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A Convenient Synthesis of Functionalized Dibenzotellurophenes and Related Compounds via the Intramolecular Telluro Coupling Reaction. The Positive Effect of Heavy Chalcogen Atoms on the Molecular Hyperpolarizability of a Captodative Conjugation System

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Nitro-containing dibenzotellurophenes and related compounds, which are otherwise laborious to obtain, were prepared by the reaction of 2,2′-diiodobiphenyl derivatives with an in situ prepared tellurium−copper slurry. Partial reduction of 3,7-dinitrodibenzotellurophene using hydrazine hydrate/palladium on charcoal led to 3-amino-7-nitrodibenzotellurophene, which was found to exhibit a relatively large third-order molecular hyperpolarizability γ (1.4×10^{-31} esu) in the measurement of degenerated four-wave mixing (DFWM) as compared with 4-amino-4′-nitrobiphenyl and other previously reported compounds, confirming the positive effect of tellurium atom on the nonlinear optical property of a captodative conjugation system.

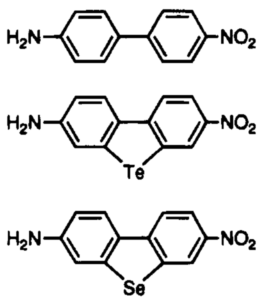
Introduction

During the past two decades, organic molecules with nonlinear optical properties have received growing attention because of their potential as materials for high density and fast optical information processing. In connection with our ongoing program, it became necessary to examine the effect of heavy chalcogen atoms, such as tellurium and selenium, on the hyperpolarizability of a capto-dative conjugation system such as that of 4-amino-4′-nitrobiphenyl (**1**). Model compounds chosen for this purpose were 3-amino-7-nitrodibenzotellurophene (**3a**) and 3-amino-7-nitrodibenzoselenophene (**4a**) (Chart 1). A search of the literature revealed no descriptions of these compounds or their immediate precursors. Thus, a synthetic investigation of new methods for the construction of this class of heteroaromatic compounds was launched.

Results and Discussion

Synthesis of Functionalized Dibenzotellurophenes and Related Compounds. At first sight, the easiest route to compounds **3a** and **4a** appeared to involve the direct nitration of dibenzotellurophene **3e**[1] and dibenzoselenophene **4e**[2] to dinitro derivatives **3b** and **4b**, followed by their partial reduction to the respective nitroamines **3a** and **4a**. However, this approach proved untenable since, as expected, the nitrating agents preferentially attack the chalcogen atom rather than the nuclear carbons. Furthermore, the preferred ring site for electrophilic attack is a position *para* to the chalcogen atom. Under forcing conditions, there resulted a complex mixture of isomeric mono- and dinitro derivatives of the corresponding nitratotelluro or -seleno compounds, often accompanied by extensive decomposition products.

Chart 1



1

3a

4a

An alternative route to compound **3a** involved an intramolecular telluro coupling reaction. A homogeneous mixture of disodium telluride and copper(I) iodide in a 1:2 molar ratio in *N*-methyl-2-pyrrolidone (NMP) produces a black slurry, supposedly composed of elemental tellurium, metallic copper, and possibly some tellurium−copper compounds of indefinite nature.[3,4] This slurry has recently been shown to act as a mild telluration agent for iodonitroarenes to afford bis(nitroaryl) tellurides in acceptable yields.[5] When this type of telluro coupling reaction was applied to 2,2′-diiodobiphenyl **2e**, we obtained the expected dibenzotellurophene **3e** in a modest yield. The generality of this synthetic approach has been confirmed by the synthesis of compounds **3b-d** from the corresponding 2,2′-diiodobiphenyl derivatives **2b-d** (Table 1). The nitro group, which does not survive when disodium telluride is employed as the tellurating agent, remained intact.

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[3] Copper telluride with a composition of Cu_2Te[4] was prepared by heating a stoichiometric mixture of elemental tellurium and copper powder in an electric furnace at 900 °C under 10^{-7} mmHg for 24 h. The structure of Cu_2Te thus obtained was confirmed by powder X-ray diffraction analysis. The compound in the form of glittering fine powder, however, showed no ability for the telluration of activated iodoarenes. After being heated with iodonitroarenes in NMP at 150 °C for 5 h, it was recovered entirely unchanged.

