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Light-Frozen Dynamic Covalent Synthesis of Electron-Deficient Conjugated Materials

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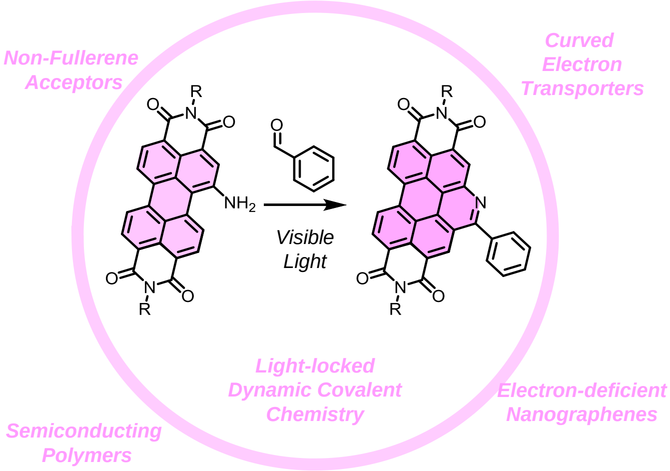
Organic electronics devices are now all around us and the chemistry of organic semiconductors of various optical and electronic properties is blooming. If the development of p-type (holes transporting, electron-rich) organic semiconductors has seen the synthesis and characterization of a wide variety of high-performing new materials, the preparation of their n-type (electron-transporting, electron-poor) equivalents is still lagging behind. This is mainly due to the difficulty to selectively and efficiently introduce electro-attracting group on conjugated molecules and to the low variety of electron-poor scaffolds available. We present here an alternative way to prepare AzaBenzannulated PeryleneDiimides (AzaBPDIs) that proceeds in three steps in one pot: an imine condensation by reaction between an amino-PDI derivative and an aldehyde, followed by a visible-light induced photocyclization and re-aromatization. This class of materials has been so far underexploited in organic electronics as previous strategies relied on poorly efficient acid-catalysed cyclisations. This light-mediated method allows us to prepare bay-extended perylenoïd materials without the need for a precious metal catalyst and the tedious preliminary bromination of the PDI core. Multimeric and heteroatoms doped materials prepared with various aromatic side-groups showed good n-type semiconducting properties and performed as modest non-fullerene acceptors in organic solar cells exhibiting high open-circuit voltages. Interestingly, the reversible and dynamic covalent character of the first step of the reaction opens a new route for the synthesis of organic semiconducting polymers, by preparing size-defined oligomers and polymers at thermodynamic equilibrium, subsequently locked by exposure to visible light into kinetically inert materials.



Références

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