Chalcogens as electron donors for selected nonlinear optic phores

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Three different heteroaromatic charge transfer chromophores, *e.g.* donor(D)–acceptor(A)-substituted thieno[3,2-*b*]thiophenes 3 and 4, D-substituted thieno[2,3-*c*]pyridinium salts 7 and 2-(2′-thienyl)pyridinium salts 10 have been prepared. Alkylchalcogenic ethers were used as D-groups. The molecular first hyperpolarizabilities *β* were determined by the EFISH method in the case of 3 and 4 and by the HRS method in the case of the ionic compounds 7 and 10. Substitution of the ether oxygen atom by sulfur increases markedly the *β* value which is not further increased by the higher chalcogens selenium and tellurium.

Introduction

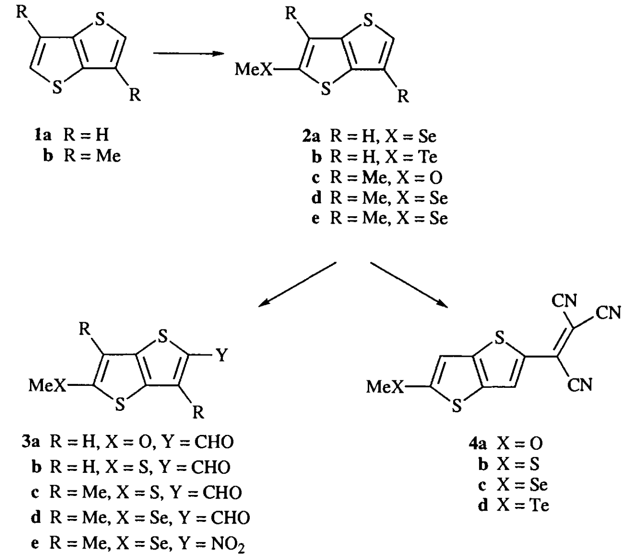
Nonlinear optics (NLO)[1] have become a focus for the attention of material scientists based on the anticipation that the transition from electronics to photonics[2] will require more efficient NLO materials. The preparation of many photonic devices requires materials with high macroscopic nonlinear optical susceptibilities (χ^2), which depend on the first molecular hyperpolarizability (β).[3] Many molecules with high β values have already been developed.[4] For applications, *e.g.* in the field of optical telecommunications, molecules with even higher NLO activities are desirable, especially for the development of efficient electro–optic polymeric materials.[5] The most common NLO chromophores contain donor (D)–acceptor (A) substituted π-systems which have the possibility of intramolecular charge transfer (CT).[6] A prototype is *p*-nitroaniline (*p*NA). It has been shown[7] that the β values of CT chromophores with aromatics as π-bridges increase with the electronic donating and attracting power of the D and A groups, respectively.

As expected it was found previously[8] that the donating power of thioethers is very much superior to that of ethers in NLO chromophores.[9] In other applications, *e.g.* organic conductors, substitution of sulfur by selenium improves the electronic properties greatly. However the possibility of heavier chalcogenes exerting an even higher electron donating effect in NLO chromophores than sulfur has remained so far an unexplored issue. In order to get a well founded answer to this question we have investigated the influence of the different chalcogenes in three different heteroaromatic systems, thieno[3,2-*b*]thiophene (**1a**), thieno[2,3-*c*]pyridinium salts (**7**) and thienylpyridinium salts (**10**).

Results and discussion

Syntheses

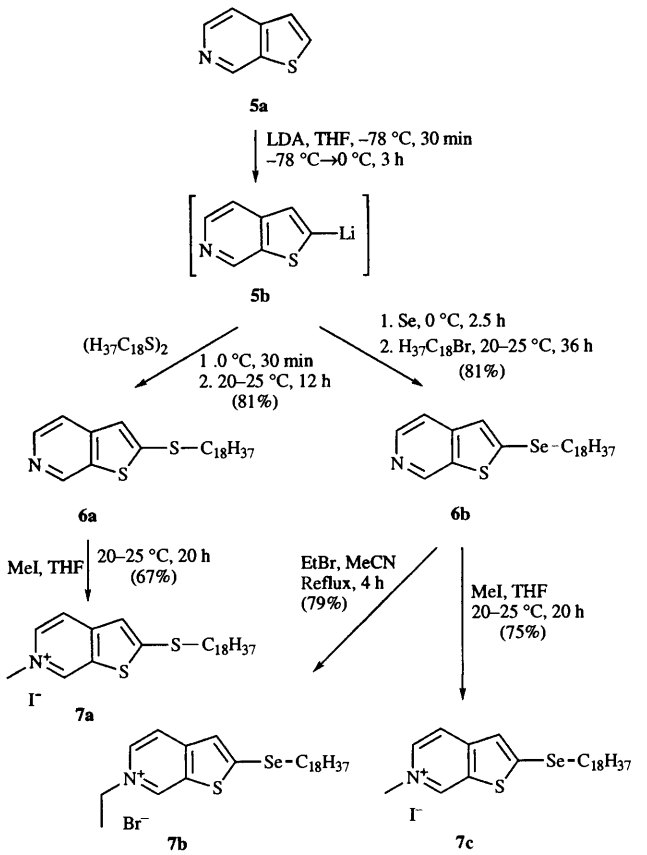
The chemistry of thieno[3,2-*b*]thiophene is closely related to that of thiophene. Thus the methyl ether **2c** could be obtained by bromination of **1b** followed by a copper catalysed substitution of the bromine with methanolate as described for thiophene[10] and the chalcogenic ethers **2a**, **2b** and **2e** by lithiation of **1a** or **1b**, followed by reaction with the elemental chalcogens and methyl iodide (Scheme 1). This procedure (yields 70–90%) proved to be superior to the reaction of the lithiated thieno[3,2-*b*]thiophenes with disulfides (**2d**, 37%).[11] Compounds **3a** and **3d** were prepared by a Vilsmeier–Haack reaction analogous to the protocol for **3b** and **3c**,[12] and **3e** by mild nitration of **2e** with copper(II) nitrate in acetic anhydride. The compounds **4** could be obtained easily in high yields by reacting the corresponding methyl chalcogenic ethers of **1a** with tetracyanoethylene in dimethylformamide.



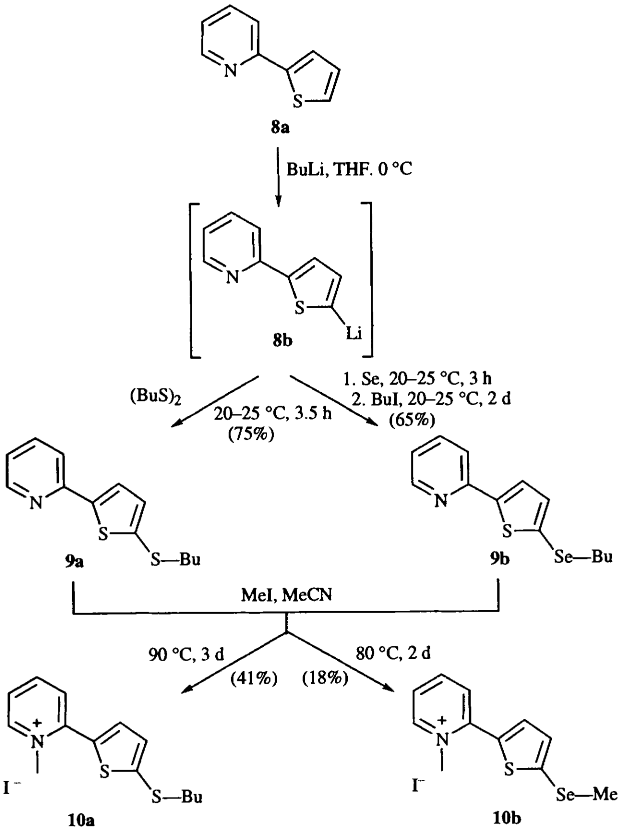
Scheme 1

The preparation of the thieno[2,3-*c*]pyridinium salts **7a**, **7b** and **7c** was furnished according to Scheme 2. Thieno[2,3-*c*]pyridine **5a** was used as starting material and was easily accessible by improved known methods.[13] Lithiation of **5a**[14] (pK_a = 5.57[15]) by LDA in THF gave high yields of only the organolithium salt **5b** (detected by the blue colour) if the reaction was warmed up from −78 to 0 °C and stirred at 0 °C for 3 h. Adding dioctadecyl disulfide to the solution of **5b** gave the thioether **6a** in 81% yield. The selenoether **6b** was prepared in 81% yield by the reaction of the lithium salt **5b** with selenium and then with 1-bromooctadecane. The selenoether **6b** was smoothly converted to the corresponding salt **7c** by treatment with iodomethane. *N*-Ethylation afforded compound **7b** under harsher conditions. The thioether **7a** was obtained by reaction of **6a** with iodomethane at room temperature.

