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Synthesis of phosphonosulfonic acid building blocks as linkers for coordination polymers

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Ten aromatic building blocks (8-11, 23-28) containing phosphonic and sulfonic acid groups within one molecule were synthesized. Twofold nucleophilic substitution starting from 1,2,4,5tetrakis(bromomethyl)benzene (1) followed by hydrolysis gave building blocks 8-11. To obtain building blocks 23-28, the respective bromobenzenesulfonic acids 13, 16, 18-20 and 22 had to be synthesized first. Palladium-catalysed cross coupling with triethylphosphite followed by hydrolysis gave the desired building blocks with phosphonic and sulfonic acid groups. Building block 9 was successfully used as a linker for the synthesis of a new La-based CP with the composition $[La_2(H_2L)_{1.5}(H_2O)_4]$.

Introduction

Coordination polymers $(CP)^1$ and metal-organic frameworks $(MOF)^2$ are intensely studied compounds with possible application in gas storage, gas separation, catalysis, drug delivery and ion conduction.^{3,4}

The most investigated frameworks are based on carboxylates as organic building blocks.⁵ Considerably less well-studied are organic phoshonates and sulfonates. This might be because single crystal growth and the prediction of the coordination chemistry of metal phosphonates is more difficult and since they mostly form non-porous dense layered materials. In the case of metal sulfonates, the relatively weak coordination of the anions to the metal nodes facilitates the formation of crystalline products, but often these networks are less robust. Nevertheless, there is a broad spectrum of phosphonate and sulfonate frameworks described to date.⁶

Especially in the field of ion conduction, the use of organic building blocks with phosphonic or sulfonic acid groups has shown promising results. While metal phosphonates are able to build stable frameworks with high proton conductivity^{7,8}, metal sulfonates seem to be more promising in sulfonate-carboxylate frameworks.⁹ In the latter case, the carboxylates coordinate to metal nodes and the sulfonate remains free. But also phosphonate-carboxylate frameworks are known for very

high proton conduction.^{4,10}

Examples^{11,12,13} of organic building blocks containing a phosphonic and a sulfonic acid group are rare, which limits the investigation of metal phosphonate-sulfonate frameworks.^{14,15–18} In case of the known frameworks, very little is known in terms of proton conduction.^{19,20} To the best of our knowledge, only four organic building blocks have been successfully used up until now. In case of flexible building blocks, only 2-phosphonoethanesulfonic acid^{18,21} and 4-phosphonobutanesulfonic acid^{17,22} have been investigated. The majority of known metal phosphonate-sulfonate frameworks have been obtained using rigid *m*- or *p*-phosphonobenzenesulfonic acid.^{15,16,19,23}

Our research focuses on the synthesis of new rigid and flexible benzene-based building blocks containing at least one sulfonic acid and one phosphonic acid group.

Results and discussion

The synthesis of aromatic building blocks containing both sulfonic and phosphonic acid groups (herein called phosphonosulfonic acids) can be divided into two approaches. Either these groups are connected directly to the aromatic ring or via a flexible spacer unit.

To obtain flexible phosphonosulfonic acids, 1,2,4,5tetrakis(bromomethyl)benzene (1) was chosen as the starting material. Nucleophilic substitution of the bromides with triethyl phosphite⁷ or sodium sulfite²⁴ at the benzyl positions has proven to be an efficient tool to introduce $-PO_3H_2$ and $-SO_3H$ groups.

