Syntheses and Properties of Ditelluroxanes and Oligochalcogenoxanes: Hypervalent Oligomers with Te–O Apical Linkages in the Main Chain

Kenji Kobayashi,*[a] Kunimasa Tanaka,[a] Hiroyuki Izawa,[a]
Yoriko Arai,[a] and Naomichi Furukawa[a, b]

Abstract: The reaction of ditelluroxanes $[Ar_2Te\text{-}O\text{-}TeAr_2]^{2+}[X]_2^-$ (**2**) (Ar = *p*-tolyl) with a telluroxide **1**, a selenoxide **7**, or a carboxylate **10** to produce oligochalcogenoxanes with hypervalent Te–O apical linkages in their main chain is described. The ^{125}Te NMR chemical shifts of **2** (**2a**: $X^- = CF_3SO_3^-$, **2b**: $X^- = CF_3CO_2^-$, **2c**: $X^- = CH_3CO_2^-$, **2d**: $X^- = Cl^-$) are shifted downfield with decreasing nucleophilicity of the counteranions. This result reflects both the cationic character and the reactivity of the Te atoms of **2**. The reaction of **2a** with one, two, three, or four equivalents of telluroxide **1a** (Ar = *p*-tolyl) selectively gave a tritelluroxane **3a**, tetratelluroxane **4a**, pentatelluroxane **5a**, and hexatelluroxane **6a**, respectively. In contrast, the reaction of **2b** with an excess of **1a** produced only tritelluroxane **3b**. An equilibrium between the oligotelluroxanes was confirmed by crossover experiments of the reactions of **2a** with **4a** and of **2a** with **1b** (Ar = Ph). The selective equilibrium formation of a selenoxaditelluroxane **8** or a bis(selenoxa)ditelluroxane **9** was achieved by the reaction of **2a** with one or two equivalents of selenoxide **7**, respectively. The association constant of **2a** with **7** to form **8** was estimated to be $K_a = (2.18 \pm 0.12) \times 10^4\,\text{M}^{-1}$ in CD_3CN at $-40\,^{\circ}C$. The reaction of **2a** with two equivalents of carboxylates **10a–d** gave a mixture of bis(carboxylate)ditelluroxanes **11a–c** and diaryldicarboxytelluranes **12b–d**, respectively, in which the product ratio of these depended upon the electron-withdrawing ability of **10**. The reaction of **3a** with two equivalents of **10a–d** afforded **11a–d** in all cases. The present results suggest that the σ^*-n orbital interaction plays an essential role in the reactivity of ditelluroxanes and in the formation of self-assembled oligochalcogenoxanes, and that a hypervalent bond via a σ^*-n orbital interaction is viable as a new supramolecular synthon for molecular assembly.

Keywords: hypervalent compounds · oligomerization · selenium · self assembly · tellurium

Introduction

Polymers containing oxo bridges between heteroatoms such as those found in polysiloxanes and polyphosphonates have attracted considerable attention in the field of material science.[1, 2] One of the characteristics of organic heteroatom chemistry is the formation of hypervalent compounds.[3] The introduction of hypervalent heteroatom moieties into polymer (oligomer) main chains would give rise to new avenue for exploration in polymer science, because the conformational and electronic properties of a polymer backbone could be changed and controlled by hypervalent bond formation in the heteroatom units.[4–9] Telluranes have a trigonal bipyramidal geometry (10-Te-4)[10] in which two of the more electronegative ligands prefer to occupy the apical positions. The two apical ligands and the central Te atom construct a three-center four-electron bond that is called a hypervalent bond with bond angles of approximately 180°.[3] Polytelluroxanes $[XPh_2Te(OTePh_2)_nOTePh_2X]$ are endowed with both of these characteristics, as the tellurium units are linked by an oxo bridge and they also possess a hypervalent Te–O apical linkage in the main chain. However, polytelluroxanes have not been extensively explored because of a lack of a general synthetic methodology. Ditelluroxanes ($n = 0$) have been synthesized from the thermal dehydration of diaryltellurium hydroxyl halides and related compounds, $Ph_2Te(OH)X$ (in which X = Cl, NSC, CF_3CO_2, etc.).[11, 12] Domasevitch et al. reported on the synthesis of a tritelluroxane (in which $n = 1$, and X = nitrosocarbamylcyanomethanide) using a dehydration procedure.[13] Seppelt and Schrobilgen et al. synthesized $Te(OTeF_5)_4$ by treating TeF_4 with $B(OTeF_5)_3$.[14] With these methods, however, the formation of oligomers higher than tritelluroxane ($n \geq 2$) has not been attained.

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[a] Dr. K. Kobayashi, K. Tanaka, H. Izawa, Y. Arai, Prof. Dr. N. Furukawa
Department of Chemistry, University of Tsukuba
Tsukuba, Ibaraki 305-8571 (Japan)
Fax: (+81)298-53-6503
E-mail: kenjinor@staff.chem.tsukuba.ac.jp

[b] Prof. Dr. N. Furukawa
Present address:
Foundation for Advancement of International Science
586-9 Akatsuka-Ushigahuchi, Tsukuba
Ibaraki 305-0062 (Japan)

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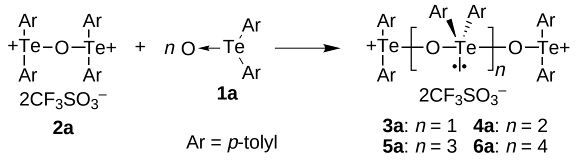
One strategy for the formation of hypervalent telluranes is to use the σ* – n orbital interaction, in which the σ* orbital of the Te–L bond of a telluronium salt interacts with the n orbital of a lone pair of electrons of a nucleophile or ligand (L).[3d, 7b] In supramolecular chemistry, the field of polymer synthesis has advanced to the stage where self-assemblies through hydrogen bonding and transition metal coordination have proved to be a reliable tool.[15, 16] Hypervalent bonds formed through σ* – n orbital interactions in heteroatoms may also be a viable alternative for self-assembled oligomer synthesis.[17] Recently, we described the synthesis of oligotelluroxanes **3a**–**6a** ($n = 1-4$) from the reaction of cationic ditelluroxane **2a** with bis(4-methylphenyl) telluroxide (**1a**) through a σ* – n orbital interaction (Scheme 1).[18] Our strategy for oligotelluroxane synthesis is based on the following aspects. 1) In **2a**, triflate as a counteranion is dissociated from tellurium atoms, which exhibit cationic character, in solution.[19] 2) These tellurium cations can then react with the oxygen atom of **1a** as a nucleophilic monomer through a σ* – n orbital interaction to produce the tritelluroxane **3a**. 3) As the terminal Te atoms in **3a** carry a positive charge, the further addition of **1a** can lengthen the main chain to selectively produce compounds **4a**–**6a**. In this paper, we report on the reactivities and properties of ditelluroxanes and oligochalcogenoxanes that include: 1) the effect of counteranions in ditelluroxanes, 2) the elucidation of the equilibrium between oligotelluroxanes, and 3) the reaction of **2a** with a selenoxide or a carboxylate as nucleophiles. We propose that a hypervalent bond formed through a σ* – n orbital interaction is viable as a new supramolecular synthon for molecular assembly.

