Linearly condensed Polythiophenes: Characteristic Molecular Aggregation of Thieno[2'',3'':4',5']thieno[2',3'-d]thieno[3,2-b]thiophene Crystals Revealed by Ultraviolet Photoelectron Spectroscopy

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Linearly-condensed polythiophenes (**4** and **5**) have been prepared and their characteristic aggregation behaviour as hydrogen-poor π compounds in the solid state has been investigated in comparison with those of the lower homologues (**2** and **3**); the photoelectron spectra of the series **2–5** were measured in the solid state as well as in the gas phase. For **4** the difference in the ionization energies for the gaseous (adiabatic; 7.22 eV) and solid (threshold; 4.86 eV) states is significant, giving rise to a large polarization energy (2.36 eV), which is larger than the calculated value (1.83 eV) based on the packing density and molecular polarizability. This has been interpreted in terms of the intermolecular orbital interactions in the solid state of **4**. Such an interaction has not been observed in the lower homologues (**2** and **3**).

The discovery of an organic superconductor under ambient pressure from bis(ethylenedithio)tetrathiafulvalene complexes (BEDT-TTF)$_2$I$_3$[1] has demonstrated that an enhancement in the spatial arrangements of intermolecular interactions is important in stabilizing the metallic states and, further, in designing organic superconductors.[2] Four sulfur atoms in the BEDT-TTF molecule, when introduced into the TTF skeleton, reinforce the interaction between quasi-one-dimensional stacks of BEDT-TTF molecules in the crystal through their side-by-side packing arrangements.

Against this background, we have investigated the linearly-condensed polythiophene **1**. This polymer molecule bears essentially no hydrogen atoms in the molecular periphery, and is therefore expected to interact efficiently intermolecularly through S – – – S contacts. Polycondensed thiophene itself has not yet been obtained. In contrast, lower homologues of a series of linearly-condensed thiophenes, *i.e.* thieno[3,2-b]thiophene[3] (**2**) and thieno[3,2-b]thieno[2',3'-d]thiophene[4] (**3**), which are regarded as the prototype of linearly-condensed polythiophenes, are already known. We have also prepared two higher homologues of this series;[5] thieno[2'',3'':4',5']thieno[2',3'-d]-thieno[3,2-b]thiophene (**4**) and dithieno[2,3-d:2',3'-d']thieno-[3,2-b:4,5-b']dithiophene (**5**), which are isoelectronic with
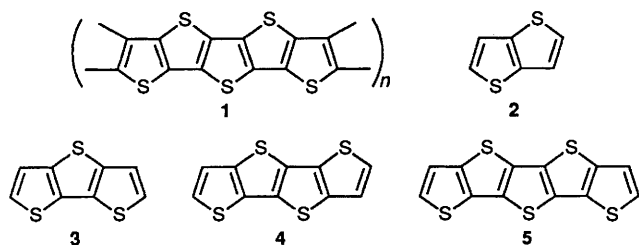
chrysene and picene, respectively, but with much fewer hydrogen atoms in the molecular periphery. The compounds in this series correspond, in terms of linear condensation, to the acenes of polynuclear aromatic hydrocarbons. In this paper we demonstrate, using photoelectron spectroscopy, characteristic molecular aggregations in crystals of **4** and **5** that are not encountered in the lower homologues **2** and **3**.

Experimental

Preparation.—Polythiophenes **4** and **5** were prepared according to the synthetic sequences[5] depicted in Scheme 1. Coupling constant values *J* are given in Hz throughout.
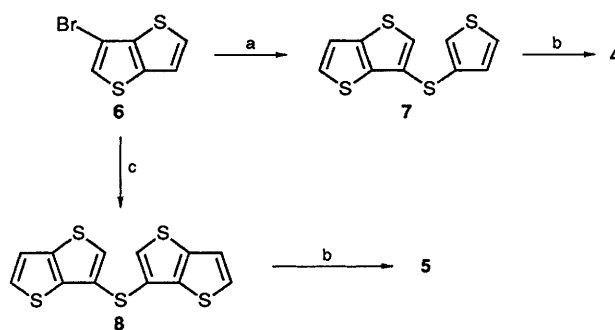
Scheme 1 *Reagents and conditions:* (a) Bu^{n}Li, Et$_2$O, −78 °C (1 h); bis(3-thienyl) disulfide, Et$_2$O, −78 °C (1 h); room temperature (2 h); (b) Bu^{n}Li, Et$_2$O, −10 °C (2 h); CuCl$_2$, room temperature (24 h); (c) Bu^{n}Li, Et$_2$O, −78 °C (1 h); bis(benzenesulfonyl) sulfide, Et$_2$O, −78 °C (1 h) → −40 °C (6 h)

