Correlation between alkyl chain length and aggregated structures in nitrogen-doped perylene diimide analogues

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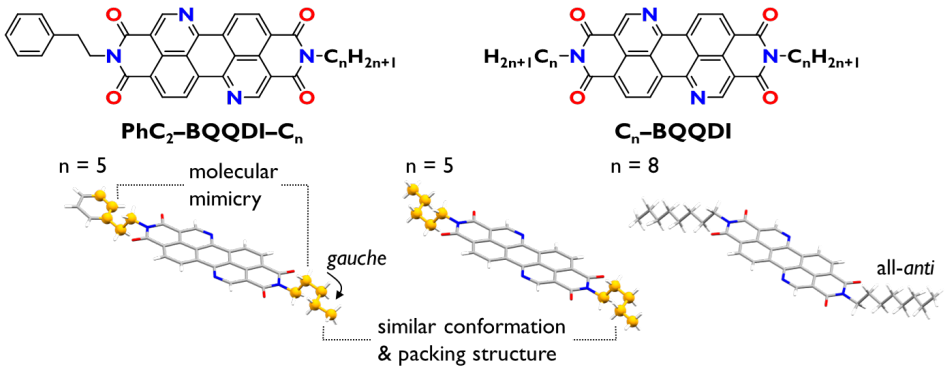
The aggregated structure is a crucial factor of materials properties. Recently, our group studied nitrogen-doped perylene diimide analogues, benzo[*de*]isoquinolino[1,8-*gh*]quinolinetetracarboxylic diimide (BQQDI), as n-type organic semiconductors.[1] The recent paper on phenethyl/alkyl asymmetrically functionalized BQQDI derivatives (PhC_2–BQQDI–C_n) has indicated that, when n = 5–7, PhC_2–BQQDI–C_n can exhibit a similar brickwork packing structure to phenethyl-functionalized BQQDI (PhC_2–BQQDI), one of the most promising BQQDI derivatives reported to date.[2] This phenomenon is attributed to a unique behavior of alkyl groups, namely, molecular mimicry, where a part of alkyl moieties adopts the *gauche* conformation to mimic the phenethyl counterpart.[2] To comprehend the intrinsic impact of alkyl chain length, in this study, symmetrically and asymmetrically functionalized BQQDI derivatives bearing alkyl substituent(s) were investigated.

Symmetrically alkyl-functionalized BQQDIs (C_n–BQQDI) and PhC_2–BQQDI–C_n were synthesized at various alkyl chain lengths (n). As represent, C_5–BQQDI was found to exhibit bulk polymorphism, with both polymorphs exhibiting the *gauche* conformation, one of which is comparable to that observed in PhC_2–BQQDI–C_5. Importantly, the *gauche* conformation is important for large intermolecular orbital overlaps. In contrast, C_8–BQQDI adopts all-*anti* conformation, leading to poorer intermolecular orbital overlaps. The comprehensive discussion and comparison of the influences on solid-state properties will be given in the presentation.



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