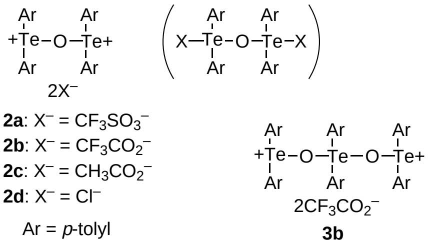


Scheme 1. Synthesis of oligotelluroxanes **3a**–**6a** from **2a** and n equivalents ($n = 1-4$) of **1a**.

Results and Discussion

Reactivity and properties of ditelluroxanes—effect of counteranions: To gain insights into the correlation between the reactivity and the cationic character of the Te atoms of ditelluroxanes, the ^{125}Te NMR chemical shifts and the reaction with bis(4-methylphenyl) telluroxide (**1a**) were investigated with respect to ditelluroxanes **2** (Ar = p-tolyl) bearing various counteranions: $X^- = CF_3SO_3^-$ (**2a**),[19] $CF_3CO_2^-$ (**2b**),[20] $CH_3CO_2^-$ (**2c**) (vide infra), and Cl^- (**2d**)[11b].

The ^{125}Te NMR chemical shifts of ditelluroxanes **2a**, **2b**, **2c**, and **2d** in CD_3CN were observed at $\delta = 1288.4$,[19] 1169.8, 964.5, and 939.8, respectively; these values are shifted downfield with decreasing nucleophilicity of the counteranions. Thus, the cationic character on the Te atom decreased in the order, **2a** > **2b** > **2c** > **2d**. The ^{125}Te NMR data suggest that the triflate of **2a** is dissociated from the Te atoms in solution, whereas the acetate and chloride of **2c** and **2d** may be tightly bound to the Te atoms. This tendency reflects the contact distances of the Te ··· X bond in the crystal structure of **2**, and the reactivity of **2** toward **1a**. The average contact distances of the Te ··· O bond in **2a**[19] and the analogue of **2b** (Ar = Ph)[11e] are 2.66 and 2.35 Å, respectively, both of which are shorter than the sum of the van der Waals radii (3.60 Å) of the Te and O atoms, but longer than the Te–O covalent bond.



2a: $X^- = CF_3SO_3^-$
2b: $X^- = CF_3CO_2^-$
2c: $X^- = CH_3CO_2^-$
2d: $X^- = Cl^-$
Ar = p-tolyl

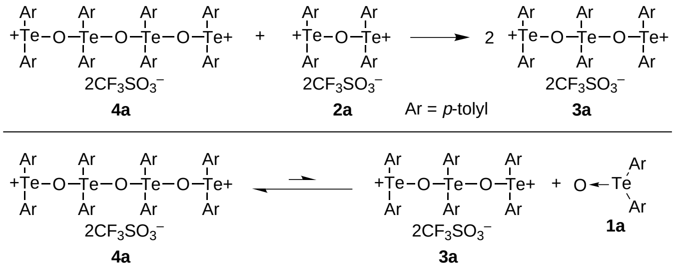
3b

As reported previously,[18] the reaction of **2a** with one, two, or three equivalents of **1a** in CH_2Cl_2 at room temperature exclusively yields the tritelluroxane **3a**, tetratelluroxane **4a**, or pentatelluroxane **5a**, respectively, depending on the stoichiometry of **1a** and **2a** (Scheme 1). The reaction of **2a** with four equivalents of **1a** results in a mixture of **5a** and hexatelluroxane **6a** in the ratio 2.5:1. Oligomers higher than **6a** ($n \geq 5$) are not formed, even when an excess of **1a** is added to **2a**. The ^{125}Te NMR chemical shifts of the terminal Te atoms in oligotelluroxanes **3a**–**6a** are shifted upfield with an increasing degree of oligomerization: $\delta = 1311.9$ (**3a**), 1263.4 (**4a**), 1242.2 (**5a**), and 1224.2 (**6a**). Hence, both the cationic character and the reactivity of the terminal Te atoms of the oligotelluroxanes decrease with increasing degree of oligomerization in the order, **2a** > **3a** > **4a** > **5a** > **6a**.

By contrast, the reactivity of **2b**–**d** toward **1a** is very different from that of **2a**. The reaction of **2b** with an equivalent of **1a** quantitatively afforded the tritelluroxane **3b**. However, the treatment of **2b** with an excess of **1a** did not produce oligomers higher than **3b**. The ^{125}Te NMR chemical shift of the terminal Te atoms in **3b** was observed at $\delta = 1182.5$, which is shifted upfield by 129 ppm relative to that of **3a**. Ditelluroxanes **2c** and **2d** were recovered unchanged even upon addition of an excess of **1a**. Thus, the reactivity of ditelluroxanes toward **1a** decreases in the order, **2a** > **2b** ≫ **2c** ≈ **2d**. These results indicate that the cationic character of the Te atoms of **2**, that is, the σ* – n orbital interaction, plays an essential role in the reactivity of **2**.

Equilibrium between oligotelluroxanes: In the present study, we found an equilibrium between the oligotelluroxanes, although the association constants could not be estimated owing to the independence of the concentrations (at least > 1 mM) in the ^{1}H and ^{125}Te NMR oligotelluroxane spectra. The following two experiments were carried out to gain insights into the equilibrium between oligotelluroxanes.

Based on the reactivity of the oligotelluroxanes mentioned above, the reaction of the tetratelluroxane **4a** with an equivalent of ditelluroxane **2a** was conducted in CH_2Cl_2 at room temperature for 12 hours (Scheme 2). This crossover experiment gave the tritelluroxane **3a** as the sole product,



Scheme 2. Crossover reaction of **4a** with an equivalent of **2a**, and equilibrium of **4a**.

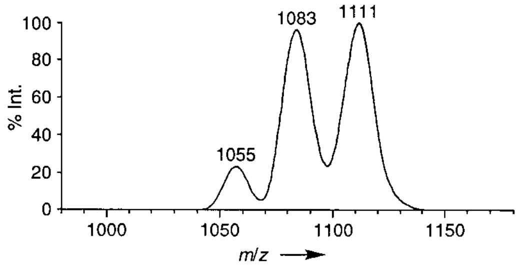
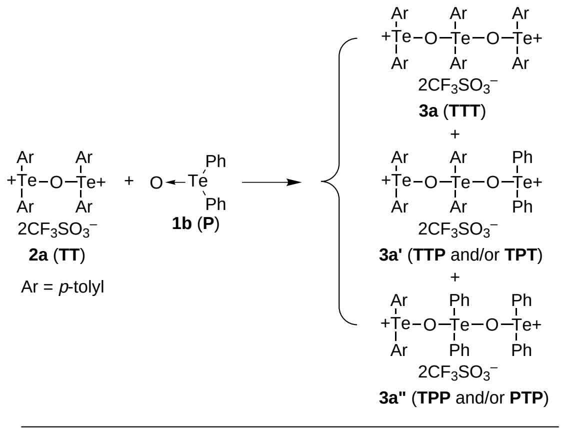


Figure 1. MALDI-TOF-MS spectrum (dithranol matrix) for the reaction mixture of **2a** and an equivalent of **1b**.

which was confirmed by ^{1}H and ^{125}Te NMR spectra, and by FAB-MS spectra of the reaction mixture. This result can be explained as follows. The tetratelluroxane **4a** slightly dissociates to form the tritelluroxane **3a** and the telluroxide **1a**. As **2a** possesses the highest reactivity toward **1a** among the series **2a**, **3a**, and **4a**,[18, 21] the dissociation of **4a** into **3a** and **1a** is promoted in the presence of **2a** and finally produces **3a**.

