

study are commercially available or can be easily synthesized. They spontaneously self-assemble in neutral water giving rise to an assembly that displays some of the most important features of a sensor, such as sensitivity and selectivity. This modular approach allows for the easy variation of the components, which makes the process of system optimization very simple. Work is in progress to extend such a concept to ligands selective towards other metal ions and to widen its scope to the sensing of neutral molecules.

Experimental Section

N-Decylglycylglycine (**1**) was synthesized following a reported procedure^[13] and was isolated as the CF₃COOH salt. All spectral and analytical data were in agreement with the proposed structure. Representative data for **1**: m.p. 109–110 °C; elemental analysis calcd for C₁₆H₂₉N₂O₅F₃: C 49.7, H 7.56, N 7.25; found: C 50.1, H 7.51, N 7.27; ¹H NMR (250 MHz, CD₃OD, 25 °C, TMS): δ = 0.94 (t, *J* = 6.5 Hz, 3H), 1.38 (m, 14H), 1.74 (m, 2H), 3.07 (t, *J* = 6.7 Hz, 2H), 3.88 (s, 2H), 4.03 (s, 2H).

Critical micellar concentrations were obtained from surface tension measurements using a Krüss K6 apparatus. Ultrafiltrations were performed with a 8010 Amicon cell equipped with a regenerated cellulose Millipore filter with a cut-off of 10⁴ Daltons. Emission spectra were recorded on a Perkin–Elmer LS-50B spectrofluorimeter. Titrations were performed in a 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid (HEPES) buffer 0.01 M, pH 7, and 25 °C. Excitation and emission wavelengths (nm) were, respectively: 375 and 500 for ANS; 286 and 360 for 1-NAFOSF; 362 and 415 for 9-anthracenecarboxylic acid (ACA); 325 and 530 for dansylamide (DANSA).

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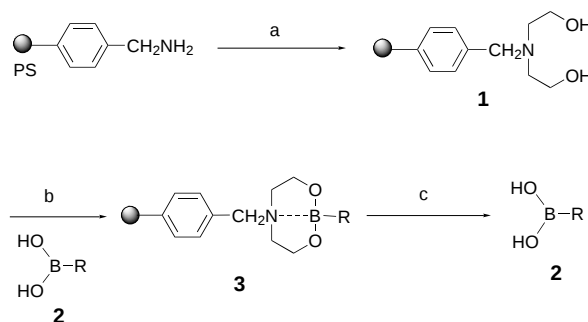
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N,N-Diethanolaminomethyl Polystyrene: An Efficient Solid Support to Immobilize Boronic Acids**

Dennis G. Hall,* Jyoti Tailor, and Michel Gravel

Insoluble resins that selectively couple to a functional group are vital in combinatorial chemistry to immobilize substrates to be derivatized by solid-phase synthesis.^[1] They are also employed as scavenger or “fishing out” resins in the solution-phase parallel synthesis of small molecule libraries.^[2] Despite the use of boronic acids as intermediates in reactions such as the Suzuki cross-coupling^[3] and in biological applications including sugar recognition^[4] and inhibition of serine proteases,^[5] there are currently no solid supports available that couple to the boronic acid functionality. Herein we report on the preparation of *N,N*-diethanolaminomethyl polystyrene (DEAM-PS), the first resin capable of immobilizing boronic acids, along with a preliminary assessment of its usefulness toward combinatorial chemistry applications. DEAM-PS resin can immobilize aryl, alkenyl, and alkyl boronic acids almost quantitatively in a wide range of organic solvents. Moreover, it is easily synthesized at low cost and can be recycled.

Diethanolamine boronate adducts have long been employed to stabilize, purify, and characterize boronic acids.^[6] We looked at several ways to derivatize polystyrene resin to include such a diethanolamine anchor. We have best achieved this goal through the reaction of aminomethylated polystyrene (AM-PS) with excess ethylene oxide at 50 °C in a THF/water solvent mixture in a sealed, pressure-resistant tube (Scheme 1). Under these conditions, quaternization to give the triethanolalkylammonium hydroxide salt and oxirane



Scheme 1. Synthesis of DEAM-PS resin **1**. Immobilization and subsequent release of boronic acids **2**. a) Ethylene oxide (excess), THF/H₂O 9/1 (sealed tube), 50 °C, 24 h; b) boronic acid **2** (see Table 1), solvent, RT, 15 min; c) THF/H₂O/AcOH 90/5/5, RT, 1 h; or THF/H₂O 9/1, RT, 2 h.

