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overlap population (COOP) analysis used in extended Hückel calculations,<sup>16,21</sup> provides a quantitative measure of bond strengths and is probably more appropriate for a calculation from first principles. All COHP curves are presented here in a format similar to COOP curves: positive values are bonding, and negative antibonding; this means we are plotting  $-COHP$  instead of COHP.

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## Efficient Intermolecular Charge Transport in Self-Assembled Fibers of Mono- and Bithiophene Bisurea Compounds\*\*

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Conjugated oligomers and polymers of thiophenes are among the most promising organic semiconducting molecular materials for application as thin film transistors<sup>[1]</sup> (TFT) and light-emitting diodes<sup>[2]</sup> (LED) in (opto)electronic devices. The basis for this is their highly favorable electronic properties, such as a small band gap, high charge-carrier mobility (although low compared to the mobility in some aromatic molecular crystals),<sup>[3]</sup> and high quantum yield for fluorescence.<sup>[4]</sup> The properties and performance of these materials, however, do not only depend on the electronic structure of the molecules themselves, but also critically on supramolecular features such as the molecular packing of the thiophene moieties and the morphology of thin films and crystals of those compounds.<sup>[5]</sup> Although full control of the molecular packing and morphology is still a far-fetched goal, progress has been made in directing the spacing and the orientation of  $\pi$ -stacked aromatic groups by making use of hydrogen bonding motifs.<sup>[6,7]</sup> A class of compounds that is particularly well suited for the spatial organization of functional entities are (bis)urea compounds.<sup>[8]</sup> We showed recently that bisurea compounds self-assemble into ribbons, which stack into sheets or lamella.<sup>[9]</sup> The bisurea compounds have an extended conformation in the ribbons and are amenable to form multiple hydrogen bonds with neighboring molecules, and thereby provide a framework for the organization of other functional entities in ribbons and lamella (Figure 1). The

- [1] The physics community is well aware of Stoner's model that deals with ferromagnetism; unfortunately, it does not provide much insight into the bonding situation. a) W. Heisenberg, *Z. Phys.* **1928**, *49*, 619; b) E. C. Stoner, *Proc. Roy. Soc. A* **1938**, *165*, 372; c) E. C. Stoner, *Proc. Roy. Soc. A* **1939**, *169*, 339. Stoner's model included an adjustable parameter  $I$  in its original formulation; in later studies various methods to calculate  $I$  were proposed, see for example d) J. F. Janak, *Phys. Rev. B* **1977**, *16*, 255; e) O. K. Andersen, J. Madsen, U. K. Poulsen, O. Jepsen, J. Kollar, *Physica B* **1977**, *86–88*, 249.
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- [12] The local magnetic moments of Figure 1d also arise as a consequence of spin polarization. In this case the narrow bands give rise to sharp peaks in the DOS. In the spin-polarized DOS of this system  $\epsilon_F$  occurs at the top of the  $\alpha$  DOS and the entire  $\beta$  DOS is found above  $\epsilon_F$ , that is, there is no occupation of the  $\beta$ -spin sub-lattice.
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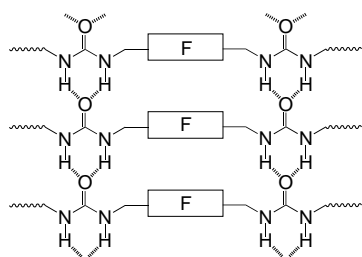
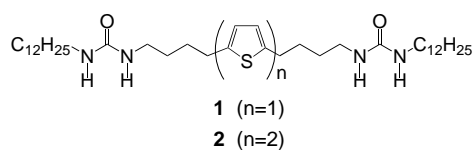


Figure 1. Ribbon of a bisurea compound used for the spatial organization of functional entities (F).

bisurea compounds **1** and **2** with a thiophene or bithiophene moiety incorporated in the spacer have been synthesized on the basis of this organization principle. The molecular packing and morphology of aggregates of these compounds, as well as the remarkably efficient charge transport in these materials, are presented here.



