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Rational Design and Synthesis of 2D/3D Conjugated Porous Polymers via Facile and 'Greener' Direct Arylation Polycondensation

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Abstract : Conjugated porous polymers (CPPs) are amorphous, insoluble and highly robust organic semiconductors that have been largely synthesized by traditional transition-metal catalyzed reactions. The distinguishing feature of CPP materials is that they combine microporosity and high surface areas with extended conjugation, making them ideal for versatile applications such as separation, catalysis and energy storage. By applying a modular approach to synthesis, chemical and electronic properties of CPPs can be tailored for specific applications making these materials economical alternatives to inorganic semiconductors. Direct arylation - an environmentally benign alternative to traditional polymerization reactions – is one such reaction that extensively over the last decade for the synthesis of linear p-conjugated polymers. In this report, we present the synthesis and characterization of a new series of robust conjugated porous polymers synthesized by facile direct arylation polymerization of thiophene-flanked acceptor building blocks with multi-brominated aryls with different geometries. We observed that the porosities and morphologies of the polymers are determined by the chemical structure of the aryl bromide used. Moreover, good control of the optical bandgap in the range 2.53 - 1.3 eV could be obtained by using different building blocks. Structure-property relationships demonstrated in this study suggest that direct arylation polymerization is an attractive synthetic tool for the rational design of porous organic materials with tunable photo-physical properties for applications in photocatalysis, energy storage and conversion.

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