Novel Aromatic Azopolymers with Regularly Interposed Tellurium Atoms in the Backbone

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Previously unknown *alt*-copoly(telluro-1,4-phenylene/azo-1,4-phenylene) and related polymers were synthesized by several different approaches, which include a) reductive polymerization of bis(4-nitrophenyl) tellurides with zinc; b) oxidative polymerization of bis(4-aminophenyl) telluride using a Cu^I/Cu^{II} redox system as catalyst under oxygen; c) electrochemical polymerization of bis(4-amino-3,5-dimethylphenyl) telluride; d) condensation polymerization of 1,4-dinitrosobenzene with bis(4-aminophenyl) telluride *Te,Te*-dichloride, and e) condensation polymerization of bis(4-nitrophenyl) telluride with bis(4-aminophenyl) telluride in the presence of sodium hydroxide. The polymers obtained were characterized by elemental analysis, ^{13}C-CPMAS NMR, IR and UV-vis spectroscopy, GPC, and inherent viscosity measurements, and their properties were examined, particularly their electrical conductivity. The electrical conductivities of the new polymers **9b**, **c** and **10** were shown to increase from below 10^{-7} up to $10^{-5} \sim 10^{-2}$ S cm^{-1} upon bromine doping in spite of their formally interrupted conjugation structure.

Since the last two decades, organotellurium compounds have been receiving increasing attention as special reagents, organic conductors, and new imaging systems[1]. However, the literature contains comparatively few reports on tellurium-containing organic polymers[2-9], among which poly(ditelluromethylene) is of special interest, since it shows a noticeably high conductivity ($\sigma \approx 10^{-3}$ S cm^{-1}) upon bromine doping in spite of its non-conjugative aliphatic nature[5]. Chemical doping presumably produces the positive holes on tellurium atoms, which are effectively transferred from chain to chain via telluride linkage.

On the other hand, poly(azo-1,4-phenylene) and its analogs have been extensively studied and amply reported in the literature[10-25]. This may be attributed to the fact that these conjugated polymers are expected to display electrical conductivity due to their moderately low band energy gap and their stability towards *p*-type chemical doping[26]. Polymerization of aromatic diamines to the conductive azo polymer systems has usually been carried out by oxidative ways and the electrical conductivity of the azo polymers obtained reaches up to $\sigma \approx 10^{-5} \sim 10^{-4}$ S cm^{-1} after chemical doping[15,18].

With these findings in mind, the idea came to us that the combination of the *n*,π-conjugative azo, π-conjugative 1,4-phenylene, and *n*-conjugative telluro functions in some alternate way may produce a novel polymer of higher electrical conductivity upon chemical doping because of the joint operation of the intrachain and interchain mechanisms of electrical conduction. However, a synthesis of such polymers has not been realized so far probably because of the difficult access to appropriate starting materials. We have recently developed a convenient method for the preparation of bis(nitroaryl) tellurides by using an in situ generated tellurium/copper couple as the tellurating agent[27]. By use of this new reagent system, a variety of bis(nitroaryl) tellurides and hence bis(aminoaryl) tellurides are readily available, thus providing a route to mixed aromatic azo-telluro polymers. In this paper we describe the synthesis and electrical properties of the previously unknown azopolymers **9b**, **c** and **10** with regularly interposed tellurium atoms in the backbone.

Results and Discussion

Synthesis of *alt*-Copoly(telluro-1,4-phenylene/azo-1,4-phenylene) 9 and Related Polymer 10

We have tried to prepare new polymers composed of telluride, 1,4-phenylene and azo functions by two different approaches, i.e. via the telluride linkage formation and via the azo linkage formation. For this purpose, many model reactions have been carried out to find out the optimum conditions for polymer synthesis.

a) Approach via the Telluride Linkage Formation

Model reactions of 4-iodo- and 4-bromoazobenzenes with disodium telluride[37] or Te-Cu reagent[27] mainly resulted in the reductive dehalogenation of starting materials to give parent azobenzene **3b** together with a complex mixture of unidentified products. Likewise, attempts to generate the 4-phenylazophenyltellurolate equivalent by lithium/halogen exchange of 4-bromoazobenzene with butyllithium

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failed. Thus, the approach via the telluride linkage formation can hardly be regarded as promising for the synthesis of the expected polymers.

