Bull. Chem. Soc. Ethiop. **2014**, 28(1), 143-148.
Printed in Ethiopia
DOI: http://dx.doi.org/10.4314/bcse.v28i1.17
ISSN 1011-3924

SHORT COMMUNICATION

HIGH YIELD SYNTHESIS OF SOME PHOSPHONIC ACID DERIVATIVES AS SURFACE TETHERS FOR ENERGY HARVESTING TECHNOLOGIES

Amshumali Mungalimane*

Department of Industrial Chemistry and Chemistry, Vijayanagara Sri Krishnadevaraya University, Jnana Sagara campus, VinayakaNagara, Cantonment, Bellary, India-583 104

(Received January 14, 2013; revised November 6, 2013)

ABSTRACT. Efficient synthesis of novel 6-(2-bromo-2-methyl propanoyloxy)hexyl phosphonic acid, dodecane di-phosphonic acid, 6-(thiophene-3-carbonyloxy)hexyl phosphonic acid, octadecyl phosphonic acid and such other derivatives are reported here. These derivatives have a potential application as tethers to nanoparticle surfaces that can promote efficient electron transfer process in solar energy conversion.

KEY WORDS: Surface tethers, Coupling reaction, Phosphonic acid derivatives, Solar energy conversion

INTRODUCTION

The quest for efficient solar energy conversion to produce electricity or chemical fuels has expanded significantly in the last decade [1-7]. As pointed out in these literatures, it is widely recognized that many of the key limitations to new energy conversion technology results from a lack of nanometer scale control of material composition and properties, linked with a clear understanding of how these properties impact on energy conversion efficiency.

The key steps in solar energy conversion, and solar photochemical formation of fuels, using small molecule, polymer, and semiconductor nanoparticle (SC-NP) composites are recognized to be (i) light absorption, (ii) exited state or exciton dissociation, (iii) charge separation, (iv) charge transport and (v) charge collection (electronic) or electrochemical fuel production. Limitations in any one of these steps translates to poor energy conversion efficiency for the entire system [8, 9]. The recent efforts in avoiding the limitations to the above steps consists of electro deposition of an ultra thin film polymer host on an activated indium tin oxide (ITO) surface providing a selective (electron blocking) back contact, and CdSe nanoparticles capped with electroactive ligands are attached electrochemically in the near surface region of the polymer film [10-12]. This provides for the direct wiring of the SC-NP to the transparent bottom contact and appears to provide a route for optimizing the use of such nanoparticles as the photoactive layer in both photo electrochemical and photovoltaic energy conversion technologies. Notable recent studies using functional ligand capping of SC-NPs have been directed towards enhancing the compatibility of the nanoparticle with polyphenylenevinylene (e.g. MEH-PPV) or polythiophene matrices [13-18], where the surface functional groups may be the trioctylphosphine oxide (TOPO) derivatives or phosphonates. In this work we prepared a library of such ITO tethering compounds, namely, 6-(2-bromo-2-methyl propanoyloxy)hexyl phosphonic acid, dodecane di-phosphonic acid, 6-(thiophene-3-carbonyloxy)hexyl phosphonic acid, octadecyl phosphonic acid have been prepared and characterized along with its intermediates. We hypothesize that these ligands would passivate the surfaces of metal chalcogenide nanoparticles and make them ameanable to inclusion in a variety of polymeric hosts and/or provide for attachment at the termini of the conducting polymeric chains.

*Corresponding author. E-mail: amshumalir@yahoo.com

EXPERIMENTAL

General methods. All reactions are carried out under argon atmosphere using standard Schlenk technique, except where otherwise indicated. All glassware are previously dried in oven at 120 ^{o}C and cooled to room temperature. 1-Bromo-6-hexanol, triethylamine, triethylphosphite, thiophene carboxylic acid, 1-bromooctadecane and 1,12-dibromododecane and 2-bromoiso-butyrylbromide were used as received from Aldrich or elsewhere. NMR experiments were carried out in Bruker AM 250 in the solvent indicated in each case at 250 and 62.5 MHz for ^{1}H and ^{13} C NMR, respectively. Chemical shifts were noted in parts per million and J values are given in hertz. Microanalyses were carried out at Indian Institute of Science, Bangalore, on LECO-CHNS analyzer, and were in a good agreement with the calculated values. High resolution mass spectrometry (HRMS) was recorded on FAB Shimadzu Instruments.