The bisurea thiophenes **1** and **2** were synthesized in several steps starting from thiophene and 2,2'-bithiophene, respectively (see experimental section). Compounds **1** and **2** are insoluble in organic solvents at room temperature, but upon heating to 50–100 °C they gradually dissolve. Upon cooling the solution to room temperature **1** and **2** precipitate in solvents such as ethanol, butyl acetate, and cyclohexane, but in tetralin and 1,2-dichloroethane organogels are formed.<sup>[9, 10]</sup> The highly efficient aggregation of these compounds is caused by the formation of hydrogen bonds between urea groups. Infrared spectroscopic analysis of the gels **1** and **2** indeed showed a strong NH band at 3330  $\text{cm}^{-1}$  and amide I and II bands at 1620  $\text{cm}^{-1}$  and 1570  $\text{cm}^{-1}$ , respectively, which correspond well with the value for the solids and are characteristic for the presence of hydrogen-bonded urea groups.<sup>[11]</sup>

Light microscopic analysis of the gels and solids **1** and **2** revealed that these compounds self-assemble into elongated twisted fibers with a breadth of 2–10  $\mu\text{m}$  and lengths of 20–100  $\mu\text{m}$ . The fibers are strongly birefringent, which indicates a high degree of molecular ordering. Analysis by electron microscopy (Figure 2) and X-ray powder diffraction showed

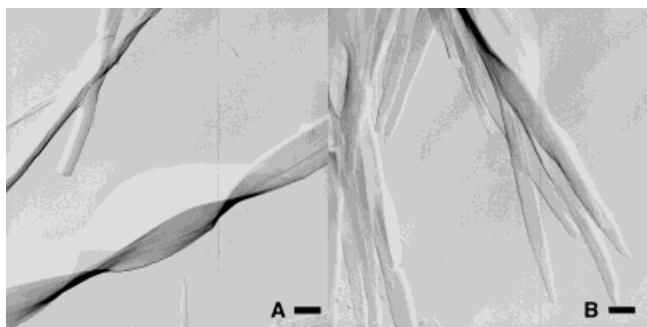


Figure 2. Electron micrographs of lamellar fibers of **1** (A) and of **2** (B). A platinum shadow has been applied with an angle of 10°. The bar corresponds to 500 nm.

that the fibers have a lamellar structure, with a spacing of 38.9 Å for **1** and 41.2 Å for **2**. These values are smaller than the molecular lengths of **1** and **2**, which amount to 51 and 53 Å, respectively. The bisurea compounds are most likely closely packed within the lamella with their long molecular axis parallel to each other and make a small angle with the normal of the lamella (Figure 3). A similar molecular

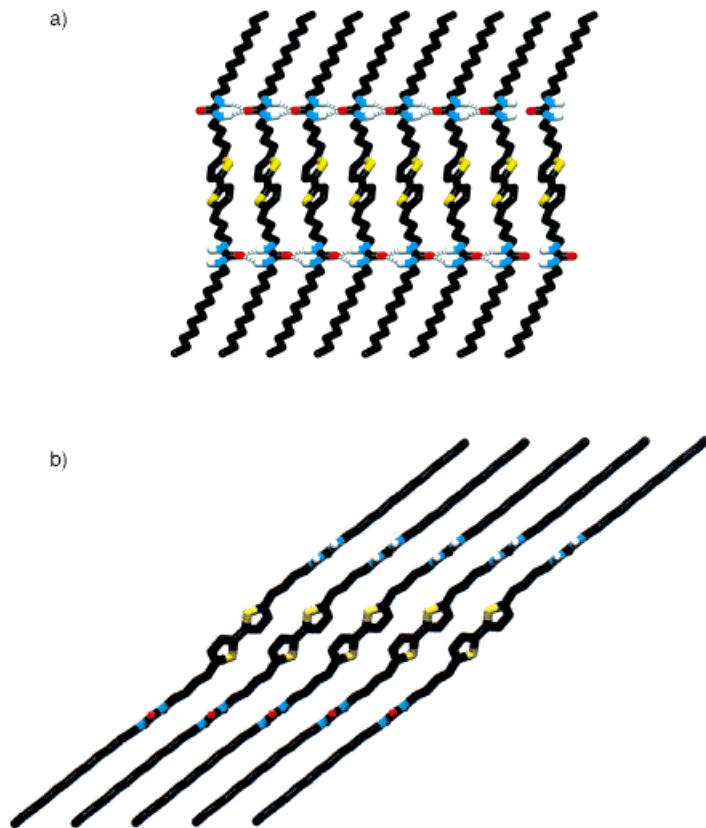
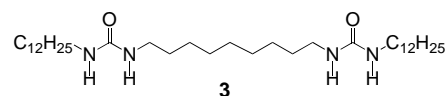