3-(3-*Thienylthio*)*thieno*[3,2-b]*thiophene* (**7**). To a solution of 3-bromothieno[3,2-b]thiophene (**6**) (4.08 g, 18.62 mmol) in anhydrous diethyl ether (20 cm^3) was added a 1.6 mol dm^{-3} solution of Bu^{n}Li in hexane (12 cm^3, 1.03 equiv.) under a nitrogen atmosphere at −78 °C. The mixture was stirred for 1 h at −78 °C, then to the resulting white suspension was added a solution of bis(3-thienyl) disulfide (4.3 g, 18.66 mmol) in Et$_2$O (10 cm^3). After being stirred for 1 h at −78 °C, the mixture was allowed to warm and was stirred at room temperature for a further 2 h after which time water (80 cm^3) was added. The aqueous phase was extracted twice with ether (30 cm^3) and the combined organic layers were washed with brine (2 × 20 cm^3) and dried over MgSO$_4$. After removal of solvent under reduced pressure the residual pale green oil was chromatographed on silica gel, using hexane as an eluent, to give crude **7** (4.5 g, 95%). Further purification by gel permeation chromatography gave analytically pure **7** (4.17 g, 88%) as a colourless oil: ^{1}H NMR (CDCl$_3$), δ_H 7.02 (m, 1 H), 7.23 (m,

1 H), and 7.25–7.4 (m, 4 H); ^{13}C NMR (CDCl$_3$), δ_C 119.5 (d), 123.1 (s), 126.2 (d), 127.2 (d), 128.0 (d), 128.5 (s), 129.8 (d), 138.8 (s) and 140.5 (s); v/cm^{-1} 3100, 1495, 1480, 1340, 1320, 1200, 1185, 1090, 970, 890, 850, 820, 775, 705, 645 and 615; MS m/z (relative intensity) 256 (50), 255 (41), 254 (M$^+$, 100), 221 (63), 209 (100) and 177 (63); λ_{max}/nm (cyclohexane) 260 (ε 13 480) and 284 (11 590) (Found: C, 47.3; H, 2.4; S, 50.7. Calc. for C$_{10}$H$_6$S$_4$: C, 47.21; H, 2.38; S, 50.41%).

Thieno[2″,3″:4′,5′]thieno[2′,3′-d]thieno[3,2-b]thiophene (**4**). A solution of Bu^{n}Li (6.3 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 10.1 mmol) was added, with stirring, to a solution of sulfide **7** (1.28 g, 5.03 mmol) in 30 cm^3 of anhydrous diethyl ether at -10 °C under a dry nitrogen atmosphere. The reaction mixture was stirred at -10 °C for 2 h before being added to a vigorously-stirred suspension of anhydrous CuCl$_2$ (1.36 g, 10.1 mmol) in diethyl ether (10 cm^3). After the mixture had been stirred for 24 h at room temperature the dark-green suspension was quenched with water (20 cm^3) and the resulting precipitate was filtered and washed with boiling benzene (100 cm^3). The combined organic phases were washed with brine (2 × 30 cm^3) and then dried (MgSO$_4$) and concentrated. The residual greenish solid was chromatographed on a silica gel column using hexane as eluent to afford **4** as colourless prisms (0.76 g, 60%); m.p. 220 °C; ^{1}H NMR (CDCl$_3$), δ_H 7.31 (2 H, d, $J =$ 5.1) and 7.37 (2 H, d, $J =$ 5.1); v(KBr)/cm^{-1} 3085, 3065, 1465, 1405, 1365, 1185, 1080, 950, 930, 890, 710 and 620; MS, m/z (relative intensity) 254 (16), 253 (14), 252 (M$^+$, 100), and 126 (18); λ_{max}/nm (CH$_2$Cl$_2$) 333 (ε 25 640), 320 (29 140), 316 (27 780), 306 (29 490), 296 (sh, 18 600) and 283 (sh, 8200) (Found: C, 47.4; H, 1.8; S, 51.0. Calc. for C$_{10}$H$_4$S$_4$: C, 47.59; H, 1.60; S, 50.81%).

