

## ABSTRACT

---

An atom-economic one-step chain-growth coordination homopolymerization providing high yields of functionalized hyper-cross-linked polyacetylenes with permanent micro/mesoporous texture and specific surface area up to 1062 m<sup>2</sup>/g was introduced and optimized. Substituted 1,3-diethynylbenzenes served as monomers simultaneously providing functionalization and hyper-cross-linking of the networks. The homopolymerization was compatible with the heteroatom groups of the monomers and allowed to prepare polyacetylene networks with the wide spectrum of univalent functional groups: -F, -Cl, -Br, -NO<sub>2</sub>, -COOCH<sub>3</sub>, -CH<sub>2</sub>OH, -COOH and -CH=O decorating the aromatic segments of the networks in a high extent (7.87 mmol/g).

A novel two-step synthesis of functionalized hyper-cross-linked polyacetylenes was introduced combining chain-growth coordination polymerization of acetylenic monomers and covalent templating using acetal and Schiff base protecting groups. By postpolymerization hydrolytic removal of the protecting segments from the primary networks, the networks with a high content (up to 9.61 mmol/g) of univalent functional groups -CH<sub>2</sub>OH, -CH=O and -NH<sub>2</sub> were prepared. These groups were placed either on the cross-linking or linear (aromatic and aliphatic) network segments, even in the vicinity of the main polyacetylene chains. The deprotection not only liberated the reactive groups but also modified the porous texture of the networks towards higher pore volume and specific surface area. In some cases, the porous texture was even completely generated by this detemplating.

The character of the functional groups and their content significantly influenced the sorption activity and selectivity of the prepared networks. In general, the presence of the functional groups increased the capacity of reversible CO<sub>2</sub> capture up to 10 wt. % (1 bar, 273 K). Networks with oxygen-containing groups showed high activity in cyclic reversible capture of water vapor from the air (up to 445 mg/g, at RH = 90 %). On the contrary, halogenated networks were active in trapping benzene vapor from the air (up to 971 mg/g, room temperature). Porous networks with aldehyde groups efficiently, selectively and reversibly chemisorbed amines and alcohols from the liquid phase (up to 350 mg/g). Functional properties of networks with aldehyde groups were possible to modify by post-polymerization covalent incorporation of variously functionalized amines while preserving the porous texture.