

Toward Better Solid-State Order and Performance of D–A Conjugated Polymers: Fluorine Substitution

This report features the work of Chain-Shu Hsu, Chien-Lung Wang and their co-workers published in *Adv. Mater.* **25**, 2445 (2013).

Donor–acceptor (D–A) conjugated polymers are promising materials for organic optoelectronic applications. A charge mobility over $5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in polymer field-effect transistors and efficiency of power conversion (PCE) over 10 % in polymer solar cells (PSC) have been realized.^{1, 2} The solid-state structural order is crucial to convert molecular properties into useful device performance. Although chemical modifications of D–A units facilitate fine tuning of molecular properties, the increased structural complications of these D–A polymers cause difficulty in identifying the key parameters to attain a highly ordered solid state. Because both molecular geometry and non-covalent intermolecular interactions govern the formation of solid-state structures, identifying the individual influences of these two parameters in the solid-state order of D–A polymers is essential for clarifying the relation between molecular structure and solid-state order. Chain-Shu Hsu and Chien-Lung Wang from National Chiao Tung University, Taiwan, have identified that the strength of non-covalent interactions plays an important role in attaining a highly ordered solid state and improved device performance of D–A polymers. Through prudent molecular design, they minimized the effect of molecular geometry, and compared systematically the strengths of non-covalent interaction, solid-state order and optoelectronic performances of a D–A polymer, PTh₄BT, and its fluorinated analogue, PTh₄FBT (Fig. 1(a)). Replacing the hydrogen substituents with fluorine on the 2,1,3-benzothiadiazole (BT) unit shows a small effect in molecular geometry, but alters significantly the dipole moments of the acceptor unit, as illustrated in the energy-minimized molecular models obtained from theoretical calculations (Fig. 1(b)). In this case, varied solid-state behavior and device performance are clearly attributed to the enhanced non-covalent interactions.

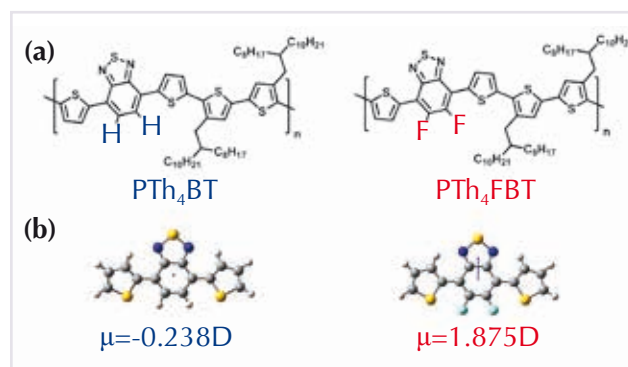


Fig. 1: (a) Molecular structures of PTh₄BT and PTh₄FBT. (b) Illustration of dipole moments of the BT and FBT acceptor units. The unit of the dipole moment is given in debye and the direction is indicated by the arithmetic sign.

The consequences of molecular modification were first examined through UV-vis absorption spectra and thermal analysis. The raised dis-aggregation temperature in solution and raised melting temperature of the bulk of PTh₄FBT are the first indications of the enhanced intermolecular non-covalent interactions. These interactions resulted in enhanced crystallinity of PTh₄FBT as indicated by the X-ray powder diffraction patterns (Fig. 2) collected *in situ*

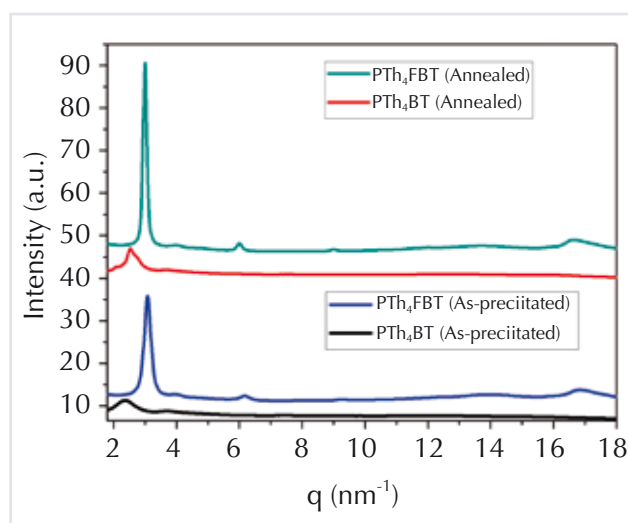


Fig. 2: X-ray powder diffraction patterns of PTh₄BT and PTh₄FBT *in situ* before and after thermal annealing.