The 2-(2′-thienyl)pyridinium salts **10a** and **10b** were synthesized according to the procedure outlined in Scheme 3.



Scheme 2



Scheme 3

The commercially available 2-(2′-thienyl)pyridine **8a** (pK_a = 3.98[16]) was regioselectively lithiated with BuLi in THF at the 5′-position as described by Kauffmann *et al.*[17] Addition of dibutyl disulfide to the solution of **8b** in THF gave the thioether **9a** in 75% yield. The conversion of **8b** into the corresponding selenoether **9a** was furnished by the procedure described for the analogous selenoether **6b**. Treatment of the ethers **9a** and **9b** with iodomethane in acetonitrile gave the desired pyridinium salts **10a** and **10b** in moderate yields. In the case of the conversion of the selenoether, an exchange of the butyl group took place to give the Se–Me product.

Linear and nonlinear optical properties

Results of electric field induced second harmonic (EFISH) measurements are reported in Table 1. It is more relevant to compare 'static' $\beta(0)$ values, giving an intrinsic estimate of the molecular nonlinearity, rather than $\beta(1.34\ \mu m)$, because resonance effects are not the same for all molecules (their transition energies being different).

Compounds **3c** and **3d** display similar linear and nonlinear optical behaviour, their transition energies are the same and also their $\beta(0)$ values. Comparison of compounds **3c** and **3d** with **4b** and **4c**, respectively, clearly confirms the well-established superiority of the tricyanovinyl moiety[18] over the aldehyde group as an electron-acceptor substituent, the $\beta(0)$ being increased by a factor close to 2.5 when using the former one.

An investigation of compounds **4a–d** provides interesting information about the relative donor strengths of X–Me groups, where X are chalcogen atoms. When the electronegativity of the chalcogen atom, going from oxygen to tellurium, decreases with a correlative increase of the atomic polarizability, then an improvement of the electron-donating character of the X–Me groups is expected. The results reported in Table 1 clearly indicate the strong superiority of sulfur over oxygen in this respect, the corresponding $\beta(0)$ value being nearly two times higher for the S–Me group as compared to a methoxy group. The $\beta(0)$ value of compound **4b** is relatively high when considering the size of the conjugated path: $\beta(0)$ is only 20% smaller than that of the classical dye DR1,[19] with a shorter conjugated path. This also indicates that the thieno[3,2-*b*]thiophene moiety is an interesting conjugated path for building highly nonlinear molecules.

Values of $\beta(0)$ for compounds **4c** and **4d** are very similar to those of compound **4b**, in spite of the lower electronegativity of Se and Te as compared to S. This paradoxical behaviour can be reasonably explained by the poor overlap of the nonbonding orbitals of Se and Te with the π-orbitals of the thiophene moiety, owing to the much larger size of these heavy atoms as compared to carbon, oxygen or even sulfur atoms. It appears from this study that using heavier atoms does not present any advantage from the increased electron donating character of the chalcogen derivatives. Sulfur illustrates the best compromise between atomic electronegativity and orbital overlap obtained presently.

Finally, measurements carried out on compound **4d** at two different fundamental wavelengths 1.34 and 1.9 μm lead to comparable $\beta(0)$ values, when considering experimental errors, thus confirming the validity of the two-level dispersion model for deducing the 'static' hyperpolarizability $\beta(0)$ values from experimental ones.

The molecules **7a–c** and **10a,b** are ionic and could therefore not be investigated with the EFISH technique. To get the experimental values of the first hyperpolarizability β of these molecules we used the hyper-Rayleigh scattering (HRS) method,[20,21] also referred to as harmonic light scattering (HLS)[22] or double quantum light scattering.[23] Table 2 lists the results of the HRS-measurements along with the UV–VIS data. All β values were determined in chloroform as solvent *versus* *p*-nitroaniline (PNA) in $CHCl_3$ as an external reference at a fundamental wavelength of 1064 nm. For PNA we used the literature value of 17×10^{-30} esu,[24] which is in good agreement with the value we determined. In addition the hyperpolarizabilities were extrapolated to zero frequency using the two-level model.

Table 1 Experimental data for **3c**, **3d**, **4a–d**: λ_{max}, ground state dipole moment μ, β measured at 1.32 μm and 'static' $\beta(0)$ values deduced from β using a two level dispersion model

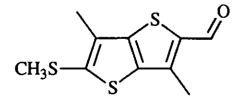
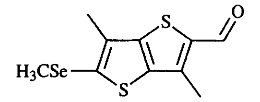
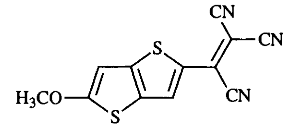
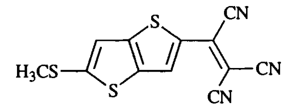
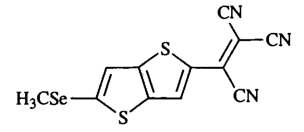
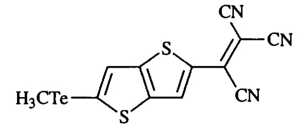
Comp.	Formula	λ_{max}/nm	μ/D	β(1.32 μm)/ 10^{-30} esu	β(0)/ 10^{-30} esu
3c		350	4.6	26	17
3d		350	4.6	22	15
4a		502	9.0	65	25
4b		516	9.5	124	43
4c		518	10	115	39
4d		538	10	125 (1.34 μm) 54 (1.9 μm)	37 33

Table 2 UV–VIS data and β resp., β_0 values of compounds **7a–c** and **10a,b**

	λ_{max} ($CHCl_3$)/nm	λ_{max} (CH_3CN)/nm	$\lambda_{cut\text{-}off}$ ($CHCl_3$)/nm	$\lambda_{cut\text{-}off}$ (CH_3CN)/nm	$\beta_{HRS,1064}$/ 10^{-30} esu	$\beta_{HRS,0}$/ 10^{-30} esu
7a	362 (4.46)[a]	352 (4.41)	480	400	36	18
7c	370 (4.48)	360 (4.35)	500	410	26	12
7b	370 (4.42)	360 (4.35)	426	412	26	12
10a	368 (4.13)	358 (3.92)	560	450	26	12
10b	374 (4.07)	370 (3.91)	*ca.* 500	456	23	10

[a] Figures in parentheses are log ε values.

A comparison of **7a** with **7c** and **10a** with **10b** reflects the same tendency seen for compounds **3c** and **3d** as well as **4b** and **4c**: the substitution of the thioether group with a selenoether group as an electron donor does *not* result in an enhancement in the value of the molecular hyperpolarizability β. On the contrary, the thioethers exhibit higher β values than their selenoether counterparts as the data from Table 2 clearly demonstrate.

A comparison between **7b** and **7c** shows another interesting phenomenon. While the absorption maxima in chloroform are exactly the same, the cut-off wavelength of **7c** (with iodide as counterion) is strongly red-shifted compared with **7b** (with bromide as counterion). This is due to an interionic charge-transfer between the iodide and the pyridinium moiety. Since this does not affect the intramolecular charge transfer of the chromophore itself no effect on the hyperpolarizability is expected. This is reflected by the experimental data for both compounds which are exactly the same.

Conclusions

Modern photonic devices require materials with high macroscopic nonlinear optical susceptibilities, which depend on the first molecular hyperpolarizability β of the incorporated nonlinear optical (NLO) molecules. These contain D/A substituted π-bridges with the possibility of an intramolecular charge transfer. The β values can be improved by modifying all three structural parameters of the NLO phores. Easily accessible but weak donors are ethers. Thioethers possess a markedly higher donating power. Thus it was an interesting question whether the higher chalcogenes can exert an even stronger electron donating effect than sulfur. Therefore we prepared three types of NLO phores with different π bridges: D/A substituted thieno[3,2-*b*]thiophenes **3** and **4**, D-substituted thieno[2,3-*c*]pyridinium salts **7** and D-substituted 2-(2′-thienyl)pyridinium salts **10** with alkylchalcogenic ethers as D-groups. The molecular first hyperpolarizabilities β were determined by the EFISH method in the case of **3** and **4** and by the HRS method in the case of the ionic compounds **7** and **10**. As expected substitution of the ether oxygen atom by sulfur increased the β value markedly, which surprisingly was not further increased using the higher chalcogens selenium and tellurium.

