

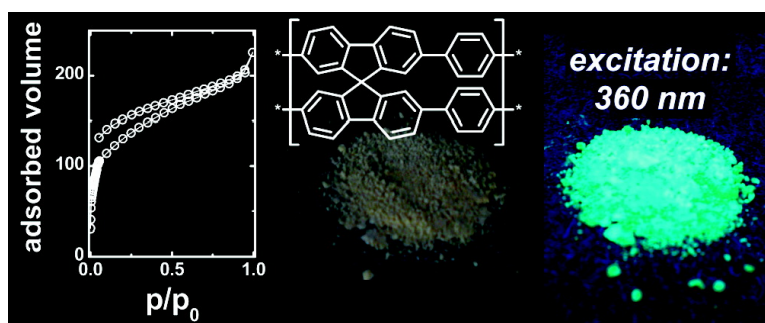
Communication

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Toward Stable Interfaces in Conjugated Polymers: Microporous Poly(*p*-phenylene) and Poly(phenyleneethynylene) Based on a Spirobifluorene Building Block

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Organic electronics is an important field of modern technology. Organic light emitting diodes (OLED) and organic solar cells are the most prominent among the various applications. Often, their performance relies on an intimate contact between a charge transport material and an optoelectronic active polymer.¹ Recent attempts toward the control of the morphology included blending, block copolymer approaches, solvent, and thermal annealing, as well as hard templating approaches.^{1–7}

Microporous materials have shown to be beneficial in a broad variety of both industrial and academic applications. However, the synthesis of purely organic, noncarbonaceous, microporous materials was up to now mainly restricted to hypercrosslinked polystyrenes.^{8,9} During the last years, a broader variety of microporous polymers (e.g., polybenzodioxanes,¹⁰ polyimides, and^{11,12} polyanilines¹³) and crystalline organic frameworks¹⁴ was introduced by various groups. Recently, also the first microporous conjugated polymers, that is, microporous poly(aryleneethynylene)s, were synthesized.¹⁵

Poly(*p*-phenylene)-type polymers are another class of conjugated polymers that have promising properties regarding their application as OLED material. It is known that blending of them with charge transport materials can enhance the electroluminescence efficiency if phase separation can be excluded.¹ A potential pathway is, therefore, the mixing of a microporous host material with dopants to form stable interpenetrating network (IPN).

Here we present the synthesis of microporous poly(*p*-phenylene)s based on the concept of intrinsic microporosity. These networks can be regarded as promising hosts for IPNs.

9,9'-Spirobifluorene (**1**) is a well-known monomer for the synthesis of materials for organic electronics,¹⁶ as well as for microporous polymers.^{11,12} It incorporates a 90° kink in every repeating unit, which prevents the otherwise stiff polymer chains from space efficient packing. Therefore, a very high, accessible free volume is obtained. Polymers based on this concept are, therefore, named polymers of intrinsic microporosity (PIM).^{10,17}

2,2',7,7'-Tetrabromo-9,9'-spirobifluorene (**2**), which is readily available from **1**,^{18,19} was used as the structure directing monomer in the synthesis of three different conjugated polymers. Figure 1 shows the chemical structure of the monomers as well as two 3D views of the spatial structure of **2**. The tetrahedral carbon atom directs the two fluorene moieties into a cross-like shape, giving rise to a contorted polymer structure.

Reaction of **2** with benzene-1,4-diboronic acid (**3**) in a mixture of *N,N*-dimethylformamide (DMF) and water (20 vol %) under the presence of palladium acetate, triphenyl phosphine, and sodium bicarbonate gave **P1**. Reaction of **2** with 4,4'-biphenyldiboronic acid (**4**) under the same conditions gave **P2**. The synthesis of **P1** and **P2** was performed under microwave heating. The microwave-

assisted synthesis turned out to be crucial for the successful quantitative and reproducible synthesis of the *p*-phenylene type networks.²⁰

P3 was synthesized in quantitative yield from **2** and 1,4-diethynylbenzene (**5**), employing known reaction conditions.¹⁵

The purified polymer networks were analyzed by means of IR spectroscopy, gas sorption, X-ray scattering, electron microscopy, and photoluminescence (PL) measurements.

Characterization of the networks by IR spectroscopy, elemental analysis, and energy dispersive X-ray spectroscopy (EDX) confirmed the chemical identity of the samples.

No palladium residues could be observed by EDX. If the electrooptic performance of such polymers would suffer from undetected Pd traces, known chemical methods for the removal of Pd should be applicable due to the microporosity of the polymers.²¹

The condensation reactions were not fully complete. Traces of bromine and oxygen, originating from unreacted end groups, were detected. This fact is not surprising, as a full condensation is not possible if the reaction is performed under kinetic control. Wide-angle X-ray scattering revealed the amorphous nature of the networks. Scanning electron microscopy showed that **P1** and **P2** are produced as small spheres (ca. 200 nm), which agglomerate and react to larger structures. **P3** shows a fiber-like structure on the micrometer scale.

The analysis of the networks by nitrogen sorption confirmed their microporous nature. Figure 1c shows the nitrogen sorption isotherms. For all polymers, a hysteresis is observed at low relative pressures. This feature is due to elastic deformations in the course of nitrogen sorption, that is, the networks are swelling.¹² Therefore, the networks can be regarded as soft matter in comparison to stiff, inorganic materials like zeolites. The hysteresis is largest for **P2**, indicating a lower degree of cross-linking. This is in accordance with the low surface area of **P2** (S_{BET} : 210 m² g⁻¹). **P1** and **P3** show a smaller hysteresis and can, therefore, be regarded as more rigid. (S_{BET} : 450 m² g⁻¹ and 510 m² g⁻¹, respectively.)

