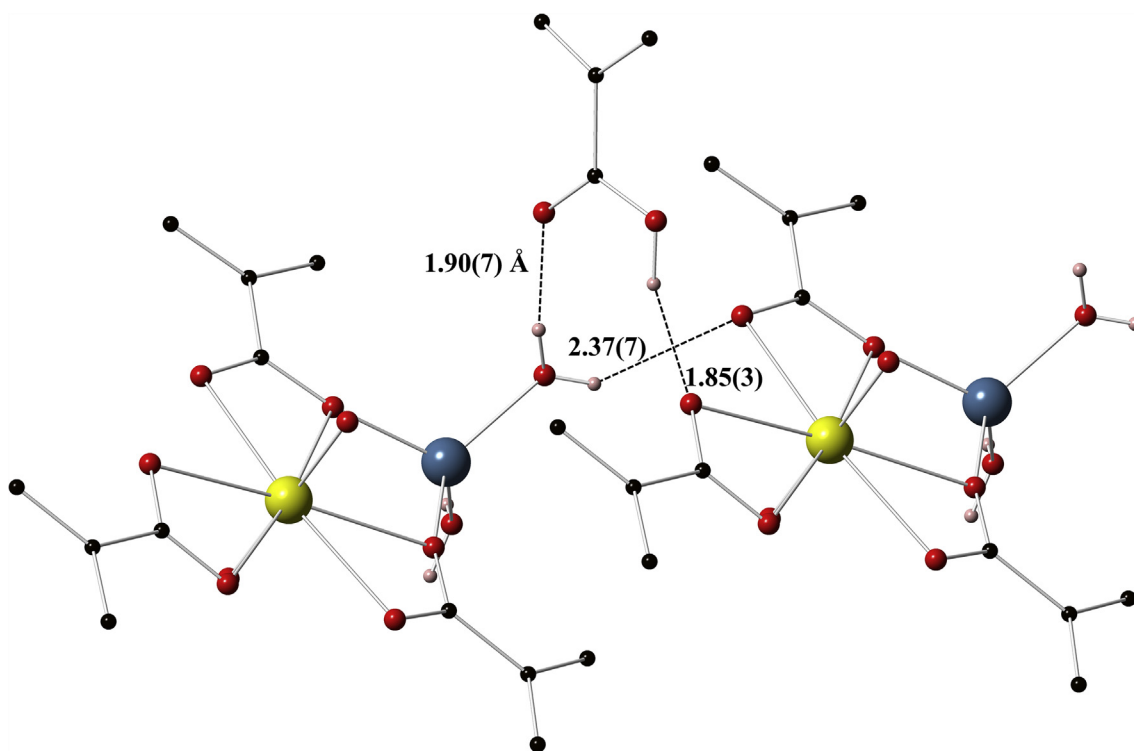


Fig. 2. Hydrogen bonding between $\{[Li(H_2O)_2][UO_2(macr)_3]\}$ units. H atoms belonging to CH_2 and CH_3 groups are omitted for clarity.

stacked by two methacrylate anions from adjacent complexes, which are located above and below at a distance of approximately 3.6–3.8 Å (calculated as the distance between the plane of the middle methacrylate anion and the atoms belonging to either of the two adjacent methacrylate anions) with the plane-plane angle being equal to 3.7° (Fig. 3). Such an arrangement of the methacrylate anions can be considered as $\pi \cdots \pi$ interactions between non-aromatic molecules, which are responsible (along with hydrogen

bonding) for the cohesion of the $\{[Li(H_2O)_2][UO_2(macr)_3]\}$ units into the layers. The methacrylic acid molecules also interact through similar interactions. Due to the presence of an inversion center between them, the methacrylic acid molecules are arranged in exactly parallel pairs of molecules separated by a distance of 3.61 Å. These interactions participate in connecting the layers into a framework because the molecules of the pair belong to adjacent layers.