Figure 3. Possible arrangement of **2** in the lamella: a) view of a hydrogen-bonded ribbon, and b) a tilted stack of ribbons that form a lamella.

arrangement has been found for lamella formed by other linear bisurea compounds such as **3**.<sup>[9]</sup>



Interestingly, UV/Vis spectroscopic analysis of both compounds showed that the formation of fibers (as in 1,2-dichloroethane gels) is accompanied by a broadening and decrease in intensity of the  $\pi-\pi^*$  absorption bands relative to homogeneous 1,2-dichloroethane solutions of **1** and **2**. These spectral changes can be attributed to a strong exciton coupling between the thiophene chromophores.<sup>[12]</sup> Apparently, the thiophene moieties are present as  $\pi$ -stacked aggregates in fibers of **1** and **2**. A blue shift of the  $\pi-\pi^*$  absorption maximum occurred from 319 nm for a solution of the bithiophene compound **2** in 1,2-dichloroethane to 310 nm for a gel of **2**, which is characteristic of the formation of *H*-aggregates.<sup>[12, 13]</sup> No shift of the  $\pi-\pi^*$  absorption maximum

has been observed in the case of compound **1** upon formation of the fibers. This points to an oblique arrangement of the monothiophene moieties in the fibers, but it should be noted that for monothiophenes the shifts of the absorption maxima as a result of exciton coupling are expected to be smaller because of the lower oscillator strength.<sup>[14]</sup>

Molecular modeling studies were used to explore the possible arrangements of **1** and **2** in the fibers. A systematic search following the cluster approach of Gavezotti<sup>[15, 16]</sup> yielded a number of stable lamellar structures within an energy range of 10 kcal mol<sup>-1</sup>. These calculated polymorphs have a common structure in that the lamella have a sandwich structure, in which the central layer of each lamella is formed by the thiophene moieties and is flanked on both sides by layers that consist of the urea groups and the hydrocarbon chains of the compounds, respectively (Figure 3). Furthermore, it was found that both urea groups form hydrogen bonds with urea groups of neighboring molecules, and thereby participate in the formation of infinite chains of hydrogen-bonded urea moieties. The average repeat distance along the direction of the hydrogen-bonded chains is 4.5 Å, which is in good agreement with the average value of 4.6 Å found for crystal structures of urea compounds.<sup>[8, 9]</sup> The clearest resemblance between the possible polymorphs is seen within the central aromatic layer where the bithiophene moieties adopt a closely packed arrangement with a face to face stacking of the thiophene moieties along the same direction as the infinite hydrogen-bonded chains. In Figure 3 one of the possible lamellar arrangements of **2** is shown, of which the thickness of 39 Å is very close to the experimentally determined spacing of 41.2 Å. In this arrangement the bithiophene moieties are cofacially stacked with an interplanar distance of 3 Å, and are displaced by 0.4 and 3.5 Å along the long and short molecular axis, respectively. Since the transition moment of the  $\pi$ - $\pi^*$  transition for bithiophenes coincides with the long molecular axis,<sup>[14]</sup> the structure shown in Figure 3 represents an *H*-aggregate, and is in excellent agreement with the experimental data presented. It should be stressed that other lamellar arrangements are also in reasonable agreement with the experimental data.

The presence of extended aggregates of  $\pi$ -stacked thiophene moieties in self-assembled fibers of **1** and **2** should provide an efficient path for charge-carrier transport within the fibers. The conductive properties of **1** and **2** were therefore studied with the pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) technique.<sup>[17]</sup> Solid-state powder samples (20–200 mg) of the materials were irradiated with 3-MeV electrons (2–20 ns pulses) from a Van de Graaff accelerator, which resulted in the creation of uniformly distributed pairs of electron-hole in low concentration in the sample. If the charge carriers formed are mobile, the conductivity of the sample will increase, which is monitored as a change in the microwave power that is reflected by the cell containing the sample. In this way, no electrode contacts are required, polarization of the sample is absent because of the ultra-high frequencies used (26.5–38 GHz), and the time scale of the observations is very short. This implies that effects arising from domain boundaries and impurities are minimized, since the charge carriers only move across short

