Bilayered crystalline organic semiconductors for solution-processed OFETs: asymmetrically-substituted smectic liquid crystal of benzo[1,2-b:4,5-b']dithiophene derivatives

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Recently we have proposed a new OFET material exhibiting high mobility of over 10 cm^2/Vs in polycrystalline thin films, i.e., Ph-BTBT-10.[1] The most unique feature of this materials is that the polycrystalline thin films as-fabricated *via* a smectic liquid crystal phase [2] are mono-layered crystals and are transformed to bilayered crystals with accompanying significant increase of FET mobility by about one-order of magnitude when thermally annealed for a short time at 120°C.

In this study, as the first example to show a fact that this unique phenomena is not limited for a particular case of Ph-BTBT-10, we designed and synthesized a new molecule of asymmetrically-substituted smectic liquid crystals with a small core of benzo[1,2-b:4,5-b']dithiophene (BDT) substituted with mono-alkyl and phenyl groups, 6-Alkyl-2-Phenyl-Benzo[1,2-b:4,5-b']dithiophene (Ph-BDT-Cn, n = 8, 14, **Fig. 1**), followed with investigated their mesomorphism and crystal properties of spin-coated thin films,[2] and characterized solution-processed OFETs before and after the thermal annealing. Both two compounds exhibited the SmE phase, and their crystalline films derived from SmE films exhibited

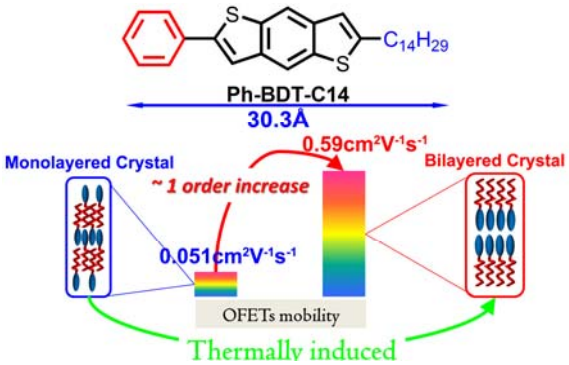

Fig. 1 Scheme illustration of OFET mobility enhancement induced by crystal-to-crystal phase transition

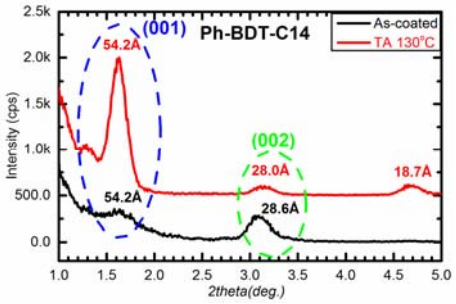

Fig. 2 XRD of thin film before & after thermal annealing

mono-layered crystals as-fabricated and transformed to bilayered crystals through a crystal-to-crystal transition when thermally annealed (**Fig. 2**). The FET mobility was significantly enhanced by a transition factor of 2 to 10, accompanied with the phase transition from mono-layered crystals to the bilayered crystals and reached up to be 0.59cm^2/Vs in spite of a small core of BDT (**Fig. 3**).

In conclusion, the phenomenon of "OFET mobility enhanced by phase transition from mono-layered crystal to bilayered crystal" is NOT a particular case for Ph-BTBT-C10, and would be general for solution-processed OFET devices fabricated with mono-alkyl SmE OFET materials featuring bilayer crystal structure.

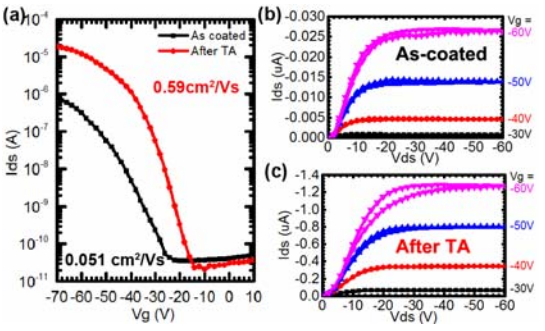

Fig. 3 FET performance of Ph-BDT-C14

References

1. H. Iino, T. Usui & J. Hanna, *Nat. Commun.*, **2015**, 6, 6828.
2. H. Iino and J. Hanna, *Adv. Mater.*, **2011**, 23, 1748.