Insights into Molecular Packing

Controlling π–π stacking in non-fullerene acceptors could be key to enhancing organic photovoltaic performance.

Organic photovoltaics (OPVs) have emerged as a promising renewable energy technology due to their lightweight, flexible, and scalable nature, making them ideal for next-generation solar energy solutions. A key factor driving the advancement of OPVs is the development of non-fullerene acceptors (NFAs), which have surpassed fullerene-based acceptors in optical absorption, tunability, and efficiency.[1] Among these, Y6-based NFAs stand out as benchmarks, enabling power conversion efficiencies (PCEs) exceeding 18% through their unique A-DA' D-A-type molecular architecture.[2] This structure, featuring a central thiadiazole (Tz) unit and a C-shaped ortho-benzodipyrrole skeleton, supports strong absorption and efficient charge transport. Despite these successes, challenges such as the synthetic complexity of Y6 and its tendency toward aggregation hinder further improvements and limit scalability.

To address these challenges, teams led by Yen-Ju Cheng (National Yang Ming Chiao Tung University) and U-Ser Jeng (NSRRC) are exploring innovative molecular designs aimed at maintaining high performance while minimizing structural complexity and aggregation. This research focused on three carefully designed NFAs—CB16, Y6-16, and SB16—to better understand the relationships between molecular structure, packing behavior, and device performance. As shown in **Fig. 1**, CB16 simplifies the Y6 architecture by removing the central Tz unit while preserving the C-shaped ortho-benzodipyrrole skeleton. This modification is intended to reduce self-aggregation and improve donor–acceptor interactions. Y6-16, a derivative of Y6 with side chains identical to those of CB16, retains the Tz unit and serves as a benchmark for comparison. Additionally, SB16 features an S-shaped para-benzodipyrrole skeleton, offering a direct comparison in molecular geometry. These three NFAs were strategically selected to elucidate how structural modifications influence molecular packing, charge transport, and overall device performance.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) and simultaneous small- and wide-angle X-ray scattering (SWAXS) provided detailed insights into the molecular packing and phase behavior of the NFAs in both neat films and when blended with the donor polymer PM6. **Figure 2** highlights the GIWAXS patterns and corresponding 1D scattering profiles, revealing the key differences in molecular packing among the three NFAs. CB16 exhibits vertically oriented π–π stacking with abundant small nanodomains, facilitating the formation of bicontinuous networks essential for efficient charge transport. This packing arrangement reflects the benefits of removing the Tz unit, which results in reduced aggregation while maintaining robust donor–acceptor interactions. By contrast, SB16 demonstrates large, phase-separated domains with poor π–π stacking due to its S-shaped geometry, resulting in suboptimal performance. Y6-16, while similar to CB16 in packing features, shows

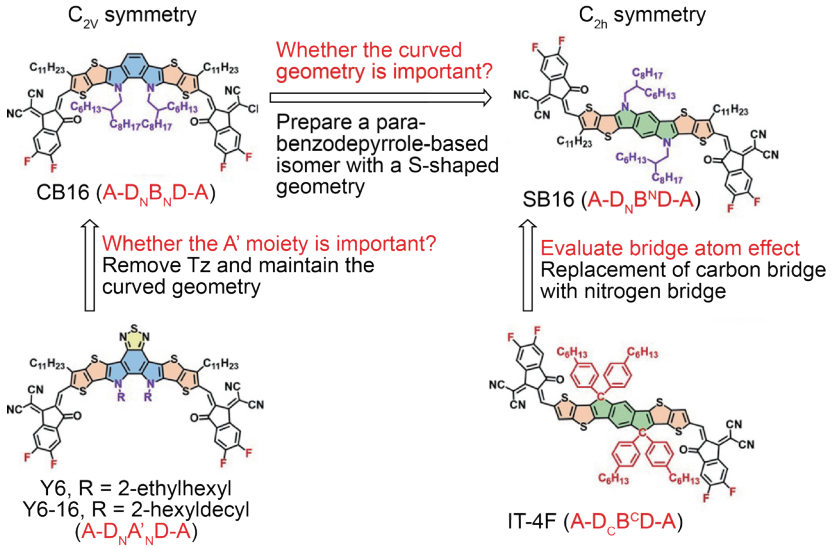

Fig. 1: Chemical structures of Y6, Y6-16, and IT-4F that inspired the design of CB16 and SB16 NFAs. [Reproduced from Ref. 3]