The synthesis of new rigid phosphonosulfonic acids is based oncombiningdifferentsyntheticapproaches.Previously,sulfonationofbenzenephosphonic acidhasbeenreported togive3-phosphonobenzenesulfonicacidand

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Electronic Supplementary Information (ESI) available: linker synthesis and characterization, $[La_4(H_2L)_3(H_2O)_8]$ synthesis and characterization, PXRD data, and X-ray crystallographic files. CCDC 1547972. For ESI and crystallographic data (CIF) see DOI: 10.1039/x0xx00000x

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(23).¹³ 5-phosphonobenzene-1.3-disulfonic acid But sulfonation of aromatic phosphonic acids has two major draw backs: long reaction times of up to 35 d and only metasubstitution due to the electron withdrawing effect of the phosphonic acid group. Therefore, Montoneri et al. synthesized 4-phosphonobenzenesulfonic acid using a different approach.¹¹ 4-Bromobenzenesulfonic acid ethyl ester was synthesized from the respective sulfonic acid chloride and sodium ethanolate. The obtained arylbromide was converted with triethyl phosphite and nickel(II) chloride to the respective arylphosphonic acid diethyl ester. This synthesis is known as the Tavs reaction.²⁵ Hydrolysis of the diester yielded 4phosphonobenzenesulfonic acid.

Sulfonation of arylbromides and bromination of arylsulfonic acids were chosen to obtain a large variety of different bromobenzenesulfonic acids. Compared to arylphosphonic acids, many different arylbromides are commercially available and the electron donating effect of the bromine allows *ortho*and *para*-sulfonation in short reaction times. Following a modified Tavs reaction using microwave-assisted heating, the respective phosphonobenzenesulfonic acids were obtained. **Synthesis of flexible phosphonosulfonic acids**

Although 1,2,4,5-tetrakis(bromomethyl)benzene (1) is commercially available, it was synthesized from durene (1,2,4,5-tetramethylbenzene) according to a literature procedure.²⁶ Nucleophilic substitution of **1** was performed with two equivalents of triethyl phosphite. Two equivalents were chosen to get di-substituted phosphonic acid ethyl esters. The remaining bromomethylene groups would allow nucleophilic substitution with sodium sulfite to introduce the sulfonic acid groups.



Scheme 1 Nucleophilic substitution of 1,2,4,5-tetrakis(bromomethyl)benzene (1) with two equivalents of triethyl phosphite. a) $P(OEt)_3$, toluene, 12 h reflux.

Due to very similar reactivities of the bromomethylene groups in the starting material and products, a mixture of the starting material and six different phosphonic acid ethyl esters (mono-, di-, tri- and tetra-phosphonic acid diethyl esters) was obtained. Column chromatography of the mixture yielded pure monosubstituted phosphonic acid diethyl ester 5 in the first fraction, a mixture of di-substituted 2, 3 and 4 in the second fraction and pure tri-substituted phosphonic acid diethyl ester 6 in the third fraction. The tetra-substituted phosphonic acid diethyl ester 7 was not isolated. A mixture of the di-substituted esters 2 and 4 were obtained from the second fraction by crystallization. Column chromatography of this mixture yielded pure 2 and pure 4. Fortunately 3 did not crystallize because separation of 2 from 3 or 4 via column chromatography is possible but separation of 3 from 4 was not successful even after several attempts. Nevertheless, these purification procedures reduced the yields, especially for the di-substituted phosphonic acid diethyl esters 2 and 4.

The ¹H-NMR and ¹³C-NMR spectra of **2** and **4** are very similar and differ only by the chemical shift of the signals. NOESY experiments of both isomers were performed for unequivocal assignment. In case of isomer **2** a NOE interaction was observed between the protons of the bromomethylene group and the phosphonic acid diethyl ester methylene group. Such a NOE interaction was not found for isomer **4**. Also, a doublet of a doublet is observed for the ¹³C-NMR signal of the methylene carbon atom connected to the phosphorus atom for isomer **4**. The coupling constants could be assigned to ¹J and ⁴J coupling with the respective phosphorus atom. For the respective carbon atom of isomer **2**, only a doublet with a ¹J coupling is observed. The ⁶J coupling to the second phosphorus atom seems to be too small.

It is important to notice that tri-substituted phosphonic acid diethyl ester **6** should be used as fast as possible for further reactions. Ethanol impurities originating from column chromatography were difficult to remove and tended to react in a nucleophilic substitution of the bromide after some time. The respective ether was observed via ¹H-NMR spectroscopy and El mass spectrometry.