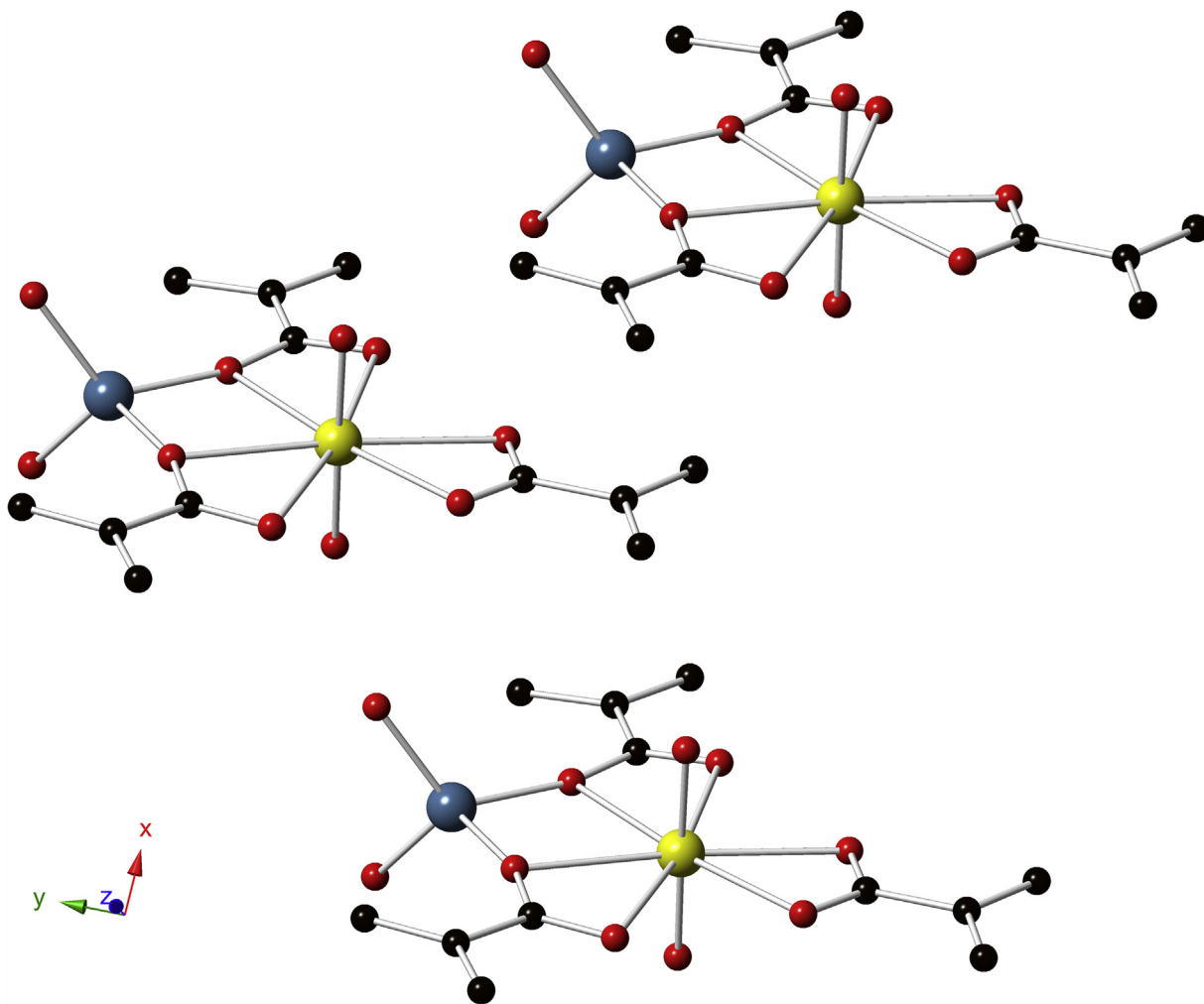


Fig. 3. Parallel orientation of the methacrylate anions in **1**.

3.2. $\text{Na}[\text{UO}_2(\text{macr})_3] \cdot \text{H}_2\text{O}$ (**2**)

The structure of **2** consists of electroneutral chains extending along the [001] direction (Fig. 4). **2** exhibits two crystallographically independent uranium and two sodium atoms. Each unique uranyl cation coordinates three methacrylate anions in its equatorial plane to form a $[\text{UO}_2(\text{macr})_3]^-$ complex. The Na1 and Na2 atoms are bound to five O atoms belonging to either of two $[\text{UO}_2(\text{macr})_3]^-$ complexes or a water molecule. The water molecule participates in hydrogen bonding with the oxo atoms of complexes

of a neighboring chain. Thus, the hydrogen bonding connects the chains into bulky layers in the *ac* plane. In contrast to the structure of **1**, the disorder of the methacrylate anions in **2** is less pronounced. However, four of the six crystallographically unique methacrylate anions have a noticeable difference in the C–C distances involving terminal C atoms within the same anion, ranging from 0.10 to 0.16 Å. It allows us to distinguish methyl and methylene groups in these cases.