Although the microporous nature of the networks is confirmed by the steep uptake of nitrogen at very low relative pressures, it is not possible to determine reliable or comparable pore size distributions (PSD). The swelling effects are neither considered in state-of-the-art methods like nonlinear density functional theory nor in traditional methods like Horvath–Kawazoe, rendering these methods physically untrustworthy.²²

Specific surface areas of microporous polymers can also be determined by small-angle X-ray scattering (SAXS).¹² The measurements give specific surface areas of 1230 m² g⁻¹ (**P1**), 860 m² g⁻¹ (**P2**), and 1030 m² g⁻¹ (**P3**), respectively (see Supporting Information). The mismatch between the surface areas determined by different methods points to the presence of closed or nonaccessible porosity.

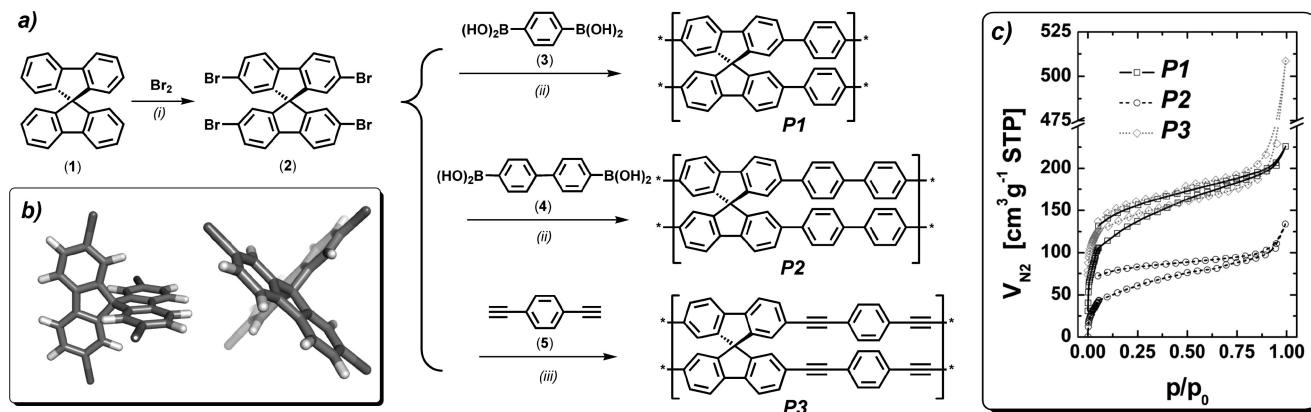


Figure 1. (a) Synthetic pathway towards the conjugated polymer networks **P1–P3**, (i) Br_2 , cat. FeCl_3 , CHCl_3 , room temperature, (ii) cat. $\text{Pd}(\text{OAc})_2$, PPh_3 , NaHCO_3 , DMF/water (4/1), μ -wave, $150\text{ }^\circ\text{C}$, (iii) cat. $\text{Pd}(\text{OAc})_2$, PPh_3 , CuI , $\text{toluene}/\text{Et}_3\text{N}$ (1/1), $80\text{ }^\circ\text{C}$; (b) two 3D views on the structure of 2,2',7,7'-tetrabromospirobifluorene (**2**); (c) nitrogen sorption isotherms of the networks **P1–P3**.

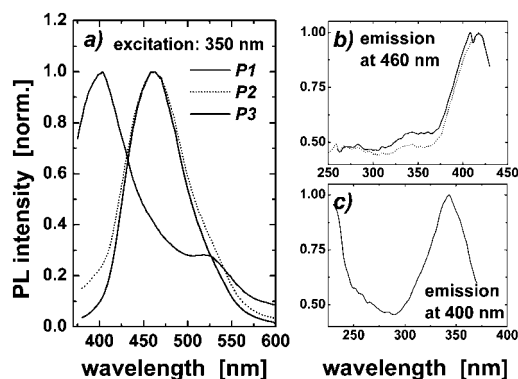


Figure 2. (a) PL spectra of **P1**, **P2**, and **P3** ($\lambda_{\text{excitation}}$: 350 nm); (b) excitation spectra of **P1** and **P2** ($\lambda_{\text{emission}}$: 460 nm); (c) excitation spectra of **P3** ($\lambda_{\text{emission}}$: 400 nm).

Figure 2 summarizes the optical properties of the materials. The photoluminescence (PL) emission spectra of **P1** and **P2** show a maximum at $\lambda = 460\text{ nm}$ (blue emission, Figure S3).

No secondary emission peak could be observed, indicating an effective prevention of aggregation. This in agreement with earlier experiments on spirobifluorene-based light-emitting materials.¹⁶

It is worth mentioning that there is nearly no influence of the comonomer on the optical properties. The correlation length in both polymers is therefore higher than the effective correlation length, indicating a rather high degree of condensation.

The PL spectrum of **P3** is dominated by a peak at 400 nm, originating from the spirobifluorene building block. A shoulder is observed at 525 nm, which is in accordance with spectra reported earlier.¹⁵

The band gaps of the polymers were estimated from the absorption edge. **P1** and **P2** have band gap energies of approximately 2.6–2.7 eV, while that of **P3** is approximately 3.1 eV. The emission properties of the materials did not change upon annealing at $150\text{ }^\circ\text{C}$ for some hours.

In conclusion, we have shown that conjugated polymers based on a spirobifluorene building unit possess microporosity, unifying two important concepts of material science in one material. This approach allows the introduction of a large, stable interface into materials with high potential for use in organic electronics. Current work is performed on the application of the concept on film forming materials, allowing the fabrication of advanced devices.

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Supporting Information Available: Synthetic procedures, analytical data, photographs, SAXS, and PSD analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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