$[Yb_2(H_2O)_5(\alpha\text{-}AsW_9O_{33})_2]^{12-}$ ion, where the Yb^{3+} ion is seven-coordinate, being bound by two two-coordinate O atoms from each $[\alpha\text{-}AsW_9O_{33}]^{9-}$ ligand and five (including one Yb–O–Yb bridging) water molecules. Single-crystal X-ray analysis is in progress. For $Na_{12}[Yb_2(H_2O)_6(\alpha\text{-}AsW_9O_{33})_2]\cdot m\,H_2O$ IR (KBr disk): $\tilde{\nu} = 938$ (m), 887 (s), 788 (m), 724 cm^{-1} (s).

[13] C. Tourné, A. Revel, G. Tourné, M. Vendrell, *C. R. Seances Acad. Sci. Ser. C* **1973**, *277*, 643. IR (KBr disk): $\tilde{\nu} = 931$ (m), 903 (s), 781 (s), 725 cm^{-1} (s).

[14] The existence of a broad asymmetric peak (at 579.4 and 580.3 nm with approximately 1:4 intensity ratio) for the $^5D_0 \rightarrow {}^7F_0$ transition in the 77 K photoluminescence spectrum (under the exposure to the 396 nm light corresponding to the $^7F_0 \rightarrow {}^5L_6$ transition) of solid **1** indicated the existence of at least two different sites (with approximate occupancy ratio of 1:4) for the Eu^{3+} luminescence. This supports the disorder (with 5/6 occupancy) for the K4 atom which is coordinated by water O atoms (O34 and O35) for $[Eu(H_2O)_2]^{3+}$, since the $^5D_0 \rightarrow {}^7F_0$ transition at about 580 nm cannot be split by any crystal field, see Supporting Information.

[15] Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-391197 **1** and CSD-391198 **2**.

Conducting Polymers

Facile Solid-State Synthesis of Highly Conducting Poly(ethylenedioxythiophene)**

*Hong Meng, Dmitrii F. Perepichka, and Fred Wudl**

Conducting polymers continue to be a rapidly expanding, significant research area, attracting scientists from different disciplines.[1–3] Though synthesis has had a major role, a large effort has been focused on materials processing in organic electronics. Thin-film organic electronic devices such as light-emitting diodes, field effect transistors, solar cells, high-storage capacitors, and various other types of semiconductor devices have been widely investigated.[4–6] Efforts have also been directed toward developing new processing techniques and exploring new materials with a higher degree of molecular order.[2,7] However, the existence of very few single-crystalline polymers and the defects associated with the usual synthetic methods constitute a serious problem for the in-depth investigation of molecular order in conducting polymers.[8]

In general, it is not possible to obtain well-defined polymer structures unless the conducting polymers can be synthesized by endogenous polymerization routes, that is, without addition of initiators or catalysts. A possible solution for this problem lies in the solid-state polymerization of a structurally pre-organized crystalline monomer. The idea of solid-state polymerization of a suitable monomer in a well-ordered crystalline state was already realized in the 1960s and 1970s with polydiacetylenes and $(SN)_x$.[9–11] However, there were no reports on the solid-state synthesis of the most widely investigated conducting polymers—the polythiophenes. The importance of this goal is emphasized by the high potential of polythiophenes for industrial applications, as compared to other conducting polymers.[12] For example, the synthesis of poly(3,4-ethylenedioxythiophene), one of the most successful conducting polymers used in industry, is still confined to chemical or electrochemical oxidation of monomer solutions.[13] As a consequence, defect sites and a relatively low degree of intermolecular order limit the number of possible applications.

On the other hand, solid-state polymerization could give rise to a nearly defect-free, highly ordered or even “single-crystalline” conjugated polymer. With this in mind, while our discovery fall short of the mark regarding high degree of order, we report the first solid-state synthesis of conducting PEDOT by facile polymerization of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) in the solid state.