[4] For a survey of Te−Cu alloys, see: *Gmelin Handbuch der Anorganischen Chemie, 60, Kupfer Teil B;* Verlag Chemie: GMBH, Weinheim, 1958; p 619.

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Table 1. Synthesis of Dibenzotellurophene and Derivatives

	biphenyl **2**			condns		dibenzotellurophene **3**[a]
	R^1	R^2	R^3	T (°C)	time (h)	yield (%)
b	NO_2	H	NO_2	140–150	10	31–52
c	NO_2	H	H	180–190	4.5	41
d	H	NO_2	H	140–150	4	40
e	H	H	H	190–200	5	42

[a] Yields refer to the isolated compounds and were not optimized.

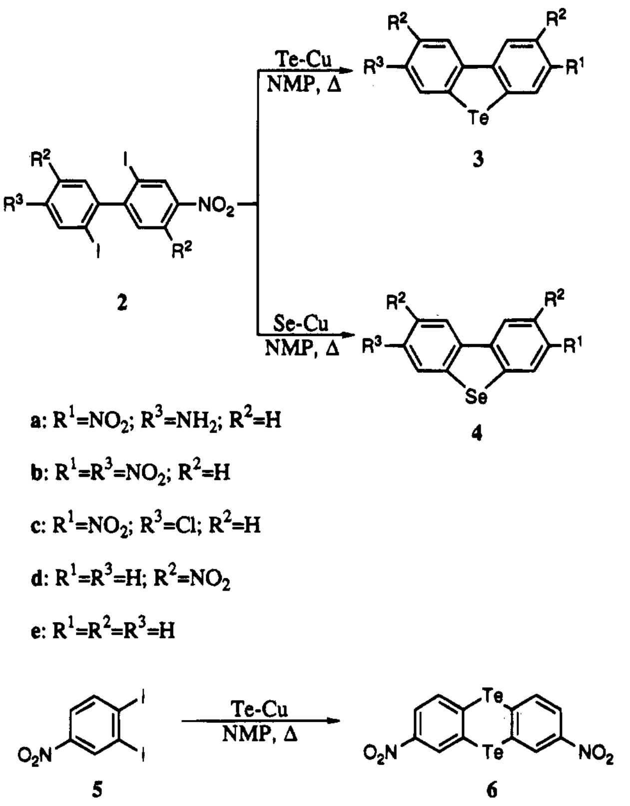
Known methods for the construction of the dibenzotellurophene framework involve the reaction of 2,2′-dilithiobiphenyl with tellurium dichloride,[6] tellurium tetrachloride,[6] tetramethoxytellurium,[6] or trimethyltellurium iodide;[7] the high-temperature reaction of biphenyl with tellurium tetrachloride,[8] the thermal cyclization of 2-biphenylyltellurium trichloride;[9] the flash thermolysis of bis(2,2′-biphenylene)tellurium,[6] the acid-mediated cyclization of 2-biphenylyl trifluoromethyl telluride;[10] and the prolonged heating of elemental tellurium with 1,2-diiodotetrafluorobenzene,[11] 2,2′-diiodooctafluorobiphenyl,[12] 2,2′-biphenylenemercury,[6] dibenzothiophene *S,S*-dioxide,[13] or thianthrene *S,S,S,S*-tetraoxide[1] at 250–450 °C. However, none of these reported methodologies appears to provide a convenient route to polyfunctionalized dibenzotellurophenes, such as compound **3a**.

A similar reaction of the tellurium-copper slurry with 1,2-diiodo-4-nitrobenzene (**5**) resulted in the formation of 2,7-dinitro-9,10-ditelluranthracene (**6**) in 12% isolated yield, although no attempt was made to optimize the yield (Scheme 1). The reported syntheses of 9,10-ditelluranthracenes involve a high-temperature reaction of elemental tellurium with tetraphenyltin,[14] 1,2-phenylenemercury,[15] or 1,2-diiodotetrafluorobenzene[16,17] and reaction of disodium telluride with 1,2-dichlorobenzene.[18]

Other binary tellurium–transition metal systems such as the Te–Fe, Te–Co, and Te–Ni slurries, prepared similarly from the reaction between disodium telluride and the respective metal salts, proved to be ineffective for the telluration of iodoarenes.