b) Approach via the Azo Linkage Formation

i) Reductive Polymerization of Bis(4-nitrophenyl) Tellurides **6**

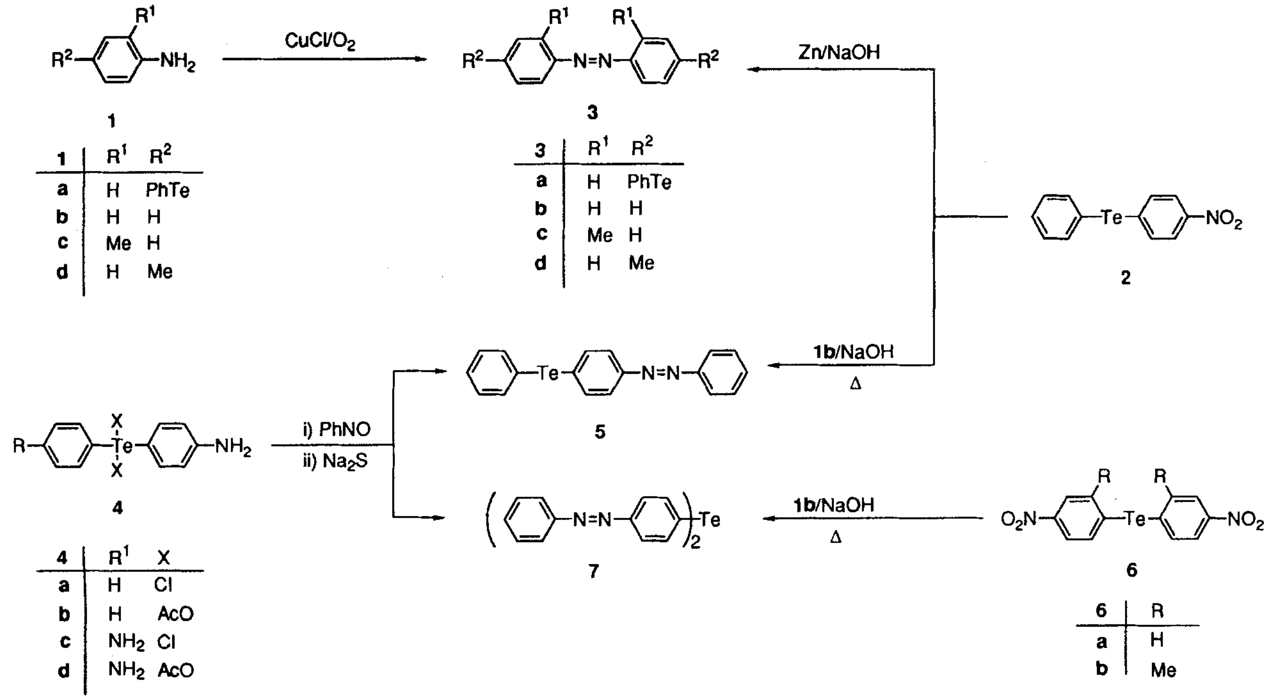
Model reaction of 4-nitrodiphenyl telluride **2** with lithium aluminum hydride (LAH) in dry ether simply resulted in the reductive detelluration to afford azobenzene **3b**, no 4,4′-bis(phenyltelluro)azobenzene **3a** being obtained. However, the reduction of telluride **2** with the Zn/NaOH system as a reducing agent successfully led to the expected telluride **3a** in 31% yield (Scheme 1).

Based on this success, the reductive polymerization of tellurides **6a** and **6b** was carried out by using the Zn/alkali reagent in ethanol/water to obtain oligomers **9a** and **9d** as an orange-colored material, the average molecular weight (M_w) of which was about 10^3 as estimated by gel permeation chromatography (GPC) (Scheme 2, *Route a*). The oligomer **9a** obtained from telluride **6a** did not provide satisfactory analytical values and was insoluble in chloroform ($CHCl_3$) and toluene, but soluble in hot *N*-methyl-2-pyrrolidone (NMP), trifluoroacetic acid, and concentrated sulfuric acid. In contrast, acceptable elemental analytical and spectral data were obtained for oligomer **9d**, which was prepared from bis(2-methyl-4-nitrophenyl) telluride **6b** by a similar reduction. The oligomer **9d** was soluble in common organic solvents such as $CHCl_3$, ethyl acetate, and toluene. Interestingly, this oligomer was found to exhibit a moderate solvatochromism; the material shows a blue shift by 20 nm (λ_{max} = 372 nm) in hexane/chloroform (30:1) relative to λ_{max} = 392 nm in $CHCl_3$. Since compound **5** corresponding to the structural unit of condensation polymers **9a–c** did not show such a solvatochromism, this interesting phenomenon could be attributed to the conformational change of the oligomer chains, depending on the solvent employed.

ii) Oxidative Polymerization of Bis(4-aminophenyl) Telluride **8a**

We tried the oxidative polymerization of bis(4-aminophenyl) telluride **8a** under homogeneous conditions by using a copper(I)/copper(II) redox system as catalyst with slow bubbling of oxygen into the solution. This procedure had earlier been employed by H. C. Bach et al.[11] for the polymerization of bis(4-aminophenyl) ether and bis(4-aminophenyl) sulfide, where they obtained *alt*-copoly(oxy-1,4-phenylene/azo-1,4-phenylene) and *alt*-copoly(thio-1,4-phenylene/azo-1,4-phenylene) of moderately high inherent viscosity in good yields by using *N,N*-dimethylacetamide (DMA) and/or pyridine as the solvent for polymerization. We applied this procedure to the polymerization of telluride **8a** and obtained polymer **9b** of moderate molecular weight (Scheme 2, *Route b*). However, the oxidative polymerization of telluride **8a** was accompanied by the formation of another type of polymers, for which we suggest the structures of polyaniline and/or aniline black type on the basis of the findings from the model reaction (Table 1). Among several aprotic solvents examined, DMA afforded the best results for the polymerization of bis(4-aminophenyl) telluride **8a**. This may be attributed to the formation of a catalytically active copper complex and the good matching of basicity between aminotelluride **8a** and DMA to ease the ligand exchange on the copper atom[11a]. Reactions performed under more vigorous conditions, i.e. high concentration and prolonged reaction time, increased considerably the molecu-

Scheme 1. Model reactions for the polymer synthesis



Scheme 2. Synthesis of polymers containing the azo 1,4-phenylene and telluro functions as backbone units