Synthesis of 6-bromohexyl-2-bromo-2-methylpropanoate. In a dry Schlenk flask equipped with a stir bar and connected to argon inlet, 2-bromo isobutarylbromide (3 g, 13.1 mmol) was added via syringe followed by 15 mL of dichloromethane. 1-Bromo-6-hexanol (2.56 g, 14.1 mmol) was then added to the above mixture and stirred for 15 min. This was kept in an ice bath and triethylamine (2 mL) was added slowly, via syringe. The mixture was allowed to warm to room temperature and stirred overnight. Next day the reaction mixture was washed several times with 10% HCl and distilled water, the solvent was removed on rotary evoparator and passed through the silica plug. Then the solvent was evaporated and concentrated. This gave almost pure product. Yield 3.4 g, (10.9 mmol 83%). ^{1}H NMR ($CDCl_3$, δ ppm) 4.17 (t, 2H, ^{3}J = 6.5 OCH_2), 3.40 (t, 2H, ^{3}J = 7.0 Br-CH_2), 1.93 (s, 6H, -CH_3), 1.87 (q, 2H, ^{3}J = 7.0 CH_2), 1.67 (q, 2H, ^{3}J = 6.75 CH_2), 1.45 (broad, 4H, CH_2). Mass spectrum: [M^+] = 327.96. Elemental analyses: $C_{10}H_{18}Br_2O_2$, calcd. C, 36.39; H, 5.50; found C, 36.37; H, 5.47.

Synthesis of 6-(diethylphosphoryl)hexyl-2-bromo-2-methyl propanoate. 6-Bromohexyl 2-bromo-2-methylpropanoate (1 g, 5.8 mmol) was mixed with triethylphosphite (1.1 mL, 8.75 mmol) and heated to 150 ^{o}C for 16 h. Excess of phosphate was removed under high vacuum diluted with dichloromethane and purified by silica gel column using 50:1 ethyl acetate and methanol mixture. Yield 1.8 g, (4.8 mmol 70%). ^{1}H NMR ($CDCl_3$, δ ppm) 4.11 (q, 6H, ^{3}J = 6.5 CH_2), 1.92 (s, 6H, CH_3), 1.73 (broad, 6H, CH_2), 1.41 (broad, 4H, CH_2), 1.31 (t, 6H, ^{3}J = 9.5 CH_2). Mass spectrum: [M+] = 386.08. Elemental analyses: $C_{14}H_{28}O_5PBr$, calcd. C, 43.42; H, 7.49; found C, 43.39; H, 7.48.

Synthesis of 6-(2-bromo-2-methylpropanoyloxy)hexyl phosphonic acid. In a Schlenk flask under argon, the 6-(diethylphosphoryl)hexyl-2-bromo-2-methyl propanoate (1.1 g, 2.84 mmol) was placed with 10 mL of dichloromethane. Bromotrimethylsilane (1.38 g, 8.5 mmol) was added to that mixture and stirred for 24 h. The excess of TMSBr in the solvent was removed under vacuum. Then 10 mL of methanol was added to this mixture and stirred for 2 h. The methanol was dried and the product was dissolve in dichloromethane and recrystallized in hexane which gave the product. Yield 0.8 g. (2.5 mmol 90%). ^{1}H NMR ($CDCl_3$, δ ppm) 1.25 (broad, 4H, CH_2), 1.69 (broad, 6H, CH_2), 1.93 (s, 6H, CH_3), 4.16 (t, 2H, ^{3}J = 6.5 OCH_2), 9.25 (broad, 2H, OH). Elemental analyses: C_{10} $H_{20}O_5BrP$, calcd. C, 36.27; H 6.09; found C, 36.26; H, 6.04. Mass spectrum: [M^+] = 330.02.

