



INTERNATIONAL Convention on Colorants - 2007



ABSTRACT

SYNTHESIS AND CHARACTERISTIC PROPERTIES OF DPP-BASED CONJUGATED POLYMERS

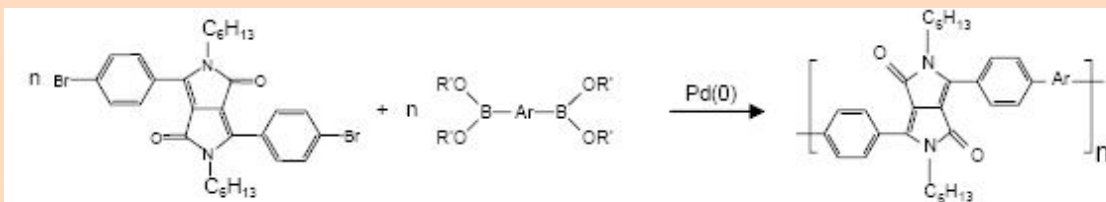
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Introduction

1,4-Diketo-3,6-diphenylpyrrolo[3,4-c]pyrrole (DPP) and some of its derivatives are commercialized as high performance pigments with exceptional light, weather and heat stability. Due to the excellent photostability and high quantum yield of fluorescence, they are potential materials for luminescent devices. In order to utilize the DPP chromophore in luminescent and other electronic devices, it is necessary to prepare soluble and film forming DPP compounds such as oligomers or polymers. Previous studies have shown that DPP-containing polymers can be prepared upon radical polymerization, polycondensation, polymer modification, or Pd-catalyzed cross-coupling reactions. The latter approach is especially interesting, because highly photoluminescent conjugated polymers containing DPP chromophores in the main chain can be obtained. The presentation deals with the synthesis of DPP-containing conjugated polymers upon Suzuki-, Stille- and Heck-coupling and electrochemical polymerization. The polymers are characterized with regard to their optical, photophysical and electrochemical properties.

Polymers prepared upon Suzuki polycondensation

Our first attempts to prepare conjugated DPP-containing polymers were based on Suzuki polycondensation of the dibromo-DPP-derivative 1 and various arene diboronic acid or diboronic ester derivatives using tetrakis(triphenylphosphine)palladium(0) as catalyst. A typical procedure is outlined in Scheme 1: Monomer 1 was obtained from dibromo-DPP upon subsequent alkylation of the lactam units using 1-bromohexane and potassium carbonate in dimethylformamide at 120°C. The polymers were synthesized and obtained as bright red powders, which could be easily dissolved in common organic solvents and processed into thin film upon solution casting (or spin coating). Molecular weights are between 6 and $24 \cdot 10^3$ Da. Optical absorption and fluorescence maxima in chloroform depend on the co monomer unit Ar, the electron-rich Ar units causing a red shift of the absorbance and fluorescence and a decrease of the band gap. All polymers exhibit large Stokes-shifts between 60 and 100 nm and low



Scheme 1) Suzuki polycondensation of DPP-containing polymer ($R' = H$ or pinacol diester).

found. Cyclovoltammetric studies indicate a quasireversible oxidation behaviour, whereas the reductive cycles are irreversible. The polymer with Ar being 2,5-dihexoxy-1,4-phenylene was also studied on its electroluminescent properties. Using a multilayer device of ITO/DPP-polymer/OXD7/Ca/Mg:Al:Zn, the polymer is electroluminescent with maximum emission at 640 nm, the turn-on voltage is 3 V. LUMO-levels of -3,3 to -3,57 eV. For some polymers, high photoluminescence quantum yields up to 85% were

Polymers prepared upon Stille and Heck coupling

In a recent study, new conjugated DPP-polymers prepared upon Stille and Heck coupling were reported. DPP-thienylene copolymers were prepared from 1 and distannyl derivatives of thiophenes and bithiophene using tetrakis(triphenylphosphine)palladium(0) as catalyst (Stille coupling). Poly(DPP-phenylenevinylene)s were synthesized upon Heck coupling of 1 and divinylbenzene. The catalyst was palladium(II)acetate/tris(o-tolyl) phosphine. The polymerization reactions are outlined in Scheme 2: All polymers are well soluble in organic solvents and exhibit a bright purple fluorescence with maxima of 600 - 635 nm in chloroform and 685 to 723 nm in the solid state. The fluorescence quantum yields are lower than for the polymers prepared upon Suzuki coupling. One reason might be a quenching caused by traces of tin, which could hardly be removed from Stille products. As indicated in the Table, the molecular weights of the poly-DPP-thienylenes are between 7 and $12 \cdot 10^3$ Da, whereas for Heck product much higher molecular weight is found. Cyclic voltammetric studies indicate reversible oxidation behaviour for poly-DPP-polythienylenes.

Bernd Teike is a Ph. D. from the University of Freiburg. He started his career as a Postdoctoral fellow at Queen Mary College, London, and then went on to become a Scientific assistant at Institute of Macromolecular Chemistry, University of Freiburg. He later became a Research chemist in chemical industry (Ciba-Geigy, Akzo). Since then he has been a Professor of Physical Chemistry, University of Cologne.