A homogeneous reaction mixture of disodium selenide and copper(I) iodide in a 1:2 molar ratio in NMP produced a dark brown slurry. When this slurry was similarly reacted with 2,2′-diiodo-4,4′-dinitrobiphenyl (**2b**), 3,7-dinitrodibenzoselenophene (**4b**) was obtained in 33% isolated yield, confirming the feasibility of this type of seleno coupling for the construction of functionalized dibenzoselenophenes. However, the dark brown slurry was most likely composed of copper selenide, accompanied by some elemental selenium and metallic copper.

Scheme 1



a: R^1=NO_2; R^3=NH_2; R^2=H

b: R^1=R^3=NO_2; R^2=H

c: R^1=NO_2; R^3=Cl; R^2=H

d: R^1=R^3=H; R^2=NO_2

e: R^1=R^2=R^3=H

Previous methods for the synthesis of the dibenzoselenophene skeleton include the cyclizations of 2-biphenylylselenenyl halides[19,20] and 2-biphenylyltrifluoromethyl selenide,[10] the high-temperature cyclization of 2-biphenylyl phenyl selenide dichloride,[21] the prolonged heating of selenium powder with 2,2′-biphenylenemercury[22] or biphenylene[23] at 275–330 °C, the cyclodehydration of diphenyl selenoxide with sodium amide,[24] the sulfur dioxide extrusion from dibenzothiophene *S,S*-dioxide with elemental selenium,[25] the removal of selenium from 9,10-diselenanthracene with copper bronze,[26] and a Bradsher-type reaction of 2-allylbenzo[*b*]selenophene with ethyl dichloroethoxyacetate.[27]

Dinitrodibenzotellurophene (**3b**) and -selenophene (**4b**) were partially reduced with hydrazine monohydrate in boiling ethanol–THF (2:1) in the presence of palladium on charcoal to produce the required aminonitro compounds **3a** and **4a** in satisfactory isolated yields.

Effect of Heavy Chalcogen Atoms on Molecular Hyperpolarizability. We have examined the macroscopic (solid phase) and microscopic (solution) nonlinear optical properties of compounds **3a** and **4a**, with a special interest in the effect of the introduction of a heavy chalcogen atom. First, the macroscopic second-order nonlinear optical properties of compounds **1**, **3a**, and **4a**

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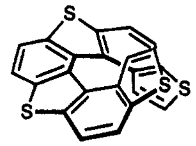
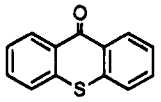
were qualitatively compared for the powdered samples by measuring the second-harmonic generation (SHG) intensity with a Nd-YAG laser at 532 nm. The SHG intensity observed for 4-amino-4′-nitrobiphenyl (**1**) was comparable with that of urea which was used as the standard. The intensity of selenophene **4a** was about three times larger, but tellurophene **3a** showed little SHG activity (< 0.2 × intensity of urea). Similar observations have recently been reported for 4-aminophenyl 4-nitrophenyl selenide and 4-aminophenyl 4-nitrophenyl telluride.[27] However, tellurophene **3a** was found to generate emission in the ultraviolet region, probably due to the third-harmonic generation (THG).

We measured the third-order nonlinear optical susceptibility $\chi^{(3)}$ of compounds **1**, **3a**, and **4a** in dilute NMP solutions at 532 nm, using the degenerated four-wave mixing (DFWM) method. The DFWM has been attracting attention because of its potential use as a phase conjugate mirror for all-optical signal processing and optical computing.[28] Many measurements of $\chi^{(3)}$ have already been made, and some organic materials are known to show large $\chi^{(3)}$ values.[29] However, there are few systematic investigations of the effect of heavy hetero atoms on the third-order molecular hyperpolarizability γ,[30] which is defined by eq $\chi^{(3)} = f^4N\gamma$, where N is the number density of molecules. The Lorentz local field factor f is obtained from the equation $f = (n^2 + 2)/3$, where n is the refractive index of NMP (1.47).

Compounds **3a** and **4a** showed relatively large third-order nonlinear optical properties compared to **1** and other previously reported compounds,[31–33] confirming the positive effect of the heavy chalcogen atoms on the γ values (Table 2). Enhancement of the γ values by the introduction of a heavy hetero atom such as tellurium may be interpreted in terms of the softness of its electronic orbitals as well as the increased planarity of the biphenyl structure. However, biphenyl and fluorene derivatives with captodative substituents in mutual conjugation gave indistinguishable THG measurements.[34]

Table 2. Third-Order Nonlinear Optical Properties of 3a and Related Compounds

compound	γ / esu [a]
1	5.1×10^{-32}
3a	1.4×10^{-31} 5.6×10^{-30} [b]
4a	1.0×10^{-31}
	6.6×10^{-33} [c]
	1.5×10^{-34} [d] 8.7×10^{-33} [b, d]
Nitrobenzene	5.2×10^{-35} [e]

[a] Measured in NMP at room temperature by DFWM with pico-order second pulses. [b] Measured in NMP at room temperature by DFWM with nano-order second pulses. [c] Taken from ref 31. [d] Taken from ref 32. [e] Taken from ref 33.