The monomer DBEDOT[14] is a white, crystalline solid, melting at 96 °C and very soluble in all common organic solvents. Its solutions in solvents such as tetrahydrofuran, hexane, xylene, chloroform, ethanol, acetone, dimethylformamide, 1,4-dioxane, and 1,2-dichlorobenzene are very stable, even on heating to reflux. However, prolonged storage of DBEDOT in the solid state at room temperature results in transformation of the sample to blue-black “crystals” or “fibers” with metallic luster, while retaining the morphology of the starting material (Figure 1). To our surprise, the blue-

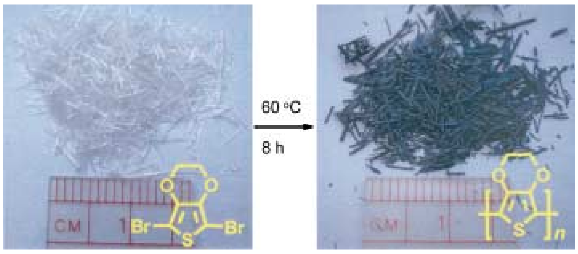

Figure 1. Photographs of crystals of DBEDOT (left) and PEDOT (right), formed on heating the crystals of the monomer at 60 °C for 8 h.

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black solid showed high conductivity, and its elemental analysis revealed that a clean polymerization reaction affording PEDOT took place (see below).

The reaction is dramatically accelerated on heating (Table 1) and is not affected by air, vacuum, or light; it can even be performed in hot water, and occurs only in the solid state. The resulting bromine-doped polymer[15] is infusible and insoluble in organic solvents and exhibits conductivity in the range of 20–80 S cm^{-1} ("crystals") and 16–30 S cm^{-1} (compressed pellets, as determined by the four-probe method), higher than that of conventional, commercial material (e.g., $FeCl_3$-synthesized PEDOT, Table 1). The conductivity showed a slight temperature dependence, with no semiconductor–metal transition down to 20 K.[16] The "as-formed" doped polymer was dried in vacuum (0.1 Torr) at 150 °C and treated with 50 % hydrazine monohydrate in acetonitrile to afford a brown, dedoped polymer (which is also insoluble in organic solvents) possessing a much lower conductivity ($<10^{-4}$ S cm^{-1}). Re-doping with iodine vapor restored the conductivity to essentially the original level (~20 S cm^{-1}).

Table 1: Conductivity σ_{rt} [S cm^{-1}] of PEDOT samples measured at room temperature.

	SSP PEDOT				$FeCl_3$-PEDOT
Temperature [°C]	ca. 20	60	80	120	0–5
Reaction time	2 years[a]	24 h	4 h	24 h	24 h
"crystals"/"fibers"	80	33	20	–	–
pellets as synthesized	30	18	16	0.1	–
pellets after I_2-doping	53	30	27	5.8	7.6
thin films	–	23	–	–	–
thin films after I_2-doping	–	48	–	–	–

[a] The monomer was stored in a closed jar for 2 years at room temperature (~20 °C).

The composition of the blue-black solid was determined by elemental analysis after vacuum drying at ambient temperature. The analysis corresponds to an empirical formula of $C_6H_4Br_{1.2}O_2S$, which suggests two Br_3^- anions and, therefore, a bipolaron per every five thiophene units.[17] Hydrazine treatment (as above) results in the almost complete removal of bromine (0.4 % Br by elemental analysis).

A powdered, dedoped sample of polymerized DBEDOT was characterized by solid-state ^{13}C NMR and FT-IR spectroscopies. The comparison of the spectra of solid-state polymerized (SSP) material with a PEDOT sample prepared by traditional $FeCl_3$ oxidation of EDOT,[13] clearly demonstrates an essentially identical structure for both materials (Figure 2). The absence of a signal at $\delta = 84.6$ ppm, characteristic for CBr (as observed for DBEDOT), and the presence of a resonance at $\delta = 108.8$ ppm, typical of C–C bonds formed at the C-2 atoms of the thiophene rings, confirm the structure.