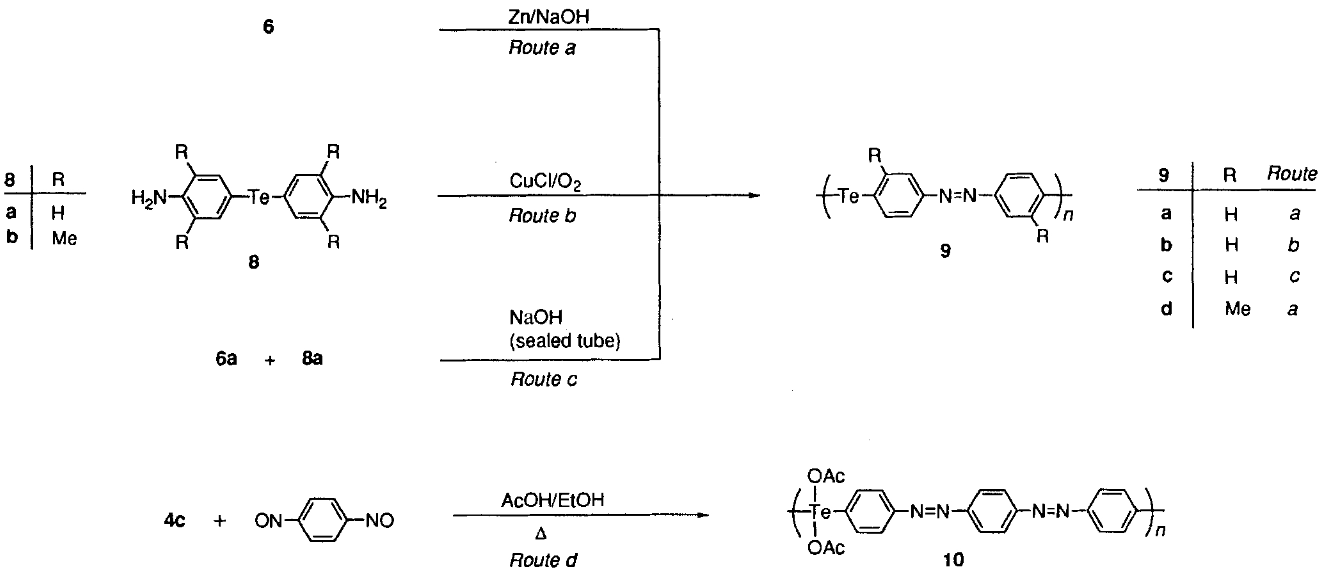


Table 1. Model reaction of aniline derivatives for oxidative polymerization

$$\mathrm{ArNH_2} \xrightarrow[\mathrm{DMA}]{\mathrm{CuCl/O_2}} \mathrm{Ar{-}N{=}N{-}Ar} + \text{Polymeric Substances}$$

Amine	Yield/%		Yield/%[a]
1a	**3a**	32	30
1b	**3b**	<1	99
1c	**3c**	20	45
1d	**3d**	52	29

[a] Yields of polymeric substances were calculated on polyaniline structure.

lar weight of the polymers and hence inherent viscosity up to 0.11 dl/g.

iii) Condensation Polymerizations of Bis(4-nitrophenyl) Telluride **6a** *with Bis(4-aminophenyl) Telluride* **8a** *and of Bis(4-aminophenyl) Telluride Te,Te-Dichloride* **4c** *with 1,4-Dinitrosobenzene*

The reaction of amines with nitro compounds at elevated temperature in the presence of alkali has long been known to produce azo compounds[38]. Since the model reaction of telluride **2** or **6a** with aniline **1b** had confirmed the azo linkage formation, the polymerization reaction of bis(4-nitrophenyl) telluride **6a** with bis(4-aminophenyl) telluride **8a** was carried out in a sealed tube in the presence of sodium hydroxide, leading to a successful production of *alt*-copoly(telluro-1,4-phenylene/azo-1,4-phenylene) **9c** (Scheme 2, *Route c*).

The dehydration reaction of an amine and a nitroso compound has long been known to be one of the efficient tools for the synthesis of azo compounds[29]. However, attempted model reaction of 4-aminodiphenyl telluride **1a** with nitrosobenzene gave azoxybenzene as the only major product. The telluride **1a** appears to have suffered oxidative decomposition during the reaction, but its oxidized product could not be identified. An alternative model reaction of 4-aminodiphenyl telluride *Te,Te*-dichloride **4a** with nitrosobenzene resulted in a successful azo linkage formation, which was confirmed by the reduction of a crude product mixture with sodium sulfide to furnish the expected 4-phenyltelluroazobenzene **5**. Thus, the latter procedure was exploited for the condensation polymerization of bis(4-aminophenyl) telluride *Te,Te*-dichloride **4c** with 1,4-dinitrosobenzene in acetic acid, which led to the formation of a new polymer **10** containing the diacetatotelluro and azo groups (Scheme 2, *Route d*). The ligand exchange on the tellurium atom was easily confirmed by ^{1}H- and ^{13}C-CPMAS NMR, which revealed a characteristic peak due to aromatic telluride diacetate.

iv) Other Attempts to Prepare Aromatic Azo-Telluro Polymers

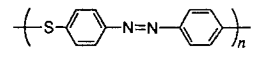
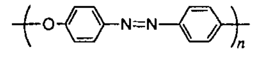
The model coupling reaction of 1,4-phenylenedidiazonium bis(tetrafluoroborate) with methyl 2,3,5,6-tetramethylphenyl telluride was attempted in methanol in the presence of sodium acetate at 0 °C. However, no azo coupling took place and only decomposition of the bisdiazonium salt occurred.

Electrochemical oxidative polymerization of bis(4-amino-3,5-dimethylphenyl) telluride **8b** was carried out in acetonitrile at 1.5 V by using sodium perchlorate as a supporting electrolyte, and a black polymeric powder was obtained. Although this product showed a UV-vis absorption at λ_{max} 520 nm in support of the formation of an azo structure, it was found to contain considerable amounts of polyanilines.