Experimental

^1H and ^{13}C NMR spectra were run on a Bruker AM 400 (400.13) and a 400 (100.61), respectively using $CDCl_3$ (TMS as internal reference) or [$^2H_6$]DMSO as solvent as well as an internal reference. *J* Values are given in Hz. The degree of substitution of the carbon atoms was determined by DEPT 135° experiments. Further assignments were made with the help of CH correlation and COLOC spectra (indicated in the ^{13}C NMR assignments by superscript CHC or COL, respectively). Mass spectra EI were recorded on a Finnigan MAT 8430 spectrometer operating at 70 eV. FAB MS (pos) were recorded on a Finnigan MAT 8340 spectrometer. Xenon was used for neutral beam production with a beam energy of 8 kV. 3-Nitrobenzyl alcohol (NBA) was used as liquid matrix. UV–VIS absorption spectra were measured with a Hewlett Packard diode array spectrophotometer 8452 A. Melting points were determined on a Kofler hot stage microscope and all values are uncorrected. Elemental analyses were carried out by the Analytisches Laboratorium des Instituts für Pharmazeutische Chemie, Technische Universität Braunschweig. Separations by column chromatography were performed on 70–230 mesh silica gel from Merck, Darmstadt, and flash chromatography on 30–60 µm, Baker, Deventer (The Netherlands). In all reactions requiring anhydrous conditions solvents were dried by distillation under nitrogen from the appropriate drying agent, glassware was flame-dried and cooled afterwards under a steady stream of nitrogen.

EFISH measurements

Hyperpolarizability (β) measurements were performed with a *Q*-switched modelocked Nd^{3+}: YAG laser emitting at 1.34 µm using the electric field induced second harmonic (EFISH) method.[25,26] The molecules measured were dissolved in chloroform and the solutions were placed in a wedge shaped cell. A high voltage electric pulse breaks the centrosymmetry of the liquid by a dipolar orientation of the molecules. Translation of this cell perpendicular to the beam direction will modulate the second harmonic signal into maker fringes. The amplitude and periodicity of the fringing pattern are respectively related to the macroscopic quadratic susceptibility $\Gamma(x)$ of the solution and to its coherence length, where x is the mass concentration. Calibrations are made with respect to the pure solvent. From the second-harmonic generation (SHG) intensity we can infer the value of the macroscopic susceptibility of the solution $\Gamma(x)$. $\Gamma(x)$ is related to the microscopic hyperpolarisabilities of the solvent γ_s and of the solute γ_c as in eqn. (1)[26] where index s

$$\Gamma(x) = \frac{Nfp}{1+x}\left(\frac{\gamma_s}{M_s} + x\frac{\gamma_c}{M_c}\right) \qquad (1)$$

stands for the solvent, index c for dissolved molecules and where γ_c is related to the second-order β and third-order γ hyperpolarizability through the relation shown in eqn. (2)

$$\gamma_c(-2\omega;\omega,\omega,0) = \gamma(-2\omega;\omega,\omega,0) + [\mu\beta(-2\omega;\omega,\omega)]/5\,KT \qquad (2)$$

where μ is the ground state dipole moment. Tests were performed at several concentrations (typically 10^{-2}–10^{-3} M or even less, depending on the solubility and the nonlinearity of the molecule). Neglecting the third-order contribution $\gamma(-2\omega;\omega,\omega,0)$[27] and assuming a two-level model for the second-order polarizability β, one can finally derive a frequency independent value $\beta(0)$[14] as shown in eqn. (3).

$$\beta_0 = \{[(\omega_0^2 - \omega^2)(\omega_0^2 - 4\omega^2)]/3\omega_0^4\}\beta(-2\omega;\omega,\omega) \qquad (3)$$

To complete these measurements the dipole moments are separately determined with a WTW dipolemeter coupled with an Abbe refractometer, in order to measure the relative permittivity and the refractive index of the solutions. From these experimental data the dipole moment can be easily deduced using the Guggenheim model.[28] The relative error on dipole moment is 5%; the total experimental error on β values does not exceed 10%. In one case (compound **4d**), we have performed the EFISH experiment at two different fundamental wavelengths: 1.34 µm and 1.9 µm. The latter wavelength was emitted by a high-pressure Raman cell pumped by a nanosecond Nd^{3+}:YAG laser at 1.06 µm. The principle of β measurement is the same but using this longer-wavelength fundamental wave precludes absorption of the harmonic wave that could appear in such coloured molecules (λ_{max} = 538 nm for **4d**) thus inducing a significant experimental error. However, comparison of $\beta(0)$ values deduced from 1.34 and 1.9 µm measurements is a good means to check the validity of the two-level model; $\beta(0)$ should have the same value for both fundamental wavelengths.

HRS measurements

The sample in the HRS experiment consists of a simple solution of a NLO-active dye in an appropriate solvent. Microscopic fluctuations in chromophore orientation and number density break the centrosymmetry of the system, so that a second-order nonlinear process can be observed. The second harmonic light is generated *via* an elastic incoherent scattering process. The intensity of the generated frequency doubled light, $I(2\omega)$ depends quadratically on the intensity of the fundamental beam, $I(\omega)$: $I(2\omega) \propto I(\omega)^2$. The hyper-Rayleigh scattering experiments were carried out at a fundamental wavelength of 1064 nm using a Q-switched modelocked Nd:YAG laser. The laser output (300 mJ) was attenuated by *ca.* 99% using several 1064 nm dichroic mirror beam-splitters. The beam was reduced to a diameter of 1.5 mm with the help of a telescope with the resulting collimated beam passing through a HRS-cell contained within a light-tight box. An 830 nm longpass filter mounted on the input of the box ensured spectral purity of the light entering the HRS cell. A combination polarizer–motor-driven half-wave-plate–polarizer was used to vary the fundamental intensity. The intensity of the second harmonic scattered light was detected with a photomultiplier tube, after passing through a 532 nm narrow-band-pass filter. The second harmonic intensity was monitored as a function of the half-wave-plate rotation angle, thus yielding sin^4 curves of the form as shown in eqn. (4), with A as the peak HRS intensity, φ the

$$I(2\omega) = A[\sin(2\varphi + \alpha)]^4 + b \qquad (4)$$

half-wave-plate rotation angle, α the half-wave-plate starting angle and b an intensity offset intrinsic to our experiment and independent of the material studied. The A-factor was determined for a series of varying chromophore concentration, yielding a straight line (when there is no significant absorption at either the fundamental or the second harmonic wavelength) with the slope $m(s)$. The A-factor was also determined for a concentration series of a reference molecule (in our case *p*-nitroaniline, see above) in the same solvent, yielding a straight line with the slope $m(r)$. With the known β value of the reference chromophore (and the same symmetry of the sample and reference molecules) the hyperpolarizability of the sample chromophore can be calculated, using eqn. (5). In the case

$$\beta_{\text{sample}} = [\sqrt{m(s)/m(r)}]\beta_{\text{reference}} \qquad (5)$$

that the sample and the reference molecule are of different symmetry, so-called orientational factors have to be used.[29] These factors take into account that for different point groups of the molecules investigated the elements of the β tensor contribute with different factors to the detected HRS intensity.

2-Methoxy-3,6-dimethylthieno[3,2-*b*]thiophene 2c

A solution of 70 mmol sodium methoxide, 5.20 g (21.0 mmol) 2-bromo-3,6-dimethylthieno[3,2-*b*]thiophene,[30] 0.34 g (2.3 mmol) sodium iodide and 1.18 g (14.8 mmol) copper(II) oxide in 70 ml methanol was refluxed for 5 days and then ice–water (100 g) was added and the reaction mixture extracted with diethyl ether. The combined diethyl ether phases were washed with water, dried and evaporated under reduced pressure. The evaporation residue yielded, after flash chromatography from light petroleum (R_f 0.41) and distillation (bp 64 °C, 0.5 Torr†), 1.95 g (9.83 mmol, 47%) of **2c** (Found: C, 54.68; H, 5.46; S, 32.45; M^+, 200, 199, 198. $C_9H_{10}OS_2$ requires C, 54.51; H, 5.08; S, 32.34%; *M*, 198.30); ν_{max}(film)/cm^{-1} 2931 (CH), 2917 (CH), 2850, 1566; δ_H($CDCl_3$) 2.17 (s, 3 H, 3-CH_3), 2.28 (d, *J* 1, 3 H, 6-CH_3), 3.89 (s, 3 H, OCH_3), 6.77 (q, *J* 1, 1 H, 5-H); δ_C($CDCl_3$) 10.5 (q, CH_3-3), 14.7 (q, CH_3-6), 62.6 (s, OCH_3), 112.4 (s, C-3), 117.7 (d, C-5), 126.7, 130.4, 137.4 (s, C-3a, 6, 6a), 159.5 (s, C-2); λ_{max}/nm (log ε) acetonitrile 278 (4.076); chloroform 280 (4.064).