[*] Prof. D. G. Hall, J. Tailor, M. Gravel
Department of Chemistry, University of Alberta
Edmonton, AB, T6G 2G2 (Canada)
Fax: (+1) 780-492-8231
E-mail: dennis.hall@ualberta.ca

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alcoholysis are known to be minimal.^[7] Indeed, the resulting resin possessed characteristics and a loading level that suggested clean and complete dialkylation of AM-PS to give DEAM-PS (**1**).^[8]

Preliminary experiments showed that resin **1** can couple almost quantitatively to equimolar amounts of arylboronic acids **2** in dry THF after a few minutes (Scheme 1). The formation of a stable resin-bound boronate adduct **3** is highly favored, and as expected,^[6] there is no need to remove the water produced in this operation. The use of glycerol-PS resin^[10] led to less than 50% coupling under the same conditions, clearly underlining the benefit of possible nitrogen coordination with DEAM-PS (**1**).^[11] The boronic ester linkage in **3** can be quickly hydrolyzed with a THF/water/acetic acid (90/5/5) mixture to release the free boronic acids (**2**). In the case of acid-sensitive boronic acids the resin can also be cleaved under neutral conditions with prolonged exposure to THF/water (9/1). Since an excess of water is sufficient to release the boronic acid, albeit slowly, resin **1** is not recommended for the immobilization of boronic acids from aqueous solvent mixtures. A solvent profile study using *p*-tolylboronic acid (**2a**) as a model and a slight excess of resin **1** (1.25 equiv) showed that a broad range of organic solvents is suitable for scavenging applications (Table 1, entries 1–6).

Resin **1** was found to be very efficient in immobilizing a wide variety of electron-rich and electron-poor arylboronic acids in near quantitative yields in THF (entries 6–12).^[12] These values were determined from the amounts of boronic acids recovered after subsequent hydrolytic release from the support. Concentration of the filtrate from exhaustive rinsing of the resin after immobilization revealed none or very little unbound boronic acid. Most interestingly, resin **1** can also couple efficiently with alkenylboronic acids (entry 13) and even with air-sensitive alkylboronic acids, although with a lower yield in this case (entry 14). The boronic acids **2a–i** were all recovered intact after cleavage from the solid support, and DEAM-PS resin **1** can be recycled with no apparent loss of efficiency after neutralization with base washings (for example, CH₂Cl₂/Et₃N 3/1).

The use of scavenger resins to eliminate excess reagents is a promising strategy in the solution-phase synthesis of parallel libraries.^[2] In this regard, DEAM-PS resin **1** could be very useful to scavenge unreacted boronic acids employed in the Suzuki cross-coupling^[3] and other reaction processes. Similarly, it can be utilized to capture boronic acid products from complex reaction mixtures either for purification or to perform solid-phase transformations.^[13] As a significant demonstration of such applications resin **1** was employed in the purification of crude dienyboronic acid **6**.^[14] The latter is produced by treating 2-methyl-1-buten-3-yne (**4**) with dicyclohexylborane followed by oxidative workup (Scheme 2). The purification of alkenylboronic acids such as compound **6** can be considerably troublesome. However, the use of resin **1** to capture **6** and eliminate excess reagents and the cyclohexanol by-products greatly facilitates its purification through simple rinsing of its resin-bound form **5**.