Electrical Conductivity of Polymers 9 and 10

Polymers **9** and **10** are deeply colored and show high glass transition points ($Tg > 300\,°C$). These polymers are insulators under neutral conditions. Upon exposure to bromine vapor, however, the compressed pellets made thereof showed relatively high electrical conductivities reaching up to semiconductive values (10^{-5}~10^{-2} S cm^{-1}) in spite of their interrupted conjugation structure. In view of the easy formation of a cationic polytelluride from an organotellurium system on treatment with halogens[39], *alt*-copoly(telluro-1,4-phenylene/azo-1,4-phenylene) **9b**, **c** are expected to form positive holes also easily on the tellurium atoms, and the holes may be transferred to the azo-1,4-phenylene moieties via intramolecular process and/or may be exchanged among the tellurium atoms via intermolecular process, thus leading to high electrical conductivity in spite of its relatively low molecular weight as compared with the other chalcogen azo polymer analogs (Table 2). The occurrence of high conductivity in polymer **10** upon bromine doping would in part be due to the hypervalent state of the tellurium atoms involved. This conductivity appreciably decreased or even disappeared after prolonged standing in air or under reduced pressure probably due to debromination, thus indicating that the induced conductivity mainly arises from the doping of the azo linkage with molecular bromine. The UV-vis peaks of these synthetic polymers **9** and **10** showed a red shift relative to the reference compounds **3a**, **5**, and **7**. This may be accounted for by the decrease of energy gap due to the extended π,π- and π,n-conjugation structures generated by the polymerization of tellurides **6** and **8** via the azo linkage formation. Further elaboration of the polymer structures and polymerization conditions would improve the electrical conductivity of this class of copolymers.

Table 2. Electrical conductivity and inherent viscosity of *alt*-copoly(telluro-1,4-phenylene/azo-1,4-phenylene) and analogs

Polymer	$[\eta]$/dlg^{-1}	σ/Scm^{-1}	
		Neutral	*p*-Type doping
9b	0.05-0.11	$\ll 10^{-7}$	$10^{-6} \sim 10^{-5}$
9c	0.08	$\ll 10^{-7}$	10^{-5}
10	0.09	10^{-7}	$10^{-3} \sim 10^{-2}$
	0.18[a] 0.17[b]	- insulator	- $10^{-5} \sim 10^{-4}$
	1.1[a] 0.72[b]	- insulator	- $10^{-5} \sim 10^{-4}$

[a] Ref.[11]. – [b] Ref.[18].

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Experimental

All melting points are uncorrected. – ^{1}H- and ^{13}C-NMR spectra of soluble organic compounds were recorded with a 200-MHz NMR spectrometer in $CDCl_3$, [D$_6$]DMSO or a 20:1 mixture of trifluoroacetic acid and [2,2,2-D$_3$]acetic acid by using tetramethylsilane as an internal reference. – ^{13}C-CPMAS (cross-polarization magic angle spinning) NMR spectra of insoluble polymers were obtained in a solid state by using adamantane as a standard. – IR spectra were measured as KBr pellets. – UV-vis spectra were recorded in chloroform, chloroform/hexane or concentrated sulfuric acid solution. – EI mass spectra were recorded at 70 eV. – Centrifugation for polymer precipitation was carried out at 8000–9000 rpm. – Thin-layer chromatography (TLC) was performed by usng Merk precoated silica gel sheets 60F-254. – Silica gel (200 mesh, Wakogel) was used for column chromatography. – Elemental analyses were performed at Microanalytical Laboratory, Institute for Chemical Research, Kyoto University.

Polymer Characterization: Polymeric substances obtained were characterized by elemental analysis, IR, UV/Vis, and NMR spectra. Inherent viscosity $[\eta]$ was measured at 57 °C with solutions of the polymers in concentrated sulfuric acid or *N*-methyl-2-pyrrolidone (NMP). Gel permeation chromatography (GPC) was performed with a Shodex A803, 804, or 805 polystyrene gel column using chloroform as the eluent for polystyrene calibration. Electrical conductivity σ was measured as compressed pellets by the four-probe method at room temp. *p*-Type doping was performed by exposing the powdered polymers to bromine vapor under nitrogen or argon for a few days at room temp.

Materials: Iodonitroarenes were obtained either commercially or by the reaction of nitroarenediazonium salts with potassium iodide[28] and further purified by recrystallization before use. 4-Iodo- and 4-bromoazobenzenes were prepared by the condensation of the corresponding aromatic amines with nitrosobenzene in acetic acid[29]. 1,4-Dinitrosobenzene was prepared according to the procedure described in ref.[30] Tellurium (99.999%), tellurium(IV) chloride (99.9%), copper(I) chloride (99.9%), copper(I) iodide (95%), palladium on carbon (10%), sodium hydride (60% dispersion in mineral oil), hydrazine monohydrate (98%), and aromatic amines **1b–d** were purchased from Wako Pure Chemical Industries. Nitrosobenzene was purchased from Tokyo Kasei Organic Chemicals and used as obtained. Azobenzenes **3b–d** were identified by direct comparison with the authentic samples[31,32]. Acetic acid was purified by heating with acetic anhydride in the presence of naphthalene-2-sulfonic acid followed by distillation under argon and stored over molecular sieves (4 Å). NMP, hexamethylphosphoric triamide (HMPA), *N,N*-dimethylacetamide (DMA), and pyridine were distilled from calcium chloride and stored over molecular sieves (4 Å).