Bis(3-thieno[3,2-b]thienyl) sulfide (**8**). To a solution of 3-bromothieno[3,2-*b*]thiophene (**6**) (2.47 g, 11.27 mmol) in anhydrous diethyl ether (10 cm^3) was added a 1.6 mol dm^{-3} solution of Bu^{n}Li in hexane (7.1 cm^3, 11.36 mmol, 1.01 equiv.) under a nitrogen atmosphere at -78 °C. The mixture was stirred for 1 h at -78 °C and then to the resulting white suspension was added a solution of bis(benzenesulfonyl) sulfide (1.722 g, 5.6 mmol, 0.5 equiv.) in Et$_2$O (20 cm^3). After being stirred for 1 h at -78 °C, the mixture was allowed to warm to -40 °C and was further stirred at this temperature for 6 h, then at room temperature for 12 h. The resulting light-brown suspension was quenched with water (50 cm^3). The aqueous layer was extracted with diethyl ether (4 × 50 cm^3) and the combined organic layers were washed with brine (2 × 30 cm^3), dried (MgSO$_4$), and concentrated. The residual brown oil was chromatographed on silica gel using hexane as an eluent to yield **8** as a light brown oil. This was further purified by gel permeation chromatography to give **8** (400 mg, 23%) as a yellow oil: ^{1}H NMR (CDCl$_3$), δ_H 7.11 (2 H, d, $J =$ 5.3), 7.23 (2 H, dd, $J =$ 1.5, 5.3) and 7.42 (2 H, d, $J =$ 1.5); ^{13}C NMR (CDCl$_3$), δ_C 119.6 (d), 120.9 (s), 128.2 (d), 128.9 (d), 138.9 (s) and 141.1 (s); v/cm^{-1} (neat) 3095, 3070, 1725, 1575, 1519, 1475, 1430, 1345, 1325, 1190, 1150, 965, 820, 715, 705, 655 and 645; MS m/z (relative intensity) 312 (24), 311 (19), 310 (M$^+$, 100), 277 (25), 265 (29) and 233 (19) (Found: C, 46.7; H, 1.9; S, 51.2. Calc. for C$_{12}$H$_6$S$_5$: C, 46.42; H, 1.95; S, 51.63%).

Dithieno[2,3-d:2′,3′-d′]thieno[3,2-b:4,5-b′]dithiophene (**5**). To a stirred solution of sulfide **8** (160 mg, 0.52 mmol) in diethyl ether (5 cm^3) was added a 1.6 mol dm^{-3} solution of Bu^{n}Li in hexane (0.7 cm^3, 1.12 mmol, 2.15 equiv.) under a nitrogen atmosphere at -10 °C. The mixture was stirred for 2 h and was then added to a vigorously-stirred suspension of anhydrous CuCl$_2$ (150 mg, 1.12 mmol) in diethyl ether (5 cm^3). The resulting mixture was stirred at room temperature for 12 h and was then quenched with 10 cm^3 of water. The dark brown precipitate was filtered and washed with boiling benzene (200 cm^3). The combined organic layers were washed with brine

(2 × 20 cm^3), dried (MgSO$_4$) and concentrated. The dark greenish residue was purified by silica gel column chromatography (hexane as eluent) to yield **5** (0.104 mmol, 20%) as a pale yellow solid: m.p. 130 °C (decomp.); ^{1}H NMR (CDCl$_3$), δ_H 7.33 (2 H, d, $J =$ 5.1) and 7.33 (2 H, d, $J =$ 5.1); MS m/z (relative intensity) 310 (12), 309 (15), 308 (M$^+$, 100) and 154 (10); λ_{max}/nm (CH$_2$Cl$_2$) 357 (ε 29 000), 342 (31 240), 327 (20 260), 317 (23 940), 305 (14 510), and 294 (6710) (Found: C, 47.0; H, 1.45; S, 51.65. Calc. for C$_{12}$H$_4$S$_5$: C, 46.73; H, 1.31; S, 51.97%).

Photoelectron Spectroscopy.—The gas-phase HeI photoelectron spectra were measured with the instrument described previously.[6] Xe gas was used as the internal standard for the calibration of the energy scale. The sample inlet and target chamber systems were heated to 150 °C during the measurements.

The solid-state ultraviolet photoelectron spectra (UPS) were obtained for vacuum-deposited films of each compound using an apparatus which was an improved version of that reported in detail previously.[7] The film preparation and *in situ* measurements of photoelectron spectra were carried out in the chamber at pressures as low as 10^{-3} Pa. Films of **2** and **3** were deposited on a copper substrate below -30 °C, while **4** was evaporated on a substrate at room temperature, although a slow decrease in the film thickness during the UPS measurement was observed with a quartz oscillator. Only for **5** were stable films at a thickness of 17–72 nm prepared on the room temperature substrate and used for the measurements.