3,6-Dimethyl-2-methylselenothieno[3,2-*b*]thiophene 2e

A mixture of 10.3 g (61.2 mmol) of **1b**, 42 ml (67.2 mmol) butyllithium (1.6 M in hexane) and 200 ml diethyl ether was refluxed (30 min). After cooling with ice, 5.1 g (64.4 mmol) of dry selenium was added under vigorous stirring. The stirring was continued for 1 h at room temp. and then 4.0 ml (64.4 mmol) methyl iodide was added under cooling with ice. The mixture was stirred for 12 h at room temp. and after cooling with ice and addition of 50 ml aqueous ammonium chloride (25%), extracted with diethyl ether. The evaporation residue of the combined, washed and dried diethyl ether phases, yielded after distillation (bp 103 °C, 0.01 Torr) 11.4 g (43.6 mmol, 71%) of compound **2e**, mp 49–52 °C (Found: C, 41.44; H, 3.83; S, 24.58; M^+, 264, 263, 262, 261, 260, 259, 258. $C_9H_{10}S_2Se$ requires C, 41.38; H, 3.86; S, 24.54%; *M*, 261.26); ν_{max}/cm^{-1} 3085 (CH), 2923; δ_H($CDCl_3$) 2.26 (s, 3 H, 3-CH_3), 2.31 (d, *J* 1, 3 H, 6-CH_3), 2.41 (s, 3 H, $SeCH_3$), 6.98 (q, *J* 1, 1 H, 5-H); δ_C($CDCl_3$) 11.7 (q, $SeCH_3$), 14.67, 14.73 (q, CH_3), 121.8 (d, C-5), 122.1, 130.0, 135.1 (s, C-2, 3, 6), 139.6, 141.4 (s, C-3a, 6a); λ_{max}/nm (log ε) acetonitrile 296sh (4.098), 286 (4.158); chloroform 298sh (4.112), 288 (4.176).

5-Methoxythieno[3,2-*b*]thiophene-2-carbaldehyde 3a

To a solution of 0.76 g (4.5 mmol) 2-methoxythieno[3,2-*b*]-thiophene[31] in 2 ml *N*,*N*-dimethylformamide, was added under cooling with ice over 30 min 0.42 ml (4.5 mmol) phosphoryl chloride. After further stirring for 30 min, the mixture was allowed to warm up to room temp. and an exothermic reaction took place. After further stirring at room temp. for 45 min followed by 30 min at 80 °C, 100 ml ice–water was added. The precipitate gave, after column chromatography from dichloromethane (R_f 0.64) and recrystallization from diethyl ether, 75.1 mg (0.38 mmol, 8%) of **3a**, mp 68 °C (Found: C, 48.43; H, 2.90; S, 32.21; M^+, 200, 199, 198. $C_8H_6O_2S_2$ requires C, 48.47; H, 3.05; S, 32.34%; *M*, 198.25); ν_{max}/cm^{-1} 1651 (C=O); δ_H($CDCl_3$) 3.99 (s, 3 H, CH_3), 6.45 (d, $J_{3/6}$ 0.6, 1 H, 6-H), 7.74 (d, $J_{3/6}$ 0.6, 1 H, 3-H), 9.82 (s, 1 H, CHO); δ_C($CDCl_3$) 60.7 (q, CH_3), 97.1 (d, C-6), 130.1 (d, C-3), 126.8, 140.8 (s, C-3a, 6a), 145.1 (s, C-2), 173.0 (s, C-5), 182.1 (s, CHO); λ_{max}/nm (log ε) acetonitrile 346 (4.389), 310sh (3.983); chloroform 352 (4.395), 316sh (3.984) [Cut-off (nm) ($CHCl_3$): 400].

3,6-Dimethyl-5-methylselenothieno[3,2-*b*]thiophene-2-carbaldehyde 3d

From 1.0 g (3.8 mmol) **2e**, 8 ml *N*,*N*-dimethylformamide and 0.56 ml (6.0 mmol) phosphoryl chloride as described for the preparation of **3a** was isolated 0.57 g (1.97 mmol, 52%) **3d**, mp 114 °C (ethanol) (Found: C, 41.30; H, 3.61; S, 22.06; M^+, 294, 293, 292, 291, 290, 289, 288, 287, 286, 284. $C_{10}H_{10}OS_2Se$ requires C, 41.52; H, 3.48; S, 22.17%; *M*, 289.27); ν_{max}/cm^{-1} 1651 (CO); δ_H($CDCl_3$) 2.34, 2.37 (s, 6 H, 3-, 6-CH_3), 2.62 (s, 3 H, $SeCH_3$), 10.06 (s, 1 H, CHO); δ_C($CDCl_3$) 11.1 (q, $SeCH_3$), 13.3, 14.5 (q, CH_3-3, 6), 130.5, 134.0, 137.6, 139.4, 141.8 (s, C-3, 3a, 5, 6, 6a), 145.3 (s, C-2), 182.6 (s, CHO); λ_{max}/nm (log ε) acetonitrile 342 (4.323), 270 (3.534); chloroform 350 (4.323), 270 (3.534) [Cut-off (nm) ($CHCl_3$): 430].

3,6-Dimethyl-5-nitro-2-methylselenothieno[3,2-*b*]thiophene 3e

A solution of 1.0 (3.8 mmol) **2e** in 10 ml acetic anhydride was dropped into an ice-cooled solution of 0.45 g copper(II) nitrate trishydrate in 15 ml acetic anhydride. After stirring at 0 °C for 4 h the mixture was poured into ice–water. Extraction with dichloromethane, evaporation of the solvent and flash chromatography of the residue from dichloromethane–light petroleum 1 : 1 (R_f 0.57) yielded 0.26 g (0.85 mmol, 22%) **3e**, mp 160 °C (Found: C, 35.76; H, 3.02; N, 4.46; S, 20.90; M^+, 311, 310, 309, 308, 307, 306, 305, 304, 303, 301. $C_9H_9NO_2S_2Se$ requires C, 35.30; H, 2.96; N, 4.57; S, 20.94%; *M*, 306.26); δ_C($CDCl_3$) 11.1 (q, $SeCH_3$), 14.4, 15.6 (q, CH_3, 6), 132.3, 133.3, 134.8, 138.4, 140.0 (s, C-2, 3, 3a, 6, 6a), 145.5 (s, C-5); ν_{max}(KBr)/cm^{-1} 2961, 2939 and 1308; δ_H($CDCl_3$) 2.37, 2.39 (s, 6 H, 3-, 6-CH_3), 2.72 (s, 3 H, $SeCH_3$); λ_{max}/nm (log ε) acetonitrile 388 (4.194), 268 (3.634), 248 (3.773); chloroform 392 (4.204), 270 (3.648), 242 (3.853) [Cut-off (nm) ($CHCl_3$): 520].

2-Methylselenothieno[3,2-*b*]thiophene 2a

Compound **2a** was prepared from 5.0 g (35.7 mmol) **1a**,[32] 24.4 ml (39 mmol) butyllithium (1.6 M in hexane), 2.92 g (37 mmol) selenium, 2.3 ml (37 mmol) methyl iodide and 100 ml dry diethyl ether as described above for the preparation of **2e**. Distillation yielded 5.50 g (23.6 mmol, 66%) of **2a** (bp 85–88 °C, 0.01 Torr) as a yellow oil of 97% purity (GC-analysis). The compound was used for the preparation of **4c** without further purification; *m*/*z* 238, 237, 236, 235, 234, 233, 232, 231, 230, 228; δ_H($CDCl_3$) 2.39 (s, 3 H, CH_3), 7.18 (d, *J* 5, 1 H, 6-H), 7.28 (s, 1 H, 3-H), 7.35 (d, *J* 5, 1 H, 5-H).

2-Methyltellurothieno[3,2-*b*]thiophene 2b

Compound **2b** was prepared from 5.0 g (35.7 mmol) **1a**, 24.4 ml (39 mmol) butyllithium (1.6 M in hexane), 4.70 g (36.5 mmol) tellurium, 2.3 ml (37 mmol) methyl iodide and 80 ml dry diethyl ether as described above for the preparation of **2e**. Distillation yielded 7.0 g (24.8 mmol, 69.5%) of **2b** (bp 109–114 °C, 0.01 Torr) as a red oil of 96.5% purity (GC-analysis), which was used without further purification; *m*/*z* 286, 285, 284, 283, 282, 281, 280, 279, 278, 277, 276; δ_H($CDCl_3$) 2.21 (s, 3 H, CH_3), 7.20 (d, *J* 5, 1 H, 6-H), 7.43 (d, *J* 5, 1 H, 3-H), 7.51 (s, 1 H, 3-H).