Experimental Section

General. All telluro and seleno coupling reactions were carried out under an atmosphere of argon; otherwise, the yields of dibenzotellurophenes and -selenophene considerably decreased.

Sodium hydride (NaH; 60% dispersion in mineral oil) was washed with dry hexane prior to use. Tellurium (99.999%), copper(I) iodide, 10% palladium on charcoal, and dimethyl sulfoxide (DMSO) were used as commercially obtained. *N*-Methyl-2-pyrrolidone (NMP) was distilled from calcium chloride and stored over 4 Å molecular sieves. Melting points are uncorrected. ^{1}H NMR spectra were recorded in CDCl_3 and/or DMSO-d_6. IR spectra were measured as KBr pellets or liquid films. Mass spectra (EI) were determined at 70 eV. Second-harmonic generation (SHG) intensity was measured for powdered samples by using a Spectron SL401 Nd-YAG laser. A degenerated four-wave mixing (DFWM) study was performed on dilute NMP solutions of the samples, employing a frequency doubled Nd-YAG laser that can generate nano- or pico-order second light pulses. As for the details of the experimental setup used for optical measurements, see ref 31.

The $\chi^{(3)}_{\text{sample}}$ value was derived from the comparison with the $\chi^{(3)}_{\text{CS2}}$ value of carbon disulfide, taken as the standard, according to eq 1 and the reflectivity R of the phase conjugate signal, defined by eq 2, was plotted against the pump intensity I, where I_1 and I_2 are pump intensities, while

$$\chi^{(3)}_{\text{sample}} = \chi^{(3)}_{\text{CS}_2}(n_{\text{sample}}/n_{\text{CS}_2})^2(R_{\text{sample}}/R_{\text{CS}_2})^{1/2}(\ln T^{-1}/T^{1/2}(1 - T)) \quad (1)$$

$$R^{1/2} = 24\pi^3\chi^{(3)}L(I_1I_2)^{1/2}/\lambda c n^2 \quad (2)$$

L, λ, c, n, T, and $\chi^{(3)}_{\text{CS2}}$ are interaction length (1 mm thick quartz cuvette), wavelength, velocity of light, refractive index, transmissivity of a given sample at 532 nm, and third-order nonlinear optical susceptibility of carbon disulfide (1.7×10^{-12} esu at average 7 ns pulse; 2.9×10^{-12} esu at average 30 ps pulse),[35] respectively.

Materials. 1,2-Diiodo-4-nitrobenzene **5** (mp 105–107 °C (lit.[36] mp 111–113 °C)) was obtained by the reaction of 2-iodo-4-nitrobenzenediazonium salt with potassium iodide.[37] 2,2′-Diiodobiphenyl (**2e**) (mp 108–110 °C (lit.[38] mp 109–110 °C)) was prepared by the decomposition of biphenyleneiodonium iodide in hot DMSO.[38] 2,2′-Diiodo-4,4′-dinitrobiphenyl (**2b**)

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(mp 144–148 °C (lit.[39] mp 146–148 °C)) was synthesized by the diiodination of 4,4′-dinitrobiphenyl with iodyl sulfate.[39] 2,2′-Diiodo-5,5′-dinitrobiphenyl (**2d**) (mp 248–250 °C (lit.[40] mp 236–238 °C); ^{1}H NMR (DMSO-d_6/CDCl$_3$) δ 8.30 (d, 2 H, J = 8.9 Hz), 8.0–8.1 (d + dd, 4 H, J = 8.9, 2.4 Hz); MS m/z 496 (M$^+$ 23), 369 (100)) was prepared by the nitration of 2,2′-diiodobiphenyl (**2e**) with nitronium triflate.[40] 4-Amino-4′-nitrobiphenyl (**1**) (mp 200–202 °C (lit.[41] mp 198 °C)) and 4-amino-4′-nitro-2,2′-diiodobiphenyl (**2a**) were prepared by carefully reducing 4,4′-dinitrobiphenyl with hydrazine monohydrate/palladium on charcoal and 2,2′-diiodo-4,4′-dinitrobiphenyl (**2b**) with sodium sulfurated borohydride,[42] respectively. 4-Chloro-4′-nitro-2,2′-diiodobiphenyl (**1c**) was prepared by the reaction of the corresponding diazonium salt with copper(I) chloride in sulfuric acid–acetic acid. The physical data of new compounds **2a** and **2c** are shown below:

4-Amino-4′-nitro-2,2′-diiodobiphenyl (2a): yield 29%; orange syrup; ^{1}H NMR (CDCl$_3$) δ 8.73 (d, 1 H, J = 2.1 Hz), 8.21 (dd, 1 H, J = 2.1, 8.4 Hz), 7.36 (d, 1 H, J = 8.4 Hz), 7.25 (d, 1 H, J = 2.2 Hz), 6.89 (d, 1 H, J = 8.2 Hz), 6.73 (dd, 1 H, J = 2.2, 8.2 Hz), 3.90 (s, br, 2 H); IR (neat) 1600, 1510, 1350 cm^{-1}; MS m/z (rel intensity) 466 (M$^+$, 60), 334 (18), 293 (20), 139 (100). Anal. Calcd for C$_{12}$H$_8$I$_2$N$_2$O$_2$: C, 30.93; H, 1.73; N, 6.01. Found: C, 31.23; H, 1.72; N, 6.00.

4-Chloro-4′-nitro-2,2′-diiodobiphenyl (2c): yield 62%; colorless syrup; ^{1}H NMR (CDCl$_3$) δ 8.77 (d, 1 H, J = 2.2 Hz), 8.29 (dd, 1 H, J = 2.2, 8.4 Hz), 7.96 (d, 1 H, J = 2.0 Hz), 7.47 (dd, 1 H, J = 2.0, 8.2 Hz), 7.37 (d, 1 H, J = 8.4 Hz), 7.11 (d, 1 H, J = 8.2 Hz); IR (neat) 1520, 1350 cm^{-1}; MS m/z (rel intensity, Cl = 35) 485 (M$^+$, 27), 358 (100), 312 (39), 150 (95). Anal. Calcd for C$_{12}$H$_6$ClI$_2$NO$_2$: C, 29.69; H, 1.25; N, 2.89. Found: C, 29.69; H, 1.34; N, 2.81.

Preparations of Disodium Telluride and Disodium Selenide. Disodium telluride was prepared as a deep purple solution by heating tellurium powder and NaH in a molar ratio of 1:2 in NMP at 100–110 °C under argon. Disodium selenide was obtained as a deep blue solution by heating selenium powder and NaH in a molar ratio of 1:2 in NMP at 90–100 °C under argon.

Reaction of 2,2′-Diiodobiphenyls 2 with the Tellurium–Copper Slurry. Typical Procedure. 2,2′-Diiodo-4,4′-dinitrobiphenyl (**2b**) (240 mg, 0.48 mmol) was added in one portion to a black slurried mixture of amorphous tellurium (1.28 g, 10.0 mmol),[43] the tellurium–copper reagent prepared in situ from disodium telluride (350 mg, 2.0 mmol) and copper(I) iodide (760 mg, 4.0 mmol), and NMP (6 mL). The resulting mixture was gradually heated to 150 °C in 30 min and kept at this temperature for several hours. The progress of the reaction was monitored by TLC and ^{1}H NMR. After cooling, the mixture was diluted with ethyl acetate (10 mL) and THF (20 mL), and the insoluble substance was filtered off. The filtrate was diluted with water (40 mL), and the organic phase was extracted with a 1:1 mixture of ethyl acetate and THF (30 mL × 2). The combined extracts were dried with Na$_2$SO$_4$ and evaporated under reduced pressure until the total volume was reduced to one fourth. Addition of hexane (60 mL) to the concentrate separated tellurophene **3b** as a reddish brown crystalline solid or a tarry matter. In the latter case, the tarry matter was placed on a short silica gel column and eluted using ethyl acetate as the solvent. A solid residue on the column top was taken up in DMSO and passed through a short silica gel column. The eluent was diluted with water to produce a solid precipitate, which was filtered off, washed, and dried. The product was difficultly soluble in common organic solvents. It was recrystallized from DMSO to provide 3,7-dinitrodibenzotellurophene (**3b**) as dark red crystals (31–52%): mp > 300 °C; ^{1}H NMR (DMSO-d_6/CDCl$_3$) δ 9.18 (d, 2 H, J = 2.0 Hz), 8.56 (d, 2 H, J = 8.6 Hz), 8.29 (dd, 2 H, J = 8.6, 2.0 Hz); IR (KBr) 1510, 1330 cm^{-1}; MS m/z (rel intensity, Te = 130) 372 (M$^+$, 60), 326 (18), 280 (20), 150 (100). Anal. Calcd for C$_{12}$H$_6$N$_2$O$_4$Te: C, 38.98; H, 1.64; N, 7.58. Found: C, 38.84; H, 1.77; N, 7.44.