The reaction of **2a** (**TT**) with an equivalent of diphenyl telluroxide **1b** (**P**) in CH_2Cl_2 at room temperature for 12 hours produced a mixture of tritelluroxanes **3a** (**TTT**), **3a′** (**TTP** and/or **TPT**), and **3a″** (**TPP** and/or **PTP**), in which **T** and **P** denote *p*-tolyl- and phenyl-substituted tellurium units, respectively (Scheme 3). The ^{125}Te NMR spectrum of the reaction mixture in [D$_8$]THF at $-90\,^{\circ}C$ exhibited several peaks in the regions $\delta = 1306-1317$ (from the terminal Te atoms) and $\delta = 1112-1117$ (from the inner Te atoms) in a total integration ratio of 2:1.[22] The MALDI-TOF-MS spectrum of the reaction mixture showed three parent peaks at *m*/*z* 1111 ([**3a** $-$ CF_3SO_3]$^+$), 1083 ([**3a′** $-$ CF_3SO_3]$^+$), and 1055 ([**3a″** $-$ CF_3SO_3]$^+$) in an intensity ratio of 3.5:3.5:1, as shown in Figure 1. Another possible **PPP** tritelluroxane was not detected in the MS spectrum. If there is no equilibrium between tritelluroxanes, only a **TTP** tritelluroxane (one of **3a′**) should be obtained. This was not the case in the present reaction. A **TTP** tritelluroxane, formed in the initial stage, may be slightly dissociated to **TT** and **P**, and/or **T** and **TP** compounds. After repetitions of association and dissociation between these species, the thermodynamic equilibrium could result in the formation of a mixture of tritelluroxanes **3a** (**TTT**), **3a′** (**TTP** and/or **TPT**), and **3a″** (**TPP** and/or **PTP**), as shown in Scheme 3.



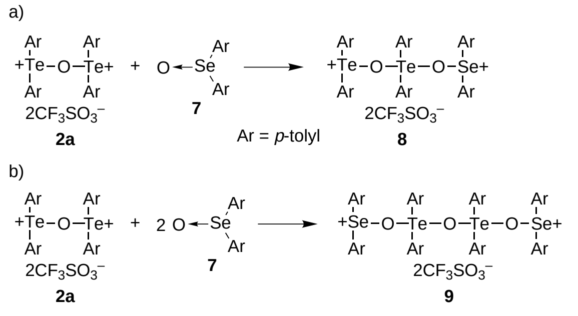
$$\mathrm{TT + P} \rightleftharpoons \mathrm{TTP} \rightleftharpoons \mathrm{T + TP}$$
$$\mathrm{TT + T} \rightleftharpoons \mathrm{TTT}$$
$$\mathrm{TP + P} \rightleftharpoons \mathrm{TPP\ or\ PTP}$$
$$\mathrm{TP + T} \rightleftharpoons \mathrm{TPT\ or\ TTP}$$

Scheme 3. Reaction of **2a** (**TT**) with an equivalent of **1b** (**P**), and equilibrium of tritelluroxanes: **T** and **P** denote *p*-tolyl- and phenyl-substituted tellurium units, respectively.

As reported previously,[18] the molecular and electronic structures of oligotelluroxanes by B3LYP density functional theory (DFT) calculations indicate that the positive charge on the terminal Te atoms decreases with increasing degree of oligomerization. It should be noted that the second O1–Te2 bond, counted from the terminal Te1 atom, is the most elongated among the Te–O bonds of the respective oligotelluroxanes, and that this bond length increases with an increasing degree of oligomerization. In all compounds, the LUMO is delocalized along the Te–O backbone and has an antibonding character between adjacent Te and O atoms; this could be a reflection of the fact that the backbone, which consists of highly polarized Te–O bonds, is a delocalized σ-electron system. These theoretical results could explain the experimental results for the reactivity and the equilibrium properties of the oligotelluroxanes.

Reaction of ditelluroxane with selenoxide—synthesis and properties of oligochalcogenoxanes: We turned our attention to the reactivity of the ditelluroxane **2a** toward a selenoxide as a homologue of telluroxide. The Se–O bond of a selenoxide is less polarized than the Te–O bond of a telluroxide, that is, the former is less nucleophilic than the latter.

The reaction of **2a** with an equivalent of bis(4-methylphenyl) selenoxide (**7**) in CH_2Cl_2 at room temperature for 12 hours quantitatively produced only the selenoxaditelluroxane **8** (Scheme 4a). Treatment of **2a** with two equivalents of **7** under the same conditions exclusively gave the bis(selenoxa)ditelluroxane **9** (Scheme 4b). The ^{125}Te NMR spectra of **8** and **9** in CD_3CN at $-40\,^{\circ}C$ showed two peaks at $\delta = 1354.2$ (from the terminal Te atoms) and 1207.6 (from the inner Te atoms) in a 1:1 integration ratio, and one peak at $\delta = 1200.1$, respectively.[23] These are in the region expected for telluranes with hypervalent Te–O apical bonds.[18] The ^{77}Se NMR spectra of **8** and **9** in CD_2Cl_2 at $-40\,^{\circ}C$ exhibited one peak at $\delta = 851.7$ and one peak at $\delta = 837.9$, respectively.[23, 24] The chemical shifts of both the inner Te atoms and the terminal Se atoms were shifted upfield with an increasing degree of oligomerization. This trend is similar to that seen for the oligotellur-



Scheme 4. Synthesis of a) selenoxaditelluroxane **8** from **2a** with an equivalent of **7**, and b) bis(selenoxa)ditelluroxane **9** from **2a** with two equivalents of **7**.

oxanes.[18] The FAB-MS spectrum of **8** (Figure 2a) showed a parent peak and distinctive fragment peaks at m/z 1063 ($[\mathbf{8}-\mathrm{CF_3SO_3}]^+$), 785 ($[\mathbf{8}-\mathrm{Ar_2SeO}-\mathrm{CF_3SO_3}]^+$), 737 ($[\mathbf{8}-\mathrm{Ar_2TeO}-\mathrm{CF_3SO_3}]^+$), 329 ($[\mathrm{Ar_2TeO{+}H}]^+$), 312 ($[\mathrm{Ar_2Te}]^+$), 279 ($[\mathrm{Ar_2SeO{+}H}]^+$), and 262 ($[\mathrm{Ar_2Se}]^+$) (Ar = p-tolyl). For compound **9** (Figure 2b), a parent peak and distinctive fragment peaks appeared at $m/z = 1341$ ($[\mathbf{9}-\mathrm{CF_3SO_3}]^+$), 1063 ($[\mathbf{9}-\mathrm{Ar_2SeO}-\mathrm{CF_3SO_3}]^+$), 785 ($[\mathbf{9}-2\,\mathrm{Ar_2SeO}-\mathrm{CF_3SO_3}]^+$), 737 ($[\mathbf{9}-\mathrm{Ar_2SeO}-\mathrm{Ar_2TeO}-\mathrm{CF_3SO_3}]^+$), 329 ($[\mathrm{Ar_2TeO{+}H}]^+$), 312 ($[\mathrm{Ar_2Te}]^+$), 279 ($[\mathrm{Ar_2SeO{+}H}]^+$), and 262 ($[\mathrm{Ar_2Se}]^+$). The isotopic distribution patterns of these peaks are consistent with those obtained by calculation. A diselenoxaditelluroxane **9′** (Se-O-Se-O-Te-O-Te sequence) as a structural isomer of **9** (Se-O-Te-O-Te-O-Se sequence) was not produced. If this had been the case, additional fragment peaks at m/z 1015 (Se-O-Se-O-Te sequence) and 689 (Se-O-Se sequence) arising from **9′** should have been observable in the FAB-MS spectrum. Thus, the reaction of **2a** with two equivalents of **7** exclusively produces the bis(selenoxa)ditelluroxane **9**, indicating that the terminal Te cation is more reactive than the terminal Se cation in **8**.