2-Methoxy-5-tricyanovinylthieno[3,2-*b*]thiophene 4a

To a stirred solution of 1.0 g (5.9 mmol) 2-methoxythieno[3,2-*b*]thiophene[31] in 15 ml *N*,*N*-dimethylformamide was added 0.9 g (7.0 mmol) of tetracyanoethylene. The dark red solution was stirred for 24 h at room temp. and subsequently poured into 50 ml of water. The precipitate was filtered off, dried and sublimed *in vacuo* (200 °C, 0.01 Torr) to yield 1.25 g (4.6 mmol, 78%) **4a** as brick-red crystals, mp 264 °C (Found: C, 53.13; H, 1.82; N, 15.52; S, 23.48; M^+, 273, 272, 271. $C_{12}H_5N_3OS_2$ requires C, 53.12; H, 1.86; N, 15.49; S, 23.63%; *M*, 271.31); ν_{max}(KBr)/cm^{-1} 2927 (CH), 2888, 2217 (CN), 1524; δ_H(DMSO) 4.09 (s, 3 H, CH_3), 7.05 (s, 1 H, 3-H), 8.45 (s, 1 H, 6-H); λ_{max}/nm (log ε) acetonitrile 498 (4.60); chloroform 502 (4.61).

2-Methylthio-5-tricyanovinylthieno[3,2-b]thiophene 4b

Compound **4b** was prepared from 5.0 g (27 mmol) 2-methylthiothieno[3,2-*b*]thiophene,[12] 4.6 g (36 mmol) tetracyanoethylene and 30 ml *N*,*N*-dimethylformamide as described for the preparation of **4a**. Sublimation *in vacuo* (170 °C, 0.01 Torr) yielded 6.95 g (24.2 mmol, 90%) **4b** as dark-blue crystals, mp 215 °C (Found: C, 50.12; H, 1.66; N, 14.48; S, 33.36; M^+, 289, 288, 287. $C_{12}H_5N_3S_3$ requires C, 50.16; H, 1.75; N, 14.62; S, 33.47%; *M*, 287.37); ν_{max}(KBr)/cm^{-1} 2924 (CH), 2218 (CN), 1526; δ_H($CDCl_3$) 2.71 (s, 3 H, CH_3), 7.14 (s, 1 H, 3-H), 8.13 (s,

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† 1 Torr = 133.322 Pa.

1 H, 6-H); δ_C(DMF) 23.6 (q, CH_3), 86.0 [s, $C(CN)_2$], 118.9, 119.1, 119.2 (s, CN), 123.8 (d, C-3), 138.5, 139.6 (s, C-6a, 3a), 138.8 (d, C-6), 145.2, 156.2, 163.2 (s, C-5, 2, *C*CN); λ_{max}/nm (log ε) acetonitrile 512 (4.61); chloroform 516 (4.60).

2-Methylseleno-5-tricyanovinylthieno[3,2-*b*]thiophene 4c

Compound **4c** was prepared from 0.5 g (2.15 mmol) 2-methylselenothieno[3,2-*b*]thiophene (**2a**), 0.51 g (4.0 mmol) tetracyanoethylene and 5 ml *N*,*N*-dimethylformamide as described for the preparation of **4a**. The precipitate was purified by flash chromatography with chloroform (R_f 0.40), yield 0.25 g (0.75 mmol, 35%) of dark-blue crystals, mp 228 °C (chloroform) (Found: C, 43.34; H, 1.55; N, 12.42; S, 19.00; M^+, 338, 337, 336, 335, 334, 333, 332, 331. $C_{12}H_5N_3S_2Se$ requires C, 43.12; H, 1.51; N, 12.57; S, 19.18%; *M*, 334.27; ν_{max}(KBr)/cm^{-1} 2915 (CH), 2209 (CN), 1512; δ_H(DMF) 3.51 (s, 3 H, CH_3), 7.80 (s, 1 H, 3-H), 8.55 (s, 1 H, 6-H); δ_C(DMF) 10.6 (q, CH_3), 81.9 [s, $C(CN)_2$], 113.8, 114.0, 114.1 (s, CN), 122.9 (d, C-3), 133.4 (d, C-6), 133.9, 134.8 (s, C-6a, 3a), 142.8, 147.2, 150.9 (s, C-5, 2, *C*CN); λ_{max}/nm (log ε) acetonitrile 510 (4.48); chloroform 518 (4.44).

2-Methyltelluro-5-tricyanovinylthieno[3,2-*b*]thiophene 4d

Compound **4d** was prepared from 1.82 g (6.5 mmol) **2b**, 1.0 g (7.8 mmol) tetracyanoethylene and 15 ml *N*,*N*-dimethylformamide as described for the preparation of **4a**. The tarry precipitate was purified by flash chromatography with chloroform (R_f 0.42), followed by sublimation *in vacuo* (130 °C, 0.01 Torr), yield 0.73 g (1.9 mmol, 29%) **4d** as dark crystals, mp 226 °C (Found: C, 37.39; H, 1.36; N, 10.49; S, 17.07; M^+, 388, 387, 386, 385, 384, 383, 382, 381, 380, 379, 378, 377. $C_{12}H_5N_3S_2Te$ requires C, 37.64; H, 1.32; N, 10.97; S, 16.75%; *M*, 382.91; ν_{max}(KBr)/cm^{-1} 2930 (CH), 2202 (CN); δ_H($CDCl_3$) 2.47 (s, 3 H, CH_3), 7.51 (s, 1 H, 3-H), 8.16 (s, 1 H, 6-H); δ_C($CDCl_3$) 12.5 (q, CH_3), 88.2 [s, $C(CN)_2$], 114.2, 114.4, 114.5 (s, CN), 122.8 (d, C-3), 137.8 (d, C-6), 140.2, 141.0 (s, C-3a, 6a), 147.2, 155.1, 158.9, (s, C-5, *C*CN); λ_{max}/nm (log ε) acetonitrile 518 (4.18); chloroform 538 (4.31).

2-Lithiothieno[2,3-*c*]pyridine 5b

To a solution of lithium diisopropylamide (LDA) (8.9 mmol) in anhydrous THF (40 ml), a solution of thieno[2,3-*c*]pyridine (**5a**)[14] (1.00 g, 7.4 mmol) in anhydrous THF (7 ml) was added at −78 °C over 30 min. Then the cooling bath with methanol was changed to an ice bath and the reaction mixture was stirred for a further 3 h.

N-Methylation of thieno[2,3-*c*]pyridyl chalcogenoethers with iodomethane (procedure 1)

A solution of the thio- or the seleno-ether (0.500 g) and iodomethane (0.2 ml, 3.2 mmol) in anhydrous THF (10 ml) was stirred at 20–25 °C for 20 h. The precipitate was filtered off, washed with *ca.* 5 ml of anhydrous THF and dried *in vacuo* (0.1 mbar‡).

2-Octadecylthiothieno[2,3-*c*]pyridine 6a

To a solution of 2-lithiothieno[2,3-*c*]pyridine (**5b**), dioctadecyl disulfide[33] (4.22 g, 7.4 mmol) was added. The reaction mixture was stirred at 0 °C for 30 min and then at 20–25 °C for 12 h. After addition of 20 ml of conc. aqueous ammonium chloride the mixture was extracted three times with 20 ml of diethyl ether and the organic phase was dried with $MgSO_4$. Purification by column chromatography (R_f 0.35, 150 g silica gel, diethyl ether) gave 2.52 g (81%) **6a** as a colourless solid, mp 49–50 °C (Found: C, 71.46; H, 10.07; N, 3.45; S, 15.37. $C_{25}H_{41}NS_2$ requires C, 71.54; H, 9.85; N, 3.34; S, 15.28); ν_{max}/cm^{-1} 2918vs (CH), 2850vs (CH), 1575w, 1471m, 839m; δ_H($CDCl_3$) 8.97 (1 H, 't', ^5J(H,H) 0.8, 7-H), 8.44 [1 H, d, ^3J(5-H, 4-H) 5.5, 5-H], 7.51 [1 H, dd, *J* 1.0, ^3J(4-H, 5-H) 5.5, 4-H], 7.18 (1 H, d, *J* 0.7, 3-H), 3.04 (2 H, t, *J* 7.4, SCH_2), 1.68–1.77 (2 H, m, SCH_2CH_2), 1.41–1.46 (2 H, m, 10-H), 1.25–1.32 (28 H, m, 11–24-H), 0.88 (3 H, t, *J* 6.9, 25-H); δ_C($CDCl_3$) 146.4 (s, C-2), 145.3 (s, C-3a), 143.53 and 143.46 (d, C-5, 7), 137.1 (s, C-7a), 123.1 (d, C-3), 116.5 (d, C-4), 36.8 (t, C-8), 32.0 (t, C-9), 29.72, 29.69, 29.65, 29.58, 29.49, 29.39, 29.36, 29.1, 28.6 (t, C-10–23), 22.7 (t, C-24), 14.2 (q, C-25); *m*/*z* (EI-MS) 419 (M^+, 64%), 168 (43), 167 (100), 57 (32); λ_{max}/nm (log ε) chloroform 240 (4.05), 256sh (3.75), 302 (4.16), 314sh (4.05), 334sh (3.03); acetonitrile 228 (4.24), 248sh (3.76), 298 (4.15), 308sh (4.06), 330sh (2.78).