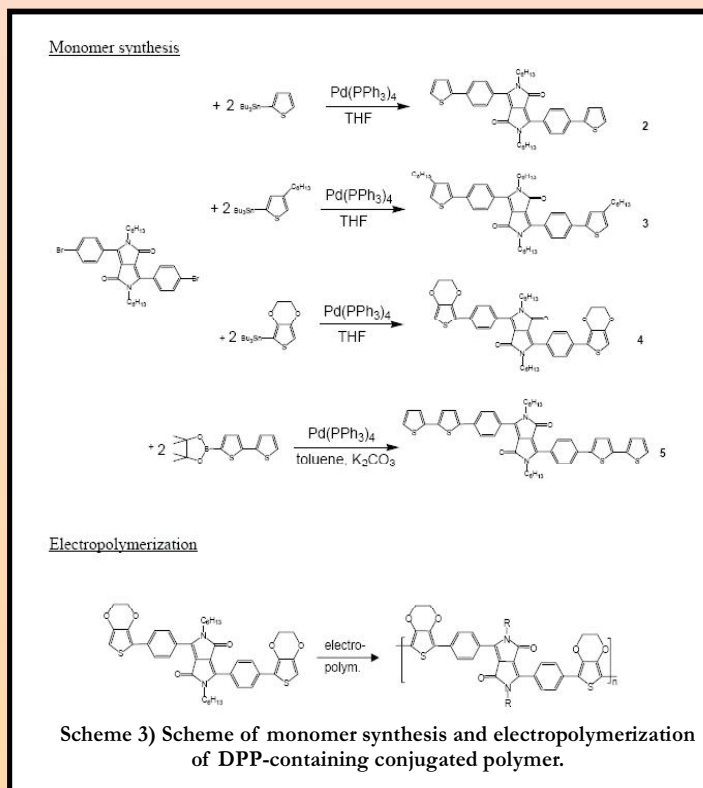
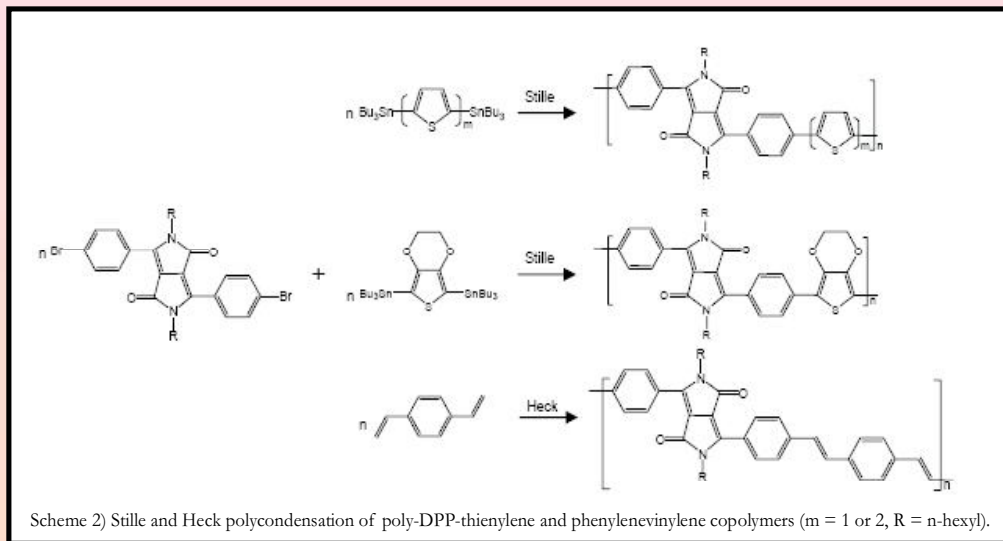


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Polymers prepared upon electrochemical polymerization

DPP-monomers (2-5) suitable for electropolymerization were synthesized upon Stille and Suzuki coupling using 1 and corresponding stannanes or boron ester derivatives as starting compounds (Scheme 3). The monomers were orange powders, which were excellently soluble in common organic solvents. Among the monomers, 4 and 5 exhibit the lowest oxidation potentials and are most suitable for electropolymerization (see also Scheme 3). The electropolymerization was carried out in a 1:1 mixture of dichloromethane and acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate. A three-electrode cell was applied with ITO as the working electrode and platinum wires as the counter and reference electrodes. The electropolymerization was followed using cyclic voltammetry. Studying monomer 4 for example, in the first cycle only the monomer oxidation at 0.83



V occurred, whereas in subsequent cycles, the polymer peaks at 0.5 to 0.6 V appeared and increased in intensity with the number of cycles.

Summary

Our studies demonstrate that DPP-containing conjugated polymers can be prepared from dialkylated dibromo-DPP 1 and various comonomers using palladium-catalyzed polycondensation reactions (such as Suzuki-, Stille- and Heck-coupling) or electrochemical polymerization. The polymers are readily soluble in common organic solvents. The solutions and films exhibit purple red colours and a purple luminescence with maxima up to 635 nm (in solution) and 723 nm (in film). The quantum yield of photoluminescence is up to 85 %. Preliminary studies indicate that the polymers are electroluminescent. Cyclic voltammetric studies show HOMO levels of the polymers between - 5.7 and - 5.1 eV and LUMO levels between - 3.7 and - 3.3 eV depending on the comonomer units. Some of the copolymers exhibit quasireversible oxidation and/or reduction behaviour. In future work, other coupling reactions will be studied and polymers containing other chromophores than DPP will be investigated.

Acknowledgements:

Financial support by Ciba Specialty Chemicals, Basle (Switzerland) is gratefully acknowledged. Drs. Roman Lenz, Matthias Duggeli and Beat Schmidhalter from Ciba thanked for helpful discussions and generously supplying dibromo DPP and dialkylated dibromo DPP.