The conductivity of polymers prepared at different temperatures is listed in Table 1. The polymers synthesized at lower temperatures show a higher conductivity, which may reflect a higher degree of order in the polymerization for these conditions. Indeed, the highest conductivity was found for the SSP sample polymerized at room temperature; however, a very long reaction time from months to about 2 years was required. On the other hand, heating above the melting point of the monomer significantly inhibits the reaction and results in dramatically reduced conductivities (0.1 S cm^{-1}).

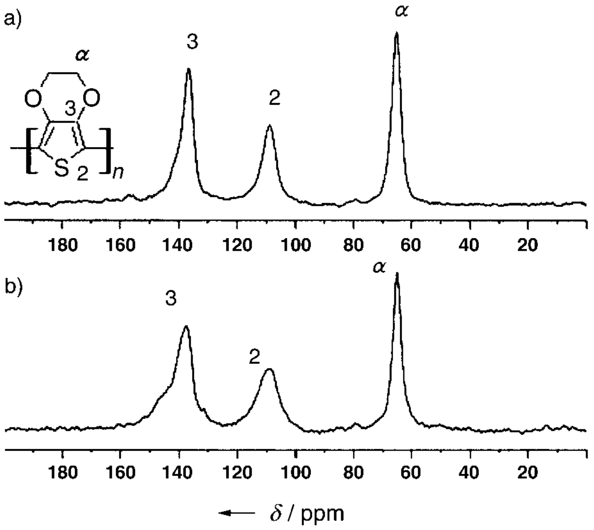

Figure 2. Solid-state ^{13}C NMR CP-MAS spectra of PEDOT prepared by a) solid-state polymerization of DBEDOT at 60 °C and b) oxidative polymerization of EDOT in solution with $FeCl_3$, after dedoping with hydrazine monohydrate in acetonitrile solution (50 %).

This observation implies that some aspects of the crystal structure may be responsible for the polymerization.[10] Figure 3 shows a crystal packing diagram of DBEDOT. Though the reaction cannot be topotactic since bromine is liberated, it does take advantage of the solid-state packing. Particularly, a short intermolecular Br–Br distance of 3.45 Å [vs the sum of van der Waals (vdW) radii of 3.9 Å] favors solid-state polymerization through the expulsion of molecular bromine and concomitant C–C bond formation at the 2- and 5-positions of the thiophene rings.[18] The molecular bromine, being a strong oxidant, dopes the formed polythiophene, providing a driving force for this unusual coupling reaction. Although the exact mechanism of the polymerization is not clear, there is a growth and decay of a free-radical species as a function of time, determined by ESR spectroscopy.[15,16] However, there is also an induction period which is ESR silent, leading us to believe that the ESR signal may not be associated with the polymerization but due to the formation of polarons in the polymer.

The approach described here offers a unique opportunity for the preparation of highly conductive, relatively well-ordered polymer films on an insulating support, which, in principle, can be utilized in the fabrication of all-organic LEDs.[5] High-vacuum (~10^{-4}–10^{-5} mbar) sublimation of DBEDOT with gentle heating of the substrate results in in-situ deposition of transparent, dark green to blue, uniform PEDOT films onto glass slides or a poly(ethyleneterephthalate) substrate (Figure 4). The average surface resistance of the films on a glass slide (average film thickness 2700 Å) is $2.1 \times 10^3\ \Omega\square^{-1}$ ($\square = 1$ cm^2) and on a plastic substrate (average film thickness 1300 Å) $3.6 \times 10^3\ \Omega\square^{-1}$. The conductivity reaches 20 S cm^{-1} and can be increased by almost a factor of 2 on further doping with iodine vapor. The very low value of