The desired phosphonobenzenesulfonic acids 8, 9, 10 and 11 were obtained by introduction of the sulfonic acid groups and hydrolysis of the phosphonic acid diethyl esters. Sulfonic acid groups were introduced by nucleophilic substitution of the bromides in 2, 4, 5 and 6 with sodium sulfite. The respective phosphonic acid diethyl esters were dissolved in acetone, added to a saturated sodium sulfite solution in water and heated for 12 h. A saturated solution was used to minimize nucleophilic side reactions with water. After removing acetone, conc. hydrochloric acid was added to hydrolyze the phosphonic acid diethyl ester and to decompose sodium sulfite. After removing the conc. hydrochloric acid, dimethylsulfoxide was added to dissolve the respective phosphonobenzenesulfonic acid. The majority of sodium chloride remained undissolved and was removed by filtration. The acids were precipitated by adding dichloromethane and filtered off. Since it is difficult to know whether the respective acids or sodium salts were obtained, ion exchange was used to

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remove the sodium ions. The four desired phosphonobenzenesulfonic acids **8**, **9**, **10** and **11** were obtained as colourless solids.



Scheme 2 Nucleophilic substitution of the bromides with sodium sulfite followed by hydrolysis of the phosphonic acid diethyl esters. a) 1. $Na_2SO_{3(aq)}$, acetone, 12 h, 100 °C; 2. $HCl_{(aq)}$, 2 d, 120 °C; 3. ion exchange.

Synthesis of rigid phosphonosulfonic acids

The general procedure for the preparation of different phosphonobenzenesulfonic acids can be divided into two steps: synthesis of the bromobenzenesulfonic acids and the Tavs reaction to introduce the phosphonic acid groups. Different approaches to obtain tri- and tetra-substituted bromobenzenesulfonic acids will be discussed.

5-Bromobenzene-1,3-disulfonic acid (13) was synthesized by bromination of benzenedisulfonic acid disodium salt (12). The starting material 12 was dissolved in conc. sulfuric acid and brominated with N-bromosuccinimide (NBS). Unbrominated starting material and dibrominated benzenedisulfonic acid were obtained as byproducts depending on the reaction time and the amount of NBS used. Starting material 12 could be separated by transferring product 13 into the organic layer with tetra-*n*-butylammonium cations. Surprisingly, the starting material 12 stayed in the aqueous layer. Since this was not the case for the dibrominated byproduct, the reaction conditions were optimized to prevent double-bromination. Stirring starting material 12 with 1.1 equivalents of NBS for 12 h at room temperature showed satisfying results. Cation-exchange after workup yielded the desired 5-bromobenzene-1,3disulfonic acid (13)



Scheme 3 Bromination of benzenedisulfonic acid disodium salt (12). a) 1. NBS, conc. sulfuric acid, 12 h, room temp.; 2. ion exchange.

In a similar approach, benzenesulfonic acid was reacted with NBS to obtain 3,5-dibromobenzenesulfonic acid (**16**). But only a mixture of different dibrominated benzenesulfonic acids was

obtained due to the electron-donating effect of the first substituted bromine. Since separation was too difficult, another approach using ipso-sulfonation of а tried.27 trimethylsilylbenzene was 3,5-Dibromo-1-(trimethylsilyl)benzene (14) was treated with trimethylsilyl chlorosulfonate to give 3,5-dibromobenzenesulfonic acid (16). The +I effect of the trimethylsilyl group surpasses the +M effect of the bromine atoms and enables an ipso-substitution. The addition of aqueous sodium hydroxide is necessary to hydrolyze the sulfonic acid trimethylsilyl ester intermediate 15.

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Scheme 4 <code>ipso-Sulfonation</code> of 14. a) CISO_3SiMe_3, 1,2-dichloroethane, 2 d, 90 °C; b) 1. NaOH_(aq); 2. ion exchange.

