Wavelength tuning of light-emitting polyarenes *via* an *m*-phenylene interrupting block: π–π* band-gap adjustment of thiophene-based conjugated polymers

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The π–π* band gap of thiophene-based conjugated polymers can be adjusted *via* the insertion of *m*-phenylene bridges into regularly defined positions.

Since the observation of electroluminescence in poly(*p*-phenylenevinylene)s,[1] efforts to find effective emissive layers in luminescent devices have been diverted from organic and inorganic materials to conjugated polymeric materials. Numerous reports have focused on effective emitting materials and the optimization of preparation conditions which would improve their luminescence efficiency[2] and stability,[3] and efforts to tune the emission wavelength.[4]

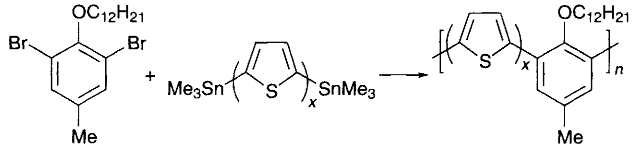
One of the most powerful strategies for wavelength tuning involves the adjustment of the π–π* band gap (energy separation between the HOMO and LUMO) of the active polymeric chain. It is well known that the band gap between the HOMO and LUMO can be adjusted by the length of conjugated π system. The more extended this is, the narrower the band gap.[5] Wavelength tuning can be successfully realized *via* block copolymers, in which π-conjugated active blocks of a regularly defined length alternate with unconjugated interrupting σ-inactive blocks of a wider band gap.[6] Wavelength tuning can also be achieved using sterically unhindered oligo(arene) active blocks of defined lengths between head-to-head dyads of alkyl-substituted hindered arenes.[7] Since the repulsive interaction, in head-to-head dyads, between the alkyl substituents on the arene rings results in a distortion of the π-conjugated backbone from coplanarity, the length of the active blocks between the head-to-head dyads can be varied in a systematic and regular manner. By this method wavelength tuning can cover the whole visible spectrum.[6,7,8]

On the other hand, π conjugation by resonance in oligo- and poly(*m*-phenylene)s does not exist between adjacent phenylene rings. Therefore, these polymers show broad band gaps and are essentially semiconductors.[9] Accordingly, if *m*-phenylene bridges are inserted into regularly defined positions of a π-conjugated backbone the bridges will act as interrupting blocks. Thus, if the length of the π-conjugated active blocks is controlled by the *m*-phenylene bridges, the π–π* band gap can be adjusted accordingly enabling tuning of wavelength emission.

In order to verify our hypothesis, we synthesized such block copolymers and probed their optoelectronic properties. We chose thiophene and oligothiophenes as active blocks because of their good environmental stability and high conductivity of the resulting polymers. In these copolymers the lengths of the π-conjugated blocks (*i.e.* the number of thiophene rings) between the consecutive *m*-phenylene bridges were successfully varied in a systematic way. To improve solubility, dodecyloxy groups were grafted onto the *m*-phenylene rings. Our preliminary results are reported below.

The general synthetic procedure for the block copolymers **6**–**9** is shown in Scheme 1. 2,6-Dibromo-1-dodecyloxy-4-methylbenzene **1** was prepared from commercially available 2,6-dibromo-4-methylphenol. 2,5-Bis(trimethyltin)thiophene **2** and ω,ω′-bis(trimethyltin)oligothiophenes **3**–**5** were prepared as described in the literature.[10] For example, compound **1** was refluxed with 2.2 equiv. of **3** in THF for 24 h in the presence of [Pd(PPh$_3$)$_2$Cl$_2$]. Copolymer **6** was purified by repetitive precipitation–centrifugation using THF and MeOH. Copolymers **7**–**9** were also prepared by a similar procedure. Copolymer **6** is a sticky dark brown liquid and **7**–**9** are brown, orange and dark red solids, respectively. All four copolymers are soluble in CHCl$_3$ and THF, and insoluble in polar organic solvents. The solubility of the copolymers decreases in going from **6** to **9**. GPC measurements upon the copolymers with polystyrene as calibration standard gave M_n = 1700 (M_w/M_n = 1.4) for **6**, 3100 (2.1) for **7**, 8700 (3.9) for **8** and 8100 (13.5) for **9**. These molecular masses appear to be relatively low, similar to observations in other copolymerizations using transition-metal-catalysed coupling at sterically congested positions adjacent to side chains.[11] In this study, however, we were not concerned with production of high-molecular mass polymers since it is well known that the electronic structure of polyarenes is invariant even at a low degree of polymerization.[12] The structures of the copolymers have been characterized by spectroscopic methods.

