Pyridine and Pyrimidine Functionalized Sulfonic Acids as Linkers for Metal Organic Frameworks

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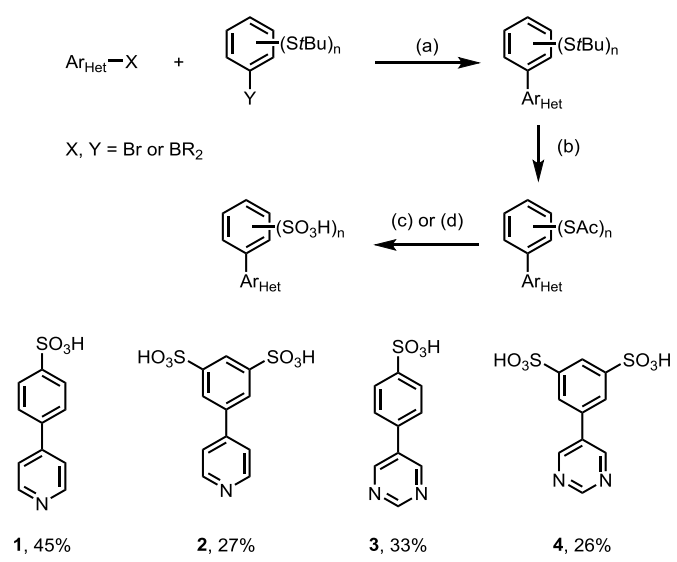
Pyridine and pyrimidine functionalized sulfonic acids were synthesized by palladium catalyzed C-C bond formation. Subsequent treatment with different metal carbonates and hydroxides delivered several sulfonates, which were characterized by X-ray diffractometry.

Introduction

Aromatic oligocarboxylic acids are the leading structural motif for linker molecules in metal organic frameworks and coordination polymers.[1] The key advantage of this compound class is the flexible accessibility of various structural subtypes with different symmetries, which is based on a rich and well developed synthetic organic chemistry targeting benzene carboxylic acids. In contrast, the synthesis of aromatic sulfonic acids is much less developed, which is mainly due to the electronically deactivating character of a sulfo group making a second sulfonation (electrophilic aromatic substitution) very difficult. However, advantageous features of sulfonic acids compared to carboxylic acids are their pronounced thermal stability and higher acidity, making them attractive target structures for the preparation of new materials.[2] Here we would now like to introduce novel hybrid linker molecules based on biaryl compounds with two type of donor moieties: Nitrogen donor functions like pyridine and pyrimidine derivatives suitable for coordination to late (soft) transition metals and sulfonate groups and for the coordination of early (hard) transition metals or lanthanides.

Preparation of functionalized sulfonic acids

In a first step, pyridine-4-boronic acid or 5-bromopyrimidine were linked with a *tert*-butyl protected thiol by a Suzuki coupling. These biaryls were then deprotected at sulfur using BBr_3/AcCl and finally oxidized with H_2O_2 in KOH/methanol to obtain the sulfonic acids **1**-**4**.



1, 45% **2**, 27% **3**, 33% **4**, 26%

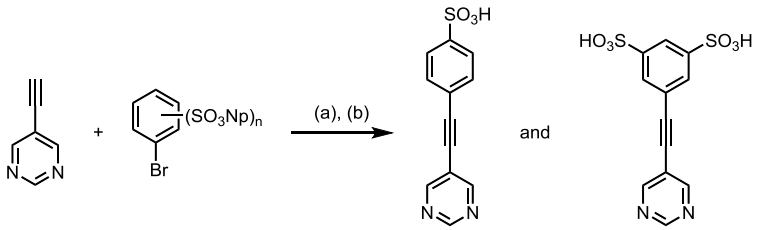
Scheme 1. Synthesis of sulfonic acid derivatives **1**-**4** (yields over four steps). Reagents and conditions: (a) 2.0 equiv. K_2CO_3, 10 mol% [$Pd(PPh_3)_4$], THF or toluene/H_2O 1:1, 100-140°C, 18 h; (b) 2.5–7.0 equiv. BBr_3, toluene/AcCl 4:1, 0°C→23°C, 3 h; (c) 2.0–4.0 equiv. KOH, 15–30 equiv. H_2O_2, MeOH, 23°C, 18 h; (d) 2.0–4.0 equiv. KOH, MeOH, 23°C, 30 min, then 15–30 equiv.H_2O_2, MeOH, 23°C, 18 h; n = 1,2; R = OH or R_2 = pin.

Acknowledgement

Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Preparation of alkyne functionalized sulfonic acids

The alkyne derivatives of the pyrimidine sulfonic acids **3** and **4** were synthesized from 5-ethynylpyrimidine **5** and bromobenzenesulfonate **6** in two steps by Sonogashira coupling and deprotection of the neopentyl sulfonate. Thus, we were able to obtain two different pyrimidine functionalized sulfonic acids **7** and **8** with alkyne spacers.



5 **6** **7**, 36% **8**, 26%

Scheme 2. Synthesis of pyrimidine sulfonic acids with ethynediyl spacer **7** and **8** (yields over two steps). Reagents and conditions: (a) 5 equiv. Et_2NH, 10 mol% [$Pd(PPh_3)_2Cl_2$], 11 mol% CuI, THF, 100°C, 18 h; (b) DMF, 155°C, 21 h; Np = neopentyl (2,2-dimethylpropyl); n = 1,2.

X-ray structure of sodium salt of compound 8

As a representative example, the X-ray structure of the sodium salt of compound **8** was obtained by conversion of the corresponding acid with sodium carbonate and recrystallization from water/DME.

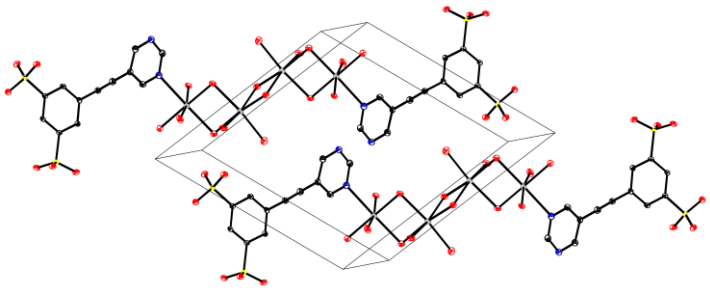


Figure 1. ORTEP representation of the sodium salt of compound **8** in the solid state. Hydrogen atoms are omitted for clarity.

[1] H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* **2013**, *341*, 1230444.

[2] T. W. T. Muesmann, M. S. Wickleder, J. Christoffers, *Synthesis* **2011**, 2775-2780.