Synthesis of tetraethyldodecane-1,12-diyldiphosphonate. 1,12-Dibromododecane (1 g, 3.05 mmol) was place in a Schlenk flask with an argon inlet and triethyl phosphate (1.01 g, 6.1 mmol) was added via syringe. The mixture was heated to 150 ^{o}C for 18 h. The excess of triethyl phosphate was removed under vaccumm at 100 ^{o}C. Dichloromethane was added to the product and the product was extracted with a dilute HCl, and $NaHCO_3$ followed by distilled water. ^{1}H

NMR $CDCl_3$, ppm 4.00 (q, 8 H, OCH_2 J = 6.75), 1.64 (q, 4H, CH_2, J = 17.5) 1.01-1.31 (q, broad, 20H). Mass spectrum: [M+] = 442.26. Elemental analyses: $C_{20}H_{44}O_6P_2$, calcd. C, 54.28; H, 10.02; found C, 54.22; H, 10.06.

Synthesis of dodecane diphosphonic acid. Tetraethyl dodecane-1,12-diyldiphosphonate (1 g, 2.6 mmol) were mixed in 15 mL of dichloromethane and bromotrimethylsilane (1.086 g, 7.1 mmol) and this mixture was allowed to stir for 24 h. Excess of bromotrimethylsilane was evaporated along with dichloromethane. Then 10 mL of methanol was added to this mixture and stirred for 3 h. After evaporation of methanol, the off-white solid was obtained. The solid was dispersed in dichloromethane, and then the dichloromethane was evaporated and dried under vacuum. Yield 0.4 g (1.3 mmol 65%). ^{1}H NMR (DMSO-D6) 1.03-1.24 (broad, CH_2, 8H), 1.46 (broad, CH_2, 6H), 0.97 (d, CH_2, 4H, J = 11.0), 9.5 (broad, OH, 4H). Mass spectrum: MH^+ 330.10. Elemental analysis: $C_{12}H_{28}O_6P_2$, calcd. C, 43.64; H, 8.54; found C, 43.60; H, 8.50.

Synthesis of 6-bromohexyl thiophene 3-carboxylate. In a 50 mL Schlenk flask fitted with argon inlet was added 3-thiophene carboxylic acid (0.5 g, 3.9 mmol), 4 dimethyl amino pyridine (0.48 g, 3.9 mmol) was added and evacuated 3 times and backfilled with argon. 25 mL of dichloromethane was added to this mixture and stirred for a few min with 0 ^{o}C. Then 1-bromo-6 hexanol (0.7 g, 3.9 mmol) was added via syringe to this. A solution of DCC (0.8 g, 3.9 mmol) in 10 mL of dichloromethane was added and this solution was allowed to warm up to room temperature and stirred overnight. The product was filtered and purified by column chromatography on silica gel using hexane/EA (8.5/1.5). Yield: 0.7 g, 83%. ^{1}H NMR: ($CDCl_3$, δ ppm, J_{Hz}), 8.09 (d-d, 1H, J = 4.25), 7.53 (m, 1H, J = 4.25), 7.27-7.33 (m, 1H, J = 12), 4.28 (t, 2H, OCH_2 J = 8.75), 3.42 (t, 2H, CH_2Br, J = 13.5), 1.82 (m, 2H, CH_2), 1.57 (m, 2H, CH_2), 1.44 (broad, 4H, CH_2). ^{13}C NMR: ($CDCl_3$, δ ppm, J_{Hz}) 162.70 (C=O), 133.79 (C-quaternary), 132.40 (C-aromatic), 127.81 (C-aromatic), 125.89 (C-aromatic), 64.53 (O-CH_2), 34.9-25.3 (C alkyl chain). Mass spectrum: [M^+] = 289.99. Elemental analysis: $C_{11}H_{15}O_2BrS$ calcd. C, 45.37; H, 5.19; S, 11.01; found, C, 45.18; H, 5.34; S, 10.94.