distances within the materials while being probed. Thus the end-of-pulse conductivity can be considered to represent the maximum value obtainable with a charge-transport device with a monodomain between the electrodes. As a consequence of the fact that a fraction of the electron-hole pairs recombines during the ionization pulse and does not contribute to the observed conductivity, the PR-TRMC technique in fact provides a lower limit for this value. From frequency-dependent conductivity measurements in the range of 28 to 38 GHz the dose-normalized end-of-pulse conductivity  $\Delta\sigma/D$  is obtained, and the lower limits of  $\Sigma\mu_{\min}$  (the sum of the mobilities of the positive and negative charge carrier) are derived from the relationship  $\Sigma\mu_{\min} = E_p(\Delta\sigma/D)$ , where  $E_p$  is the average electron-hole pair formation energy.

Figure 4 shows the result of the PR-TRMC experiments on virgin samples of **1** and **2**. For comparison the results obtained for linear bisurea compound **3**, which contains only alkyl chains and urea groups, are also included. A very low

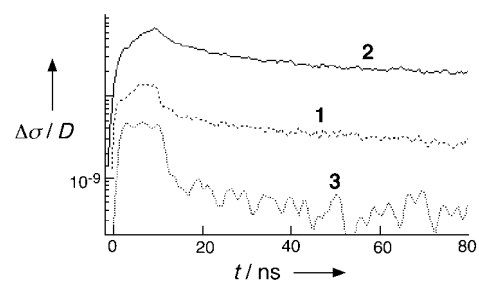


Figure 4. Radiation-induced conductivity transients of the three bisurea compounds **1**–**3**, as obtained with the PR-TRMC technique (10 ns pulse length, microwave frequency = 34 GHz). The dose-normalized conductivity ( $\Delta\sigma/D$ ) is in  $\text{Sm}^2\text{J}^{-1}$ .

conductivity signal close to the detection limit of the system is observed for **3**, which indicates that the charge carriers have a very low mobility. Note that the initial part of the signal (during the 10 ns excitation pulse) is mainly a result of the presence of remnant air in the sample. The remaining transient observed after the pulse, which decays within 20 ns to the noise level, might be attributed to a conductivity change of  $\Delta\sigma/D = 9 \times 10^{-10} \text{ Sm}^2\text{J}^{-1}$  at most, which corresponds to  $\Sigma\mu_{\min} < 2 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  for **3**. In contrast, the conductivity signal of **1** ( $\Delta\sigma/D = 8 \times 10^{-9} \text{ Sm}^2\text{J}^{-1}$ ) is dramatically higher than that of **3** and is relatively long-lived, which shows that the introduction of a thiophene unit in the bisurea compound leads to the occurrence of efficient charge-transport pathways ( $\Sigma\mu_{\min} = (1 \pm 0.2) \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  for **1**). Interestingly, the signal of **2** shows a substantial increase in the conductivity ( $\Delta\sigma/D = 4 \times 10^{-8} \text{ Sm}^2\text{J}^{-1}$ ) relative to **1**, which might be attributed to the much better  $\pi$  overlap that is achieved between neighboring molecules as a consequence of the presence of two central thiophene units. The mobility value of **2** ( $\Sigma\mu_{\min} = (5 \pm 0.2) \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) is in fact much higher than that of a cyclohexyl end-capped bithiophene oligomer ( $\Sigma\mu_{\min} = 4 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) studied before with the PR-TRMC technique<sup>[18]</sup> and also higher than that of unsubstituted quaterthiophene mentioned in the same study ( $\Sigma\mu_{\min} < 1 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ). Thus, the solid-state ordering achieved by

the bisurea moieties in **2** results in a clearly increased mobility relative to these two small oligothiophenes. Earlier PR-TRMC experiments on the conductivity of various alkyl-substituted polythiophenes<sup>[9]</sup> yielded a mobility  $\Sigma\mu_{\min} = 7 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , irrespective of the length of the alkyl side chain. Remarkably, the value of **2** is already close to that of the polymers, although the former contains only two conjugated thiophene units!

