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Practical, high-yield synthesis of thiol-terminated diacetylenes for formation of conductive monolayers

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Abstract

Self-assembled monolayers of thiol terminated conjugated diacetylenes can be cross-linked using ultraviolet light to form highly conjugated polydiacetylenic conductive monolayers¹; however, the reported syntheses of the diacetylene monomers present numerous problems that prevent the wide spread application of these in functional materials. We report a redesigned four-step synthesis that proceeds in 75–80 % overall yields and allows gram scale production of an array of thiol terminated conjugated diacetylenes, thereby allowing examination and application of these low-dimensional conductive materials.

Graphical Abstract

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Supplementary data

Supplementary data includes detailed syntheses for both the successful and unsuccessful strategies, NMR spectra and data, mass spectra and data. Data associated with this article can be found in the online version at <https://doi.org/10.1016/j.tetlet>

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Keywords

conjugated diacetylene; self-assembled monolayer; conductive monolayer; photonics

Monolayers and nanoscale thin films of conducting and semiconducting polymers have wide spread applications such as in photonics, flexible electronics, batteries, and solar energy harvesting.²⁻⁴ Polyacetylenic materials, especially thin films, have many advantages in these applications.^{2, 5-7} One approach to forming 2-dimensional conductive materials of polyacetylene is to pre-form self-assembled monolayers (SAM) of monomeric precursors to the polymer and then polymerize these into the film using UV light (Scheme 1).^{1, 8-11} The key to the practical applications of 2-dimensional polyacetylene films by the SAM approach is the efficient synthesis and purification of the thiol terminated hydrocarbon containing conjugated diacetylenes. Changing the functional group designed to bind to the surface affords compounds that form SAMs on other substrates, for example phosphates bound to group III nitrides,¹² carboxylates bound to indium tin oxide,¹³ or insulators such as sapphire or highly ordered pyrolytic graphite.¹⁴

Though the synthesis of the diacetylene monomers used to form SAMs was first reported over 20 years ago,^{9, 10} there are few reports by other groups using this approach to these compounds or similar derivatives. The reported four step synthesis suffers from several low yield reactions, requires low temperatures in ultradry solvents, and the last step, wherein NaSH is added the 50°C, likely yields a thiophene as the significant side product.^{15, 16} Using this synthesis, we were repeatedly unsuccessful in isolation significant amounts of the intermediates and the final products despite using freshly dried solvents, inert atmosphere, and freshly purified reagents.

An alternative approach reported by Evans and coworker somewhat later starts with a terminal alkyne, forms the iodated derivative, couples this with a second alkyne alcohol using base and a Cu(I) catalyst, tosylation of the alcohol, and substitution of the tosylate with NaSH.¹⁷ This latter method is reported to go in 30–40% overall yields, and avoids many to the pitfalls of the former but the thiophene issue remains. Similar approaches to the synthesis of diacetylene alcohol were reported later, including a 14-(9H-9-carbazolyl)-tetradeca-10,12-diyn-1-yl disulfide, and the heneicosa-10,12-diyn-1-yl disulfide.^{11, 18} Wolf and coworkers use a much larger monomer based on a propionic ester, $[S(CH_2)_2COO(CH_2)_9CC-CC(CH_2)_{13}CH_3]_2$ deposited as the disulfide, and presumably the enhanced intermolecular interactions of the liquid crystal forming monomers aids in the formation of ordered films.¹⁹

Several attempts to synthesize the targeted diacetylated thiols (see ESI) were unsuccessful. The first attempt began with 1,4-bis(trimethylsilyl)-1,3-butadiyne as a starting material, 9, 20, 21 stoichiometric addition of MeLi.LiBr to selectively deprotect one of acetylenes, adding base to form the acetylide, followed by substitution of bromopentane in dry hexamethylphosphoramide (HMPA). However, no product formation was observed. This could be because the MeLi.LiBr reagent used in the reaction can lead to formation of several side products, thus not allowing the substitution of the bromopentane.²² Replacing the MeLi.LiBr with MeLi was also unsuccessful and little product was observed. In both cases

we observe formation of black solution within 10 min of adding bromopentane in dry HMPA. HMPA is generally used to reduce the polymer formation, which is the most possible side products in this reaction scheme. Attempts to use tetrahydrofuran (THF) instead of HMPA also did not yield product, but it took more than 12 hours before a black solution formed.

Next, we attempted to form the unsymmetrical diacetylene thiols via a Cadiot Chodkiewicz type reaction starting with alkynes^{11, 17} using Cu(I) as catalyst forming iodoalkyne *in situ*,²³ but no product was observed.

The synthesis reported herein proceeds in 75–80% overall yields via a modified Cadiot Chodkiewicz reaction conditions via bromoalkyne, and the thioacetate product allows long term storage without resorting to using the disulfides. Disulfides often times significantly complicate the formation of SAMs because of redox reactions with the gold surface, slower kinetics, and there can be morphological differences between monolayers formed by the thio versus the disulfide.²⁴ The thiol is readily deprotected under mild basic conditions (Scheme 2).