Synthesis of 6-(diethoxy phosphoryl)hexyl thiophene-3-carboxylate. 6-Bromo hexyl (3-thiophne) carboxylic acid (0.7 g, 2.4 mmol) and triethyl phosphate (0.79 g, 4.8 mmol) were mixed together in a Schlenk flask under argon atmosphere and heated to 145 ^{o}C for 18 h with a closed argon inlet. Then the temperature of the oil bath is reduced to 90 ^{o}C and excess of triethyl phosphite was removed under vacuum. Yield: 0.71 g, 78%. ^{1}H NMR: ($CDCl_3$, δ ppm, J_{Hz}), 8.10 (d-d, 1H, J = 4.25), 7.51 (d-d, 1H, J = 6.0), 7.29 (q, 1H, J = 15.75), 4.27 (t, 2H, OCH_2), 4.09 (q, 4H, $POCH_2$, J = 21.75), 1.75 (broad, 6H, CH_2), 1.45 (broad, 4H, CH_2), 1.26 (t, 6H. CH_3). ^{13}C NMR ($CDCl_3$, δ ppm, J_{Hz}): 162.73 (C=O), 133.84 (C-quaternary), 132.43 (C-aromatic), 127.94 (C-aromatic), 125.90 (C-aromatic), 64.55 (O-CH_2), 34.9-25.3 (C of alkyl chain). Mass spectrum: [M^+] = 348.1. Elemental analyses: $C_{15}H_{25}O_5PS$, calcd. C, 51.71; H, 7.23; S, 9.20; found, C, 52.00; H, 7.11; S, 8.99.

Synthesis of 6-(thiophene-3-carbonyloxy)hexyl phosphonic acid. 6-Hexyl (3-thiophene carboxylic) phosphonite (0.7 g, 2.0 mmol) was placed in a Schlenk flask with 10 mL of dichloromethane. TMSBr (0.6 g, 4 mmol) was added via syringe and stirred for overnight. Next day the dichloromethane and the excess of TMS-Br were removed under vacuum. 15 mL of methanol was added to this mixture and stirred for 3 h. The methanol was removed under vacuum and the viscous oily product obtained and it solidifies on cooling. This product was stirred vigorously in boiling hexane and allowed to settle, cooled and filtered. Procedure was repeated 3 times to get rid of oily impurities. And the white product was obtained. ^{1}H NMR: ($CDCl_3$, δ ppm, J_{Hz}) 10.15 (broad, 2H, OH), 8.09 (d-d, 1H, J = 18.75), 7.52 (d-d, 1H, J = 19), 7.29 (m, 1H, J = 23), 4.27 (q, PCH_2, J = 25.5), 1.8 (b, 4H, CH_2), 1.75 (b, 2H, CH_2), 1.69 (b, 4H,

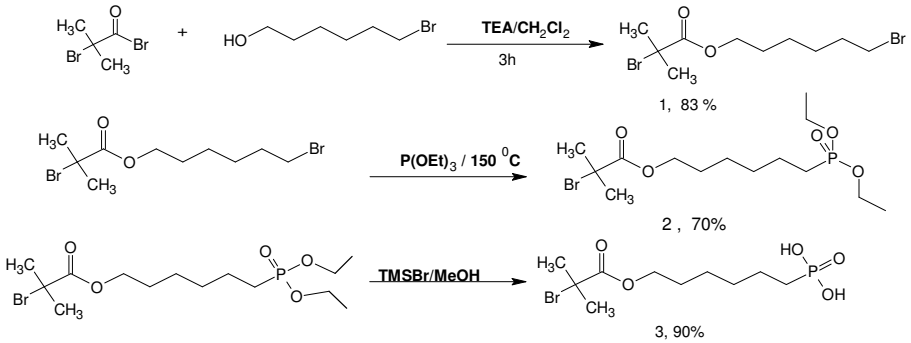
CH_2). Mass spectrum: [M+] = 292.05. Elemental analyses: $C_{11}H_{17}O_5PS$, calcd. C, 45.20; H, 5.86; S, 10.97; found, C 45.00; H, 5.92; S, 10.44.

