

Hyperbranched polyarylethenes synthesized by successive C-H vinylation

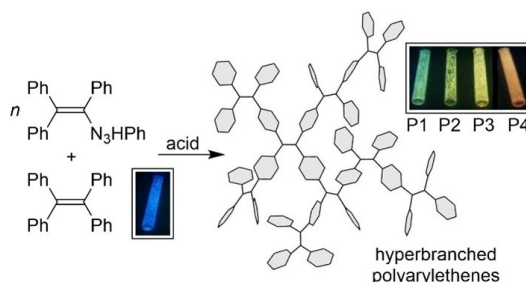
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Since the aggregation-induced emission (AIE) phenomenon was discovered for tetraphenylethene (TPE) in 2007,¹ polymers based on tri- and tetraphenylethene have received renewed interest.² These polymers stand out for highly functional properties such as enhanced AIE, high luminescence quantum yield in the solid state, high porosity, and response to additives. As a consequence, polyarylethenes were applied as effective sensors for explosives and metal ions, as gas sorption compounds, and as light-emitting materials.^{3,4}

Polyarylethenes are generally synthesized from monomers featuring reactive functional groups (halogens, boronic acids, terminal alkynes) using C–C coupling reactions,² reductive olefinations, or cyclotrimerizations.⁴ The existing approaches are effective and high-yielding. However, the final polymeric products remain chemically unstable due to the presence of the functional groups on the ends or in the periphery.

Here we show a novel procedure for the synthesis of polyarylethenes. As coupling polymerization, we employ a C–H vinylation of aromatic cores mediated by acid-induced cleavage of a triazene (Scheme 1).



Scheme 1. Synthesis of polyarylethenes via C–H polyvinylation.

The methodology allows obtaining 'inert' polyarylethenes without reactive functional groups in good yield. The branched polyarylethenes were characterized by NMR, HRMS, GPC, TGA, and elemental analysis. They show a size-dependent luminescence and a double emission in the solid state and in aggregates. The unusual AIE behaviour allows ratiometric detection of metal ions in water solutions.

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