Both crystallographic sorts of Na atoms have a coordination polyhedron in the shape of a pentagonal bipyramid. The $\text{Na}1\text{O}_5$

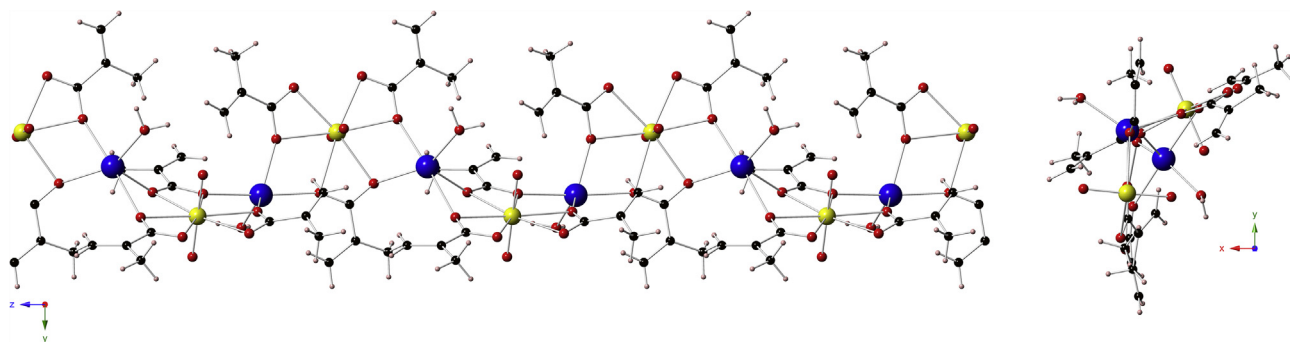


Fig. 4. A view on the chains in $\text{Na}[\text{UO}_2(\text{macr})_3] \cdot \text{H}_2\text{O}$ (**2**) along the *a* (left) and *c* (right) axes. Na atoms are shown in blue. (Color online.)

coordination polyhedron is quite distorted, which is supported by the sodium atom D_A value equal to 0.24 Å (shows the shift of a central atom from the centroid of its VDP; the higher the D_A value the more distorted the environment of the atom is [43]). The Na2 atom has a less distorted polyhedron, as indicated by its D_A value of 0.07 Å. The Na1 coordination polyhedron distortion stems from a shift of the water molecule with respect to the remaining four oxo atoms from the $[\text{UO}_2(\text{macr})_3]^-$ complexes. In both cases there are almost linear “axial” ONaO fragments (the angles are 175.7 and 173.7° for the atoms Na1 and Na2, respectively) that involve O atoms from the two neighboring uranyl complexes. In the more even Na_2O_5 coordination polyhedron, the equatorial angles are equal to 110.5(2)°, 123.0(2)°, and 125.3(2)°, whereas in Na_1O_5 these are 111.2(2)°, 101.6(2)°, and 146.8(3)°. In both cases, the first angle involves only the O atoms of the uranyl complexes, and the other two indicate the relative positions of the water molecule in the equatorial plane. Distorted coordination polyhedra are common for Na atoms due to the ionic nature of the Na–O bond and the absence of a predetermined geometry. However, as can be seen from the D_A value of 0.06(6) Å averaged over 974 crystallographically unique NaO_n coordination polyhedra, an even environment is preferred in NaO_n coordination polyhedra [49]. The positions of the water molecules are therefore favored by hydrogen bonding. Indeed, in both cases, the water molecules occupy a position which allows for stronger hydrogen bond formation.