Of particular interest to combinatorial chemistry is the use of resin **1** to immobilize functionalized boronic acid templates and plan different solid-phase transformations. For instance,

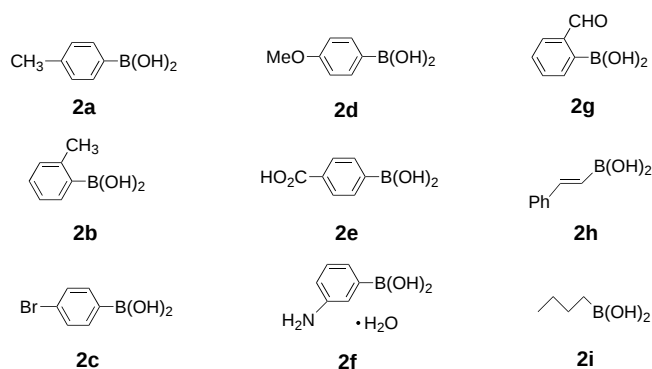
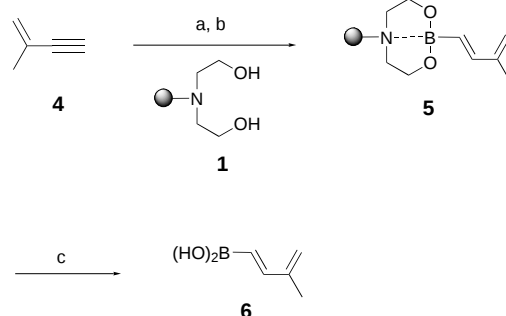


Table 1. Coupling of different boronic acids **2** with DEAM-PS resin **1**.^[a]

Entry	Boronic acid	Solvent	Yield [%] ^[b]	Purity [%] ^[c]
1	2a	CH ₂ Cl ₂	> 95	> 95
2	2a	DMF	87	> 95
3	2a	toluene	> 95	> 95
4	2a	CH ₃ OH	53	> 95
5	2a	Et ₂ O	90	> 95
6	2a	THF	> 95	> 95
7	2b	THF	> 95	> 95
8	2c	THF	> 95	> 95
9	2d	THF	> 95	> 95
10	2e	THF	> 95	> 95
11	2f	THF	> 95	> 90
12	2g	THF	90	> 95
13	2h	THF	91	> 90
14	2i	THF	50	> 90

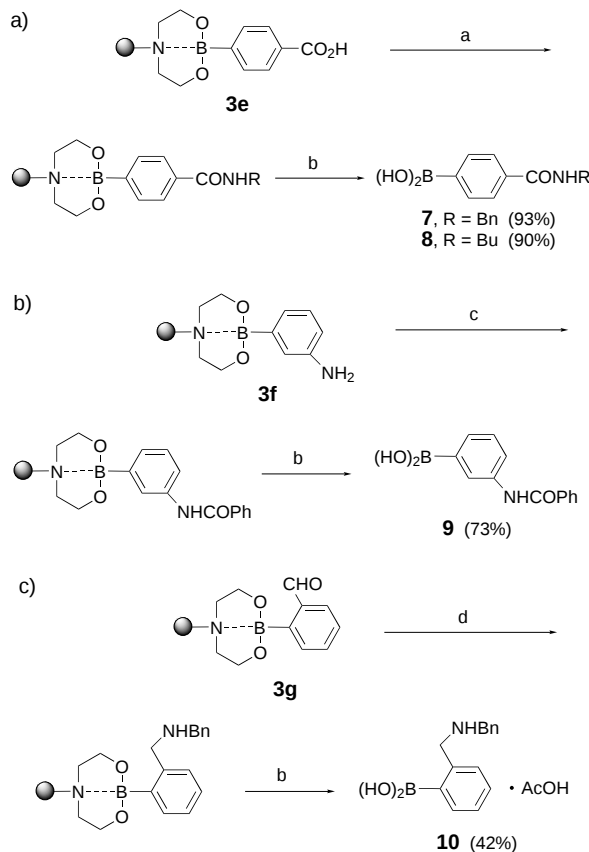
[a] The coupling reactions were conducted by shaking a slight excess of resin **1** (200 mg, 0.92 mmol g⁻¹ substitution) with the boronic acid (0.8 equiv) in the indicated solvent (2 mL) at RT for 15 min in a polypropylene vessel equipped with a fritted filter. [b] Based on the amount of boronic acid recovered after cleavage of the resin for 1 h in a THF/H₂O/AcOH mixture (90/5/5). A slight imprecision must be ascribed to these values as a result of exhaustive drying, which may lead to partial dehydration to give boronic acid anhydrides. [c] Estimated through comparison of the ¹H NMR spectra of the recovered boronic acids and the starting material.



