CONFINED CONJUGATION FOR ADJUSTABLE OPTICAL PROPERTIES

M. Baumgarten,1,2 D. Caparros,1 T. Yüksel,1 S. Karabunarliev,1,2 W. Rettig3
1Max-Planck-Institute for polymer research, Ackermannweg 10, D-55128
Mainz, Germany; e-mail: baumgart@mpip-mainz.mpg.de
2Technical University, Bourgas, BG
3Humboldt University, Berlin, Germany

Introduction

Although many conjugated polymers are already available they most often are synthesized by very diverse methods. As a kind of construction set we used AB type building blocks to get simple access to fully conjugated polymers enabling control of conjugation in extended \( \pi \)-systems by changes in topology and geometry.1 Thereby meta-phenylene or bianthrylene bridging of intermediate \( \pi \)-systems as stilbenes or terthiophenes has been used so far given in Scheme 1.2,3 While 1 can be seen as prototype of a polaronic ferromagnet upon charging. Its absorption and fluorescence is independent of the number of repeat units and color tuning is easily available varying the size of the intermediate \( \pi \)-chromophore.

Scheme 1: \( \pi \)-conjugated polymers with well defined conjugation length by bridging different \( \pi \)-subunits through meta-phenylene 1 and bianthrylene 2, and their para-phenylene 3 connection for comparison.

Results and Discussion

Towards soluble meta-terphenylenevinlenes we used the alkylated 1,3-dibromobenzene 5 and coupled it with the 4,4’-diboronacid-stilbene 6 (Scheme 2). Although the degree of polymerization differed depending on the solubility enhancing alkyl-substituents, virtually no difference in the optical spectra of the polymers 1a-c could be obtained in solution. But upon spin coating on quartz an increased Stokes shift was detected, indicating some aggregation, although the fluorescence maximum (461 nm) still appeared in the blue spectral region (Figure 1).

In order to diminish aggregation and to enhance the solubility further substituted stilbenes were prepared by McMurry reaction of the ketone precursors. Here the cis/trans ratio sensitively depends on the catalyst used, starting with TiCl\(_3\)/DME nearly pure cis-isomers (>90%) were obtained for 4,4’-dibromo-7,7’-dialkyl-stilbenes 7a,b as evidenced also by Raman spectroscopy. Therefore, the absorption spectra of the polymers are hypsochromically shifted (260 nm for 1d and 330 nm for 1e on quartz), while the fluorescence appears in the same spectral range, stemming from the trans-isomers (450 nm for 1d and 490 nm for 1e on quartz), which act as an energetic sink. Especially for 1e no further Stokes shift appears when comparing fluorescence in solution and from film.

Scheme 2. Preparation of polymers 1a-c by Suzuki coupling

Figure 1. fluorescence excitation spectra of 1c.

Scheme 3. Alkyl- and alkylphenyl-substituted poly-meta-terphenylenevinlenes 1d,e poly-para-terphenylenevinylene 1f and poly-meta-phenyl-terthiophenes 1g.

In order to verify the topological approach by meta-phenylene bridging and compare to geometric influences we also synthesized a poly-para-terphenylenevinylene 1f, where the two solubilizing alkyl groups at the phenyl unit induce relatively strong steric hindrance. For 1f the absorption and fluorescence maxima are nearly identical to those from 1a-c.

For extending the approach and demonstrating its broad variability, besides stilbenes, we also tested alkylated terthiophene as intermediate \( \pi \)-
system leading to polyphenylmerthiophene 1g. The absorption then occurred at \( \lambda_{\text{max}} \approx 420-430 \text{ nm} \) and the fluorescence appears already in the green spectral region (500-550 nm). Here again the maxima of optical bands can be shifted by varying the length of the thiophene segment.

When further working on synthesis of substituted stilbenes we found better access to trans-configuration when changing the catalyst in the McMurry reaction. Then the pure trans-dibromostilbenes 7a,b could be separated for direct polymerization according to Yamamoto, yielding novel polybiphenylenevinylene 3a,b (see Figure 2).

For compounds of type 2 we started from diiodobianthryl which is better suited for coupling with the stilbenes than dibromobianthryl. As a reference compound also distilbenylbianthryl 2c was synthesized (abs.: 405 nm; fluor.: 448 nm) and found to be comparable with the higher oligomers 2a (406 nm; fluores.: 459 nm). In depth studies of 2c indicated further that the fluorescence maxima are strongly dependent on the polarity of the solvents and the temperature. To verify the nature of these effects the bianthrylene in the center was changed to a single dialkylated anthracene 2b (Scheme 1).

Poly(9,10-anthrylene-4,4'-stilbenylene) 2b now obtained with high molecular weight (\( \text{Mn} > 6 \times 10^4 \)) possesses the same fluorescence as the bianthynestilbenylene 2a with orthogonal subunits. Further work is directed to elucidate these effects.

**Conclusions**

As outlined in the result section, the use of 1,3-phenylene and 9,10-bianthryl bridging of conjugated moieties like stilbenes and thiophenes can be used in a broad variety for the synthesis of new fully conjugated polymers with well defined conjugation independent of the number of repeat units. The conjugated polymers described are thermally very stable making them useful also for device application. Moreover the optical absorption and fluorescence properties can easily be shifted by extension or reduction of the size of the intermediate \( \pi \)-moieties. The solvatochromic and thermotropic fluorescence changes in 2b,c are certainly intriguing and will be studied in more detail.

**Acknowledgements:** This work was supported by the Volkswagenstiftung, the Fond der chemischen Industrie and the Max-Planck society. We thank Mr. Zimmer (Mainz) and Mrs. Rothe (Berlin) for the fluorescence measurements and Dr. Oda and Prof. Neher (Potsdam) for a single layer LED device based on 1c.

**References**