Another tri-substituted bromobenzenesulfonic acid was obtained using a modification of a published procedure.²⁸ 1,4-Dibromobenzene (**17**) was sulfonated with fuming sulfuric acid (20-30 % SO₃) to give 2,5-dibromobenzenesulfonic acid (**18**). After stirring for 2 h at 150 °C, the suspension became a clear solution. A mixture of the mono- and disulfonated dibromobenzenes was obtained in a ratio of 3:2. Optimization of the reaction conditions in favor of the mono-sulfonated product **18** was not successful. Using a weaker sulfonation agent like conc. sulfuric acid led to unexplainable side reactions. Reducing the reaction time favored mono-sulfonateination but at the same time not all starting material **17** was converted. Nevertheless, 2,5-dibromobenzenesulfonic acid (**18**) was obtained after separation from the disulfonated byproducts **19** and **20**.



 $\label{eq:Scheme 5} Scheme 5 \mbox{ Mono-sulfonation of 1,4-dibromobenzene (17). a) 1. Furning sulfuric acid (20 - 30 \% SO_3), 2 h, 150 °C; 2. ion exchange.$

As described in the literature²⁹, double-sulfonation of 1,4dibromobenzene (**17**) gives two isomers which are perfect precursor for the synthesis of tetra-substituted phosphonobenzenesulfonic acids.



 $[\]label{eq:scheme-f-$

By increasing the reaction time to 24 h and raising the temperature to 200 °C, only the disulfonated isomers 2,5-

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dibromobenzene-1,3-disulfonic acid (**19**) and 2,5dibromobenzene-1,4-disulfonic acid (**20**) were obtained. Contrary to the literature, both isomers were characterized.

Double-sulfonation was also possible for 1,3-dibromobenzene (**21**). Treatment with fuming sulfuric acid (65 % SO₃) gave 4,6-dibromobenzene-1,3-disulfonic acid (**22**). No disulfonated isomer was observed as well as any mono- or triple-sulfonation.



Scheme 7 Double-sulfonation of 1,3-dibromobenzene (21). a) 1. Fuming sulfuric acid (65 % SO₃), 5 h, 120 °C; 2. ion exchange.

The second step to obtain the tri- and tetra-substituted phosphonobenzenesulfonic acids involves the introduction of phosphonic acid groups. Conversion of the described bromobenzenesulfonic acids in a modified Tavs reaction²⁵ gave the respective phosphonic acid diethyl esters. The most common reaction conditions for arylbromides and aryliodides in a Tavs reactions are: high temperature (up to 200 °C), nickel(II) chloride as catalyst and triethyl phosphite as reagent and solvent. In addition, changing the catalyst to palladium(II) chloride and using microwave-assisted heating showed promising results in the literature.³⁰ Palladium(II) chloride gave better yields for bromoaryls in general and in the presence of a sterically demanding group in the ortho-position. Microwaveassisted heating was chosen because the necessary high temperatures (≥ 200°C) are easier to accomplish and the reaction time is much shorter compared to ordinary heating.

These conditions were adapted for all the Tavs reactions performed. Nevertheless, some optimizations had to be carried out to get satisfying results. Since acidity of the sulfonic acid might be problematic for the reaction and the workup, the respective tetra-*n*-butylammonium sulfonates were used. In contrast to sodium sulfonates, the organic sulfonates possess a better solubility and have a lower melting point. Both aspects ensure that the sulfonate mixes and reacts with triethyl phosphite. The synthesis of sulfonic acid esters, as described by Montoneri *et al.*¹¹, becomes irrelevant. The tetra-*n*-butylammonium sulfonates are easy and fast to obtain by treating the respective sulfonic acid with tetra-*n*-butylammonium hydroxide.

This procedure was successfully used for the conversion of trisubstituted bromobenzenesulfonic acids **13** and **16**. Subsequent hydrolysis of the respective phosphonic acid diethyl esters with conc. hydrochloric acid gave 5-phosphonobenzene-1,3-disulfonic acid (**23**) and 3,5-diphosphonobenzenesulfonic acid (**24**).