Scheme 2. Purification of dienyboronic acid **6** with resin **1** following dicyclohexylboration/oxidation of **4**. a) Addition of **4** to (C₆H₁₁)₂BH (1.0 equiv) in THF, 0 °C, 0.5 h; RT, 0.5 h; then (CH₃)₃NO · 2H₂O (2.0 equiv), 0 °C to RT, 12 h; b) DEAM-PS resin **1** (0.5 equiv), CH₂Cl₂, 1.5 h; c) THF/H₂O 9/1, RT, 1.5 h, 95% (overall yield based on **1**).

this would allow the elaboration of diverse libraries of new arylboronic acids with potential use as inhibitors of serine proteases.^[15] In addition, whereas boronic acids are important building blocks for solid-phase Suzuki reactions in combina-

torial chemistry,^[16] few are commercially available. The *N,N*-diethylaminomethyl-PS boronate linkage (**3**, Scheme 1) was found to be resistant to standard carbodiimide methods for amide bond formation. Benzylamine and butylamine were coupled with high efficiency to resin-bound *p*-carboxyphenylboronic acid (**3e**), to afford the corresponding amides **7** and **8** in high yields after cleavage (Scheme 3a).^[17] Similarly, resin-



Scheme 3. Immobilization and solid-phase transformations of resin-bound arylboronic acids **3e–g**. Synthesis of new boronic acid derivatives **7–10**. a) RNH_2 (2.5 equiv), *N*-hydroxybenzotriazole $\cdot$ H_2O (2.5 equiv), *N,N'*-diisopropylcarbodiimide (2.5 equiv), DMF, RT, 6 h; b) THF/ H_2O /AcOH 90/5/5, RT, 1 h; c) PhCOCl (10 equiv), iPr_2EtN (11 equiv), THF, RT, 24 h; d) PhCH₂NH₂ (2.0 equiv), $NaBH(OAc)_3$ (2 equiv), $(ClCH_2)_2$, RT, 2 h.

bound *m*-aminophenylboronic acid (**3f**) was transformed into anilide **9** upon treatment with benzoyl chloride (Scheme 3b) and reductive amination of **3g** with benzylamine afforded **10** (Scheme 3c).^[17] Further work on applications of DEAM-PS resin is currently in progress.

Experimental Section

Preparation of DEAM-PS resin **1**: 1% DVB (DVB = divinylbenzene) cross-linked aminomethylated polystyrene (3.0 g, 1.00 mmol g⁻¹ substitution) was weighed out in a large thick-walled pressure tube equipped with a stirring bar. A THF/water solvent mixture (9/1, 25 mL) was added, followed by excess ethylene oxide (ca. 2 mL). The tube was quickly closed through its teflon screw cap equipped with a seal and immersed into an oil bath at 50–55 °C. The tube was hand shaken periodically when magnetic stirring became inefficient. After 24 h the tube was allowed to cool to RT and uncapped. The tube contents were passed through a medium-porosity fritted glass filter and the resin was rinsed with THF (5 $\times$), CH_2Cl_2 /Et₃N (3/

1, 3 $\times$), then CH_2Cl_2 (5 $\times$), and dried under high vacuum for a few days (the resin was pulverized to powder after a few hours of drying), to afford 3.35 g of a white colored resin (theoretical: 3.26 g, 0.92 mmol g⁻¹).