Results and Discussion

Photoelectron Spectra.—Of primary interest in this study is the solid-state characterization of the polythiophenes. It will also be important, however, to consider first the photoelectron spectra of the isolated molecule to provide a context for the discussion on the aggregation properties. The gas-phase HeI photoelectron spectra for the series **2**–**4** are shown in Fig. 1. Photoelectron spectra for polythiophenes **2**[8] and **3**[9] have already been reported and are in good agreement with the present spectra. The first ionization energy values of **2**–**4** obtained from the spectra are listed in Table 1 together with the data for some related compounds.

The lowest ionization energy decreases with increasing number of the thiophene rings. A similar trend is observed for the second-band ionization energies. The lowest ionization energy of **4** is 7.52 eV; this value is as small as that of chrysene (7.59 eV) as the isoelectronic aromatic hydrocarbon,[10] but is larger than those of Wetiz-type donors[11] such as TTF. Polythiophene **4** formed a 1:1 charge–transfer complex[12] with TCNQ and, moreover, compound **3** yielded a 1:1 complex of a mixed stack with TCNQ.*

Each spectrum in Fig. 1 shows fairly sharp spectral features in the low ionization range, *viz.* less than 11 eV. For **4**, five bands can easily be distinguished in such an energy range. In order to assign them, we have performed MINDO/3 calculations using the structural data obtained from X-ray analysis.[12] The calculated orbital energies of **4** correspond fairly well to the observed ionization energies (Fig. 2) according to Koopmans' theorem.[14] Thus, the three bands are assigned, from the first one, to the $\pi 9(a_u)$, $\pi 8(a_u)$ and $\pi 7(b_g)$ molecular orbitals, respectively. The fourth band is, however, not distinctively

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* Polythiophene **3** has been reported by Taliani[13] to form a 1:1 charge–transfer complex with TCNQ, although the X-ray crystal structure has not been solved. We have carried out an X-ray analysis for this complex and revealed the mixed stacks. The structural details are to be published elsewhere.
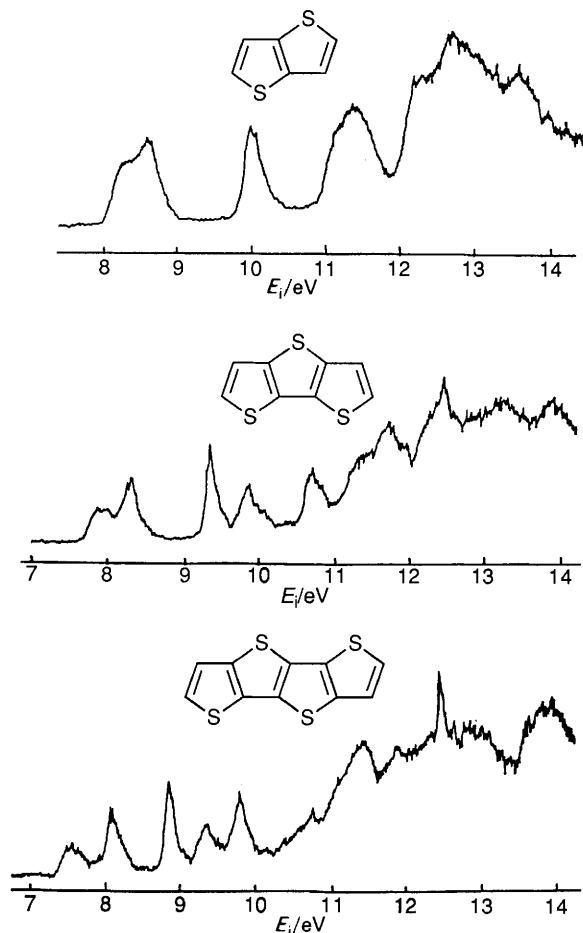
Fig. 1 Photoelectron spectra of a series of polythiophenes

Fig. 2 Correlation of the observed ionization energies and calculated energy levels. The calculated MOs $(-E/\text{eV})$ and their schematic drawing are given by MINDO/2.