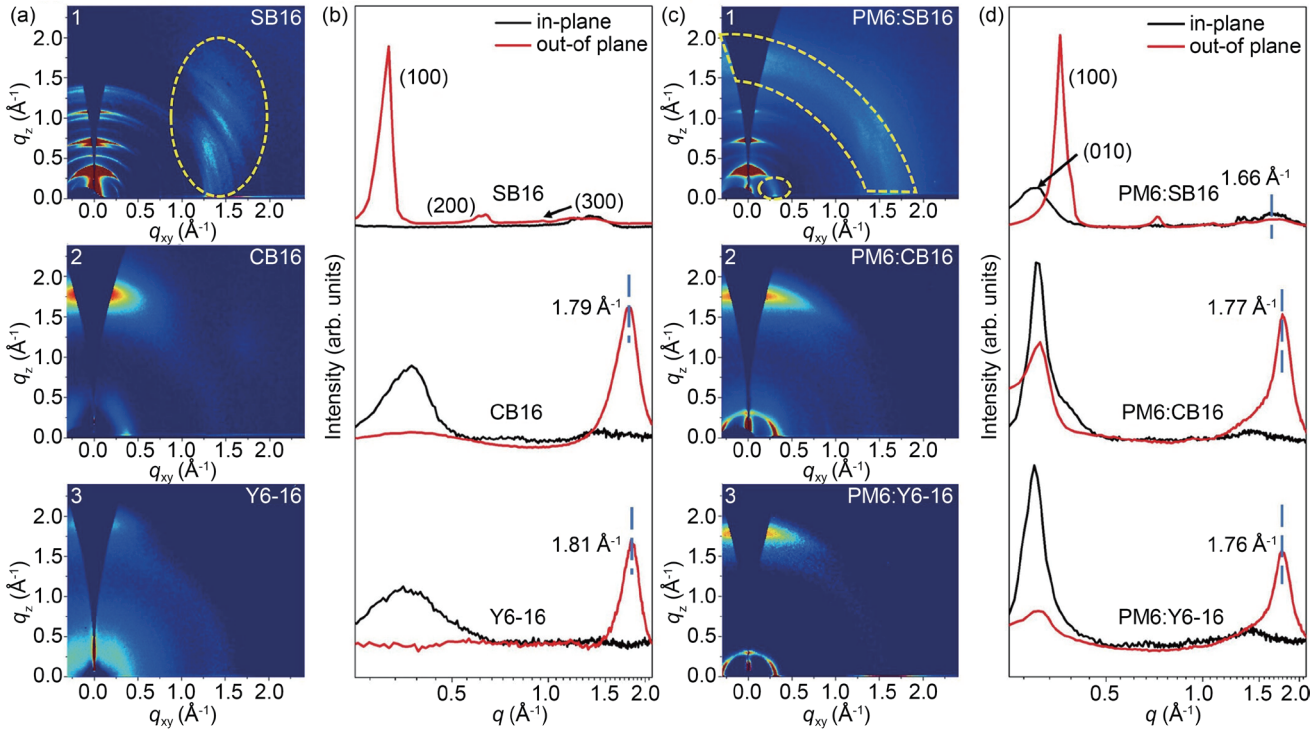

Fig. 2: 2D GIWAXS patterns of the SB16 (a-1), CB16 (a-2), and Y6-16 (a-3) and their blended films PM6:SB16 (c-1), PM6:CB16 (c-2), and PM6:Y6-16 (c-3) and their corresponding 1D scattering profiles along the in-plane and out-of-plane directions for the neat films (b) and blended films (d), respectively. [Reproduced from Ref. 3]

slightly reduced donor–acceptor interactions due to the presence of the Tz unit. In device studies, CB16, when blended with PM6, achieved a remarkable PCE of 18.32% in binary OPV devices, surpassing both those of Y6-16 and SB16. The enhanced performance of CB16 is attributed to its optimized molecular packing, reduced aggregation, and efficient charge transport properties. By removing the Tz unit, CB16 not only simplifies molecular design but also balances structural simplicity with high performance, making it a promising candidate for scalable OPV applications. The contrast in performance between CB16 and SB16 underscores the critical role of molecular geometry, with the C-shaped architecture of CB16 and Y6-16 offering significant advantages over the S-shaped design.

In summary, this study provides insights into the structure–property–performance relationships of NFAs. The C-shaped A-DNBND-A skeleton in CB16 plays a crucial role in promoting efficient π–π stacking, reducing aggregation, and enhancing donor–acceptor interactions. The removal of the Tz unit simplifies synthesis while improving phase separation and charge transport, demonstrating the potential for designing high-performance NFAs with reduced complexity. Furthermore, advanced synchrotron-based characterization techniques such as GIWAXS and SWAXS at **TLS 23A1** proved invaluable for revealing the molecular packing behaviors and guiding rational molecular design. By leveraging rational sample design and state-of-the-art characterization methods, this study not only advances the understanding of NFAs but also paves the way for future innovations in OPVs. The findings emphasize the importance of integrating molecular design, structural analysis, and device optimization to overcome limitations in existing NFAs. (Reported by Hao Ming Chen, National Taiwan University)

This report features the work of Yen-Ju Cheng and U-Ser Jeng published in J. Am. Chem. Soc. ***146****, 833 (2024).*

TLS 23A1 Small/Wide Angle X-ray Scattering

- GIWAXS, GISAXS
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References

1. C. Yan, S. Barlow, Z. Wang, H. Yan, A. K. Y. Jen, S. R. Marder, X. Zhan, Nat. Rev. Mater. **3**, 18003 (2018).
2. G. Zhang, F. R. Lin, F. Qi, T. Heumüller, A. Distler, H.-J. Egelhaaf, N. Li, P. C. Y. Chow, C. J. Brabec, A. K.-Y. Jen, H.-L. Yip, Chem. Rev. **122**, 14180 (2022).
3. Y.-J. Xue, Z.-Y. Lai, H.-C. Lu, J.-C. Hong, C.-L. Tsai, C.-L. Huang, K.-H. Huang, C.-F. Lu, Y.-Y. Lai, C.-S. Hsu, J.-M. Lin, J.-W. Chang, S.-Y. Chien, G.-H. Lee, U-Ser Jeng, Y.-J. Cheng, J. Am. Chem. Soc. **146**, 833 (2024).