Fibers of linear bisurea compounds have a common feature in that they have excellent thermal stability, because of the presence of infinite chains of hydrogen bonded urea groups. The high thermal stability of fibers of **1** and **2** is reflected by their melting temperatures of 143 °C and 177 °C, respectively. Above these temperatures the compounds slowly decompose. Temperature-dependent conductivity measurements for both compounds showed that up to their melting points no large changes in conductivity occurred. Thus, the degree of organization achieved by the intermolecular hydrogen bonding is maintained over a large temperature range.

In conclusion, the mobilities measured for the bisurea thiophenes when compared to (oligo)thiophenes and especially the lower members, are remarkably high, especially when one takes into consideration that only a small fraction of the volume of the material consists of the aromatic thiophene part, with the larger volume fraction being occupied by insulating alkyl chains. For this reason, the high charge mobility in these materials must arise from the well-defined arrangement of the thiophene moieties in closely packed layers within the material. The molecules presented in this study are forced to adopt this arrangement as a result of the presence of the urea groups, which results in a close packing of the thiophenes and hence an efficient pathway for charge transport. Therefore, these thiophenes modified with bisurea units, with the capability for self-organization through hydrogen bonding, are promising candidates for inclusion in charge-transport devices based on organic semi-conducting layers. Research in this direction is in progress.

### Experimental Section

The synthesis and properties of compound **3** can be found in ref. [9].

**2,5-Di(4-chlorobutyl)thiophene (4):** A solution of 2.5 M *n*-BuLi in hexanes (104 mL, 260 mmol) was added to a solution of thiophene (10.15 g, 121 mmol) in THF (150 mL), followed by the addition of 1-bromo-4-chlorobutane (42.8 g, 250 mmol). The initial rise in temperature of the reaction mixture was controlled by means of a cold water bath, and then the mixture was stirred overnight at 40–50 °C. After aqueous work-up and extraction of the product with diethyl ether, a dark brown residue was obtained, which was purified by column chromatography (basic Al<sub>2</sub>O<sub>3</sub>, activity I, pentane). A colorless liquid was obtained (30.5 g, 115 mmol, 95.0%). <sup>1</sup>H NMR: (200 MHz, CDCl<sub>3</sub>):  $\delta = 1.77\text{--}1.90$  (m, 8H), 2.81 (t, <sup>3</sup>J(H,H) = 6.8 Hz, 4H), 3.57 (t, <sup>3</sup>J(H,H) = 3.7 Hz, 4H), 6.60 (s, 2H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta = 28.7, 29.2, 31.7, 44.7, 123.8, 142.4$ ; MS:  $m/z$ : 264 [M<sup>+</sup>].

**2,5-Di(4-azidobutyl)thiophene (5):** Compound **4** (12.28 g, 46.3 mmol) was added to a suspension of NaN<sub>3</sub> (8.26 g, 127 mmol) in DMSO (100 mL) and then the temperature raised to 50 °C. The mixture was then stirred overnight. After aqueous work-up and extraction of the product with diethyl ether a yellowish liquid was obtained, which was purified by column chromatography (basic Al<sub>2</sub>O<sub>3</sub>, activity I, pentane/CH<sub>2</sub>Cl<sub>2</sub> 9/1) to yield a colorless liquid (12.78 g, 45.9 mmol, 99%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.41\text{--}1.50$  (m, 4H), 1.58–1.65 (m, 4H), 2.66 (t, <sup>3</sup>J(H,H) = 7.0 Hz, 4H),

2.71 (t, <sup>3</sup>J(H,H) = 7.5 Hz, 4H), 6.51 (s, 2H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta = 28.8, 29.8, 33.0, 41.8, 123.3, 142.7$ ; MS:  $m/z$ : 278 [M<sup>+</sup>].

**2,5-Di(4-aminobutyl)thiophene (6):** 10% Pd/C (120 mg) was added to a solution of **5** (12.08 g, 43.4 mmol) in ethanol (150 mL). A balloon filled with hydrogen gas was mounted on top of the flask and the mixture was stirred vigorously at room temperature. Analysis of the mixture by <sup>1</sup>H NMR spectroscopy showed that the reaction was complete after almost 5 h. The catalyst was filtered off and the solvent removed in vacuo to yield a colorless liquid (9.82 g, 43.4 mmol, 100%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.41\text{--}1.50$  (m, 4H), 1.58–1.65 (m, 4H), 2.66 (t, <sup>3</sup>J(H,H) = 7.0 Hz, 4H), 2.71 (t, <sup>3</sup>J(H,H) = 7.5 Hz, 4H), 6.51 (s, 2H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta = 28.8, 29.8, 33.0, 41.8, 123.3, 142.7$ ; MS:  $m/z$ : 226 [M<sup>+</sup>].