2-Octadecylthio-6-methylthieno[2,3-*c*]pyridinium iodide 7a

According to procedure 1: **6a** (0.500 g, 1.2 mmol) yielded 0.45 g (67%) of **7a** as a pale yellow solid, mp 125 °C (Found: C, 55.52; H, 8.10; N, 2.54; S, 11.51. $C_{26}H_{44}INS_2$ requires C, 55.60; H, 7.90; N, 2.49; S, 11.42); ν_{max}/cm^{-1} 2921vs (CH), 2849vs (CH), 1625m, 1421s, 841m; δ_H($CDCl_3$) 10.11 (1 H, s, 7-H), 8.67 [1 H, dd, ^3J(5-H, 4-H) 6.7, *J* 1.2, 5-H], 8.02 [1 H, d, ^3J(4-H, 5-H) 6.7, 4-H], 7.37 (1 H, s, 3-H), 4.61 (3 H, s, NCH_3), 3.23 [2 H, t, ^3J(H,H) 7.3, SCH_2], 1.77–1.86 (2 H, m, 9-H), 1.44–1.52 (2 H, m, 10-H), 1.24–1.35 (28 H, m, 11–24-H), 0.88 (3 H, t, ^3J 6.8, 25-H); δ_C($CDCl_3$) 164.0 (s, C-2), 149.6 (s, C-3a, 8.67^{COL}), 139.4 (d, C-7, 10.11^{CHC}), 137.8 (d, C-5, 8.67^{CHC}), 136.4 (s, C-7a, 7.37^{COL}), 118.5 (d, C-3, 7.37^{CHC}), 118.0 (d, C-4, 8.02^{CHC}), 48.3 (q, NCH_3), 36.1 (t, SCH_2), 31.9, 29.67, 29.62, 29.54, 29.42, 29.32, 29.06, 28.7, 28.6 (t, C-9–23), 22.7 (t, C-24), 14.1 (q, C-25); *m*/*z* (FAB MS) 434 (Cat., 100%), 182 (73), 181 ({Cat. − $C_{18}H_{37}$}, 35); λ_{max}/nm (log ε) chloroform 244 (4.32), 300 (4.02), 362 (4.46); acetonitrile 242 (4.46), 314sh (3.89), 352 (4.41).

2-Octadecylselenothieno[2,3-*c*]pyridine 6b

To the solution of 2-lithiothieno[2,3-*c*]pyridine **5b**, selenium (0.76 g, 9.6 mmol) was added at 0 °C. The reaction mixture was stirred for 2.5 h and then treated with 1-bromooctadecane (2.50 g, 7.5 mmol). After stirring for 36 h at 20–25 °C, the work-up was carried according to the preparation of **6a**. Purification by column chromatography over 300 g silica gel (R_f 0.66, ethyl acetate–CH_2Cl_2, 1 : 1) and recrystallization from diethyl ether gave 2.78 g (81%) of **6b** as a colourless solid, mp 49–50 °C (Found: C, 64.38; H, 9.17; N, 2.96. $C_{25}H_{41}NSSe$ requires C, 64.35; H, 8.86; N, 3.00); ν_{max}/cm^{-1} 2917vs (CH), 2849vs (CH), 1572m, 850s; δ_H($CDCl_3$) 9.02 (1 H, s, 7-H), 8.44 [1 H, d, ^3J(5-H, 4-H) 5.5, 5-H], 7.57 [1 H, dd, *J* 0.9, ^3J(4-H, 5-H) 5.5, 4-H], 7.35 (1 H, s, 3-H), 3.04 (2 H, t, ^3J 7.5, $SeCH_2$), 1.73–1.82 (2 H, m, 9-H), 1.34–1.44 (2 H, m, 10-H), 1.24–1.30 (28 H, m, 11–24-H), 0.88 (3 H, t, ^3J 6.8, 25-H); δ_C($CDCl_3$) 145.7 (s, C-3a), 143.1 (d, C-5), 142.9 (d, C-7), 139.2 (s, C-7a), 136.5 (s, C-2), 127.3 (d, C-3), 116.7 (d, C-4), 31.9, 31.0, 30.3, 29.72, 29.68, 29.64, 29.62, 29.57, 29.49, 29.38, 29.0 (t, C-8–23), 22.7 (t, C-24), 14.1 (q, C-25); *m*/*z* (EI-MS) 467 (M^+, ^{80}Se, 76%), 465 (M^+, ^{78}Se, 39), 386 (31), 215 ($M^+ - C_{18}H_{36}$, ^{80}Se, 100), 213 ($M^+ -$ $C_{18}H_{36}$, ^{78}Se, 50), 57 (42), 43 (63); λ_{max}/nm (log ε) chloroform 252sh (3.83), 308 (4.13), 358sh (2.85); acetonitrile 252 (3.78), 304 (4.13).

2-Octadecylseleno-6-methylthieno[2,3-*c*]pyridinium iodide 7c

According to procedure 1: **6b** (1.1 mmol) yielded 0.50 g (75%) of **7c** as a pale yellow solid, mp 105 °C (Found: C, 51.28; H, 7.55; N, 2.37; S, 5.18. $C_{26}H_{44}INSSe$ requires C, 51.32; H, 7.29; N, 2.30; S, 5.27%); ν_{max}/cm^{-1} 2921vs (CH), 2849vs (CH), 1626m, 1419s, 844m; δ_H($CDCl_3$) 10.17 (1 H, s, 7-H), 8.71 [1 H, d, ^3J(5-H, 4-H) 6.7, *J* 1.3, 5-H], 8.09 [1 H, d, ^3J(4-H, 5-H) 6.7, 4-H], 7.58 (1 H, s, 3-H), 4.64 (3 H, s, NCH_3), 3.27 (2 H, t, ^3J 7.4, $SeCH_2$), 1.81–1.90 (2 H, m, 9-H), 1.42–1.50 (2 H, m, 10-H), 1.24–1.34 (28 H, m, 11–24-H), 0.88 (3 H, t, ^3J 6.8, 25-H); δ_C($CDCl_3$) 154.9 (s, C-2), 149.5 (s, C-3a, 8.71^{COL}), 139.5 (d, C-7, 10.17^{CHC}), 138.7 (s, C-7a, 7.58^{COL}), 137.8 (d, C-5, 8.71^{CHC}), 123.2 (d, C-3, 7.58^{CHC}), 118.3 (d, C-4, 8.09^{CHC}), 48.4 (q, NCH_3), 31.9,

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‡ 1 bar = 10^5 Pa.

31.2, 29.68, 29.66, 29.61, 29.53, 29.43, 29.31, 29.0 (t, C-8–23), 22.6 (t, C-24), 14.1 (q, C-25); *m*/*z* [FAB MS (pos.)] 482 (Cat., ^{80}Se, 100%), 229 (Cat. − $C_{18}H_{37}$, ^{80}Se, 50), 227 (Cat. − $C_{18}H_{37}$, ^{78}Se, 27); λ_{max}/nm (log ε) chloroform 242 (4.31), 292 (4.06), 370 (4.48); acetonitrile 244 (4.45), 310sh (3.67), 360 (4.35).

2-Selenooctadecyl-6-ethylthieno[2,3-*c*]pyridinium bromide 7b
A solution of **6b** (0.750 g, 1.6 mmol) and bromoethane (10 ml) in acetonitrile (30 ml) was refluxed for 4 h. After cooling to 20–25 °C the precipitate was filtered off, washed with 5 ml diethyl ether and dried *in vacuo* (0.1 mbar) to give 0.73 g (79%) of **7b** as a colourless solid, mp 101–102 °C (Found: C, 56.09; H, 8.09; N, 2.23. $C_{27}H_{46}BrNSSe$ requires C, 56.34; H, 8.06; N, 2.43); ν_{max}/cm^{-1} 2917vs (CH), 2852s (CH), 1622m, 1423m; δ_H($CDCl_3$) 10.60 (1 H, s, 7-H), 8.80 [1 H, dd, ^3J(5-H, 4-H) 6.7, *J* 1.3, 5-H], 8.05 [1 H, d, ^3J(4-H, 5-H) 6.7, 4-H], 7.53 (1 H, s, 3-H), 4.98 (2 H, q, ^3J 7.3, NCH_2), 3.26 (2 H, t, ^3J 7.4, SeCH_2), 1.81–1.89 (2 H, m, 9-H), 1.74 (3 H, t, ^3J 7.3, NCH_2CH_3), 1.41–1.48 (2 H, m, 10-H), 1.24–1.32 (28 H, m, 11–24-H), 0.88 (3 H, t, ^3J 6.8, 25-H); δ_C($CDCl_3$) 155.0 (s, C-2), 149.5 (s, C-3a), 139.4 (d, C-7), 139.2 (s, C-7a), 136.5 (d, C-5), 123.1 (d, C-3), 118.4 (d, C-4), 56.4 (t, NCH_2), 31.9, 31.1, 29.8, 29.7, 29.56, 29.45, 29.35, 29.0 (t, C-8 bis C-23), 22.7 (t, C-24), 17.4 (q, NCH_2CH_3), 14.1 (q, C-25); *m*/*z* [FAB MS (pos.)] 496 (Cat., ^{80}Se, 100%), 494 (Cat., ^{78}Se, 55), 243 (Cat. − $C_{18}H_{37}$, ^{80}Se, 14), 241 (Cat. − $C_{18}H_{37}$, ^{78}Se, 8); *m*/*z* [FAB MS (neg.)] 658 (Cat. + 2 ^{81}Br$^-$, 16%), 656 (Cat. + ^{79}Br$^-$ + ^{81}Br$^-$, 30), 654 (Cat. + 2 ^{79}Br$^-$, 25), 81 (^{81}Br$^-$, 99), 79 (^{79}Br$^-$, 100); λ_{max}/nm (log ε) chloroform 244 (4.20), 322sh (3.77), 3.70 (4.42); acetonitrile 244sh (4.24), 318sh (3.78), 360 (4.35).

