

## Molecular Semiconductor Wires

# New polyrotaxanes reduce intermolecular interactions

To exploit molecular semiconductors we need to be able to control intermolecular interactions. Franco Cacialli and co-workers from UCL, Cambridge, Oxford and Berlin (*Nature Materials*, November 2002) have recently developed a class of semiconducting conjugated molecular wires with reduced intermolecular interactions. The material has been engineered at the supramolecular level by threading a luminescent conjugated macromolecule, through non-conjugated insulating  $\alpha$  or  $\beta$ -cyclodextrin rings.

A rotaxane is a supramolecular assembly of a dumbbell locked through the cavity of a macrocycle. The synthetic strategy employed to make polyrotaxanes has three key steps; *threading* of the insulating molecular 'bead' onto the monomer unit which will form the conjugated backbone; *coupling* of threaded monomer units and *capping* with bulky stopper units to prevent the outer 'bead' molecules from falling off.

In Cacialli *et al*'s work, polyrotaxanes were prepared by Suzuki coupling – reacting bulky aryl iodides with diboronic acids and cyclodextrins molecules in aqueous sodium carbonate containing palladium(II) acetate. 1-Iodonaphthalene-3, 6-disulphonate disodium salt was used as the bulky stopper moiety. This synthesis makes use of the hydrophobic effect to promote the threading mechanism. The monomer is hydrophobic, and the insulating outer molecule has a hydrophobic interior so it can accommodate the guest. The outer molecules hydrophilic exterior

renders it water-soluble. The chemical structures of the polyrotaxanes are shown in fig 1.

This is the first example of genuine conjugated polyrotaxanes with stoppers at both ends of the chains to prevent unthreading. The resulting supramolecules are insulated molecular wires that display the basic semiconducting and optical properties of the uninsulated chains and can be used as molecular materials. There is also reduced aggregation of the polymer chains, allowing solution processing of individual polyrotaxane wires onto substrates.

The level of threading (an average of 0.9 to 1.6 macrocycles per repeat unit) leaves some of the  $\pi$ -systems exposed, explaining why satisfactory conductivity is maintained in spite of the insulating sheath.

Scanning force microscopy showed a difference in aggregation behaviour between threaded and non threaded polymer cores. The new cyclodextrin sheathed polymers are not closely packed, allowing individual molecular rods to be distinguished - evidence of strongly reduced inter-strand interactions. In contrast, the uninsulated polymers assembled into domains consisting of  $\pi$ - $\pi$  stacked rods.

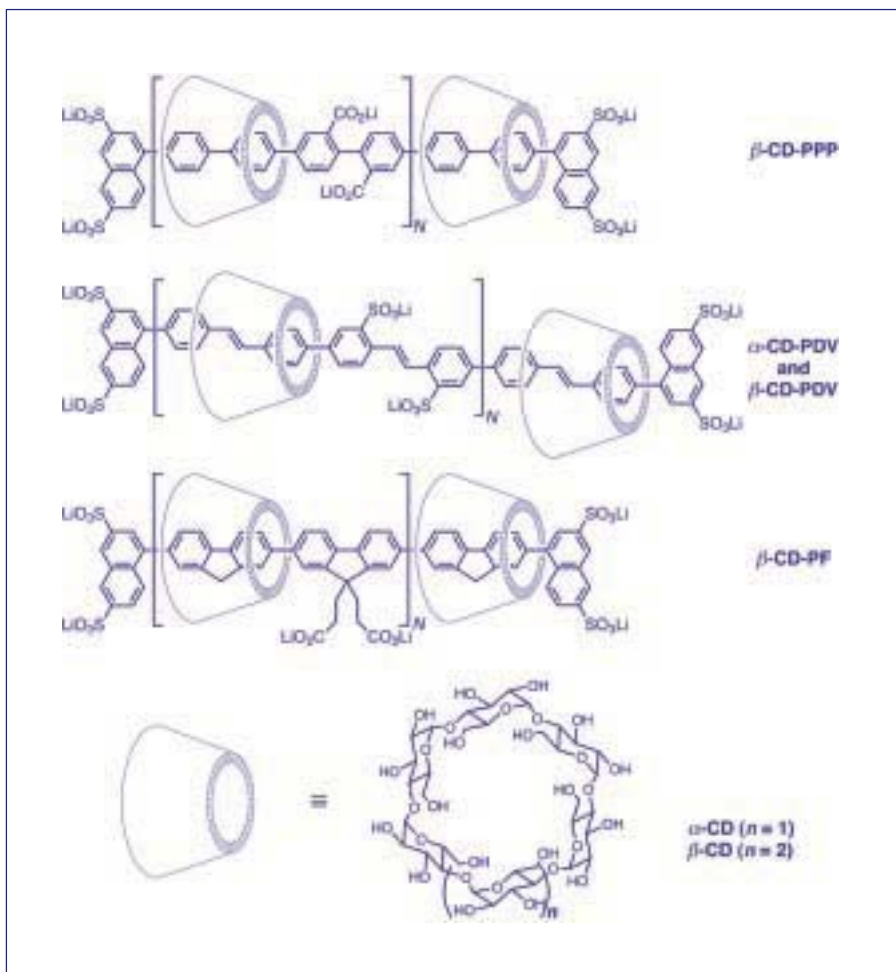
Close-packing leads to the formation of intermolecular excited states due to  $\pi$ - $\pi$  interactions in luminescent materials. This reduces the photoluminescence efficiency and causes a red-

shift of the luminescence spectrum – undesirable for the fabrication of emitting devices. LEDs fabricated from the new polyrotaxane materials show that the supramolecular architecture has a beneficial effect. The rotaxinated conjugated polymers have considerably higher photoluminescent efficiencies in comparison to their unrotaxinated equivalents. The effect is even greater in crude polymer samples that contained remnants of the palladium catalyst – demonstrating that the cyclodextrins protect against quenching of the luminescence by the metallic contaminants.

The results gained by Cacialli and co-workers demonstrate the potential for control of solid state intermolecular interactions through the use of supramolecular chemistry. Additionally, the new materials' greater solubility in water, allows spin-coating without toxic solvents and paves the way for bio-compatible processes and structures. The exploitation and control of individual chains is crucial for manipulation of single organic wires in nanoelectronics. This work shows a possible pathway to future molecular semiconductor wires.

*Cyclodextrin-threaded conjugated polyrotaxanes as insulated molecular wires with reduced interstrand interactions.*

F Cacialli, J S Wilson, J J Michels, C Daniel, C Silva, R H Friend, N Severin, P Samorì, J P Rabe, M J O'Connell, P N Taylor and H L Anderson *Nature Materials*, 2002, 1, 160



**6** **Figure 1** Chemical structures of the polyrotaxanes used in this work. The chemical structures of the cyclodextrin-threaded conjugated polyrotaxanes with poly(para-phenylene), and poly(4,4'-diphenylene vinylene) and polyfluorene cores ( $\beta$ -CD-PPP,  $\alpha$ - and  $\beta$ -CD-PDV and  $\beta$ -CD-PF respectively).

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