Conjugated starshaped oligothiophenes

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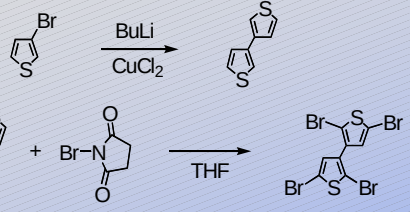
Introduction

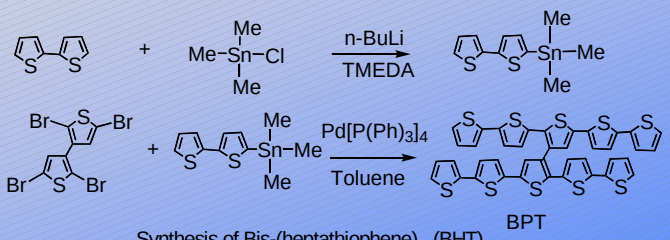
Of late polythiophenes have received increasing attention because of their numerous applications in areas such as energy storage and electrocromic devices[1]. One important field where thiophene-based π-conjugated oligomers and polymers have been widely investigated are organic semiconductors for application in organic field-effect transistors (OFETs)[2][3]. Solution-processible conjugated materials are among the most promising candidates for a cheap electronic and optoelectronic technology on plastic substrates.The morphologic stability of oligo-and polythiophenes while preparing and usage of OFETs are very important for such applications. In this current work the target was to increase the solubility and morphologic stability of oligothiophenes without any substitution of the thiophene backbone with alkyl chains via synthesis of starshaped oligothiophenes. The starshaped oligothiophenes Bis-(terthiophene) (BTT), Bis-(pentathiophene) (BPT) and Bis-(heptathiophene) (BHT) have been synthesized in a Stille type aryl-aryl-coupling procedure with $Pd[P(Ph)_3]_4$ as catalyst using 2,2´,5,5´-tetrabromo-substituted 3,3´-bithienyl as precursor. Herein we describe the synthesis and the optical properties of these oligomers.

Synthesis

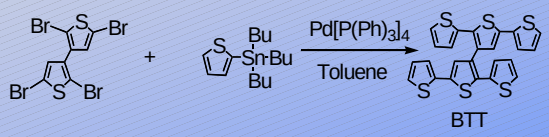
Synthesis of 2,2´,5,5`-Tetrabromo-3,3´-Bithiophenyl



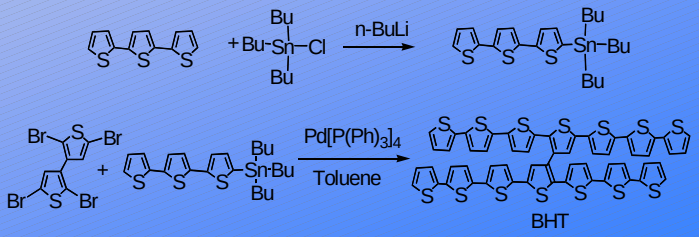
Synthesis of Bis-(pentathiophene) (BPT)



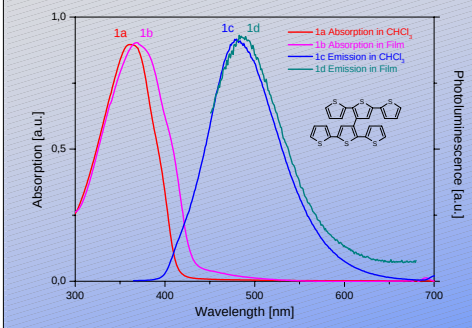
Synthesis of Bis-(terthiophene) (BTT)



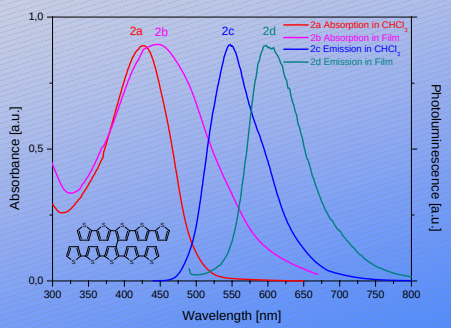
Synthesis of Bis-(heptathiophene) (BHT)



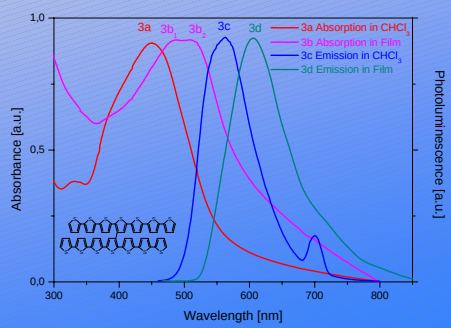
UV-Vis and photoluminescence spectra of BTT in solution and film



UV-Vis and photoluminescence spectra of BPT in solution and film



UV-Vis and photoluminescence spectra of BHT in solution and film



DSC-results	BTT	BPT	BHT
Glass transition temperature T_g/ °C	not observed	74	146
Melting point T_m / °C	187	167	not observed

Optical properties	BTT / λ_{max}[nm]	BPT / λ_{max}[nm]	BHT / λ_{nm}[nm]
Absorbance in solution	(1a) 361	(2a) 426	(3a) 451
Absorbance in film	(1b) 368	(2b) 446	($3b_1$ / $3b_2$) 509 / 564
Emission in solution	(1c) 480	(2c) 547	($3c_1$) 564
Emission in film	(1d) 483	(2d) 598	(3d) 606

Result and Discussion

(1) Starshaped thiophene-oligomers are obtained in good yields and are soluble in common organic solvents

(2) With increasing of the thiophene chainlength the absorption and emission maxima are bathocromically shifted

(3) Bathocromic shift (~50nm) of PL on going from solution to solid state is attributed to formation of ordered aggregates in the oligomers BPT and BHT

(4) In DSC-measurements BTT shows only a melting-point T_m, BPT shows a glass transition temperature Tg and melting-point, but BHT only a glass transition temperature Tg

(5) The oligomers are attractive candidates as active semiconducting layers in oligomer-based organic field effect transistors (OFETs)

References

[1] S.Tanaka and M.Kumei; *J.Chem.Soc., Chem.Comm.***1995**,815

[2] Remi de Bettignies, Y.Nicolas,P.Blanchard,E.Levillian,J.-M.Nunzi and J.Roncali; *Advanced Materials* **2003**,*22*,1939

[3] H.Sirringhaus, N.Tessler, H.Friend, *Science***1998**,*280*,1741