Synthesis of Organic Tellurium Compounds Used as Substrate or Reference for Comparison

4-Nitrodiphenyl Telluride (**2**): To a stirred solution of diphenyl ditelluride (3.06 g, 7.47 mmol) in HMPA (20 ml) was added sodium borohydride (570 mg, 15 mmol) at 80–90 °C under argon. After disappearance of the color of the ditelluride, ethanol (2 ml) was added to the solution until the liberation of hydrogen gas ceased. Subsequently, copper(I) iodide (3.10 g, 16.3 mmol) was added. As soon as the resulting mixture turned black, powdered 4-iodonitrobenzene (3.72 g, 14.9 mmol) was introduced in one portion and the mixture was maintained at 90–100 °C with vigorous stirring. The progress of the reaction was monitored by TLC. After 2.5 h the mixture was diluted with 10% HCl (200 ml) to separate a black tarry matter, which was taken up into ethyl acetate (100 ml), and the resulting solution was filtered through a short silica gel column. The filtrate was dried with Na_2SO_4, then the solvent was evaporated under reduced pressure. The residue was chromatographed over silica gel to afford unchanged iodoarene (300 mg, 1.2 mmol) from hexane eluates and compound **2** (3.35 g, 10.3 mmol) from hexane/ethyl acetate (4:1) eluates: Yield 75% (based on unrecovered starting material), m.p. 110–112 °C (ref.[33] m.p. 110–112 °C). – ^{1}H NMR ($CDCl_3$): δ = 7.8–8.0 (m, 4H, aromatic H), 7.2–7.6 (m, 5H, aromatic H). – MS (EI), *m/z* (%, Te = 130): 329 (46) [M$^+$], 207 (34) [M$^+$ – $O_2NC_6H_4Te$], 153 (52), 77 (100).

4-Aminodiphenyl Telluride (**1a**): A mixture of telluride **2** (830 mg, 2.5 mmol), hydrazine monohydrate (640 mg, 13 mmol), 10% Pd-C (300 mg), and EtOH (20 ml) was heated at reflux for 5 h, during which time the initial yellow color of the mixture gradually faded to colorless. After compound **2** was consumed (TLC), the reaction mixture was cooled and Pd-C was removed by filtration. The filtrate was concentrated under reduced pressure to afford a brown residue, which was chromatographed over silica gel with CH_2Cl_2/hexane (1:1) as the eluent to give telluride **1a**: Yield 380 mg (51%), pale brown crystals, m.p. 67–70°C. – ^1H NMR ($CDCl_3$): δ = 7.64 (d, J = 8.5 Hz, 2H, aromatic H), 7.45–7.55 (m, 2H, aromatic H), 7.1–7.2 (m, 3H, aromatic H), 6.58 (d, J = 8.5 Hz, 2H, aromatic H), 3.8 (br., 2H, NH_2). – $C_{12}H_{11}NTe$ (296.8): calcd. C 48.56, H 3.74, N 4.72; found C 48.45, H 3.67, N 4.76.

Bis(4-nitrophenyl) Telluride (**6a**): To a black slurry of Te-Cu couple[27] prepared in situ from dissodium telluride (20.0 mmol) and copper(I) iodide (7.60 g, 39.9 mmol) in dry NMP (40 ml) under argon was added all at once 4-iodonitrobenzene (4.98 g, 20.0 mmol) in NMP (20 ml) and the resulting mixture was kept at 140–150°C for several hours. During this period, the color of the heterogeneous mixture gradually changed from black to yellow. After the starting material was consumed (TLC), the mixture was poured into 5% HCl (100 ml) to afford a black precipitate, which was filtered through a thin layer of Celite and washed with water (3 × 50 ml). The organic phase of the residue was extracted with $CHCl_3$ (2 × 100 ml). The combined extracts were dried with $MgSO_4$ and the solvent was evaporated under reduced pressure to furnish a yellow solid, which was recrystallized from $CHCl_3$/hexane (1:1) or chromatographed over silica gel with CH_2Cl_2/hexane (1:2) as the eluent to give telluride **6a** as yellow crystals (44–63%): m.p. 173–175°C (ref.[34] 170–172°C). Small amounts of the accompanying biaryl could be easily removed by recrystallization.

Bis(2-methyl-4-nitrophenyl) Telluride (**6b**) was similarly prepared from 2-iodo-5-nitrotoluene: Yellow crystals (50–57%), m.p. 126–129°C (ref.[27] 127–130°C).

Bis(aminoaryl) Tellurides (**8a** *and* **8b**): Tellurides **8** were prepared by two different procedures involving the reaction of tellurium(IV) chloride with the corresponding aniline (Method A) and the catalytic reduction of bis(nitroaryl) tellurides **6** with hydrazine monohydrate (Method B). The latter method proved to give better results.

Method A: See experimental section in ref.[35a]

Method B. – Typical Procedure: To a mixture of telluride **6a** (1.86 g, 5.00 mmol) and hydrazine monohydrate (750 mg, 15 mmol) in EtOH (10 ml) was added 10% Pd-C (200 mg) at around 50°C and the resulting black mixture was heated at reflux for 5 h, during which time the color of the mixture gradually changed from yellow to colorless. After the telluride **6a** was consumed (TLC), Pd-C was filtered off and the filtrate was concentrated under reduced pressure. The brown residue was chromatographed over silica gel with CH_2Cl_2/hexane (1:1) as the eluent to give bis(4-aminophenyl) telluride **8a** as colorless crystals (1.06 g, 68%): m.p. 128–131°C (ref.[35b] 127–128°C).