Immobilization of **3e**, followed by amide coupling with butylamine and cleavage to give **8**: A slight excess of *p*-carboxyphenylboronic acid (**2e**) (45 mg, 0.27 mmol) was added to a polypropylene filter vessel containing a suspension of resin **1** (200 mg, 0.18 mmol) in dry THF (2 mL). The vessel was shaken for 2 h after which the resin was rinsed with dry THF (5 $\times$) and dry DMF (2 $\times$). Unbound boronic acid (13 mg) was recovered from the first three THF rinses, which corresponds almost exactly to the theoretical unbound excess. Dry DMF (2 mL) was then added to resin **3e** and a solution of *N*-hydroxybenzotriazole (70 mg, 0.46 mmol) and butylamine (50 μ L, 0.46 mmol) in DMF (1 mL) was added to the suspension. The latter was homogenized by gentle vortexing followed by the addition of diisopropylcarbodiimide (72 μ L, 0.46 mmol). The vessel was shaken for 5 h then rinsed with dry DMF (3 $\times$) and dry THF (5 $\times$). The resulting resin was treated with a THF/water/acetic acid mixture (90/5/5, 2 mL) for 1 h. The liquid phase was drained and the resin rinsed with the above cleavage mixture (1 $\times$) and THF (3 $\times$). The combined filtrates were concentrated and dried under high vacuum (>12 h) to afford arylboronic acid **8** as a white powder (41 mg, 90%). ¹H NMR (300 MHz, 5% D₂O in CD₃OD, 25 °C): δ = 7.7–8.0 (m, 4H; Ar), 3.37 (t, ³*J*(H,H) = 7 Hz, 2H; NCH₂), 1.59 (m, 2H; CH₂CH₂CH₃), 1.40 (m, 2H; CH₂CH₃), 0.96 (t, ³*J*(H,H) = 7 Hz, 3H; CH₃); ¹³C NMR (75 MHz, 5% D₂O in CD₃OD, 25 °C): δ = 170.4 (CONH), 134.9, 134.8, 129.6, 127.1 (4s, Ar), 40.7 (NCH₂), 32.6 (CH₂CH₂CH₃), 21.1 (CH₂CH₃), 14.1 (CH₃); MS (positive ES): *m/z* (%): 244 (45) [*M*⁺+Na], 222 (100) [*M*⁺]; HR-MS (positive ES): *m/z*: calcd for C₁₁H₁₇NO₃B [*M*⁺]: 222.1303; found: 222.1301.

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Electrochemical Synthesis of $\text{Ba}_2\text{Ag}_8\text{S}_7$, a Quasi-One-Dimensional Barium Silver(I) Sulfide Containing Mixed $\text{S}^{2-}/\text{S}_2^{2-}$ Ligands**

He Li and Shiou-Jyh Hwu*

There has been renewed interest in the synthesis of solid-state inorganic materials by means of chemical electrolysis.^[1, 2] The versatility of the electrochemical technique for exploratory synthesis has been demonstrated by a number of recent reports in materials synthesis.^[2] Compared to conventional thermal methods, electrochemical synthesis allows greater control over the electronic state of extended solids and possibly structural frameworks as well as product stoichiometry. We have enjoyed numerous successes in the electrochemical crystal growth of copper(I) sulfides in nonaqueous solvents.^[3] Systematic studies on the electrochemically grown series of compounds $\text{KCu}_{7-x}\text{S}_4$, for example, have revealed some unusual stoichiometry-dependent transport anomalies.^[2a, 3] In light of the fascinating physical properties, we have expanded our search of new coinage metal chalcogenides to include silver. We report here a novel barium silver(I) sulfide obtained in our recent exploratory synthesis of alkaline earth silver(I) sulfides. The $\text{Ba}_2\text{Ag}_8\text{S}_7$ structure is quasi-one-dimensional and contains mixed S^{2-} and S_2^{2-} ligands. This discovery provides new insights with respect to possible electrochemical routes for the rational synthesis of inorganic solids.

[*] Prof. S.-J. Hwu, H. Li
Department of Chemistry
Clemson University
Clemson, SC 29634-0973 (USA)
Fax: (+1) 864-656-6613
E-mail: shwu@clemson.edu