**2,5-Di(4-(3-dodecyl-ureido)butyl)thiophene (1):** A solution of dodecylisocyanate (1.89 g, 8.95 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added to a solution of **6** (0.98 g, 4.33 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The resulting mixture was stirred for three hours, during which period a white precipitate formed. The solvent was removed in vacuo to yield an off-white solid. This solid was dissolved in refluxing toluene/propanol (9/1), and then cooled down to room temperature and filtered under suction. This procedure was repeated three times, after which the product was obtained as a white powder (1.88 g, 2.90 mmol, 67%). M.p. 143 °C (decomp.); <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]DMSO):  $\delta = 0.88$  (t, <sup>3</sup>J(H,H) = 6.6 Hz, 6H), 1.28 (brs, H), 1.37–1.51 (m, H), 1.57–1.66 (m, H), 2.73 (t, <sup>3</sup>J(H,H) = 7.3 Hz, 4H), 3.01 (m, 8H), 5.45 (brs, 4H), 6.59 (s, 2H); elemental analysis: calcd: C 70.3, H 11.2, N 8.6, S 4.9%; found: C 70.0, H 11.1, N 8.6, S 4.9; IR (nujol):  $\tilde{\nu} = 3322$  (NH), 1620 (amide I), 1574 (amide II) cm<sup>-1</sup>; UV/Vis (1,2-dichloroethane, 80 °C):  $\lambda_{\max}(\epsilon) = 242$  (6850) nm.

**5,5'-Di(4-chlorobutyl)-2,2'-bithiophene (7):** This compound was synthesized as described for **4**, starting from 2,2'-bithiophene. After purification by column chromatography (basic Al<sub>2</sub>O<sub>3</sub>, activity I, pentane/CH<sub>2</sub>Cl<sub>2</sub> 7/1) a slightly yellow solid was obtained in 93% yield; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.81\text{--}1.90$  (m, 8H), 2.84 (t, <sup>3</sup>J(H,H) = 6.8 Hz, 4H), 3.56 (t, <sup>3</sup>J(H,H) = 3.7 Hz, 4H), 6.68 (d, <sup>3</sup>J(H,H) = 3.7 Hz, 2H), 6.92 (d, <sup>3</sup>J(H,H) = 3.7 Hz, 2H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta = 28.7, 29.3, 31.8, 44.7, 122.8, 125.0, 135.5, 143.5$ ; MS:  $m/z$ : 346 [M<sup>+</sup>].

**5,5'-Di(4-azidobutyl)-2,2'-bithiophene (8):** This compound was synthesized as described for **5**, starting from **7**. After purification by column chromatography (basic Al<sub>2</sub>O<sub>3</sub>, activity I, pentane/CH<sub>2</sub>Cl<sub>2</sub> 7/1) a slightly yellow solid was obtained in 98% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.66\text{--}1.81$  (m, 8H), 2.84 (t, <sup>3</sup>J(H,H) = 7.1 Hz, 4H), 3.31 (t, <sup>3</sup>J(H,H) = 6.6 Hz, 4H), 6.69 (d, <sup>3</sup>J(H,H) = 3.7 Hz, 2H), 6.93 (d, <sup>3</sup>J(H,H) = 3.7 Hz, 2H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta = 28.1, 28.5, 29.5, 51.0, 122.7, 124.9, 135.4, 143.4$ ; MS:  $m/z$ : 360 [M<sup>+</sup>].

**5,5'-Di(4-aminobutyl)-2,2'-bithiophene (9):** This compound was synthesized as described for **6**, starting from **8**. Compound **9** was obtained as a colorless liquid that solidified on standing (yield 100%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.48\text{--}1.58$  (m, 4H), 1.64–1.76 (m, 4H), 2.73 (t, <sup>3</sup>J(H,H) = 7.0 Hz, 4H), 2.80 (t, <sup>3</sup>J(H,H) = 7.3 Hz, 4H), 6.66 (d, <sup>3</sup>J(H,H) = 3.6 Hz, 2H), 6.89 (d, <sup>3</sup>J(H,H) = 3.6 Hz, 2H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta = 28.7, 29.8, 33.1, 41.8, 122.7, 124.9, 135.4, 143.4$ ; MS:  $m/z$ : 308 [M<sup>+</sup>].