Table 1 Ionization energies in the gaseous[a] and solid states and polarization energies[b] for polythiophenes and some related compounds

Compound	$E_i^v(g)/\text{eV}$	$E_i^a(g)/\text{eV}$	$E_i^{th}(s)/\text{eV}$	P_+ eV
2	8.12	7.9	6.23	1.7
3	7.78	7.55	5.94	1.61
4	7.52	7.22	4.86	2.36
5	—	—	4.68	—
Phenanthrene	7.86[c]	7.72[c]	6.08[f]	1.64
Chrysene	7.59[c]	7.51[c]	5.8[g]	1.7
Picene	7.52[c]	7.5[c]	5.7[h]	1.8
Anthracene	7.41[c]	7.36[c]	5.67[i]	1.69
Naphthacene	6.97[c]	6.89[c]	5.10[g]	1.8
Pentacene	6.61[c]	6.58[c]	4.85[j]	1.7
BEDT-TTF	6.5[d]	6.21[d]	4.78[d]	1.43
TMTSF[k]	6.58[e]	6.27[e]	4.84[d]	1.43

[a] Superscripts a and v indicate adiabatic and vertical values, respectively. [b] $P_+ = E_i^a(g) - E_i^{th}(s)$: polarization energy. [c] Ref. 10. [d] Ref. 22. [e] R. Gleiter, M. Kobayashi, J. Spanget-Larsen, J. P. Ferraris, A. N. Bloch, K. Bechgaard and D. O. Cowan, Ber. Bunsenges. Physik. Chem., 1979, 79, 1218. [f] N. Sato, unpublished results. [g] Ref. 16. [h] S. Hino, Ph.D. Thesis, University of Tokyo, 1975. [i] B. M. Schmid, N. Sato and H. Inokuchi, Chem. Lett., 1983, 1897. [j] N. Sato, K. Seki, H. Inokuchi and Y. Harada, Chem. Phys., 1986, 109, 157. [k] Tetramethyltetraselenafulvarene.

Fig. 3 Schematic drawing of a qualitative interaction diagram between decapentaene orbitals and four sulfur p orbitals, focusing on the four highest occupied orbitals of 4

assigned to the calculated MO ($\pi 6$ or σ), only from the MINDO calculations. The HOMO level ($\pi 9$) of 4 has only a very small amplitude on the sulfur atoms, while the $\pi 8$ (the next HOMO) and $\pi 7$ MOs have a large amplitude in these positions. These results are consistent with the spectral profiles, when the half-width of the first four bands in Fig. 1 is examined. In general, bonding orbitals lead to spectral peaks broader than those for
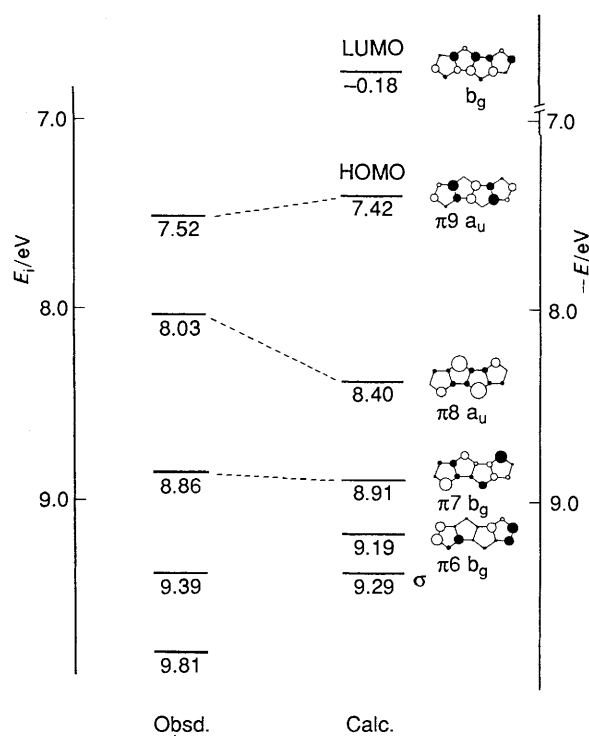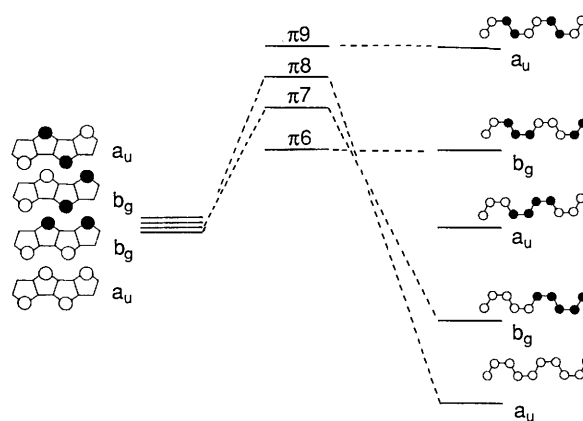
non-bonding orbitals.[15] The second and third bands in the spectrum are obviously sharp, so that these bands are relevant to the large contribution from the non-bonding orbitals localized on the sulfur atoms.