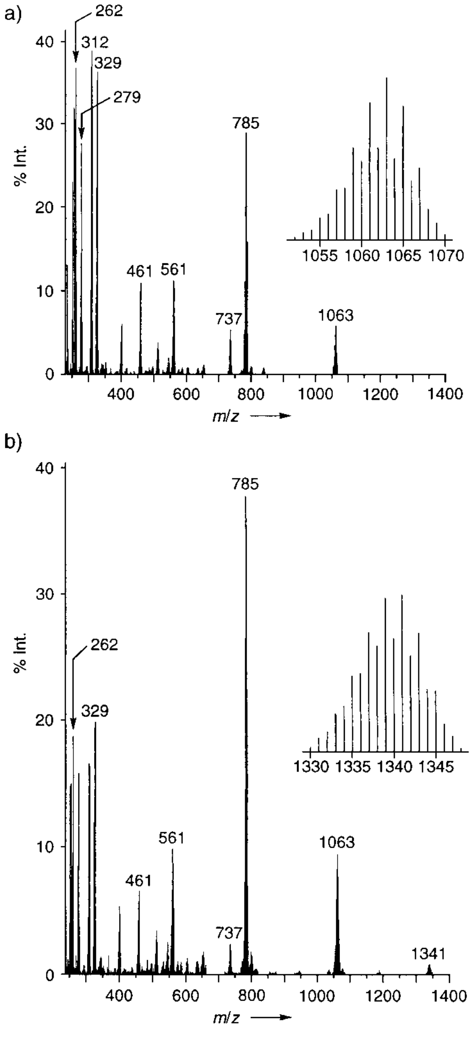
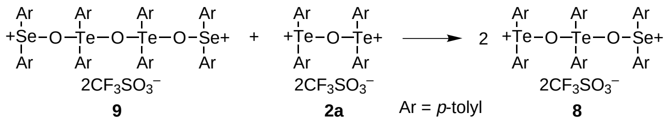


Figure 2. FAB-MS spectra (2-nitrophenyl octyl ether matrix): a) **8** and b) **9**.

As a crossover experiment, the reaction of the ditelluroxane **2a** with an equivalent of bis(selenoxa)ditelluroxane **9** in $\mathrm{CH_2Cl_2}$ at room temperature for 12 hours afforded the selenoxaditelluroxane **8** exclusively (Scheme 5). This result indicates that **9** is slightly dissociated to **8** and to the selenoxide **7**. Among the series of compounds **2a**, **8**, and **9**, compound **2a** shows the dominant reaction with **7**. Therefore, the dissociation of **9** into **8** and **7** could be promoted in the presence of **2a** to finally form **8**. In contrast to the oligotelluroxanes, the ^{1}H NMR spectra of **8** and **9** showed a concentration dependence, suggesting that they are in equilibrium. The ^{1}H NMR spectrum of **8** when diluted in $\mathrm{CD_3CN}$ at −40 °C is shown in Figure 3, for which the ratio of **2a** to **7** was maintained at 1:1.[23] In the aromatic region, four sets of doublet peaks from **8** appeared at $\delta = 7.21$, 7.27, 7.38, and 7.47 at an integration ratio of 8:4:4:8 at concentrations greater than 50 mM (region A). On dilution, a new doublet peak appeared at $\delta = 7.61$ and increased in intensity; this indicates



Scheme 5. Crossover reaction of **9** with an equivalent of **2a**.

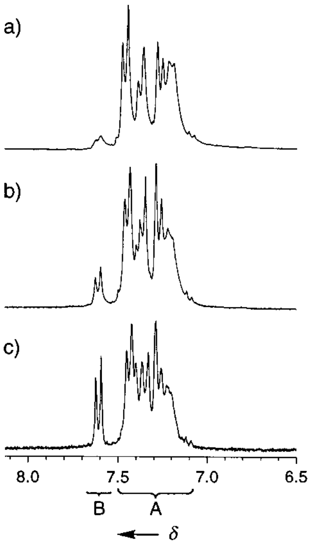


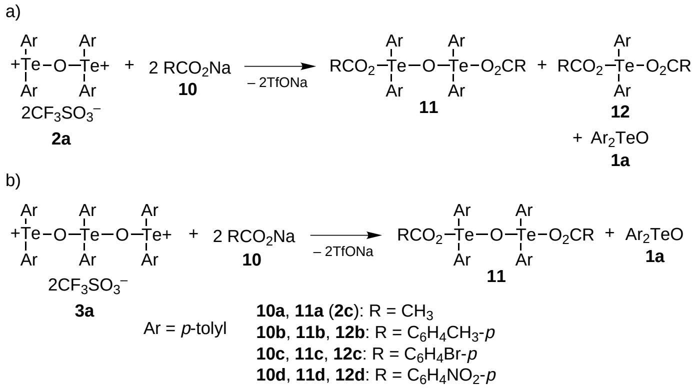
Figure 3. ^{1}H NMR spectra for a 1:1 mixture of **2a** and **7** to form **8** in $\mathrm{CD_3CN}$ at −40 °C: a) 40 mM, b) 8 mM, and c) 1 mM.

an overlap of one of the two doublet peaks of **2a** with one of the two doublet peaks of **7** (region B), while the other peaks from these doublets were in region A. Based on the integration changes of region B with region A as a function of the concentration, the association constant of **2a** with **7** to form **8** was estimated to be $K_a = (2.18 \pm 0.12) \times 10^4\,\mathrm{M}^{-1}$ in CD_3CN at $-40\,^{\circ}C$. The association constant of $K_a = (3.35 \pm 0.12) \times 10^5\,\mathrm{M}^{-1}$ in CD_2Cl_2 at $-40\,^{\circ}C$ is 15 times higher than that in CD_3CN, indicating that the association of **2a** with **7** is favorable in a less polar solvent.