Besides hydrogen bonding, there are $\pi \cdots \pi$ interactions between the methacrylate anions of adjacent chains as well. The abovementioned bulky layers, being formed from the chains by hydrogen bonding, also interact with each other through the $\pi \cdots \pi$ interactions of the methacrylate anions. In order to estimate the contribution of different types of interactions, we calculated characteristics of the molecular VDP [44,45]. According to the obtained data (Table 2), hydrogen bonds (H/O contacts) and dispersion interactions (H/H and H/C contacts) contribute most in the overall molecular VDP surface area. A similar distribution of contributions is observed in some other molecular uranyl carboxylate structures [48,50,51]. The presence of faint C/C and C/O contacts, which are 1.1 and 0.6%, respectively, may be attributed to π -interactions among the methacrylate anions. The remaining Na/H contact may be assigned to an interchain pseudo-agostic interaction [52].

3.3. $\text{Rb}[\text{UO}_2(\text{macr})_3]$ (**3**), $\text{Tl}[\text{UO}_2(\text{macr})_3]$ (**4**) and $\text{Cs}[\text{UO}_2(\text{macr})_3]$ (**5**)

Because of the similar sizes of the Rb^+ and Tl^+ cations, **3** and **4** are isostructural and crystallize in the monoclinic $P2_1$ space group, whereas their Cs analog **5** has trigonal (R3) symmetry. Despite the difference in symmetry, these compounds have similar structures and thus are described together. In **3–5**, there are two crystallographically unique U atoms, both forming $[\text{UO}_2(\text{macr})_3]^-$ complexes. Each $[\text{UO}_2(\text{macr})_3]^-$ complex binds three monovalent cations via pairs of O atoms from adjacent carboxylate groups (Fig. 5). The monovalent cations are 6-coordinated, with a severely distorted octahedral geometry, and are coordinated by the O atoms of three $[\text{UO}_2(\text{macr})_3]^-$ complexes. The methyl and methylene

groups within the methacrylate anions were distinguished by the differences in the bond lengths involving the terminal C atoms, which span the range 0.04–0.19 Å. However, in the cases with rather small differences, 0.04–0.07 Å, a proper group cannot be assigned undoubtedly, and the corresponding methacrylate anions are likely disordered.

Similar compositions, coordination numbers and local geometries of the cations in **3–5** allow the suggestion that these compounds belong to a single isorecticular series. For topological analysis, the structures of **3–5** were reduced to the metal–oxygen MUO_6 frameworks by removing the C and H atoms which do not contribute to the connectivity between the metal centers, and the coordination sequences, showing the amount of metal atoms in a n^{th} coordination sphere, were calculated [51,53]. The coordination sequences are listed in Table S1 and support the suggestion that compounds **3–5** are isorecticular. The same topology is also observed in the metal–oxygen framework of the cubic acetate $\text{Na}[\text{UO}_2(\text{CH}_3\text{COO})_3]$, acrylates $\text{M}[\text{UO}_2(\text{CH}_2=\text{CHCOO})_3]$ ($\text{M} = \text{K}, \text{NH}_4, \text{Rb}, \text{Cs}$) and crotonates $\text{M}[\text{UO}_2(\text{CH}_3\text{CH}=\text{CHCOO})_3]$ ($\text{M} = \text{K}, \text{Rb}$) [17,18,54]. Along with the recently reported ammonium and potassium analogs, $\text{K}[\text{UO}_2(\text{macr})_3]$ and $\text{NH}_4[\text{UO}_2(\text{macr})_3]$ (sp. gr. $P2_1$) [55], **3–5** are the first examples of complexes with this stoichiometry and topology, having non-cubic symmetry. The structures of **3–5** contain no common symmetry operators since there is only a 2_1 screw axis in **3** and **4** ($P2_1$ sp.gr.) and a threefold axis in **5** (R3). Nevertheless, both these space groups are subgroups of the general $P2_13$ space group. Therefore, both these structural types were obtained by slight distortions of the cubic structural type, which was observed in the abovementioned acetate, acrylate and crotonate compounds. The symmetry decrease in the methacrylate series may be due to the alteration of the ligand to monovalent cation volume ratio compared to the compounds of the cubic series [56]. However, the crotonate complexes $\text{M}[\text{UO}_2(\text{CH}_3\text{CH}=\text{CHCOO})_3]$ ($\text{M} = \text{K}, \text{Rb}$) and their methacrylate counterparts $\text{M}[\text{UO}_2(\text{CH}_2=\text{C}(\text{CH}_3)\text{COO})_3]$ ($\text{M} = \text{K}, \text{Rb}$) are isomeric, thus they should have similar ratios and the symmetries. The difference in their symmetries evidences the fact that not only the volume of the ligand, but also its structure plays an important role in the symmetry of the crystals of tris(carboxylato)uranylates. However, the overall motif of the structures and their topology is not affected by the ligand isomerization.