A simple discussion leads to an assumption that the occupied π orbitals of 4 are derived from the interaction of the five occupied π-MOs of the all-cis decapentacene molecule and the 3p-π orbitals of the four sulfur atoms. The qualitative orbital interaction diagram, which brings about the highest four occupied orbitals of 4, is shown in Fig. 3. The HOMO, i.e., $\pi 9$, is mostly derived from the decapentacene HOMO which possesses no correct symmetry with which to interact with the sulfur fragment. On the other hand, the lowest energy MO of decapentaene interacts most effectively with four sulfur atoms to form the $\pi 8$ orbital by an out-of-phase-type (antibonding-type) combination of the a_u group orbital of the four sulfur orbitals. The $\pi 7$ orbital is also formed by the combination of the sulfur

and polyene orbitals. Thus, the sulfur p-electrons are mainly localized in the $\pi 8$ and $\pi 7$ orbitals. These are similar in nature to the HOMO levels of **2** and **3**, as illustrated in Fig. 4, in which correlations of the HOMO and the next HOMO ionization bands for a series of polythiophenes are depicted. The HOMO levels of the polythiophene series shift progressively to the higher energy side with successive increases in the polyene HOMO orbital that makes a large contribution to the HOMO of the polythiophenes.
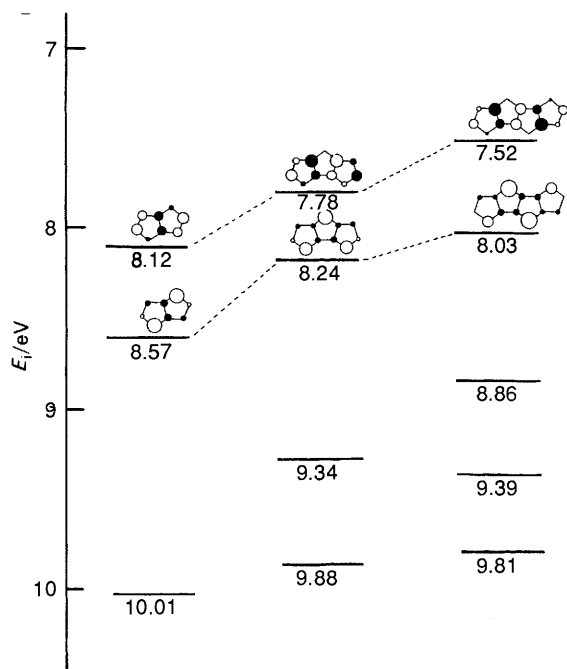

Fig. 4 PE band energy diagram for the series of polythiophenes **2–4**

Photoemission in Solids.—The photoemission spectra of **2–5** were measured in the solid state by using their polycrystalline thin films prepared by vacuum deposition. As depicted in Fig. 5, the spectra, at least in the photon energy range employed for the present study, are of unresolved features, being fairly common for the solid-state photoelectron spectra.[16,17] The threshold ionization energies, $E_i^{th}(s)$, which represent the ionization energy of a molecule in the bulk of the solid, are listed in Table 1 together with the adiabatic (threshold) ionization energy $E_i^a(g)$, determined for a molecule in the gas phase. The values of $E_i^{th}(s)$ decrease with an increase in the number of thiophene rings, as observed in the gas-phase spectra. Thus, of the four compounds polythiophene **5** shows a significantly low ionization energy (4.68 eV), which is comparable to the values observed for graphite (4.74 eV).[18] The ionization energy of an organic molecular solid is in principle smaller than that of its constituent molecule in the gas phase. The difference corresponds to a stabilization energy for a molecule ionized in the solid, which results from electrostatic polarization on the surrounding molecules induced by the ionic charge; the energy is termed polarization energy P_+.[19] Thus, the polarization energy is defined[16] in eqn. (1), where $E_i^{th}(s)$ is the threshold ionization

$$P_+ = E_i^a(g) - E_i^{th}(s) \tag{1}$$

energy in the solid state and $E_i^a(g)$ is the adiabatic ionization energy in the gaseous state. The polarization energies of the polythiophenes and some related compounds are also listed in Table 1.