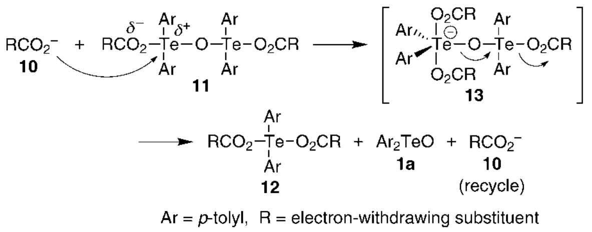
The reaction of **2a** with an excess of **7** did not produce any higher oligomers than **9** as judged from the ^1H and ^{77}Se NMR spectra.[25] The vapor pressure osmometry (VPO) of a mixture of **2a** and ten equivalents of **7** in $CHCl_3$ at 35 °C exhibited a number-average molecular weight of 409.3, which is consistent with that of 411.8, which corresponds to a mixture of **9** and eight equivalents of **7**. Thus, the formation of the bis(selenoxa)ditelluroxane **9** is the limit of the present reaction scheme (at least in solution).[26, 27]

Reaction of ditelluroxane or tritelluroxane with carboxylates: The reactivities of the ditelluroxane **2a** and tritelluroxane **3a** toward sodium carboxylates **10**, which are more nucleophilic than both a telluroxide and a selenoxide, were investigated.

The reaction of **2a** with two equivalents of acetate (**10a**) in CH_3CN at room temperature for 24 hours exclusively produced the bis(carboxylate)ditelluroxane **11a** (**2c**) (vide supra). On the other hand, the reaction of **2a** with two equivalents of *p*-methylbenzoate (**10b**) under the same reaction conditions yielded a mixture of **11b** and the diaryldicarboxytellurane **12b**[28] in a ratio of 1:0.3,[29, 30] together with the telluroxide **1a** (Scheme 6a). The reaction of **2a** with two equivalents of *p*-bromobenzoate (**10c**) gave a mixture of **11c** and **12c** in a ratio of 1:1,[29, 30] together with **1a**. By contrast, the reaction of **2a** with two equivalents of *p*-nitrobenzoate (**10d**) afforded only **12d**,[29] together with **1a**. Thus, in the reaction of **2a** with sodium carboxylates **10**, a more electron-donating **10** preferentially affords the bis(carboxylate)ditelluroxanes **11**, whereas a more electron-withdrawing **10** affords the diaryldicarboxytelluranes **12**. This tendency may be ascribed in part to the electrophilicity of the Te atom of **11**. On increasing the electron-withdrawing ability of a ligand **10** in **11**, the Te–O_2CR bond would be loosened, and the Lewis acidity on the Te atom would increase.[31] Such a bis(carboxylate)ditelluroxane would still possess a capacity for a further nucleophilic addition of **10** to form a transient pentacoordinate tellurate anion **13**,[31] which could be decomposed to produce the thermodynamically more stable **12**, **10**, and **1a** (Scheme 7). A ligand **10** with an electron-withdrawing ability may act as a catalyst for the decomposition of **11**.



Scheme 6. a) Reaction of **2a** with two equivalents of **10**, and b) reaction of **3a** with two equivalents of **10**.



Scheme 7. A possible reaction mechanism for the formation of **12** from **11** and **10**.

In all cases, the reaction of the tritelluroxane **3a** with two equivalents of **10a–d** in CH_3CN at room temperature for 24 hours exclusively produced bis(carboxylate)ditelluroxanes **11a–d**,[29] respectively, together with **1a** (Scheme 6b). This result can be related to the equilibrium of **3a**, as mentioned above. The ^{125}Te NMR chemical shifts of **11a–d**, which are in a similar region to telluranes with hypervalent Te–O_2CR apical bonds,[28] are shifted downfield with the increasing electron-withdrawing ability of a ligand **10**,[29] suggesting that the Lewis acidity on the Te atom of **11** increases in this order.

Conclusion

We have demonstrated that the σ* – n orbital interaction plays an essential role in the reactivity of the ditelluroxanes **2** (Ar = *p*-tolyl) and in the formation of self-assembled oligochalcogenoxanes that are composed of a hypervalent Te–O apical linkage in the main chain. Both the cationic character and the reactivity of the Te atoms of **2** increase with decreasing nucleophilicity of the counteranions (X^-): **2a** ($X^- = CF_3SO_3^-$) > **2b** ($X^- = CF_3CO_2^-$) ≫ **2c** ($X^- = CH_3CO_2^-$) > **2d** ($X^- = Cl^-$). The selective formation of the tritelluroxane **3a**, tetratelluroxane **4a**, pentatelluroxane **5a**, and hexatelluroxane **6a** has been achieved by the reaction of **2a** with one, two, three, or four equivalents of telluroxide **1a** (Ar = *p*-tolyl), respectively. The equilibrium between the oligotelluroxanes was elucidated from crossover experiments of the reactions of **2a** with **4a** and of **2a** with **1b** (Ar = Ph). We have also demonstrated the selective equilibrium formation of the selenoxaditelluroxane **8** and the bis(selenoxa)ditelluroxane **9** by the reaction of **2a** with one or two equivalents of selenoxide **7**, respectively. This is the first example of the synthesis of oligochalcogenoxanes composed of hypervalent tellurium and selenium units linked by an oxo bridge. The reaction of **2a** with two equivalents of carboxylates **10a–d** yielded a mixture of bis(carboxylate)ditelluroxans **11a–c** and diaryldicarboxytelluranes **12b–d**, respectively. The product ratio of this mixture depends on the electron-withdrawing ability of **10**, while the reaction of the tritelluroxane **3a** with two equivalents of **10a–d** afforded **11a–d** in all cases. The results presented here could provide a basis for the use of hypervalent bonds through a σ^*-n orbital interaction in heteroatoms as a new supramolecular synthon for self-assembled oligomer (polymer) synthesis.[15–17, 32] Assembly of polychalcogenoxanes in the solid state, and the reaction of **2a** with oxides of Group 15 and 17 elements will be the subject of a future study.

Experimental Section

General: ^{1}H, ^{77}Se, and ^{125}Te NMR spectra were recorded on a JEOL JNM-EX270 (^{1}H 270 MHz, ^{77}Se 51.4 MHz, ^{125}Te 85.2 MHz) spectrometer. Chemical shifts of ^{77}Se and ^{125}Te NMR spectra were reported relative to $(CH_3)_2Se$ and $(CH_3)_2Te$, respectively. FAB-MS spectra were measured on a JEOL JMS-SX102 A spectrometer with 2-nitrophenyl octyl ether as a matrix. MALDI-TOF-MS spectra were obtained on a Shimadzu/KRATOS KOMPACT-MALDI III spectrometer with dithranol as a matrix. IR spectra were recorded on a JASCO FT/IR-5000 spectrometer by using KBr pellets or a thin film on NaCl plates. Vapor pressure osmometry (VPO) measurement was made with a Corona-117 vapor pressure osmometer. CH_2Cl_2, $CHCl_3$, and CH_3CN were distilled from CaH_2 under N_2. NMR solvents of CD_2Cl_2, CD_3CN, and [D$_8$]THF were dried over molecular sieves 4 A. Oligotelluroxanes **2a–6a** were prepared according to the literature.[18, 19]

Ditelluroxane 2b: This compound was prepared by a modified procedure of the literature.[11e] Two equivalents of CF_3CO_2H (0.47 mL, 6.10 mmol) was added at room temperature to a solution of **1a** (1.00 g, 3.07 mmol) in MeOH (30 mL). After stirring for 1 h, an equivalent of H_2O (55 μL, 3.06 mmol) was added to the reaction mixture, which was stirred at room temperature for additional 12 h. After evaporation of solvents, the residue was precipitated from CH_2Cl_2/hexane to give **2b** (1.29 g, 98 % yield) as a white powder. M.p. 165–166 °C (decomp); ^{1}H NMR (CD_3CN, 23 °C): $\delta = 2.41$ (s, 12 H), 7.38 (d, $J = 7.9$ Hz, 8 H), 7.87 (d, $J = 7.9$ Hz, 8 H); ^{125}Te NMR (CD_3CN, 23 °C): $\delta = 1169.8$; FAB-MS: m/z: 749 $[M - CF_3CO_2]^+$; elemental analysis calcd (%) for $C_{32}H_{28}F_6O_5Te_2$: C 44.60, H 3.27; found: C 44.54, H 3.49.