Scheme 8 Tavs reaction and hydrolysis to obtain 23 and 24. a) $1.NBu_4OH$; 2. $P(OEt)_{3}$, $PdCl_2$, MW; 3. $HCl_{(aq)}$; 4. ion exchange.

An unexpected side reaction reduced the yields of the three phosphonobenzenesulfonic acids **25**, **26** and **27** significantly. An ethylphosphinic acid ethylester group was partly introduced instead of the desired phosphonic acid diethyl ester group.



Scheme 9 The observed ethylphosphinic acid ethylester group

¹H-NMR spectra showed characteristic signals for an ethyl group connected directly to a phosphorus atom and a second set of aromatic signals. For all three cases, integration of the signals showed that the byproduct possesses one ethylphosphinic acid ethylester group and one phosphonic acid diethyl ester group. It remains unclear why and how this side reaction takes place. But it was observed only when a sulfonate group was in ortho position to a bromine atom. After ester hydrolysis, the phosphinic acid byproducts could be recrystallization. Pure 2,5separated bv diphosphonobenzenesulfonic acid (25), 2,5diphosphonobenzene-1,4-disulfonic acid (26) and 4,6diphosphonobenzene-1,3-disulfonic acid (27) were obtained.



Scheme 10 Synthesis of phosphonobenzenesulfonic acids 25, 26 and 27. a) 1.NBu₄OH; 2. P(OEt)₃, PdCl₂, MW; 3. HCl_(an); 4. ion exchange.



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Different side reactions were observed during the synthesis of 2,5-diphosphonobenzene-1,3-disulfonic acid (28). The Tavs reaction at the bromine in the 5-position works very well but the conversion of the bromine in the 2-position is very slow. ¹H-NMR spectra suggested that either the bromine atom did not react at all or it was substituted by a hydrogen atom. The desired product 28 was obtained in a mixture which mainly contains byproducts 29 and 23. 2,5-Diphosphonobenzene-1,3disulfonic acid (28) could be obtained by recrystallization in low yield.



Scheme 11 Synthesis of 2,5-diphosphonobenzene-1,3-disulfonic acid (28) with nonisolated byproducts 29 and 23. a) 1.NBu₄OH; 2. P(OEt)₃, PdCl₂, MW; 3. HCl_(aq); 4. ion exchange.

Synthesis of a La-based coordination polymer

Reactions were performed under hydrothermal conditions using $La(NO_3)_3 \cdot 6H_2O$ and the flexible linker 9 (H₆L, [2,5bis(phosphonomethyl)-benzene-1,4-diyl]bis(methylsulfonic acid).³¹ A new La-based CP with the composition $[{\rm La}_4({\rm H}_2{\rm L})_3({\rm H}_2{\rm O})_8]$ was obtained. The crystal structure of this compound was determined from single-crystal X-ray diffraction data and phase purity was confirmed by powder Xray diffraction (Fig. S1 and Fig. S2). The compound $[La_4(H_2L)_3(H_2O)_8]$ crystallizes in the monoclinic space group C2/m. The asymmetric unit contains two La³⁺ ions and two linker molecules on special positions and four water molecules (Figure 1).



Figure 1 Extended asymmetric unit of compound $[La_4(H_2L)_3(H_2O)_8]$ with 50% thermal ellipsoids, La-O bonds are presented by dashed lines. H atoms are omitted for clarity. [Symmetry code: (i) x + 0.5, y + 0.5, z; (ii) x + 0.5, y - 0.5, z; (iii) x,1 - y, z; (iv) x, - y, z; (v) x, y - 1, z]

Both La³⁺ ions (La1 and La2) are eightfold coordinated in a distorted square antiprismatic fashion by two water molecules

and six oxygen atoms from five or four different linker molecules for La1 and La2, respectively. Due to statistical incorporation of phosphonate and sulfonate groups the structure was refined with an occupancy of 0.5 for sulfur and phosphorus atoms at each position. All sulfonate/phosphonate groups coordinate two La³⁺ ions in a [2, 1 1 0] fashion and connect the linker molecule to six La³⁺ ions, four monodentate and two chelating (Fig. S3). Every La³⁺ ion is bound to two other La³⁺ ions by three sulfonic/phosphonic groups, forming chains along the *b* axis (Figure 2).