The P_+ value is interpreted in terms of two factors: the molecular polarizability and the molecular packing in the solid.[16] As a result, P_+ values become larger when molecules are closely packed and/or the molecular polarizability of the surrounding molecules is large. As shown in Table 1, for aromatic hydrocarbons with planar molecular structures the P_+ value is almost the same (ca. 1.7 eV).[16] This can be attributed to an inherent balance between the two factors: the
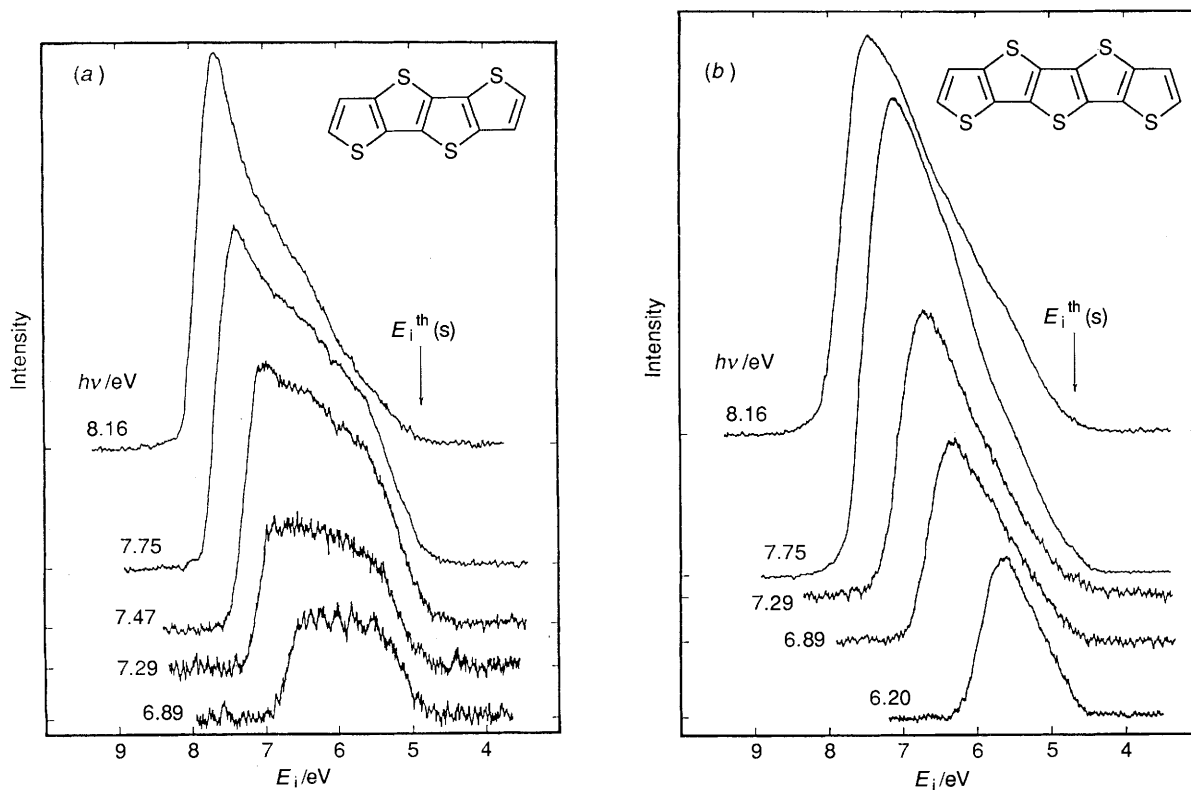

Fig. 5 Photoelectron spectra of solid-state polythiophenes: (*a*) **4**; (*b*) **5**. Incident photon energy is written beside each spectrum.

Table 2 Mean molecular polarizabilities, packing densities and calculated polarization energies of polythiophenes

Compound	$\bar{\alpha}/$ 10^{-39} F m^2	Z/V $/10^{27}$ m^{-3}	$P_+^{calc}/$ eV	$P_+^{obs}/$ eV
2	1.69	6.62	1.90	1.7
3	2.29	4.97	1.75	1.61
4	2.92	4.26	1.83	2.36
5	3.52	(3.8)^a	(1.9)^a	(2.3)^a

^{a} Estimated value, see text.

increase in molecular size, which causes a decrease in the molecular packing density, balances with a parallel increase in polarizability due to an extension of the region for electron delocalization. The common value of P_+ also appears to be held in the case of polythiophenes **2** and **3**: the P^+ value of **3** (1.61 eV) and **2** (1.7 eV) is comparable to those of the isoelectronic polynuclear aromatic hydrocarbons. Thus, the molecular packing in solid **2** and **3** is estimated to be of common molecular solids and also to balance with the large molecular polarizability due to sulfur atoms introduced in the molecular framework.

