Design and synthesis of benzo[*de*]isoquinolino[1,8-*gh*]quinoline diamides π-electron systems

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Synthetically versatile electron-deficient π-electron systems are urgently needed for organic electronic applications, yet their design and synthesis are challenging due to the low reactivity from large electron affinities.[1] The high-performance benzo[*de*]isoquinolino[1,8-*gh*]quinolinetetracarboxylic diimide (BQQDI) n-type organic semiconductors[2] (Figure 1) possess deep-lying lowest unoccupied molecular orbital (LUMO) levels that are necessary for air-stable electron transports in transistors, but this very electronic feature limits their synthetic and application versatilities. In the current molecular design, we remove a CO group from each imide of the BQQDI to introduce the novel benzo[*de*]isoquinolino[1,8-*gh*]quinoline diamide (BQQDA) π-electron system (Figure 1).[3] The push-pull nature of the condensed amide moieties as opposed to the strongly electron-deficient imide provide versatility in chemical functionalization to tailor the BQQDA π-electron system for various electronic applications. We demonstrate an effective synthetic method to furnish the target amide-containing BQQDA parent structure via organocatalysis, and highly selective functionalization can be performed on the condensed amide moieties as well as on the *bay* positions of the nitrogen-containing skeleton. Fine-tuning of the fundamental properties and supramolecular packing motifs are achieved via chemical modifications (Figure 1), and the cyanated BQQDA organic semiconductor demonstrates a high air-stable electron-carrier mobility. Besides their uses in transistors, the photochemical properties of the BQQDA π-electron systems also show promise for optoelectronic applications.

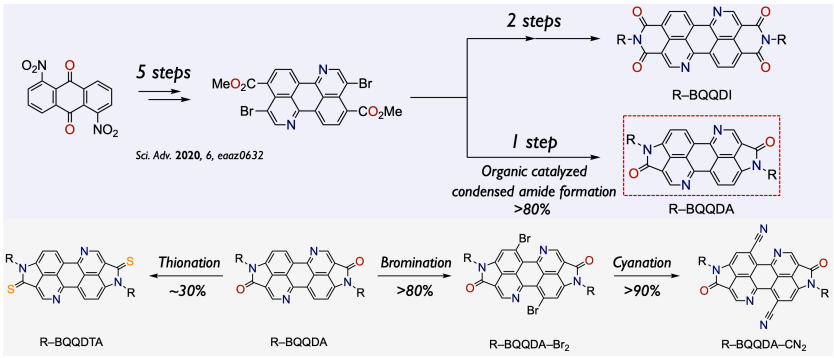

Figure 1 The synthetic routes for R–BQQDI, R–BQQDA and various chemical modifications of the BQQDI π-electron system.

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