2-(5′-Butylthio-2′-thienyl)pyridine 9a
To a solution of 2-(2′-thienyl)pyridine (2.33 g, 14.5 mmol) in 120 ml anhydrous THF (120 ml), 9.1 ml (14.6 mmol) of butyllithium (1.6 M in hexane) was added under cooling with ice.[17] After 30 min dibutyl disulfide (2.8 ml, 14.7 mmol) was added. The reaction mixture was stirred under cooling by ice for a further 3 h and then at 20–25 °C for 20 min. After hydrolysis with 50 ml of ice–water, the phases were separated and the aqueous phase was extracted three times with 30 ml of diethyl ether. The combined organic phases were dried with $MgSO_4$ and purified by column chromatography over 250 g silica gel (R_f 0.48, CH_2Cl_2) to yield 2.71 g (75%) of **9b** as a pale yellow oil (Found: C, 62.61; H, 6.21; N, 5.61. $C_{13}H_{15}NS_2$ requires C, 62.61; H, 6.06; N, 5.62%); ν_{max}/cm^{-1} 2958w (CH), 2929w (CH), 2871w (CH), 1587s, 1465s, 1435m; δ_H($CDCl_3$) 8.55 (1 H, dt, 6-H), 7.67 (1 H, td, 4-H), 7.59 (1 H, dt, 3-H), 7.41 (1 H, d, ^3J 3.8, 3′-H), 7.13 (1 H, m, 5-H), 7.06 (1 H, d, ^3J 3.8, 4′-H), 2.88 (2 H, t, ^3J 7.4, SCH_2), 1.60–1.72 (2 H, m, SCH_2CH_2), 1.38–1.48 (2 H, m, CH_2CH_3), 0.91 (3 H, t, *J* 7.3, CH_3); δ_C($CDCl_3$) 152.2 (s, C-2, 8.55^{COL}), 149.6 (d, C-6, 8.55^{CHC}), 146.9 (s, C-2′, 7.06^{COL}), 138.2 (s, C-5′, 7.41^{COL}), 136.7 (d, C-4, 7.67^{CHC}, 8.55^{COL}), 133.0 (d, C-4′, 7.06^{CHC}), 124.6 (d, C-3′, 7.41^{CHC}), 122.0 (d, C-5, 7.13^{CHC}), 118.4 (d, C-3, 7.59^{CHC}), 38.2 (t, SCH_2), 31.5 (t, SCH_2CH_2), 21.6 (t, CH_2CH_3), 13.6 (q, CH_3); *m*/*z* (EI-MS) 249 (M$^+$, 100%), 193 (93), 192 (40), 149 (24); λ_{max}/nm (log ε) chloroform 260sh (3.80), 326 (4.22); acetonitrile 266sh (3.77), 322 (4.24).

1-Methyl-2-(5′-butylthio-2′-thienyl)pyridinium iodide 10a
To a solution of **9a** (0.74 g, 3.2 mmol) in acetonitrile (20 ml), iodomethane (6 ml) was added. The reaction mixture was stirred at *ca.* 90 °C for 3 days. The solvent was then evaporated and the resulting residue was purified by column chromatography over 25 g silica gel (ethanol). Drying and recrystallization from acetone gave 0.51 g (41%) of **10a** as yellow crystals, mp 75–76 °C (Found: C, 42.68; H, 4.59; N, 3.55. $C_{14}H_{18}INS_2$ requires C, 42.97; H, 4.64; N, 3.58%); ν_{max}/cm^{-1}(film) 3068m, 1616m, 1524s, 1414vs, 1279s, 1185m, 778s; δ_H([$^2H_6$]DMSO) 9.10–9.12 (1 H, m, 6-H), 8.57 (1 H, dt, ^3J 7.9, *J* 1.1, 4-H), 8.21 (1 H, dd, ^3J 8.0, *J* 1.2 Hz, 3-H), 8.05–8.10 (1 H, m, 5-H), 7.74 [1 H, d, ^3J(3′-H, 4′-H) 3.9, 3′-H], 7.38 [d, ^3J(4′-H, 3′-H) 3.9, 1 H, 4′-H], 4.33 (s, 3 H, NCH_3), 3.05 (2 H, t, ^3J 7.3, SCH_2), 1.59–1.67 (2 H, m, SCH_2CH_2), 1.37–1.47 (2 H, m, CH_2CH_3), 0.89 (3 H, t, ^3J 7.4, CH_2CH_3); δ_C([$^2H_6$]DMSO) 147.8 (s, C-2, 4.33^{COL}), 147.2 (d, C-6, 9.11^{CHC}, 4.33^{COL}), 145.0 (d, C-4, 8.57^{CHC}), 143.2 (s, C-5′, 7.74^{COL}), 134.4 (d, C-3′, 7.74^{CHC}), 131.6 (s, C-2′, 7.38^{COL}), 131.3 (d, C-4′, 7.38^{CHC}), 130.0 (d, C-3, 8.21^{CHC}), 126.1 (d, C-5, 8.08^{CHC}), 47.6 (d, NCH_3), 36.6 (t, SCH_2), 30.7 (t, SCH_2CH_2), 20.9 (t, CH_2CH_3), 13.4 (q, CH_2CH_3); *m*/*z* [FAB MS (pos.)] 264 (Cat., 100); λ_{max}/nm (log ε) chloroform 294 (4.14), 368 (4.13); acetonitrile 248 (4.28), 358 (3.92).

2-(5′-Butylseleno-2′-thienyl)pyridine 9b
To a solution of 2-(2′-thienyl)pyridine **8a** (2.70 g, 16.2 mmol) in anhydrous THF (120 ml), 10.2 ml (16.3 mmol) of BuLi solution (1.6 M in hexane) was added under cooling by ice. After addition of powdered selenium (1.28 g, 16.2 mmol) the reaction mixture was stirred at 20–25 °C for 3 h. Then 1-iodobutane (1.9 ml, 16.7 mmol) was added at 4 °C and the reaction mixture was stirred at 20–25 °C for 48 h. Work-up as described for **6b** gave 3.12 g (65%) of **9b** as a pale yellow oil [R_f(CH_2Cl_2) = 0.51] (Found: C, 52.89; H, 5.23; N, 4.55. $C_{13}H_{15}NSSe$ requires C, 52.70; H, 5.10; N, 4.73%); ν_{max}(film)/cm^{-1} 2958w–m (CH), 2929m (CH), 2871w (CH), 1584m, 1465s, 1435s; δ_H($CDCl_3$) 8.55 (1 H, dt, 6-H), 7.67 (1 H, td, 4-H), 7.59 (1 H, dt, 3-H), 7.41 (1 H, d, ^3J 3.8, 3′-H), 7.16 (1 H, d, ^3J 3.8, 4′-H), 7.11–7.15 (1 H, m, 5-H), 2.88 (2 H, t, ^3J 7.4, SeCH_2), 1.67–1.76 (2 H, m, $SeCH_2CH_2$), 1.37–1.47 (2 H, m, CH_2CH_3), 0.90 (3 H, t, *J* 7.3, CH_3); δ_C($CDCl_3$) 152.1 (s, C-2, 8.55^{COL}), 149.6 (d, C-6, 8.55^{CHC}, 7.67^{COL}), 148.9 (s, C-2′, 7.16^{COL}), 136.7 (d, C-4, 7.67^{CHC}, 8.55^{COL}), 135.6 (d, C-4′, 7.16^{CHC}), 127.4 (s, C-5′, 7.41^{COL}), 125.0 (d, C-3′, 7.41^{CHC}, 7.16^{COL}), 122.0 (d, C-5, 7.14^{CH}, 8.55^{COL}, 7.59^{COL}), 118.5 (d, C-3, 7.59^{CHC}, 7.13^{COL}), 32.3 (t, SeCH_2), 31.4 (t, $SeCH_2CH_2$), 22.7 (t, CH_2CH_3), 13.5 (q, CH_3); *m*/*z* (EI-MS) 297 (M$^+$, ^{80}Se, 100%), 295 (M$^+$, ^{78}Se, 52), 241 (97), 240 (78), 238 (52), 161 (67), 160 (32); λ_{max}/nm (log ε) chloroform 280sh (3.90), 324 (4.20); acetonitrile; 278sh (3.89), 322 (4.21).