In contrast to **2**, **3** and aromatic hydrocarbons, polythiophene **4** has a significantly large polarization energy $P_+ = 2.36$ eV, i.e., a drastic decrease of ionization energy on going from the gaseous molecule to the solid state. This indicates that the balance between the molecular packing and the molecular polarizability is no longer held for **4**. The crystal structure analysis has demonstrated an over-tightly packed arrangement of **4** with notably short intermolecular sulfur–sulfur contacts,[12] whereas no such short contacts are found in the crystals of **3**[13] and **2**.[20] Thus, the characteristics in the molecular packing should contribute to the large P_+ value of **4**.

An approximate relation (in SI units) of P_+ in organic molecular solids is given by eqn. (2):[16]

$$P_+ = 6.99\,(e/4\pi\varepsilon_0)^2\bar{\alpha}p^{4/3} \qquad (2)$$

where e and ε_0 are the elementary charge and the permittivity of a vacuum, respectively, $\bar{\alpha}$ is the mean value of the molecular polarizability and p is the molecular-packing density in the solid, which is identical to the number density of molecules defined as Z/V using the crystallographic data. An $\bar{\alpha}$ value calculated from a δ-function model[21] is often in good agreement with that obtained using eqn. (2) from the P_+ and p values (see, e.g., ref. 22). We have thus calculated the mean molecular polarizabilities for **2–5** * from the molecular structure data, and further evaluated the polarization energies by applying the crystal structure data.

The correlation between the evaluated value P_+ and the value obtained experimentally is good for **2** and **3**, whereas for **4** the estimated polarization energy is much smaller than the observed value. This implies that an ionized molecule of **4** is stabilized in the solid much more than expected from the large mean polarizability, which is explained by an additional sulfur atom with a further extended π-system and from the over-tight molecular packing density. The observed large P_+ value can therefore result from an additional intermolecular interaction other than the van der Waals interaction.

In this connection, the polarization energy of polythiophene **5** should be noted. The mean molecular polarizability calculated for the series of polythiophenes increases successively by almost the same magnitude (ca. 0.6×10^{-39} F m^2) per annelated

thiophene ring (Table 2). A P_+ value for **5** could be evaluated as ca. 1.9 eV from eqn. (2) using the calculated $\bar{\alpha}$ value and a molecular packing density p. On the other hand, the ionization energies of **5** in the gas phase could also be estimated to be 6.9–7.0 eV for the adiabatic value and ca. 7.3 eV for the vertical value by simple extrapolation from those for the lower homologues listed in Table 1. Here again, we remark that the threshold ionization energy of **5** in the solid state is significantly low (4.68 eV). Now we have two P_+ values for **5** from different bases, i.e. 1.9 eV from the approximate relation above and 2.2–2.3 eV from the difference in ionization energies between the gaseous and solid states. The disagreement between these values leads to the tentative conclusion that, also for **5**, an additive intermolecular interaction may be operating in the solid state.

Orbital Interactions.—There appears to be a distinct change in molecular aggregation characteristics between **3** and **4** in the series of polythiophenes. Higher homologues in the series show over-tight molecular aggregation, as expected from our strategy for molecular design using polythiophenes. This could begin to explain the additive intermolecular interaction disclosed for **4** (and possibly also for **5**) by the difference between the observed and the estimated polarization energy.

The short intermolecular S–S contact allows an efficient overlap of the sulfur-originating molecular orbitals between adjacent molecules. In this case, such a MO splits to form a pair of bonding and antibonding orbitals, the latter resulting in a rise of the occupied electron level. In the case of **4**, however, the HOMO is not a sulfur-originating orbital, but mainly derives from the polyene π orbitals with little contribution from the sulfur lone-pair electrons. By an intermolecular orbital interaction through the sulfur atoms, a mixing of the next HOMO could therefore be possible. The highest occupied level of **4** in the solid state is raised much more than expected from only a common and weak interaction between the next HOMOs: this could be explained by an orbital rearrangement induced by mixing between the next HOMOs in a complex manner.

In conclusion, we have disclosed a strong intermolecular interaction, a kind of electron exchange due to intermolecular orbital interactions, in solid **4** and **5**. Such an interaction is characteristic of higher homologues of polythiophenes; we assume that a kind of self-assembling interaction is operative in the hydrogen-poor, lengthy π-molecules such as **4** and **5**, and in the extreme case, for **1**.

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