3-Chloro-7-nitrodibenzotellurophene (3c): purified by chromatography on silica gel; yield 41%; orange crystals, mp 280–281 °C (ethyl acetate); ^{1}H NMR (DMSO-d_6/CDCl$_3$) δ 9.10 (d, 1 H, J = 2.0 Hz), 8.2–8.5 (m, 4 H), 7.50 (d, 1 H, J = 2.0 Hz); IR (KBr) 1510, 1340 cm^{-1}; MS m/z (rel intensity, Te = 130, Cl = 35) 361 (M$^+$, 77), 315 (42), 150 (100). Anal. Calcd for C$_{12}$H$_6$ClNO$_2$Te: C, 40.12; H, 1.68; N, 3.90. Found: C, 40.82; H, 1.69; N, 3.91.

2,8-Dinitrodibenzotellurophene (3d): difficultly soluble in common solvents; yield 40%; red solid, mp > 300 °C (DMSO); ^{1}H NMR (DMSO-d_6/CDCl$_3$) δ 9.18 (s, 2 H), 8.49 (d, 2 H, J = 8.8 Hz), 8.13 (d, 2 H, J = 8.8 Hz); IR (KBr) 1510, 1340 cm^{-1}; MS m/z (rel intensity, Te = 130) 372 (M$^+$, 56), 242 (100), 150 (90). Anal. Calcd for C$_{12}$H$_6$N$_2$O$_4$Te: C, 38.98; H, 1.64; N, 7.58. Found: C, 38.73; H, 1.85; N, 7.31.

Dibenzotellurophene (3e): purified by chromatography on silica gel; yield 42%; pale yellow crystals, mp 90–92 °C (hexane–CHCl$_3$; lit.[9] mp 94.5 °C).

3,7-Dinitrodibenzoselenophene (4b). 2,2′-Diiodo-4,4′-dinitrobiphenyl (**2b**) (800 mg, 1.6 mmol) dissolved in NMP (3 mL) was added in one portion to a dark brown mixture of selenium powder (400 mg, 5.1 mmol) and the selenium–copper reagent prepared *in situ* from disodium selenide (540 mg, 4.3 mmol) and copper(I) iodide (1.66 g, 8.72 mmol), and NMP (8 mL). The resulting mixture was gradually heated to 160 °C in 3 h and kept at this temperature for 2 h. The progress of the reaction was monitored by TLC and ^{1}H NMR. When the starting material had disappeared, the mixture was diluted with ethyl acetate (10 mL) and THF (20 mL), and the insoluble substance was filtered off through a thin layer of Celite. The filtrate was diluted with water (40 mL), and the organic phase was extracted with a 1:1 mixture of ethyl acetate and THF (30 mL × 2). The combined extracts were dried with Na$_2$SO$_4$. Addition of hexane (30 mL) to the dried solution precipitated a black polymeric substance, which was removed by filtration. The filtrate was evaporated under reduced pressure until the volume was reduced to one third. The concentrate thus obtained was diluted with hexane (80 mL) to give selenophene **4b** as a reddish brown solid (170 mg; 33%): mp > 300 °C; ^{1}H NMR (DMSO-d_6/CDCl$_3$) δ 9.19 (d, 2 H, J = 2.1 Hz), 8.66 (d, 2 H, J = 8.7 Hz), 8.36 (dd, 2 H, J = 8.8, 2.1 Hz); IR (KBr) 1520, 1350 cm^{-1}; MS m/z (rel intensity, Se = 80) 322 (M$^+$, 95), 276 (33), 230 (39), 150 (100). Anal. Calcd for C$_{12}$H$_6$N$_2$O$_4$Se: C, 44.88; H, 1.88; N, 8.72. Found: C, 44.76; H, 2.08; N, 8.71.