Phenyl 4-Aminophenyl Telluride Te,Te-Dichloride (**4a**): To an ice-cooled solution of 4-aminodiphenyl telluride **1a** (860 mg, 2.9 mmol) in dry dichloromethane (5 ml) was added with vigorous stirring sulfuryl chloride (390 mg, 2.9 mmol) dissolved in the same solvent (1 ml). The reaction was complete within a few minutes. Addition of hexane (10 ml) to the resulting solution gave dichloride **4a** as a white precipitate. After the mixture had been kept in the refrigerator for 1 h, the precipitate was isolated by filtration (970 mg, 91%). – Colorless crystals, m.p. >120°C (dec.). – ^1H NMR ($[D_6]$DMSO): δ = 8.0–8.1 (m, 2H, aromatic H), 7.79 (d, J = 8.6 Hz, 2H, aromatic H), 7.5–7.6 (m, 3H, aromatic H), 6.91 (d, J = 8.6 Hz, 2H, aromatic H). In the ^1H-NMR spectrum the amino groups exhibited very broad signals which could not be assigned. – $C_{12}H_{11}Cl_2NTe$ (367.8): calcd. C 39.19, H 3.02, N 3.81; found C 39.05, H 3.22, N 3.35.

Bis(4-aminophenyl) Telluride Te,Te-Dichloride (**4c**): To an ice-cooled solution of telluride **8a** (1.55 g, 4.97 mmol) in dry dichloromethane (10 ml) was added with vigorous stirring sulfuryl chloride (670 mg, 5.0 mmol) dissolved in the same solvent (3 ml). Subsequent addition of hexane (20 ml) to the resulting solution gave dichloride **4c** as a white precipitate. After standing in a refrigerator for 3 h, it was filtered off (1.86 g, 98%). – Pale yellow crystals, m.p. >140°C (dec.). – ^1H NMR ($[D_6]$DMSO): δ = 7.74 (d, J = 8.6 Hz, 4H, aromatic H), 6.92 (d, J = 8.6 Hz, 4H, aromatic H), 5.8 (br., 4H NH_2). – $C_{12}H_{12}Cl_2N_2Te$ (382.8): calcd. C 37.66, H 3.16, N 7.32; found C 37.37, H 3.12, N 7.25.

Bis(4-aminophenyl) Telluride Te,Te-Diacetate (**4d**): To a well stirred suspension of silver acetate (560 mg, 3.4 mmol) in ethanol (5 ml) was added dichloride **4c** (580 mg, 1.5 mmol) in one portion and the resulting heterogeneous mixture was stirred overnight in the dark at room temp. Insoluble deposit was filtered off and washed with hot ethanol (3 × 5 ml). The filtrate was concentrate in vacuo to afford a colorless solid, which was recrystallized from ethanol/hexane (3:1) to give compound **4d** (530 mg, 82%). – M.p. >130°C (dec.). – ^1H NMR ($[D_6]$DMSO): δ = 7.38 (d, J = 8.4 Hz, 4H, aromatic H), 6.64 (d, J = 8.4 Hz, 4H, aromatic H), 5.4–5.7 (4H, two broad peaks, NH_2), 1.85 (s, 6H, $COCH_3$). – IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1}, 1640, 1590, 1500, 1380, 1300, 1180, 1050, 1010, 820. – $C_{16}H_{18}N_2O_4Te$ (429.9): calcd. C 44.70, H 4.22, N 6.52; found C 44.64, H 4.30, N 6.46.

4-Phenyltelluroazobenzene (**5**): Telluride **2** (250 mg, 0.76 mmol) was heated with an excess of aniline **1b** (3.00 g, 32.2 mmol) in the presence of sodium hydroxide (200 mg, 5.0 mmol) at 180°C for 0.5 h to afford a dark red mixture, which was extracted several times with ether. The combined extracts were concentrated in vacuo. The resulting red oil was chromatographed on silica gel with hexane as the eluent to give compound **5** as orange crystals (100 mg, 34%). – M.p. 72–75°C (hexane/$CHCl_3$ = 1:1). – ^1H NMR ($CDCl_3$): δ = 7.7–8.0 (m, 8H, aromatic H), 7.45–7.55 (m, 3H, aromatic H), 7.2–7.4 (m, 3H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 114.0, 120.5, 122.9, 123.6, 128.4, 129.0, 129.8, 131.1, 137.4, 138.9, 152.0, 152.7. – MS(EI) m/z: (%, Te = 130): 388 (17) [M$^+$], 283 (16) [M$^+$ – PhN_2], 207 (14), 77 (100). – IR (KBr): $\tilde{\nu}$ = 1470 cm^{-1}, 1440, 1390, 1300, 1100, 1010, 830, 770, 690. – UV-vis ($CHCl_3$ or hexane/$CHCl_3$ = 30:1): λ_{max} = 384 nm, 323. – $C_{18}H_{14}N_2Te$ (385.9): calcd. C 56.02, H 3.66, N 7.26; found C 56.00, H 3.56, N 7.29.

Alternatively, compound **5** was prepared by the reaction of 4-aminodiphenyl telluride *Te,Te*-dichloride **4a** with nitrosobenzene in acetic acid (50°C, 5 h) leading to 4-phenyltelluroazobenzene *Te,Te*-diacetate **4b**, which, without being isolated, was reduced with sodium sulfide to telluro-azo compound **5** in 20% yield.