Ditelluroxane 2d: This compound was prepared according to the literature.[11b] Yield 44 % (pale yellow powder); m.p. 160–161 °C (decomp); ^{1}H NMR (CD_3CN, 23 °C): $\delta = 2.41$ (s, 12 H), 7.38 (d, $J = 7.9$ Hz, 8 H), 7.89 (d, $J = 7.9$ Hz, 8 H); ^{125}Te NMR (CD_3CN, 23 °C): $\delta = 939.8$; FAB-MS: m/z: 673 $[M - Cl]^+$; elemental analysis calcd (%) for $C_{28}H_{28}Cl_2OTe_2$: C 47.59, H 3.99; found: C 47.38, H 3.91.

Tritelluroxane 3b: A 1:1 mixture of **2b** (120 mg, 0.139 mmol) and **1a** (45.3 mg, 0.139 mmol) under Ar was dissolved in CH_2Cl_2 (2 mL). The resulting mixture was stirred at room temperature for 12 h and then poured into hexane (50 mL) to give **3b** (158 mg, 96 % yield) as a white powder. M.p. 92–95 °C (decomp); ^{1}H NMR (CD_3CN, −40 °C): $\delta = 2.33$ (s, 6 H), 2.34 (s, 12 H), 7.09 (d, $J = 8.1$ Hz, 4 H), 7.15 (d, $J = 8.1$ Hz, 8 H), 7.41 (d, $J = 8.1$ Hz, 4 H), 7.51 (d, $J = 8.1$ Hz, 8 H); ^{125}Te NMR (CD_3CN, −40 °C): $\delta = 1160.5$, 1182.5 (integration ratio 1:2); FAB-MS: m/z (%): 1075 (7) $[M - CF_3CO_2]^+$, 749 (76) $[M - \mathbf{1a} - CF_3CO_2]^+$, 561 (17) $[M - (CH_3C_6H_4)_2Te - CH_3C_6H_4 - 2\,CF_3CO_2]^+$, 425 (67) $[M - 2(\mathbf{1a}) - CF_3CO_2]^+$, 329 (48) $[\mathbf{1a}{+}H]^+$, 312 (100) $[\mathbf{1a} - O]^+$; elemental analysis calcd (%) for $C_{46}H_{42}F_6O_6Te_3 \cdot H_2O$: C 45.83, H 3.68; found: C 45.75, H 3.77.

Reaction of tetratelluroxane 4a with ditelluroxane 2a: A 1:1 mixture of **4a** (44.4 mg, 0.0280 mmol) and **2a** (26.1 mg, 0.0279 mmol) in CH_2Cl_2 (2 mL) under Ar was stirred at room temperature for 12 h. After evaporation of solvent, **3a** was obtained quantitatively as a white powder.[18] M.p. 216–218 °C (decomp); ^{1}H NMR (CD_3CN, −40 °C): $\delta = 2.33$ (s, 6 H), 2.34 (s, 12 H), 7.14 (d, $J = 8.1$ Hz, 4 H), 7.27 (d, $J = 8.6$ Hz, 8 H), 7.44 (d, $J = 8.6$ Hz, 8 H), 7.47 (d, $J = 8.1$ Hz, 4 H); ^{125}Te NMR (CD_3CN, −40 °C): $\delta = 1124.7$, 1311.9 (integration ratio 1:2); ^{125}Te NMR ([D$_8$]THF, −90 °C): $\delta = 1112.0$, 1306.4 (integration ratio 1:2); FAB-MS: m/z (%): 1111 (13) $[M - CF_3SO_3]^+$, 785 (39) $[M - \mathbf{1a} - CF_3SO_3]^+$, 561 (18) $[M - (CH_3C_6H_4)_2Te - CH_3C_6H_4 - 2\,CF_3SO_3]^+$, 461 (26) $[M - 2(\mathbf{1a}) - CF_3SO_3]^+$, 329 (58) $[\mathbf{1a}{+}H]^+$, 312 (100) $[\mathbf{1a} - O]^+$; elemental analysis calcd (%) for $C_{44}H_{42}F_6O_8S_2Te_3 \cdot H_2O$: C 41.36, H 3.47; found: C 41.09, H 3.37.

Reaction of 2a with telluroxide 1b: A 1:1 mixture of **2a** (58.3 mg, 0.0624 mmol) and **1b** (18.6 mg, 0.0625 mmol) in CH_2Cl_2 (2 mL) under Ar was stirred at room temperature for 12 h. After evaporation of solvent, the residue, which could not be separated, was directly used for measurements of ^{125}Te NMR and MALDI-TOF-MS spectroscopies (see, text).

General procedure for the reaction of 2a with selenoxide 7: CH_2Cl_2 (2 mL) was added to a mixture of **2a** (100 mg, 0.107 mmol) and an equivalent of **7** (29.7 mg, 0.107 mmol) under Ar. The resulting solution was stirred at room temperature for 12 h and then poured into hexane (50 mL) to precipitate **8** (125 mg, 96 % yield) as a pale yellow powder. When two equivalents of **7** (59.4 mg, 0.214 mmol) were used under the same conditions, **9** (151 mg, 95 % yield) was obtained as a pale yellow powder.

Selenoxaditelluroxane 8: M.p. 83–86 °C (decomp); ^{1}H NMR (CD_3CN, −40 °C): $\delta = 2.33$ (s, 18 H), 7.21 (d, $J = 8.1$ Hz, 8 H), 7.27 (d, $J = 8.1$ Hz, 4 H), 7.38 (d, $J = 8.1$ Hz, 4 H), 7.47 (d, $J = 8.1$ Hz, 8 H); ^{1}H NMR (CD_2Cl_2, −40 °C): $\delta = 2.32$ (s, 18 H), 7.10 (br s, 8 H), 7.18 (br s, 8 H), 7.40 (br s, 8 H); ^{125}Te NMR (CD_3CN, −40 °C): $\delta = 1207.6$, 1354.2 (integration ratio 1:1); ^{77}Se NMR (CD_2Cl_2, −40 °C): $\delta = 851.7$; IR (KBr): $\tilde{\nu} = 797$, 759, 640 cm^{-1}; FAB-MS: m/z (%): 1063 (15) $[M - CF_3SO_3]^+$, 785 (73) $[M - \mathbf{7} - CF_3SO_3]^+$, 737 (14) $[M - \mathbf{1a} - CF_3SO_3]^+$, 561 (29) $[M - (CH_3C_6H_4)_2Se - CH_3C_6H_4 - 2\,CF_3SO_3]^+$, 461 (28) $[M - \mathbf{7} - \mathbf{1a} - CF_3SO_3]^+$, 329 (92) $[\mathbf{1a}{+}H]^+$, 312 (100) $[\mathbf{1a} - O]^+$, 279 (71) $[\mathbf{7}{+}H]^+$, 262 (93) $[\mathbf{7} - O]^+$; elemental analysis calcd (%) for $C_{44}H_{42}F_6O_8S_2SeTe_2$: C 43.64, H 3.50; found: C 44.02, H 3.59.