**5,5'-Di(4-(3-dodecylureido)butyl)-2,2'-bithiophene (2):** This compound was synthesized as described for **1**, starting from **9**. M.p. 177 °C (decomp.); <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]DMSO):  $\delta = 0.88$  (t, <sup>3</sup>J(H,H) = 6.6 Hz, 6H), 1.28 (brs, H), 1.37–1.42 (m, 4H), 1.45–1.54 (m, 4H), 1.61–1.69 (m, 4H), 2.79 (t, <sup>3</sup>J(H,H) = 7.3 Hz, 4H), 2.97–3.09 (m, 8H), 5.38 (brs, 2H), 5.44 (brs, 2H), 6.73 (d, <sup>3</sup>J(H,H) = 3.6 Hz, 2H), 6.94 (d, <sup>3</sup>J(H,H) = 3.6 Hz, 2H); elemental analysis: calcd: C 69.0, H 10.2, N 7.7, S 8.8; found: C 68.5, H 10.3, N 7.6, S 8.7; IR (nujol)  $\tilde{\nu} = 3352, 3324$  (NH), 1616 (amide I), 1572 (amide II) cm<sup>-1</sup>; UV/Vis (1,2-dichloroethane, 80 °C):  $\lambda_{\max}(\epsilon) = 319$  (12300) nm.

**Gelation experiments:** The gelation experiments and characterization of the gels and solid fibers by DSC, light and electron microscopy, and X-ray powder diffraction have been carried out as described before for other bisurea compounds.<sup>[9]</sup> A gel of **1** (3 mm) or **2** (2.5 mm) in 1,2-dichloroethane was prepared in a 1 mm quartz cell for UV/Vis measurements. UV/Vis spectra were recorded at temperatures ranging from 20 °C to 80 °C at 10 °C intervals.

**Molecular modeling:** Calculations were done using the Charmm molecular mechanics package<sup>[16]</sup> and QUANTA96, distributed by Molecular Simulations Incorporated. Preliminary calculations were done in the gas phase

with a dielectric constant of 1 and with a nonbonded cut-off range of 15 Å, with a switch function operating from 11 to 14 Å. For the final energy minimization the Ewald summation with a cut-off of 20 Å for nonbonding interactions was used. Electrostatic point charges were taken from templates provided by QUANTA. For the generation of a systematic search a charmm script was written, which is an implementation of the cluster search method of Gavezotti<sup>[15]</sup> but limited to translational symmetry operations. Each search started with a different conformation of the bisurea compound, and gave 5–10 trial structures. These trial structures were then energy minimized to an energy gradient of 0.00005.

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## Fast Experiments for Charge-Density Determination: Topological Analysis and Electrostatic Potential of the Amino Acids L-Asn, DL-Glu, DL-Ser, and L-Thr\*\*

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X-ray diffraction experiments not only give atomic positions from which the geometry of a chemical structure can be determined, but the exact charge density distribution  $\rho(\mathbf{r})$  can also be deduced,<sup>[1]</sup> which is an observable in contrast to the wave-function in the Schrödinger equation. To accomplish this the experiment has to be carried out up to high resolution ( $d \leq 0.5 \text{ \AA}$  or  $\sin\theta \lambda^{-1} \geq 1.0 \text{ \AA}^{-1}$ ) and at the lowest temperature possible. With conventional diffractometers and serial (scintillation) detection this required measurement periods of several weeks or even months, even for structures of moderate size (20–30 atoms), so that the method, although known since the 1960s,<sup>[2]</sup> was hardly applied and led only to more qualitative results. In the meantime several developments have changed the situation drastically.

By means of Bader's theory of "atoms in molecules", which was developed on a quantum chemical basis, a topological analysis of  $\rho(\mathbf{r})$  allows a well-defined partitioning of a chemical structure into sub-molecular regions (atoms or functional groups).<sup>[3]</sup> This initiated the generation of appro-

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