The absorption and emission spectra of copolymers in CHCl$_3$ solution are shown in Fig. 1. The spectra show the expected gradual bathochromic shift of λ_{max} in going from **6** to **9**. Thus, the absorption maximum increases from **6** (λ_{max} = 310) to **7** (λ_{max} = 390) to **8** (λ_{max} = 406) to **9** (λ_{max} = 421). Copolymers **6**–**9** exhibit blue, yellow–green, orange and red emissions, respectively, upon UV–VIS excitation (λ > 350 nm) both in the solid state and in CHCl$_3$ solution. The emission maximum increases from **6** (λ_{max} = 408) to **7** (λ_{max} = 492) to **8** (λ_{max} = 526) to **9** (λ_{max} = 534). As shown in Fig. 2 the variation of the absorption and emission maximum energies as a function of the inverse number of thiophene rings (1/*n*) between consecutive *m*-phenylene bridges is linear. Our present data are in good agreement with previous reports for β-substituted oligothiophenes.[13] Thus, the *m*-phenylene block can clearly play a role as an interrupting block. While the absorption spectra show structureless bands, the emission spectra exhibit fine structure. Such a difference between the absorption and emission has been observed for other thiophene oligomers and is ascribed to a greater rigidification of the polymers in their first relaxed excited state than in ground state.[13,14] The rotational energy barrier of the adjacent rings is smaller in the ground state and



1

	x		*x*
2	1	**6**	1
3	2	**7**	2
4	3	**8**	3
5	4	**9**	4

Scheme 1 *Reagents and conditions*: [Pd(PPh$_3$)$_2$Cl$_2$], THF, reflux, 24 h

contributes to the molecular disorder. Thus it gives rise to inhomogeneous broadening and hence a structureless absorption. On the other hand, the resolution of vibronic fine structures of the emission bands decreases in going from **6** to **9**. Although a detailed explanation for these spectral characteristics must await further research, it may indicate that chain rigidification decreases with a decrease in concentration of *m*-phenylene bridges (*i.e.* an increase in the number of thiophene rings).

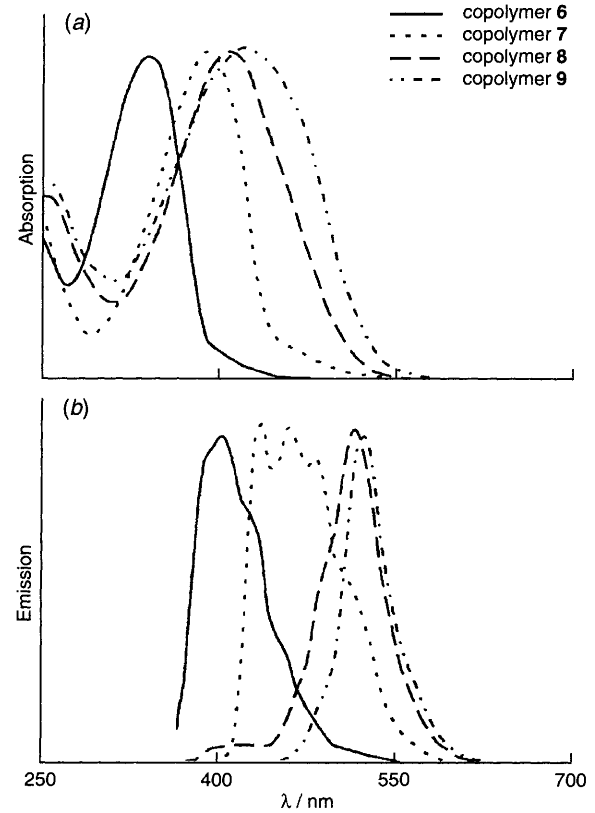


Fig. 1 Normalized spectra of (*a*) absorption and (*b*) emission from copolymers **6**–**9** in $CHCl_3$ solution

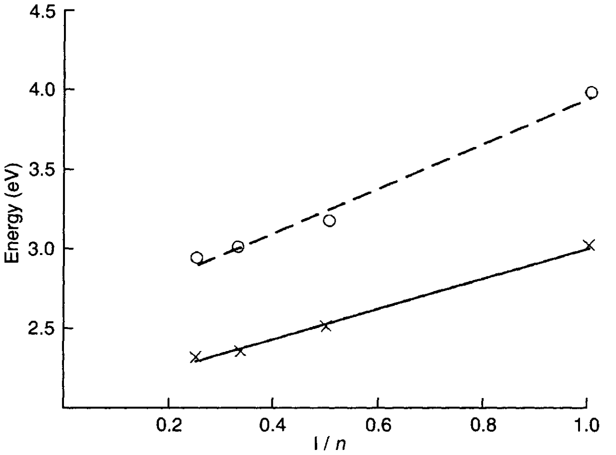


Fig. 2 Variation of absorption and emission maximum energies of copolymers **6**–**8** in $CHCl_3$ solution as a function of the inverse number of thiophene rings (1/*n*) between consecutive *m*-phenylene bridges. (×) = absorption; (○) = emission.

In conclusion, we have shown that the *m*-phenylene bridge can act as an interrupting block in π-conjugated polymers. Present ideas for π–π* band-gap adjustment should be extended to the other aromatic bridges, *e.g.* 1,3-, 1,6- and 1,8-linkages in naphthalene systems, and further 2,4-linkage in thiophene, furan, pyrrole *etc.* We are currently pursuing this approach as well as investigating the LED performances of the present copolymers.

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