Model Reactions for the Synthesis of the Azo-1,4-Phenylene/Telluro Polymers

1. *Reduction of 4-Nitrodiphenyl Telluride* (**2**) *with a Zinc/Alkali System:* A mixture of telluride **2** (360 mg, 1.1 mmol), zinc dust (670 mg, 10 mmol), powdered sodium hydroxide (600 mg, 15 mmol), ethanol (5 ml), and benzene (3 ml) was heated at reflux for 10 h. Insoluble inorganic solid was removed by filtration and the filtrate was concentrated in vacuo. The residue was chromatographed on silica gel with hexane as the eluent to give 4,4′-bis-

(phenyltelluro)azobenzene **3a** (100 mg, 31%): – Orange yellow crystals, m.p. 130–134°C (ethyl acetate). – ^{1}H NMR ($CDCl_3$): δ = 7.5–7.9 (m, 12H, aromatic H), 7.2–7.4 (m, 6H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 113.9, 120.2, 123.6, 128.5, 129..8, 137.3, 138.9, 151.9. – IR (KBr): $\tilde{\nu}$ = 1470 cm^{-1}, 1440, 1390, 1300, 1150, 1000, 840, 760, 690. – MS (EI), *m/z* (%, Te = 130): 594 (11) [M$^+$], 283 (48), 207 (51), 77 (100). – UV-vis ($CHCl_3$): λ_{max} = 407 nm, 330 (sh). – $C_{24}H_{18}N_2Te_2$ (589.6): calcd. C 48.89, H 3.08, N 4.75; found C 48.02, H 3.16, N 4.84.

2. *Oxidation of Aromatic Amines with a CuCl/O$_2$ System. – Typical Procedure:* A mixture of 4-methylaniline **1d** (430 mg, 4.0 mmol), CuCl (100 mg, 1.0 mmol), and DMA (3 ml) was heated at 60–80°C for 2 h, while a stream of oxygen was slowly bubbled through it. During this period the solution gradually turned red and a black solid separated. This polymeric by-product was filtered off, washed successively with 10% HCl, water, ethanol, and ethyl acetate, and dried. The filtrate was concentrated in vacuo and the residue was extracted with ethyl acetate (3 × 20 ml). The combined extracts were dried with Na_2SO_4 and the solvent was evaporated under reduced pressure to afford a red oil, which was chromatographed over silica gel with hexane as the eluent to give 4,4'-dimethylazobenzene **3d** (220 mg, 52%). – M.p. 140–144°C (ref.[32] 145–146°C). – MS(EI), *m/z* (%): 210 (26) [M$^+$], 91 (100).

Polymeric by-product: Yield 120 mg (29% based on polyaniline); black powder. – T*g* >300°C. – IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1}, 1650, 1500, 850, 800, 700. – UV-vis (H_2SO_4): broad absorption at 300–590 nm. Results of the model oxidative reaction are compiled in Table 1.

3. *Reaction of 4-Aminodiphenyl Telluride* (**1a**) *with Nitrosobenzene:* To a solution of telluride **1a** (350 mg, 1.2 mmol) in acetic acid (5 ml) was added nitrosobenzene (130 mg, 1.2 mmol) in one portion and the resulting mixture was stirred under argon at room temp. The reaction was intermittently monitored by TLC. After 1 h acetic acid was distilled off under reduced pressure and the residue was chromatographed on silica gel with hexane/ethyl acetate (5:1) as the eluent to give azoxybenzene (m.p. 33–34°C, ref.[36] 33–33.5°C) in 87% yield. The expected 4-phenyltelluroazobenzene **5** could not be obtained. A highly polar by-product might be some oxidized species of the telluride, but it could not be identified.

4. *Reaction of Bis(4-aminophenyl) Telluride Te,Te-Dichloride* (**4c**) *with Nitrosobenzene:* To a solution of dichloro telluride **4c** (400 mg, 1.0 mmol) in a mixture of dry acetic acid (20 ml) and ethanol (10 ml) was added powdered nitrosobenzene (480 mg, 4.5 mmol) in one portion at room temp. and the mixture was heated at 50°C for 5 h under argon. MS spectral inspection of the resulting dark red mixture showed a peak at *m/z* 492 (Te = 130) attributable to bis(phenylazophenyl) telluride. An NMR spectrum of the crude product exhibited signals due to *Te*-acetate (δ = 1.9) and aromatic protons (δ = 7.5–8.2), indicating the ligand exchange between the chlorine atom and acetoxy group during the reaction. Addition of hexane to the mixture produced a dark red tarry material which, on treatment with sodium sulfide in methanol, gave bis(4-phenylazophenyl) telluride **7** (70 mg, 14%). – Orange crystals, m.p. 197–202°C (hexane/ethyl acetate/EtOH, 1:1:1). – ^{1}H NMR ($CDCl_3$): δ = 7.7–8.1 (m, 12H, aromatic H), 7.4–7.6 (m, 6H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 119.0, 123.0, 123.8, 129.1, 131.2, 138.5, 152.3, 152.6. – IR (KBr): $\tilde{\nu}$ = 1480 cm^{-1}, 1450, 1380, 1290, 1150, 1000, 830, 770, 680. – MS (EI), *m/z* (%, Te = 130): 492 (17) [M$^+$], 387 (10), 105 (18), 77 (100). – UV-vis ($CHCl_3$): λ_{max} = 380 nm, 317. – $C_{24}H_{18}N_4Te$ (490.0): calcd. C 58.83, H 3.70, N 11.43; found C 58.93, H 3.89, N 11.27.

This telluride was also accessible by the reaction of telluride **6a** with aniline: A mixture of nitrotelluride **6a** (100 mg, 0.27 mmol), aniline **1b** (1.0 g, 11 mmol) and sodium hydroxide (100 mg, 2.5 mmol) was heated at 180°C for 15 min in the presence of molecular sieves (4 Å). During this period, the reaction mixture turned dark red. Usual workup furnished telluride **7** in 38% yield.