2,7-Dinitro-9,10-ditelluranthracene (6). A mixture of 1,2-diiodo-4-nitrobenzene (**5**) (640 mg, 1.7 mmol), amorphous tellurium (1.28 g, 10.0 mmol),[43] and the tellurium–copper reagent prepared *in situ* from disodium telluride (610 mg, 3.5 mmol), copper(I) iodide (1.33 g, 7.0 mmol), and NMP (10 mL) was heated at 100–110 °C for 3 h and then kept at 150–160 °C for 4 h. Ordinary workup of the reaction mixture followed by chromatographic purification of the product on silica gel gave compound **6** as a yellow solid (50 mg; 12%): mp > 300 °C (DMSO–ethyl acetate); ^{1}H NMR (DMSO-d_6/CDCl$_3$) δ 8.73 (d, 2 H, J = 2.4), 8.26 (d, 2 H, J = 8.6), 7.99 (dd, 2 H, J = 8.6, 2.4); IR (KBr) 1500, 1350 cm^{-1}; MS m/z (rel intensity, Te = 130) 502 (M$^+$, 32), 372 (42), 326 (20), 150 (97), 75 (100). Anal. Calcd for C$_{12}$H$_6$N$_2$O$_4$Te$_2$: C, 28.98; H, 1.22; N, 5.63. Found: C, 29.67; H, 1.42; N, 5.80.

3-Amino-7-nitrodibenzotellurophene (3a). To a suspension of tellurophene **3b** (220 mg, 0.59 mmol) and palladium on charcoal (300 mg) in a mixture of ethanol (40 mL) and THF (20 mL) was added hydrazine monohydrate (440 mg, 8.8 mmol), and the resulting mixture was heated at reflux for 3 h. The progress of the reaction was monitored by ^{1}H NMR (DMSO-d_6). After disappearance of the starting material, the insoluble substance was filtered off and the filtrate was

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(43) The yield of dibenzotellurophenes **3** could be increased appreciably (7–15%) by carrying out the telluro coupling reaction in the additional presence of amorphous tellurium, which was prepared by diluting a wine red solution of tellurium in concentrated sulfuric acid with ice–water, followed by filtration, washing, and thorough drying.

evaporated under reduced pressure to furnish compound **3a** as orange crystals (100 mg; 50%): mp 242–244 °C (hexane–CHCl$_3$); ^{1}H NMR (DMSO-d_6/CDCl$_3$) δ 8.66 (d, 1 H, J = 2.4 Hz), 8.25 (dd, 1 H, J = 9.0, 2.4 Hz), 7.93 (d, 2 H, J = 9.0 Hz), 7.18 (d, 1 H, J = 2.2 Hz), 6.83 (dd, 1 H, J = 9.0, 2.2 Hz), 4.00 (s, br, 2 H); IR (KBr) 1580, 1500, 1320 cm^{-1}; MS m/z (rel intensity, Te = 130) 342 (M$^+$, 100), 296 (31), 166 (40), 139 (78). Anal. Calcd for $C_{12}H_8N_2O_2Te$: C, 42.42; H, 2.37; N, 8.24. Found: C, 42.03; H, 2.33; N, 8.08.

3-Amino-7-nitrodibenzoselenophene (4a). This compound was similarly obtained by the reduction of compound **4b**: yield 55%; reddish orange crystals, mp 252–255 °C (hexane–CHCl$_3$); ^{1}H NMR (DMSO-d_6/CDCl$_3$) δ 8.68 (d, 1 H, J = 2.1 Hz), 8.26 (dd, 1 H, J = 8.8, 2.2 Hz), 7.97 (d, 1 H, J = 8.8 Hz), 7.95 (d, 1 H, J = 8.5 Hz), 7.16 (d, 1 H, J = 2.2 Hz), 6.85 (dd, 1 H, J = 8.5, 2.2 Hz), 4.05 (s, br, 2 H); IR (KBr) 1600, 1510, 1310 cm^{-1}; MS m/z (rel intensity, Se = 80) 292 (M$^+$, 100), 246 (50), 219 (39), 171 (28), 139 (33). Anal. Calcd for $C_{12}H_8N_2O_2Se$: C, 49.50; H, 2.77; N, 9.62. Found: C, 49.46; H, 2.78; N, 9.47.

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