Bis(selenoxa)ditelluroxane 9: M.p. 74–76 °C (decomp); ^{1}H NMR (CD_3CN, −40 °C): $\delta = 2.30$ (s, 24 H), 7.14 (d, $J = 8.1$ Hz, 8 H), 7.24 (d, $J = 8.1$ Hz, 8 H), 7.34 (d, $J = 8.1$ Hz, 8 H), 7.47 (d, $J = 8.1$ Hz, 8 H); ^{1}H NMR (CD_2Cl_2, −40 °C): $\delta = 2.31$ (s, 12 H), 2.32 (s, 12 H), 7.06 (d, $J = 8.1$ Hz, 8 H), 7.21 (d, $J = 8.4$ Hz, 8 H), 7.25 (d, $J = 8.4$ Hz, 8 H), 7.40 (d, $J = 8.1$ Hz, 8 H); ^{125}Te NMR (CD_3CN, −40 °C): $\delta = 1200.1$; ^{77}Se NMR (CD_2Cl_2, −40 °C): $\delta = 837.9$; IR (KBr): $\tilde{\nu} = 802$, 755, 638 cm^{-1}; FAB-MS: m/z (%): 1341 (3) $[M - CF_3SO_3]^+$, 1063 (29) $[M - \mathbf{7} - CF_3SO_3]^+$, 785 (100) $[M - 2(\mathbf{7}) - CF_3SO_3]^+$, 737 (8) $[M - \mathbf{7} - \mathbf{1a} - CF_3SO_3]^+$, 561 (31) $[M - \mathbf{7} - (CH_3C_6H_4)_2Se - CH_3C_6H_4 - 2\,CF_3SO_3]^+$, 461 (21) $[M - 2(\mathbf{7}) - \mathbf{1a} - CF_3SO_3]^+$, 329 (52) $[\mathbf{1a}{+}H]^+$), 312 (44) $[\mathbf{1a} - O]^+$, 279 (42) $[\mathbf{7}{+}H]^+$, 262 (49) $[\mathbf{7} - O]^+$; elemental analysis calcd (%) for $C_{58}H_{56}F_6O_9S_2Se_2Te_2 \cdot H_2O$: C 46.25, H 3.88; found: C 46.12, H 4.17.

Reaction of 9 with 2a: A 1:1 mixture of **9** (41.6 mg, 0.0280 mmol) and **2a** (26.1 mg, 0.0279 mmol) in CH_2Cl_2 (2 mL) under Ar was stirred at room temperature for 12 h. After evaporation of solvent, **8** was obtained in quantitative yield.

^{1}H NMR titration of 8: A stock solution of **8** (8.00 mM) in CD_3CN or CD_2Cl_2 was diluted by 6.00, 4.00, 2.00, 1.00, 0.500, and 0.250 mM. After 12 h at room temperature, the ^{1}H NMR spectra of these samples were taken at −40 °C to measure integrations of regions A and B (see, text).

VPO measurement for a mixture of 2a and 7:[33] A mixture of **2a** (21.6 mg, 0.0231 mmol) and ten equivalents of **7** (64.1 mg, 0.231 mmol) in CH_2Cl_2 (2 mL) under Ar was stirred at room temperature for 12 h. After evaporation of solvent, the residue was dissolved in $CHCl_3$ and diluted by 8.55, 6.84, 5.13, 4.28, 3.42, and 1.71 g L^{-1}. The ΔV of these samples was measured at 35 °C. Calibration curves were generated by using benzil and sucrose octaacetate as molecular weight standards.

General procedure for the reaction of 2a with sodium carboxylate 10: A heterogeneous mixture of **2a** (100 mg, 0.107 mmol) and two equivalents of **10a–d** in CH_3CN (4 mL) under Ar was stirred at room temperature for 24 h; the mixture gradually turned into a pale yellow homogeneous solution. After evaporation of solvent, the residue was triturated with benzene (10 mL) and then filtered. The filtrate was concentrated to give **11a** (**2c**) from **10a**, **12d** from **10d**, a mixture of **11b** and **12b** from **10b**, and a mixture of **11c** and **12c** from **10c** in quantitative yields. The mixtures for **11b**/**12b**, and **11c**/**12c** could not be separated due to decomposition on silica gel chromatography.[30]

Diaryldicarboxytellurane 12b: ^{1}H NMR (CD_3CN, 23 °C): $\delta = 2.32$ (s, 6 H), 2.35 (s, 6 H), 7.30 (d, $J = 8.4$ Hz, 4 H), 7.34 (d, $J = 8.1$ Hz, 4 H), 7.76 (d, $J = 8.4$ Hz, 4 H), 7.80 (d, $J = 8.1$ Hz, 4 H); ^{125}Te NMR (CD_3CN, −40 °C): $\delta = 978.3$; FAB-MS: m/z: 447 $[M - CH_3C_6H_4CO_2]^+$.

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Diaryldicarboxytellurane 12c: ^{1}H NMR ([D$_8$]THF, 23 °C): $\delta = 2.23$ (s, 6H), 7.28 (brs, 4H), 7.40 (brs, 4H), 7.51 (brs, 4H), 7.75 (brs, 4H); ^{125}Te NMR ([D$_8$]THF, −40 °C): $\delta = 994.6$; FAB-MS: m/z: 511 $[M - BrC_6H_4CO_2]^+$.

Diaryldicarboxytellurane 12d: Yield 95% (deep yellow powder); m.p. 244–246 °C (decomp); ^{1}H NMR (CD$_3$CN, 23 °C): $\delta = 2.41$ (s, 6H), 7.42 (d, $J = 8.3$ Hz, 4H), 7.88 (d, $J = 8.3$ Hz, 4H), 8.09 (d, $J = 8.2$ Hz, 4H), 8.21 (d, $J = 8.2$ Hz, 4H); ^{125}Te NMR (CD$_3$CN, −40 °C): $\delta = 1001.4$; FAB-MS: m/z (%): 478 (100) $[M - O_2NC_6H_4CO_2]^+$, 329 (38) $[\mathbf{1a}{+}H]^+$, 312 (98) $[\mathbf{1a} - O]^+$; elemental analysis calcd (%) for $C_{28}H_{22}N_2O_8Te$: C 52.38, H 3.45, N 4.36; found: C 52.16, H 3.60, N 4.24.

General procedure for the reaction of 3a with sodium carboxylate 10: A heterogeneous mixture of **3a** (63.3 mg, 0.0502 mmol) and two equivalents of **10a–d** in CH$_3$CN (4 mL) under Ar was stirred at room temperature for 24 h; the mixture gradually turned into a pale yellow homogeneous solution. After evaporation of solvent, the residue was triturated with benzene (10 mL) and then filtered. The filtrate was concentrated to give **11a–d** in quantitative yields.