Figure 2 Excerpt of the structure of [La4(H2L)3(H2O)8]. Chains are formed by interconnections of La^{3+} ions through sulfonate/phosphonate groups. LaO₈ polyhedra in light blue and sulfonate/phosphonate groups as purple tetrahedra.

Each chain is interconnected via the organic moieties to three other chains and a double layer in the *a*-*b* plane with diamond shaped pores along the b axis is formed (Figure 3). Taking the van der Waals radii into account, the diameter of the pores is 3.8 Å (Fig. S5). They are interconnected by smaller pores along the c axis to form a three dimensional network of infinite channels that amounts to 30 % of the crystal space. This is shown by the calculation of the Connolly surface (Fig. S4).



Figure 3 Excerpt of the structure of [La4(H2L)3(H2O)8]. Double layer, in the a-b plane with diamond shaped pores along the b axis. The orange sphere with a diameter of 6.8 Å is used for easier visualisation. LaO₈ polyhedra in light blue and sulfonic/phosphonic groups as purple tetrahedra.

Considering the IR-spectra as well as the synthetic conditions, the pores are filled with disordered water molecules. Based on the distances between oxygen atoms in the crystal structure, the presence of hydrogen bonds can be postulated. Thus, the double layers are connected by hydrogen bonds between the oxygen atoms O1 and O2 which are two coordinating water

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molecules connected to La1 and La2, respectively, and O10 (Tab. S2). The latter oxygen atom (O10) belongs to a sulfonate/phosphonate group. Due to charge balancing, two protons must be present in the structure. Since these could not be localised, we postulate that $-PO_3H$ groups are formed, which is supported by IR spectroscopy (Fig. S6). The presence of hydrogen acceptor and donor groups in combination with the coordinating water molecules within the pores makes this CP a potential candidate for proton conduction.

Up to now only two mixed-linker lanthanum arylphosphonatosulfonates have been reported.³² The pure tetrasulfono or tetraphosphono linker molecules 1,2,4,5tetrakis(sulfonomethyl)-benzene 1,2,4,5-tetrakis and (phosphonomethyl)-benzene have also been reported but only one lanthanum tetraphosphonate (PCMOF-5) has been prepared with the latter linker. The compound crystallizes in a three dimensional framework structure. As observed in the title compound, the La³⁺ ions exhibit a distorted square antiprismatic coordination environment. In PCMOF-5, one of the four functional groups does not coordinate to the metal ion but protrudes into the pore making the pore surface highly acidic.'

Conclusions

In summary, ten aromatic building blocks (8-11, 23-28) with phosphonic and sulfonic acid groups were synthesized in batch sizes and up to several grams. For the literature-known building block 23, complete characterization and a new synthetic route was provided. Building blocks 8-11 possess a flexible methylene unit between each functional group and the benzene ring. The more rigid building blocks 23-28 have their functional groups directly connected to the benzene ring. Due to the coordinating ability of phosphonic and sulfonic acid groups, all ten building blocks might be used as linkers for CP or MOF synthesis. First attempts used flexible building block 9 as a linker in hydrothermal reactions with $La(NO_3)_3 \cdot 6H_2O$. A new La-based CP with the composition $[La_4(H_2L)_3(H_2O)_8]$ was discovered. Single-crystal X-ray diffraction data showed free hydrogen acceptor and donor groups within the pores. These results indicate the potential of these new organic building blocks for the preparation of proton conducting materials.

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