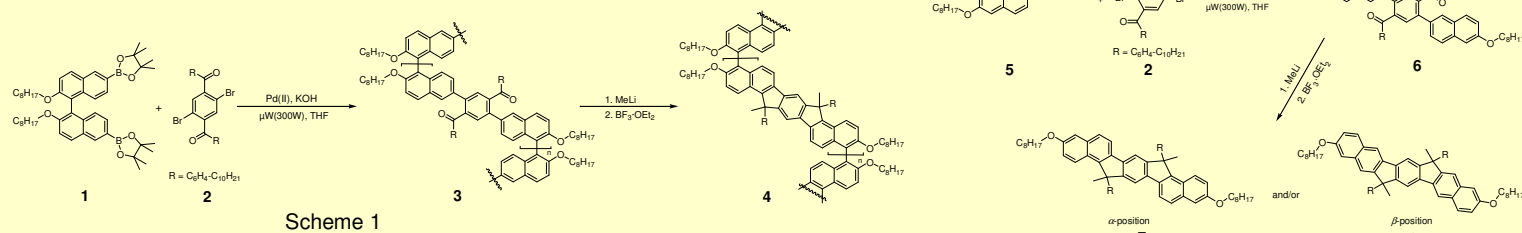


Introduction:

Of late there is substantial research towards the design of organic materials as active components media in optoelectronic devices such as organic light emitting diodes (OLEDs), solar cells and lasing materials.^[1] Aromatic ladder polymers possess a unique set of characteristic properties due to their planarized structure and initial results show them to be useful candidates in such applications.^[2] It is expected that the bulky binaphthyl structure may be useful in reducing intermolecular interactions of the polymer chains which can lead to bathochromically shifted emission bands or a reduction in luminescence quantum yields.^[3] Furthermore, the binaphthyl-building block provides the possibility to introduce main-chain chirality.^[4]

Synthesis:



- Polyketone **3** is achieved via our standard microwave-assisted protocol^[5] to give a polymer with $M_n = 13,250$ (PD = 1.5)
- Cyclization is realised by two polymer analogue steps to provide the ladder polymer **4** with $M_n = 20,200$ (PD = 2.3)
- Modelcompound **7** was synthesized to analyze the structural uniformity after cyclization (Scheme 2)

NMR-Spectroscopy:

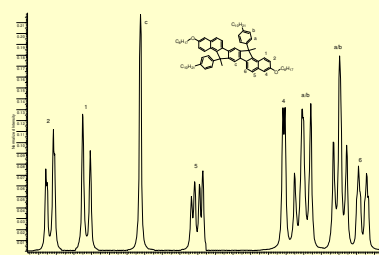


Fig.1: ¹H NMR of **7** in the aromatic region

- ¹H and ¹³C NMR spectra of **7** shows that cyclization occurs exclusively in the α -position of the naphthalene moiety
- Comparison of the NMR data of the model compound **7** and the polymer **4** indicates that similar cyclization patterns occur in the polymer

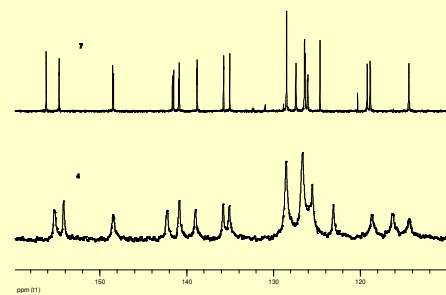


Fig.2: Comparison of the ¹³C NMR data of **7** and **4**

Optical Properties:

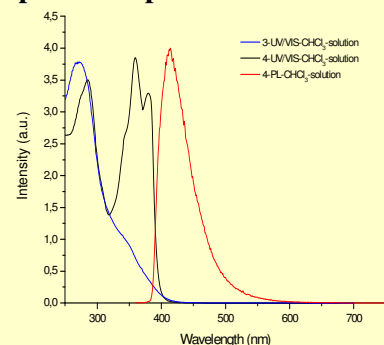


Fig.3: UV/Vis and PL of **3** and **4**

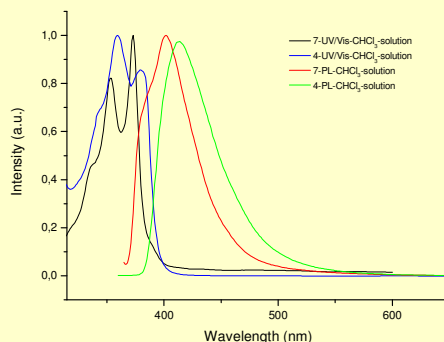


Fig.4: Comparison of **4** with **7**

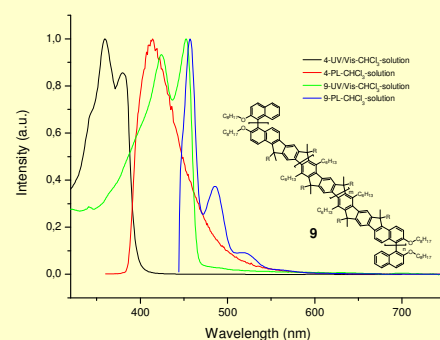


Fig.5: Comparison of **4** with **9**

- Cyclization of **3** to **4** is evidenced by the appearance of intense π - π^* transitions at 359 and 379 nm (Fig.3) in the UV/Vis spectra
- Polymer **4** and the model compound **7** show similar optical properties, but the slight bathochromic shift of λ_{max} in **4** indicates weak interaction through the binaphthyl moiety

- Statistical copolymerisation to **9** (0.1 mol of **1**, 1.0 mol of **2**, 0.9 mol of 2,5-dihexyl-phenyl-ene-1,4-diboronic-ester) allows the introduction of randomly distributed binaphthyl units
- The generation of elongated ladder segments results in bathochromically shifted UV/Vis and PL bands
- The composition of the reaction mixture allows some tuning of the optical properties

Conclusions & Outlook:

- A microwave-assisted synthetic protocol towards binaphthyl linked step-ladder polymers was developed
- Model compound **7** indicates a regioselective cyclization pattern
- Statistical copolymerisation of **9** leads to binaphthyl-linked ladder polymers which allows tuning of the optical properties
- Incorporation of binaphthyl units allows the generation of main-chain chiral polymers (*in process*)

References & Acknowledgement:

- [1] (a) Tasch, S. et al. *Appl. Phys. Lett.* **1996**, *68*, 1090. (b) Kraft, A. Grimsdale, A.C., Holmes, A.B. *Angew. Chem. Int. Ed.* **1998**, *37*, 402. [2] Scherf, U. *J. Mater. Chem.* **1999**, *9*, 1843. [3] Grimsdale, A.C et al. *Adv. Mater.* **2002**, *12*, 729. [4] Pu, L. *Chem. Rev.* **1995**, *98*, 2405. [5] Nehls, B.S et al. *Macromolecules* Submitted.

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