

Hyperbranched polyarylethenes synthesized by successive C-H vinylation

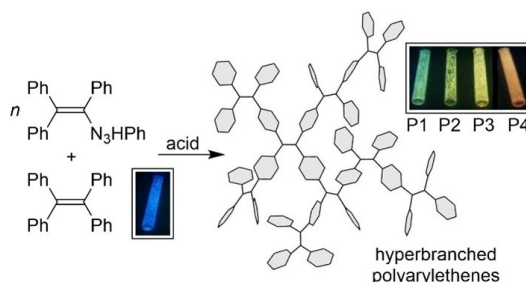
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Since the aggregation-induced emission (AIE) phenomenon was discovered for tetraphenylethene (TPE) in 2007,¹ polymers based on tri- and tetraphenylethene have received renewed interest.² These polymers stand out for highly functional properties such 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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