New developments in surface-enhanced solid-state NMR spectroscopy and their applications

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A key challenge in the development of modern materials and pharmaceuticals is to determine at the atomic scale their structure and dynamics. Recently, Dynamic nuclear polarization (DNP) has developed into a powerful analytical technique to enhance the sensitivity of magic angle spinning (MAS) solid-state NMR spectroscopy of materials and pharmaceuticals.¹

In this presentation, we will first present some recent results, where we used molecular modelling in combination with proton NMR spectroscopy under very fast magic-angle spinning (MAS) and DNP surface-enhanced NMR spectroscopy (DNP SENS) to characterise the polymer backbone group conformations and packing arrangement in the high-mobility donor–acceptor copolymer diketopyrrolo-pyrrole-dithienylthieno[3,2-b]thiophene (DPP-DTT). We found that the bulk polymer adopts a highly planar backbone conformation with a laterally-shifted donor-on-acceptor stacking arrangement. The same planar backbone structure and intermolecular stacking arrangement is preserved in the films following solution processing and annealing, thereby rationalizing the favourable device properties of DPP-DTT, and providing a protocol for the study of other thin film materials.² DNP SENS NMR enabled high-quality one- and two-dimensional 13C NMR data to be obtained in a few hours for the thin-film samples.

We will then show how high DNP enhancements can be preserved at room temperature by using solvents having a high glass transition temperature. In particular, by dissolving BDPA and TEKPOL in ortho-terphenyl (OTP), enhancement factors of around 80 and 40 were obtained at 240 K (i.e. at the glass transition temperature of OTP) and of up to 10-20 were obtained in the metastable phase at ambient temperature and at both 9.4 and 18.8 T.³ The method was successfully applied to monitor molecular dynamic transitions in pharmaceutically relevant solid samples, like Ambroxol and Ibuprofen.


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