Preparation of Polymers Composed of the Azo 1,4-Phenylene and Telluro Groups as Backbone Units

1. *Reductive Polymerization (Route a). – Typical Procedure:* A mixture of bis(2-methyl-4-nitrophenyl) telluride **6b** (410 mg, 1.0 mmol), zinc dust (1.3 g, 20 mmol), sodium hydroxide (410 mg, 10 mmol), ethanol (4 ml), and water (0.5 ml) was heated at 70–80°C for 24 h. Insoluble inorganic precipitate was filtered off and washed thoroughly with hot chloroform (3 × 100 ml). The filtrate was diluted with hexane (200 ml) and kept at room temp. overnight to afford *alt*-copoly(telluro-2-methyl-1,4-phenylene/azo-3-methyl-1,4-phenylene) **9d** as an orange powdery precipitate (110 mg, 33%). – T*g* = 135–150°C. – ^{1}H NMR ($CDCl_3$): δ = 7.1–8.4 (br., 6H, aromatic H), 2.4–2.7 (br, 6H, CH_3). – IR (KBr): $\tilde{\nu}$ = 1510 cm^{-1}, 1460, 1340, 1020, 840. – M_w = 2 × 10^3 (by GPC). Oligomer **9d** exhibited solvatochromism: λ_{max} = 392 nm ($CHCl_3$), 372 nm (hexane/$CHCl_3$ = 30:1). – $(C_{14}H_{12}N_2Te)_n$ $(335.9)_n$: calcd. C 50.07, H 3.60, N 8.34; found C 50.18, H 3.68, N 8.23.

2. *Oxidative Polymerization (Route b). – Typical Procedure:* Bis(4-aminophenyl) telluride **8a** (310 mg, 0.99 mmol) was dissolved in a mixture of DMA (2 ml) and CuCl (100 mg, 1.0 mmol) and the resulting mixture was heated at 70–80°C in a slow stream of oxygen. As the reaction proceeded, the mixture gradually became viscous and a black powdery solid began to separate. In order to keep the mixture in a state of slurry, additional portions (3 × 0.3 ml) of DMA were added to the reaction mixture at 4-h intervals. After 16 h the mixture was diluted with 10% HCl (25 ml) and a black polymeric product was collected by filtration and washed successively with 5% aqueous ammonia, water, ethanol, chloroform, and finally ethyl acetate. After each washing, the polymeric substance was collected by centrifugation. *alt*-Copoly(telluro-1,4-phenylene/azo-1,4-phenylene) **9b** thus obtained was dried under reduced pressure and stored under argon in the dark. – Yield 30–69%. – Black powder, T*g* >300°C. – ^{1}H NMR (soluble part in CF_3COOH/[2,2,2-D_3]acetic acid/TMS): δ = 7.7–8.5 (aromatic H). – ^{13}C CPMAS NMR: δ = 120–160 (br., C_{arom}). – IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1}, 1640, 1590, 1490, 1390, 1000, 820. – UV-vis (H_2SO_4): λ_{max} = 274 nm, 470 (sh), 200–570 (br.). – $[\eta]$ = 0.05–0.11. – σ <10^{-7} S cm^{-1} (neutral), 10^{-6} ~ 10^{-5} S cm^{-1} (Br_2 doping). – $(C_{12}H_8N_2Te)_n$ (307.8): calcd. C 46.83, H 2.62, N 9.10; found C 47.44, H 3.42, N 8.66.

3. *Condensation Polymerization (Route c). – Typical Procedure:* A mixture of telluride **6a** (180 mg, 0.48 mmol), telluride **8a** (210 mg, 0.67 mmol), sodium hydroxide (90 mg, 2.3 mmol), and molecular sieves (4 Å) (pellets, 10 mg) was heated in a sealed tube at 200–210°C for 3 h. Usual workup provided *alt*-copoly(telluro-1,4-phenylene/azo-1,4-phenylene) **9c** as a dark brownish powder (70 mg, 20%). – T*g* >300°C. – IR (KBr): $\tilde{\nu}$ = 1570 cm^{-1}, 1490, 1470, 1340, 1290, 1000, 830. – ^{13}C CPMAS NMR: δ = 120–150 (br., C_{arom}). – UV-vis (H_2SO_4): λ_{max} = 500 nm, 426, 213. – $[\eta]$ = 0.08. – σ <10^{-7} S cm^{-1} (neutral), 10^{-5} S cm^{-1} (Br_2 doping). – $(C_{12}H_8N_2Te)_n$ $(307.8)_n$: calcd. C 46.83, H 2.62, N 9.10; found C 45.25, H 2.79, N 8.65.

4. *Condensation Polymerization (Route d). – Typical Procedure:* Bis(4-aminophenyl) telluride *Te,Te*-dichloride **4c** (250 mg, 0.65 mmol) and 1,4-dinitrosobenzene (90 mg, 0.66 mmol) were stirred in a mixture of acetic acid (4 ml) and ethanol (3 ml) in the presence of molecular sieves (4 Å) (pellets, 20 mg) under reflux for 19 h. After usual workup, *alt*-copoly[*Te,Te*-diacetoxytelluro-1,4-phen-

ylene/bis(azo-1,4-phenylene)] **10** was obtained as a black solid (100 mg, 29%). – Tg >300°C. – IR (KBr): $\tilde{\nu}$ = 1600 (C=O) cm^{-1}, 1510, 1290, 1180, 830, 770, 670. – ^{13}C CPMAS NMR: δ = 20–30 (CH_3COO), 120–150 (C_{arom}), 175–185 (CH_3COO). – UV-vis (H_2SO_4) λ_{max} = 721, 305 nm. – $[\eta]$ = 0.09. – $\sigma = 10^{-7}$ S cm^{-1} (neutral), $10^{-3} \sim 10^{-2}$ S cm^{-1} (Br_2 doping). – $(C_{22}H_{18}N_4O_4Te)_n$ $(530.0)_n$: calcd. C 49.86, H 3.42, N 10.57; found C 50.00, H 3.18, N 10.55.

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