1-Methyl-2-(5′-methylseleno-2′-thienyl)pyridinium iodide 10b
To a solution of selenoether **9b** (2.00 g, 6.8 mmol) in acetonitrile (30 ml), iodomethane (5 ml) was added and the solution was stirred at 80 °C for 41.5 h. The solvent was evaporated and the resulting residue was dried *in vacuo* (0.1 mbar), washed twice with boiling diethyl ether (4 ml) and then treated with boiling acetone (10 ml). The yellow precipitate was filtered off and dried *in vacuo* (0.1 mbar), to yield 0.50 g (18%) of **10b** as yellow crystals, mp 142–143 °C (Found: C, 33.48; H, 3.09; N, 3.39. $C_{11}H_{12}INSSe$ requires C, 33.35; H, 3.05; N, 3.54%); ν_{max}/cm^{-1} 1622vs, 1571s, 1531vs, 1411s, 1281s, 1174s, 777vs; δ_C([$^2H_6$]-DMSO) 9.09–9.12 (1 H, m, 6-H), 8.57 (1 H, dt, *J* 8.1, *J* 1.2, 4-H), 8.20 (1 H, dd, *J* 8.1, *J* 1.2, 3-H), 8.05–8.09 (1 H, m, 5-H), 7.72 [1 H, d, ^3J 3.9, 3′-H], 7.44 (1 H, d, ^3J 3.9, 4′-H), 4.33 (3 H, s, NCH_3), 2.53 (3 H, s, SeCH_3); δ_C([$^2H_6$]DMSO) 147.9 (s, C-2), 147.1 (d, C-6, 9.11^{CHC}), 145.0 (d, C-4, 8.57^{CHC}), 134.9 (s, C-5′, 7.72^{COL}), 134.7 (d, C-3′, 7.72^{CHC}), 133.0 (s, C-2′, 7.44^{COL}), 132.2 (d, C-4′, 7.44^{CHC}), 129.9 (d, C-3, 8.20^{CHC}), 126.1 (d, C-5, 8.07^{CHC}), 47.6 (q, NCH_3), 11.1 (q, SeCH_3); *m*/*z* [FAB MS (pos.)] 667 (2 Cat. + I$^-$, ^{80}Se, 4%), 665 (2 Cat. + I$^-$, $^{78/80}$Se, 4), 663 (2 Cat. + I$^-$, ^{78}Se, 2), 270 (Cat., ^{80}Se, 100), 268 (Cat., ^{78}Se, 51); λ_{max}/nm (log ε) chloroform 290 (4.08), 374 (4.07); acetonitrile 248 (4.28), 266sh (3.99), 370 (3.91).

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References

1 (*a*) N. Bloembergen, *Nonlinear Optics*, ed. W. A. Benjamin, New York, 1965; (*b*) W. Nie, *Adv. Mater.*, 1993, **5**, 520; (*c*) R. W. Munn and C. N. Ironside, *Principles and Applications of Nonlinear Optical Materials*, Chapman and Hall, London, 1993; (*d*) P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley, New York, 1991; (*e*) D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 690.

2 D. F. Eaton, G. R. Meredith and J. S. Miller, *Adv. Mater.*, 1991, **3**, 564.

3 *Molecular Nonlinear Optics: Materials, Physics and Devices*, ed. J. Zyss, Academic Press, New York, 1994.

4 S. R. Marder and J. W. Perry, *Adv. Mater.*, 1993, **5**, 804.

5 D. M. Burland, R. D. Miller and C. A. Walsh, *Chem. Rev.*, 1994, **94**, 31.

6 For a review see *Nonlinear Optical Properties of Organic Molecules and Crystals*, eds. D. S. Chemla and J. Zyss, Academic Press, Boston, 1987.

7 See K. J. Drost, A. K.-Y. Jen and V. P. Rao, *CHEMTECH*, 1995, **25**, 16.

8 See Ch. Bubeck, A. Laschewsky, D. Lupo, D. Neher, P. Ottenbreit, W. Paulus, W. Prass, H. Ringsdorf and G. Wegner, *Adv. Mater.*, 1991, **3**, 54.

9 (*a*) M. Barzoukas, D. Josse, J. Zyss, P. Gordon and J. O. Morley, *Chem. Phys.*, 1989, **139**, 359; (*b*) D. W. Robinson, H. Abdel-Halim, S. Inoue, M. Kimura and D. O. Cowan, *J. Chem. Phys.*, 1989, **90**, 3427.

10 (*a*) J. Sicé, *J. Am. Chem. Soc.*, 1953, **75**, 3697; (*b*) M. A. Keegstra, T. H. A. Peters, L. Brandsma, *Synth. Commun.*, 1990, **20**, 213.

11 A. Bugge, *Chem. Scr.*, 1973, **3**, 190.

12 P. Boldt, M. Blenkle, I. Cabrera, D. Lupo and W. Hickel, *Nonlinear Optics*, 1994, **8**, 173.

13 (*a*) J. P. Maffrand and F. Eloy, *J. Heterocycl. Chem.*, 1976, **13**, 1347; (*b*) H. Nerenz, dissertation in progress, Technical University of Braunschweig.

14 J. M. Hoffman and K. L. Shepard, USP 4731368/1988 (*Chem. Abstr.*, 1988, **109**, 54762n).

15 W. Friedrichsen, in *Comprehensive Heterocyclic Chemistry*, eds. A. R. Katritzky and C. W. Rees, Pergamon Press, Oxford, 1984, vol. 4, 973.

16 H. Sigel, H. Wynberg, T. J. van Bergen and K. Kahmann, *Helv. Chim. Acta*, 1972, **55**, 610.

17 Th. Kauffmann, A. Mitschker and A. Woltermann, *Chem. Ber.*, 1983, **116**, 992.

18 H. E. Katz, K. D. Singer, J. E. Sohn, C. W. Dirk, L. A. King and H. M. Gordon, *J. Am. Chem. Soc.*, 1987, **109**, 6561.

19 K. D. Singer, J. E. Sohn, L. A. King, H. M. Gordon, H. E. Katz and C. W. Dirk, *J. Opt. Soc. Am. B: Opt. Phys.*, 1989, **6**, 1339.

20 K. Clays and A. Persoons, *Phys. Rev. Lett.*, 1991, **66**, 2980.

21 R. W. Terhune, P. D. Maker and C. M. Savage, *Phys. Rev. Lett.*, 1965, **14**, 681; P. D. Maker, *Phys. Rev. A*, 1970, **1**, 923.

22 J. Zyss, C. Dhenaut, T. Chauvan and I. Ledoux, *Chem. Phys. Lett.*, 1993, **206**, 409.

23 R. Bersohn, Y.-H. Pao and H. L. Frisch, *J. Chem. Phys.*, 1966, **45**, 3184.

24 M. Stähelin, D. M. Burland and J. E. Rice, *Chem. Phys. Lett.*, 1992, **191**, 245.

25 J.-L. Oudar, *J. Chem. Phys.*, 1977, **67**, 446.

26 I. Ledoux and J. Zyss, *Chem. Phys.*, 1982, **73**, 203.

27 M. Barzoukas, P. Fremaux, D. Josse, F. Kajzar and J. Zyss, *Mater. Res. Soc. Symp. Proc.*, 1988, **109**, 171.

28 E. A. Guggenheim, *Trans. Faraday Soc.*, 1949, **45**, 714.

29 J. Zyss, T. C. Van, C. Dhenaut and I. Ledoux, *Chem. Phys.*, 1993, **177**, 281.

30 G. Martelli, L. Testaferri, M. Tiecco and P. Zanirato, *J. Org. Chem.*, 1975, **40**, 3384.

31 L. Testaferri, M. Tiecco and P. Zanirato, *J. Org. Chem.*, 1975, **40**, 3392.

32 Y. L. Gol'dfarb, V. P. Litvinow and S. A. Ozolin, *Bull. Acad. Sci. USSR, Div. Chem. Sci., Engl. Transl.*, 1965, 486.

33 S. Chorbadzhiev, God Sofii. Univ. 'Kliment Okhridski', *Khim. Fak.*, 1979, **73**, 65 (Pub. 1983) (*Chem. Abstr.*, 1984, **101**, 130 174z).

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