3.4. Non-linear optical properties

Similar to the previously studied acrylate analogs, the reported methacrylate compounds exhibit non-linear optical (NLO) properties, which were measured by SHG techniques. For comparison, all the Q values (showing the SHG response relative to the response of $\alpha\text{-SiO}_2$) are summarized together with the previously reported ones in the following table:

$\text{R}[\text{UO}_2\text{L}_3]$	$\text{R} = \text{K}^+$	NH_4^+	Rb^+	Cs^+
L = acrylate	16.0	1.2	4.5	4.1
L = methacrylate	3.5	3.3	5.9	8.6

Table 2
Interchain contacts in $\text{Na}[\text{UO}_2(\text{macr})_3] \cdot \text{H}_2\text{O}$ (**2**).

Contact type	k_{ij}	$d_{\text{min}}, \text{Å}$	$d_{\text{max}}, \text{Å}$	$S_{ij}, \text{Å}^2$	$\delta_{\text{AZ}}, \%$
C/O	13	3.17	4.20	3.4	1.1
C/C	10	3.46	4.45	1.8	0.6
H/O	80	1.87	4.82	134.2	44.4
H/C	43	2.76	4.39	38.4	12.7
H/H	77	2.22	4.52	121.5	40.2
Na/H	5	3.73	4.55	2.9	1.0
Sum	227	1.87	4.82	302.2	100.0

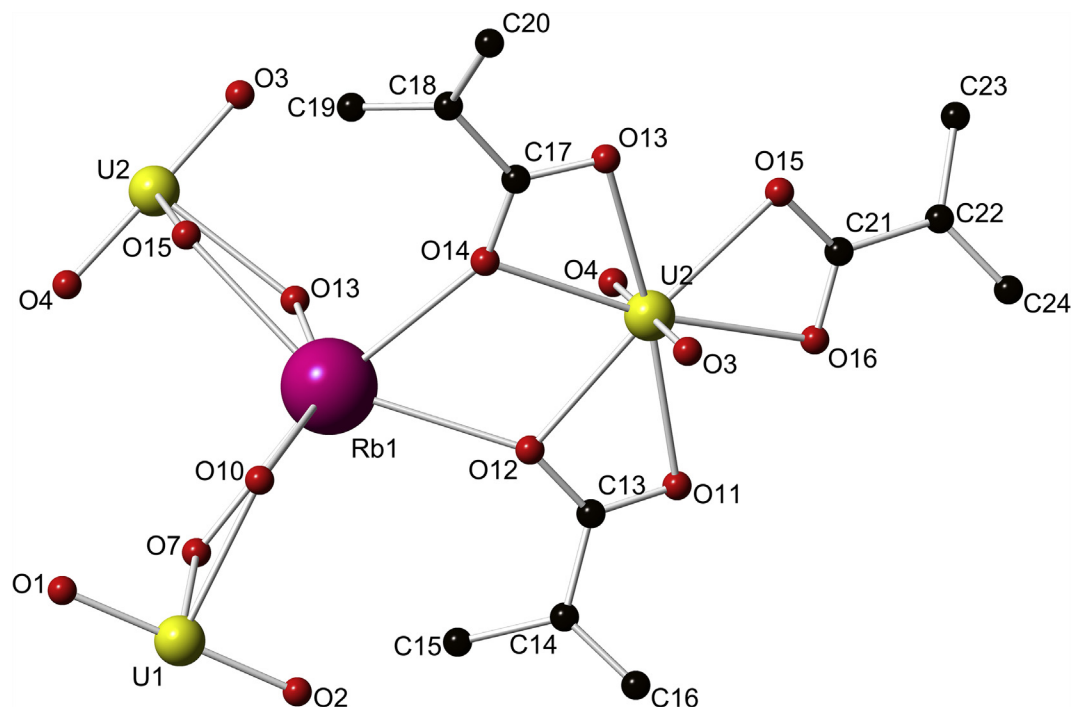


Fig. 5. A fragment of the crystal structure of $\text{Rb}[\text{UO}_2(\text{macr})_3]$ (**3**). For the sake of clarity, only one $[\text{UO}_2(\text{macr})_3]^-$ complex is shown.