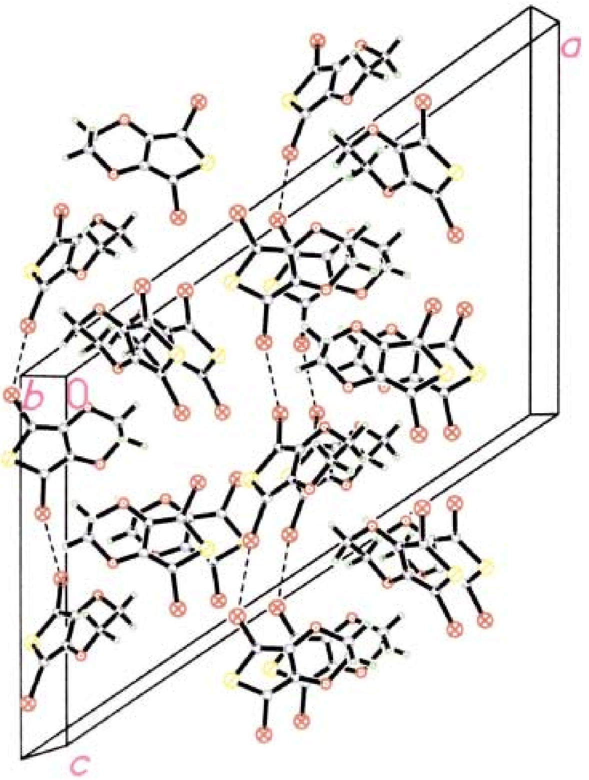

Figure 3. View of the X-ray crystallographically determined (monoclinic) structure of monomer DBEDOT: (⊗) bromine, (○) carbon, (○) hydrogen, (⊘) sulfur, (-----) short contacts between neighboring bromine atoms. The unit cell parameters are: $a = 25.27$, $b = 5.01$, $c = 15.67$ Å, $\alpha = 90$, $\beta = 123.96$, $\gamma = 90°$.

Figure 4. Photographs of transparent conducting films made by in-situ sublimation solid-state polymerization onto a plastic substrate (top) and a glass slide (bottom).

the surface resistance of the present thin films is comparable with that of recently reported films of PEDOT processed with glycerol or sorbitol (surface resistance: $\sim 10^3\ \Omega\square^{-1}$, conductivity: $\sim 10\ \mathrm{S\,cm^{-1}}$).[19]

Figure 5 shows the UV-Vis spectra of the PEDOT films "as formed" and after "dedoping" (incomplete, note broad band at 1800 nm). The onset absorption at ca. 750 nm corresponds to an optical bandgap of 1.65 eV. This value is in the range of values reported for PEDOT samples synthesized by other methods (1.6–1.7 eV).[13]

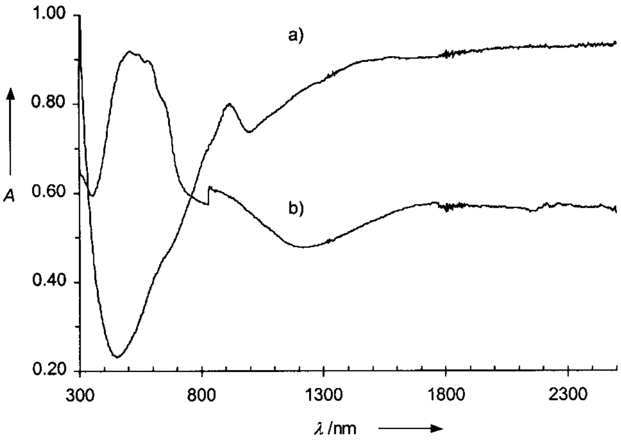

Figure 5. UV-Vis-NIR spectra of polymer films on glass slide substrates: a) "as-formed" on sublimation, b) after dedoping with hydrazine monohydrate in acetonitrile (50%).

The cyclic voltammogram (CV) of the as-prepared film on a platinum plate (Figure 6) shows an oxidation peak (*p* doping) at +0.07 V vs Ag/Ag$^+$, and the corresponding dedoping peak at −0.62 V. The film is very stable to repeated scanning from −1.0 to +0.2 V (less than 1% drop in current on 50 scans, without special precautions such as inert atmosphere). The bandgap determined from the onset of E^{pa} and E^{pc} potentials is 1.65 eV, in full agreement with the optical bandgap value.