The synthesis starts with treating heptyne with NBS using a catalytic amount of Ag(NO₃) to yield 95% 1-bromohept-1-yne, which is then coupled to a second terminal alkyne with a pent-4-yn-1-ol or hex-5-yn-1-ol using a catalytic amount of Cu(Cl) and base thus forming the diacetylene in about 90%.²⁵ Pent-4-yn-1-ol or hex-5-yn-1-ol were then converted to mesylated derivatives followed by simply stirring these diacetylene alcohols with potassium thioacetate at room temperature yields the acetate protected thiol in about 95% overall yield. Since the thiols are not stable these thioacetate diacetylenes were prepared so can be stored for several years. Acetate protected group can then be deprotected under mild basic conditions (NaOMe in MeOH under ambient condition). The deprotection was achieved in about 95%. All the product formation except for the 1bromohept-1-yne was confirmed by ¹H NMR, ¹³C NMR and mass spectrometry. The intermediate might not be very stable.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References and notes

1. Kim T; Crooks RM; Tsen M; Sun LJ Am. Chem. Soc 1995, 117, 3963.
2. Ugur A; Katmis F; Li M; Wu L; Zhu Y; Varanasi KK; Gleason KK Adv. Mater 2015, 27, 4604. [PubMed: 26224113]
3. Dou L; Liu Y; Hong Z; Li G; Yang Y Chem. Rev 2015, 115, 12633. [PubMed: 26287387]
4. Saranya K; Rameez M; Subramania A Eur. Polymer J 2015, 66, 207.

5. Bharti M; Singh A; Samanta S; Aswal DK Prog. Mater. Sci 2018, 93, 270.
6. Nam S; Seo J; Song M; Kim H; Ree M; Gal Y-S; Bradley DDC; Kim Y Org. Electronics 2017, 48, 61.
7. Shi Y; Peng L; Ding Y; Zhao Y; Yu G Chem. Soc. Rev 2015, 44, 6684. [PubMed: 26119242]
8. Kim T; Chan KC; Crooks RM J. Am. Chem. Soc 1997, 119, 189.
9. Kim T; Crooks RM Tetrahedron Lett. 1994, 35, 9501.
10. Kim T; Ye Q; Sun L; Chan KC; Crooks RM Langmuir 1996, 12, 6065.
11. Kulyashova AE; Sorokoumov VN; Popik VV; Balova IA Tetrahedron Lett. 2013, 54, 2235.
12. Li F; Shishkin E; Mastro MA; Hite JK; Eddy CR; Edgar JH; Ito T Langmuir 2010, 26, 10725. [PubMed: 20524692]
13. Toshihiko T; Yoshiaki H; Michio S Japanese J. Appl. Phys 1995, 34, 3250.
14. Verveniotes E; Okawa Y; Makarova MV; Koide Y; Liu J; Smid B; Watanabe K; Taniguchi T; Komatsu K; Minari T; Liu X; Joachim C; Aono M Phys. Chem. Chem. Phys 2016, 18, 31600. [PubMed: 27834980]
15. Kagan J; Arora SK J. Org. Chem 1983, 48, 4317.
16. Maretina IA; Trofimov BA Russian Chem. Rev 2000, 69, 591.
17. Mowery MD; Evans CE Tetrahedron Lett. 1997, 38, 11.
18. Alloisio M; Demartini A; Cuniberti C; Petrillo G; Thea S; Giorgetti E; Giusti A; Dellepiane GJ Phys. Chem. C 2007, 111, 345.
19. Batchelder DN; Evans SD; Freeman TL; Haeussling L; Ringsdorf H; Wolf HJ Am. Chem. Soc 1994, 116, 1050.
20. Holmes AB; Jones GE Tetrahedron Lett. 1980, 21, 3111.
21. Jones GE; Kendrick DA; Holmes AB Org. Synth 1987, 65, 52.
22. Semenov SN; Blacque O; Fox T; Venkatesan K; Berke HJ Am. Chem. Soc 2010, 132, 3115.
23. Hsieh H-Y; Lee W-C; Senadi GC; Hu W-P; Liang J-J; Tsai T-R; Chou Y-W; Kuo K-K; Chen C-Y; Wang J-JJ Med. Chem 2013, 56, 5422.
24. Srisombat L; Jamison AC; Lee TR Colloids Surf., A 2011, 390, 1.
25. Nie X; Wang GJ Org. Chem 2006, 71, 4734.

Tetrahedron

- The synthesis of thiol-terminated diacetylenes reported herein proceeds in 75–80% overall yields
- Used sequential ‘acetylene zipper’ reaction, a Sonagashira coupling procedure for diacetylene formation
- Thioacetate product allows long term storage without resorting to using the disulfides

Scheme 1.

Formation of 2-dimensional polyacetylenes, adapted from ref. 10. The number of methylene groups, m and n , can vary, $R = \text{CH}_3, \text{OH}, \text{COOH}, \text{COOR}'$.

Scheme 2.

An alternative, high yield approach to the synthesis of two conjugated diacetylene thiols.