

Tuning of energy transfer and charge photogeneration in small molecule based bulk heterojunction via molecular engineering revealed by time-resolved spectroscopy.

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Their well-defined structure and molecular weight give small molecules an edge compared to polymers as organic semiconductors.^[1] However, the absence of long-range intrachain conjugation means intermolecular interactions play a crucial role. Here, we present two novel small molecules, in which π -stacking is turned on and off via molecular engineering of sidechains, as indicated by 1H–1H double quantum–single quantum (DQ–SQ) NMR experiments (Fig. 1). Time-resolved photoluminescence studies show that suppressing the π -stacking results in a slower diffusion of excitons. When implementing these molecules in bulk heterojunctions, the lack of diffusion in turn limits charge generation as evidenced by transient absorption spectroscopy (TAS), see Fig. 1. In addition, TAS shows that the weakness of intermolecular interactions hinders the diffusion of charges away from the heterojunction interface, as indicated by increased geminate recombination and a long-lasting electro-absorption signal. Additional evidence of for slower charge transport is provided by the relatively large apparent reaction order of non-geminate recombination, which is an indication of recombination of separated charges largely influenced by trapping events.

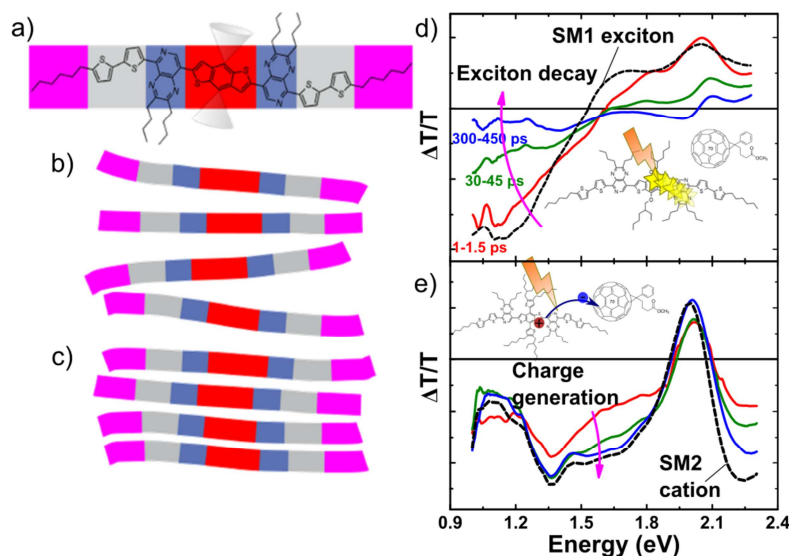


Figure 1: a), b) and c) Schematic representation of the molecular packing inferred from 1H-1H DQ-SQ NMR spectra^[2]. a) shows the common core structure of the 2 molecules, b) depicts the lesser backbone correlated extent of packing in SM1-based films, c) emphasizes the packing observed in SM2-based films favorable to π -stacking. d) and e) sub-nanosecond transient absorption spectra of SM1:PC₇₁BM and SM2:PC₇₁BM blends, respectively, together with the reference spectra of SM1 excitons obtained from films of pristine SM1 10 ps after photoexcitation and SM2 cations obtained from SM2:PC₇₁BM blends films, 10 ns after photoexcitation.

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References:

- [1] S. D. Collins, N. A. Ran, M. C. Heiber, T.-Q. Nguyen, *Adv. Energy Mater.*, **2017**, 7 (1), 1602242
- [2] J. Wolf, M. Babics, K. Wang, Q. Saleem, R.-Y. Liang, M. R. Hansen, P. M. Beaujuge, *Chem. Mater.*, **2016**, 28 (7), 2058
- [3] O. Alqahtani, M. Babics, J. Gorenflot, V. Savikhin, T. Ferron, A. H. Balawi, A. Paulke, Z. Kan, M. Pope, A. J. Clulow, D. Neher, M. F. Toney, F. Laquai, P. M. Beaujuge, B. A. Collins, "The case for moderate domain purity to enhance charge generation and collection in small molecules organic solar cells", Manuscript in preparation.