In conclusion, we described an unprecedented catalyst-free coupling reaction of heteroaromatic halides, which provides a facile synthesis of highly conducting poly(ethylenedioxythiophene)s through solid-state polymerization of a substituted dibromothiophene derivative. This method allows fabrication of conducting films, which may be utilized in a variety of electronic devices. Although there are many challenges ahead, the present example of solid-state polymerization can be regarded as an important step towards the synthesis of a higher quality, solid-state polymerized conducting polythiophene derivative. Research directed to achieve a higher degree of order in the condensed state of conducting polymers using this strategy is in progress in our group.

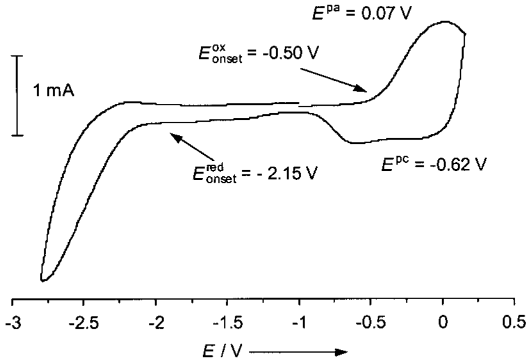

Figure 6. CV of a solid-state polymerized thin film deposited on a platinum plate. 0.1 M Bu_4NPF_6 in MeCN; scan rate 50 mV s^{-1}. Fc/Fc$^+$ shows + 0.14 V under these conditions.

Experimental Section

DBEDOT was obtained according to ref. [14] with 76% yield: m.p. 96 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 4.27$ ppm (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 139.6$, 85.4, 64.9 ppm; CP-MAS ^{13}C NMR (75 MHz, solid state, 25 °C, TMS): $\delta = 140.3$, 84.6, 65.1 ppm; MS (70 eV): m/z (%): 302 (55) [M^+], 300 (100), 298 (55); elemental analysis: found: C 23.79, H 1.28, Br 53.00, S 10.86; calcd for $C_6H_4Br_2O_2S$: C 24.02, H 1.34, Br 53.27, S 10.69.

PEDOT: In a typical experiment, DBEDOT (0.01–2 g) was incubated at 60 °C for 24 h and dried in vacuum (0.1 mbar) at room temperature to give black crystals of bromine-doped PEDOT; elemental analysis: found: C 28.87, H 1.65, Br 38.42, S 12.90; calcd for $C_6H_4Br_{1.2}O_2S(H_2O)_{0.6}$: C 28.01, H 3.50, Br 38.73, S 12.45.

The well-ground material was additionally dried in vacuum (0.1 mbar) at 150 °C overnight, then stirred with hydrazine hydrate (50% aqueous solution, in MeCN) overnight, filtered, and washed with neat MeCN. Vacuum drying afforded a nearly fully dedoped PEDOT; elemental analysis: found: C 46.84, H 2.42, N ~2, Br 0.42, S 19.04; calcd for $C_6H_4O_2Br_{0.01}S(NH_2NH_2{\cdot}3\,H_2O)_{0.12}$: C 47.63, H 3.44, N 2.22, Br 0.53, S 21.19. CP-MAS ^{13}C NMR (75 MHz, solid state, 25 °C, TMS): $\delta_c = 136.5$, 108.7, 64.9 ppm; IR (KBr): $\tilde{\nu} = 1650$, 1431, 1358, 1203, 1066, 984, 918, 832, 690 cm^{-1}.

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Asymmetric Michael Addition

Highly Enantioselective Organocatalytic Conjugate Addition of Malonates to Acyclic α,β-Unsaturated Enones**

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Even though the first reports of enantioselective organocatalysis by Wiechert et al. and Hajos and Parrish appeared almost three decades ago,[1] the field of asymmetric catalysis has been dominated by metal catalysis. It is only recently that asymmetric organocatalysis has received renewed attention and become the focus of intense research efforts.[2] This is primarily due to the operational simplicity, the cheap catalysts, and the obvious industrial applications.

Recently, a number of reports on organocatalytic transformations has appeared covering a wide range of reactions including Diels–Alder reactions,[3] aldol reactions,[4] Mannich

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