It can be seen from this table that on the contrary to the acrylate series, where SHG decreases with the increase of the monovalent cation size, the highest Q value among the methacrylate series is observed in $\text{Cs}[\text{UO}_2(\text{CH}_2=\text{C}(\text{CH}_3)\text{COO})_3]$, which contain the largest monovalent cation. We have not revealed a single value that would explain the controversial behavior of the non-linear activity in both series, as well as in the other tris(carboxylato)uranyl complexes with NLO properties. It is likely, that there are some competing factors, e.g. the nature of the ligand, size of the monovalent cations, mutual packing of complexes, etc., which complicate the explanation of the observed tendency. Despite this, it is clear that in the methacrylate series the symmetry (and the arrangement of the structural units thereof) changes in a way that enhances the SHG response. The geometric changes probably relate to the mutual orientation of tris(methacrylato)uranyl complexes and monovalent cations. Indeed, in the methacrylate series the SHG response increases along with the steadiness of the monovalent cation environment, which can be expressed as the G_3 value (the lower the G_3 value, the steadier the environment of the atom) [43]. The average G_3 parameter of the monovalent cations in the methacrylate series is equal to 0.082657, 0.081626 and 0.080701 for $\text{R} = \text{K}$, Rb and Cs , respectively. However, in the acrylate series, the G_3 values are approximately the same and do not explain the observed tendency.

4. Conclusion

A series of uranyl methacrylate complexes with monovalent cations, $[\text{Li}(\text{H}_2\text{O})_2][\text{UO}_2(\text{macr})_3] \cdot 2\text{Hmacr}$ (**1**, $\text{macr} = \text{CH}_2\text{C}(\text{CH}_3)\text{COO}^-$), $\text{Na}[\text{UO}_2(\text{macr})_3] \cdot \text{H}_2\text{O}$ (**2**), $\text{Rb}[\text{UO}_2(\text{macr})_3]$ (**3**), $\text{Tl}[\text{UO}_2(\text{macr})_3]$ (**4**), and $\text{Cs}[\text{UO}_2(\text{macr})_3]$ (**5**), has been synthesized. All the compounds contain the $[\text{UO}_2(\text{macr})_3]^-$ complex as the main structural unit. Depending on the nature of the monovalent cation, these compounds adopt molecular (**1**), chain (**2**) or framework (**3–5**) structures. In the structures of **1** and **2**, hydrogen bonding ensures cohesion of molecular and chain fragments into layers, which are connected through π -interactions between the

methacrylate groups of adjacent layers. The method of molecular Voronoi–Dirichlet polyhedra shows excessive hydrogen bonding and dispersive forces in the interchain interactions in **2**.

The structures of **3–5** were shown to be isorecticular with some previously reported cubic uranyl carboxylates. Among them are isomeric crotonates $\text{M}[\text{UO}_2(\text{CH}_3\text{CH}=\text{CHCOO})_3]$ ($\text{M} = \text{K}$, Rb). Despite the same topology, composition and size of the ligands, the symmetry of the methacrylate compounds **3** and **4** is lower (monoclinic $\text{P}2_1$ space group) compared to their crotonate analogs (cubic $\text{P}2_13$ space group), which points to the importance of the ligand structure in the structure distortion in **3** and **4**.

All the studied non-centrosymmetric compounds, except the Tl-containing one, which was not obtained in the form of a pure phase, exhibit non-linear optical properties. The SHG response grows as the environment of the monovalent cation becomes more even.

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Appendix A. Supplementary data

CCDC 1515291–1515295 contains the supplementary crystallographic data for **1–5**. These data can be obtained free of charge via <http://dx.doi.org/10.1016/j.poly.2017.04.041>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2017.04.041>.

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