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Prior to this study, all the reported $\text{A}/\text{Ag}^{\text{I}}/\text{S}$ compounds (A^+ = alkali metal cation, TI^+ , NH_4^+) contained monovalent electropositive cations. A dozen sulfides based on the general formula $m\text{A}_2\text{S} \cdot n\text{Ag}_2\text{S}$ have been reported thus far. For silver-rich phases ($m = 1$; $\text{A}_2\text{S} \cdot n\text{Ag}_2\text{S}$), there exist TIAgS ($n = 1$),^[4] $\text{A}_2\text{Ag}_4\text{S}_3$ ($\text{A} = \text{K}, \text{Rb}$; $n = 2$),^[5] AAg_3S_2 ($\text{A} = \text{Rb}, \text{Cs}, \text{TI}$; $n = 3$),^[6] $\text{A}_2\text{Ag}_6\text{S}_4$ ($\text{A} = \text{Na}, \text{K}$; $n = 3$),^[7] AAg_5S_3 ($\text{A} = \text{K}, \text{Rb}$; $n = 5$),^[8] and CsAg_7S_4 ($n = 7$).^[8] For $m = 3$, the only known phase is Na_3AgS_2 ($\equiv 3\text{Na}_2\text{S} \cdot \text{Ag}_2\text{S}$).^[9] In addition, $\text{TI}\text{Ag}_{5.4}\text{S}_{3.5}$,^[10] a nonstoichiometric compound whose structure has not yet been reported, is known. The compounds listed above were synthesized by high-temperature and/or high-pressure techniques, whereby no compound containing polysulfide has yet been isolated. The silver-based polysulfides known, thus far, are $[\text{Ag}_2\text{S}_{20}]^{4-}$, $[\text{Ag}(\text{S}_9)]^{1-}$, and $[\text{Ag}(\text{S}_5)]^{1-}$.^[11] The title compound, $\text{Ba}_2\text{Ag}_8\text{S}_7$, was prepared by electrolysis, a method in favor of selective synthesis of low-dimensional conducting solids.^[2a] It is the first ternary alkaline earth metal silver sulfide known.

Single crystals of $\text{Ba}_2\text{Ag}_8\text{S}_7$ were grown from a BaS_3 /ethylenediamine solution in a simple two-electrode chemical cell. The crystal structure was determined by single-crystal X-ray diffraction methods.^[12] The UV/Vis diffuse reflectance spectrum of $\text{Ba}_2\text{Ag}_8\text{S}_7$ was taken in the range of 200 nm (6.2 eV) to 2500 nm (0.50 eV).^[13]

The crystal structural analysis of $\text{Ba}_2\text{Ag}_8\text{S}_7$ reveals an interesting “stingray” pattern. Figure 1 shows a projected view of the structure where the extended Ag–S framework

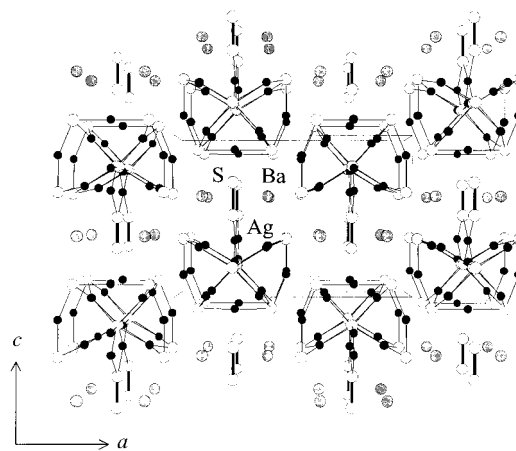


Figure 1. A projected view onto the ac plane of the $\text{Ba}_2\text{Ag}_8\text{S}_7$ structure revealing a stingray pattern; see text for details.

exhibits arrays of alternating stingray units. The structure propagates along the $[100]$ direction with respect to the 2_1 screw axis. The parallel arrays of stingray units are stacked head-to-tail in the $[001]$ direction to create voids where the barium atoms reside.

$\text{Ba}_2\text{Ag}_8\text{S}_7$ adopts a pseudo-one-dimensional structure with respect to the $\infty^1[\text{Ag}_8\text{S}_7]$ columns. The projected view of the column resembles the shape of the aforementioned stingray. Figure 2 presents a tilted view showing the coordination environments of the silver atoms. Each column is made of fused $[\text{Ag}_8\text{S}_5]$ units, each of which is weakly linked to one end of an $[\text{S}_2]$ unit. The $[\text{Ag}_8\text{S}_5]$ unit structure consists of a stacked