Bis(carboxylate)ditelluroxane 11a (2c): Yield 96% (white powder); m.p. 116–118 °C (decomp); ^{1}H NMR (CD$_3$CN, 23 °C): $\delta = 1.86$ (s, 6H), 2.37 (s, 12H), 7.18 (d, $J = 8.2$ Hz, 8H), 7.54 (d, $J = 8.2$ Hz, 8H); ^{125}Te NMR (CD$_3$CN, −40 °C): $\delta = 964.5$; FAB-MS: m/z (%): 695 (14) $[M - CH_3CO_2]^+$, 371 (66) $[M - \mathbf{1a} - CH_3CO_2]^+$, 329 (75) $[\mathbf{1a}{+}H]^+$, 312 (100) $[\mathbf{1a} - O]^+$; elemental analysis calcd (%) for $C_{32}H_{34}O_5Te_2$: C 50.99, H 4.55; found: C 50.79, H 4.22.

Bis(carboxylate)ditelluroxane 11b: Yield 94% (white powder); m.p. 244–246 °C (decomp); ^{1}H NMR (CD$_3$CN, 23 °C): $\delta = 2.29$ (s, 6H), 2.31 (s, 12H), 7.21 (d, $J = 8.1$ Hz, 8H), 7.62 (d, $J = 8.1$ Hz, 8H), 7.68 (d, $J = 8.0$ Hz, 4H), 7.83 (d, $J = 8.0$ Hz, 4H); ^{125}Te NMR (CD$_3$CN, −40 °C): $\delta = 1063.5$; FAB-MS: m/z (%): 771 (19) $[M - CH_3C_6H_4CO_2]^+$, 447 (100) $[M - \mathbf{1a} - CH_3C_6H_4CO_2]^+$, 329 (26) $[\mathbf{1a}{+}H]^+$, 312 (53) $[\mathbf{1a} - O]^+$; elemental analysis calcd (%) for $C_{44}H_{42}O_5Te_2$: C 58.33, H 4.67; found: C 58.04, H 4.34.

Bis(carboxylate)ditelluroxane 11c: Yield 89% (white powder); m.p. 234–236 °C (decomp); ^{1}H NMR ([D$_8$]THF, 23 °C): $\delta = 2.36$ (s, 12H), 7.19 (d, $J = 8.2$ Hz, 8H), 7.43 (d, $J = 8.4$ Hz, 4H), 7.59 (d, $J = 8.2$ Hz, 8H), 7.69 (d, $J = 8.4$ Hz, 4H); ^{125}Te NMR ([D$_8$]THF, −40 °C): $\delta = 1080.3$; FAB-MS: m/z (%): 837 (5) $[M - BrC_6H_4CO_2]^+$, 511 (91) $[M - \mathbf{1a} - BrC_6H_4CO_2]^+$, 329 (49) $[\mathbf{1a}{+}H]^+$, 312 (100) $[\mathbf{1a} - O]^+$; elemental analysis calcd (%) for $C_{42}H_{36}Br_2O_5Te_2$: C 48.70, H 3.50; found: C 48.94, H 3.82.

Bis(carboxylate)ditelluroxane 11d: Yield 93% (deep yellow powder); m.p. 237–239 °C (decomp); ^{1}H NMR (CD$_3$CN, 23 °C): $\delta = 2.35$ (s, 12H), 7.18 (d, $J = 8.4$ Hz, 8H), 7.58 (d, $J = 8.4$ Hz, 8H), 7.88 (d, $J = 8.2$ Hz, 4H), 8.06 (d, $J = 8.2$ Hz, 4H); ^{125}Te NMR (CD$_3$CN, −40 °C): $\delta = 1074.2$; FAB-MS: m/z (%): 802 (19) $[M - O_2NC_6H_4CO_2]^+$, 478 (59) $[M - \mathbf{1a} - O_2NC_6H_4CO_2]^+$, 329 (48) $[\mathbf{1a}{+}H]^+$, 312 (100) $[\mathbf{1a} - O]^+$; elemental analysis calcd (%) for $C_{42}H_{36}N_2O_9Te_2$: C 52.12, H 3.75, N 2.89; found: C 51.88, H 4.04, N 2.74.

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[20] Alcock et al. have prepared the analogue of **2b** (Ar = Ph).[11e]

[21] The competitive reaction of a 1:1 mixture of **3a** and **4a** with an equivalent of **1a** gives only **4a**.[18]

[22] The ^{125}Te NMR spectrum of **3a** in [D$_8$]THF at −90 °C showed two peaks at $\delta = 1306.4$ and 1112.0 in an integration ratio of 2:1.

[23] To obtain well-resolved signals in the ^{1}H, ^{77}Se, and ^{125}Te NMR spectra of **8** and **9**, the measurements were carried out at −40 °C.

[24] The ^{77}Se NMR chemical shift of **7** in CD_2Cl_2 at −40 °C was observed at $\delta = 837.0$.

[25] The ^{77}Se NMR chemical shifts for a mixture of **2a** with *n* equivalents of **7** in CD_2Cl_2 at −40 °C (integration ratio in parenthesis): $n = 3$, $\delta = 831.4$ and 830.5 (0.5:1); $n = 4$, $\delta = 833.2$ and 829.2 (1:1); $n = 6$, $\delta = 835.4$ and 827.7 (2:1); $n = 8$, $\delta = 836.6$ and 827.6 (3:1); $n = 10$, $\delta = 837.0$ and 827.6 (4:1).

[26] In the IR spectra of **7** and **9** (KBr), the Se−O stretching band appeared at $\tilde{\nu} = 826$ and 802 cm^{-1}, respectively. However, the IR spectra for a mixture of **2a** and *n* equivalents ($n = 3-10$) of **7**, after evaporation of solvents, showed shifts (20–15 cm^{-1}) to lower wavenumbers of the ν_{Se-O} for **7**.

[27] The melting points for a mixture of **2a** and *n* equivalents of **7** decreased in the order: **2a**, 273–274 °C;[19] **7**, 90–91 °C; $n = 1$ (**8**), 83–85 °C; $n = 2$ (**9**), 74–76 °C; $n = 4$, 46–47 °C; $n = 6$, wax; $n = 8$, wax; $n = 10$, viscous oil.

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[29] The ^{125}Te NMR chemical shifts of **11** and **12** at −40 °C: $\delta = 964.5$ (**11a** (**2c**), CD_3CN), 1063.5 (**11b**, CD_3CN), 1080.3 (**11c**, [D$_8$]THF), 1074.2 (**11d**, CD_3CN); $\delta = 978.3$ (**12b**, CD_3CN), 994.6 (**12c**, [D$_8$]THF), 1001.4 (**12d**, CD_3CN).

[30] The product ratios of **11b** and **12b**, and **11c** and **12c**, were estimated by the integration ratios of the ^{125}Te and ^{1}H NMR spectra of the mixture.

[31] It is known that a tellurane with an electron-withdrawing ligand is Lewis acidic and reacts further with a ligand anion to produce a pentacoordinate tellurate anion.[14b]

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