

Christoph Kahrs,<sup>[a]</sup> Mathias Wickleder<sup>[b]</sup> and Jens Christoffers\*<sup>[a]</sup>

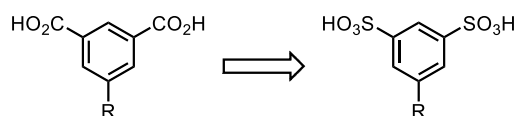
[a] Institut für Chemie, Carl von Ossietzky Universität Oldenburg, D-26111 Oldenburg

[b] Department für Chemie, Universität zu Köln, Greinstr. 6, D-50939 Köln

Sulfonic acids serve as interesting, yet not intensively studied alternatives to carboxylic acids as linker units in coordination polymers. In this study, we present the synthesis of hybrid sulfonic acids with polar, rigid biphenyl moieties and disordered highly fluorinated alkyl chains.

## Introduction

As an alternative for the well-known carboxylic acids, we aim to synthesize new sulfonic acids as linker moieties in metal organic frameworks. Sulfonic acids exhibit interesting properties, which pays for their challenging synthesis compared to carboxylic acids.

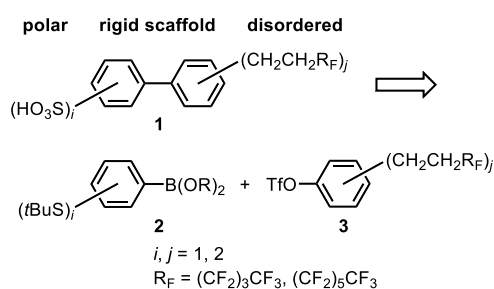


- well-known structures
- easy synthesis
- variety of metal organic frameworks
- less investigated
- challenging synthesis
- few coordination polymers

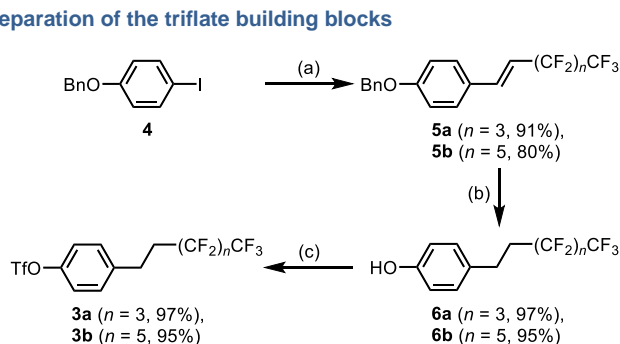
### advantages of sulfonic acids

- high acidity (use of metall oxides, hydroxides and carbonates)
- additional oxygen atoms (different coordination types)
- sulfonates are thermally more stable (up to 200°C)

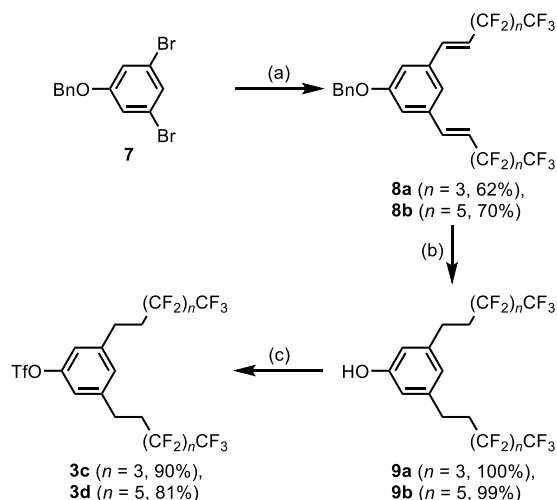
Herein, we report the synthesis of sulfonic acids **1** consisting of three entities: (1) polar, hydrophilic aromatic sulfonic acids, which might define proton conducting materials in the solid state or could form crystalline salts with various metal cations; (2) a rigid biphenyl scaffold being the structural element for inducing crystallinity of the material; and (3) hydrophobic perfluorinated residues creating domains without well-defined crystalline order.<sup>[1]</sup>



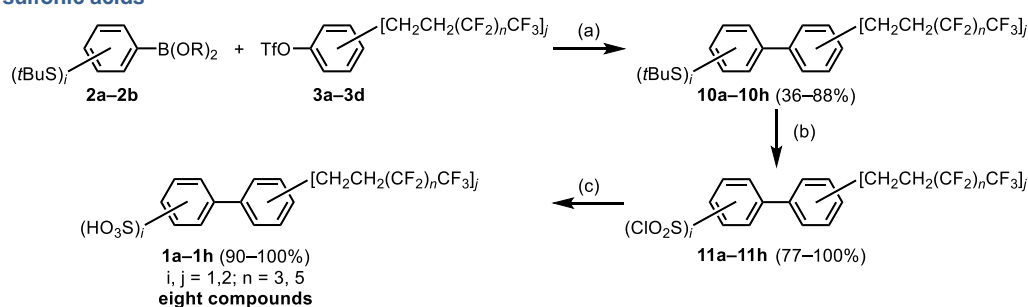
## Preparation of the triflate building blocks



**Scheme 1.** Reagents and conditions: (a) 10-20 equiv.  $\text{CH}_2=\text{CH}(\text{CF}_2)_n\text{CF}_3$ , 10 mol%  $\text{Pd}(\text{OAc})_2$ , 20 mol%  $\text{P}(\text{otol})_3$ , 5-10 equiv.  $\text{K}_2\text{CO}_3$ , DMF, 140°C, 18 h; (b) 10 mol% Pd-C, 4 bar  $\text{H}_2$ , EtOAc, 70°C, 18 h; (c) 1.2 equiv.  $\text{Tf}_2\text{O}$ , 2.0 equiv. pyridine,  $\text{CH}_2\text{Cl}_2$ , 23°C, 1.5 h.



## Preparation of the sulfonic acids



**Scheme 2.** Reagents and conditions: (a) 5 mol%  $[\text{Pd}_2\text{dba}_3]$ , 20 mol% SPhos, 2.0 equiv.  $\text{K}_2\text{CO}_3$ , toluene/ $\text{H}_2\text{O}$  1:1, 140°C, 18 h; (b) 4 x *i* equiv. NCS, 1.1 x *i* equiv. HCl, MeCN, 0°C, 1 h, 23°C, 1 h; (c)  $\text{H}_2\text{O}$ , 100°C, 18 h.

## Acknowledgement

Financial support from the Deutsche Forschungsgemeinschaft and the Heinz Neumüller Stiftung is gratefully acknowledged.