at **BL23A1** and **BL01C2** of the TLS. The diffraction pattern of PTh₄FBT as precipitated shows diffraction features much more intense than those of PTh₄BT. The diffraction signals located at scattering vector (q) = 3.00, 6.00 and 9.00 nm⁻¹ are indexed as (100), (200) and (300) diffractions, respectively, of a long-range ordered lamellar structure of PTh₄FBT with d -spacing 2.09 nm. The intense (010) diffraction signal located at $q = 16.8$ nm⁻¹ indicates an ordered π - π stacking with d -spacing 0.37 nm. Annealing the samples at 200 °C for 1 min improved the solid-state order of both polymers. In the case of PTh₄FBT, the correlation length of the lamellar structure (L_{100}) increased from 22.7 to 38.8 nm, and that of π - π stacking (L_{010}) from 5.8 to 6.0 nm, as summarized in Table 1. The crystallinity of PTh₄BT remained poor; no indication of ordered π - π stacking was observed even after the thermal treatment.

The degree of solid-state structural order shows a satisfactory correlation with the hole mobility (μ_h) of the polymers. PTh₄FBT delivered $\mu_h = 2.91 \times 10^{-2}$ cm² V⁻¹ s⁻¹ with I_{on}/I_{off} ratio 1.44×10^7 in its thin film as cast. μ_h increased significantly to 0.29 cm² V⁻¹ s⁻¹ with I_{on}/I_{off} ratio 5.13×10^7 after the thermal annealing. The improved solid-state order and L_{hkl} enabled PTh₄FBT to deliver the greatest μ_h among the BT-quarterthiophene-based alternating copolymers.^{3, 4}

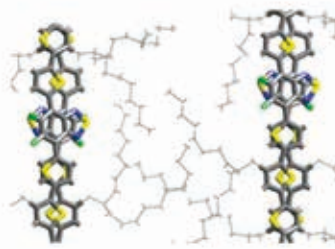
The PSC performance of PTh₄FBT was evaluated in both a conventional architecture – indium tin oxide (ITO)/PEDOT:PSS (40 nm)/PTh₄FBT:PC₇₁BM (95 nm)/Ca (35 nm)/Al (100 nm) and inverted architecture – ITO/ZnO (30 nm)/PTh₄FBT:PC₇₁BM (95 nm)/MoO₃ (6 nm)/Ag (150 nm). Their performance was measured under AM-1.5 illumination at 100 mW/cm². A conventional device using a PTh₄FBT:PC₇₁BM (1:1, mass/mass) blend as active layer exhibited $V_{oc} = 0.78$ V, $J_{sc} = 12.17$ mA/cm², FF = 67.5 %, delivering PCE = 6.41 %. The inverted device with an identical active layer exhibited $V_{oc} = 0.77$ V, $J_{sc} = 13.51$ mA/cm², FF = 65.6%, delivering the greatest PCE = 6.82 %. The electron-withdrawing fluorine substituents of PTh₄FBT resulted in a lower-lying E_{HOMO} and enabled PTh₄FBT to have an increased V_{oc} . Because of synergy with an

Table 1: Average correlation lengths, L_{100} and L_{010} , of PTh₄FBT deduced from the X-ray powder diffraction *in situ*.

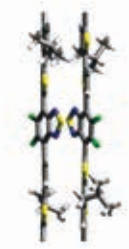
	L_{100} (nm)	L_{010} (nm)
As cast	22.7	5.8
Annealed	38.8	6.0

*Illustration of the ordered packing

lamellar structure



π - π stacking



improved solid-state order, PTh₄FBT also attained the greatest PCE among the BT-quarterthiophene-based alternating copolymers.

In summary, through appropriate molecular design, detailed solid-state analysis and evaluation of the device performance, the work revealed the importance of the strength of non-covalent interaction in attaining a highly ordered solid state and optoelectronic performance, and promoted a comprehensive consideration for future polymer design.

References

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