Synthesis of octadecyl diethyl phosphonate. To 1 g of 1-bromooctadecane, 2 g of diethyl phosphite was added under closed argon atmosphere and heated to 150 ^oC. Then excess of triethyl phosphite was removed under high vacuum at 90 ^oC. ^1H NMR: ($CDCl_3$, ppm, J Hz): 4.07 (t, 4H, OCH_2 J = 13.25), 1.65 (broad, 4H, CH_2-CH_2), 1.24 (s, 32H, CH_2), 0.866 (t, 3H, CH_3). ^{13}C NMR: 14.58 (CH_3), 16.97 (d, CH_3), 22.85-32.39 (C-alkyl chain), 33.31 (C-PCH_2), 61.81 (d-O-CH_2). Mass Spectrum: [M+] = 390.32. Elemental analyses: $C_{22}H_{47}O_3P$, calcd. C, 67.65; H, 12.13; found, C, 67.64; H, 12.10.

Synthesis of octadecyl phosphonic acid. Octadecyl diethyl phosphonite (1.2 g) and 10 mL of dichloromethane were placed in a Schlenk flask under argon. TMSBr (2.0 g, 4 mmol) was added via syringe and stirred for overnight. Next day the dichloromethane and the excess of TMS-Br were removed under vaccum. 15 mL of methanol was added and stirred for 3 h. The methanol was removed under vacuum, thus the off white crystalline solid was obtained. This product was stirred vigorously in boiling hexane and allowed to settle, cooled and filtered. Procedure was repeated 3 times to get rid of oily impurities. And the white product was obtained. ^1H NMR: ($CDCl_3$, δ ppm, J_{Hz}) 8.73 (b, 2H, OH), 1.90 (m, 2H, PCH_2 = 26.75), 1.616 (broad, 2H, CH_2), 1.39 (b, 2H, CH_2), 1.19 (s, 30H, CH_2-alkyl), 0.877 (t, CH_3, 3H, J = 13.0). Mass spectrum: [M^+] = 334.26. Elemental analyses: $C_{18}H_{39}O_3P$, calcd. C, 64.64, H, 11.75; found, C, 64.62; H, 11.72.

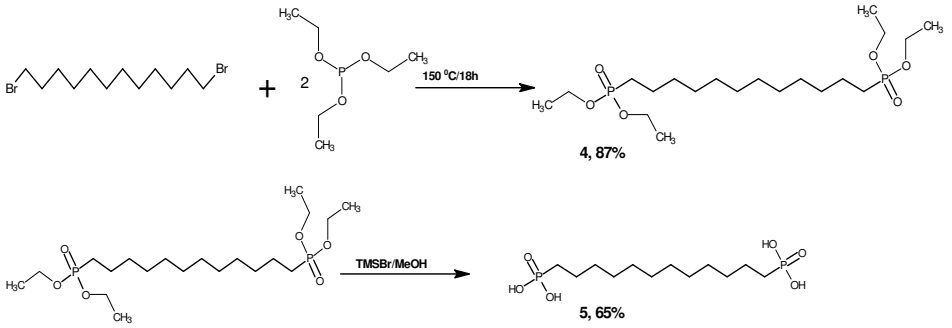
RESULTS AND DISCUSSION

The compounds selected for the synthesis is based on their suitability as ITO, SC-NP tethers and the simplicity in the synthesis. Thus for synthesizing the 6-(2-bromo-2-methyl propanoyloxy) hexyl phosphonic acid, (**3**), 2-bromoisobutyryl bromide was made to react with 1-bromo-6-hexanol in dichloromethane, gives the product (**1**) with the yield of 83%. Product (**1**) was then mixed with triethylphosphite and heated to 150 ^oC for 16 h to give the product (**2**) which was further purified by using silica gel column using 50:1 ethyl acetate and methanol mixture. The product (**2**) was treated with TMSBr for hydrolysis. The excess TMSBr was removed and washed with methanol several times to remove phosphonite impurities. After several washings in the methanol and dissolving the product in the minimum amount of dichloromethane, and processed for re crystallization in hexane to give pure product (**3**). The overall reaction is as shown in the Scheme 1.

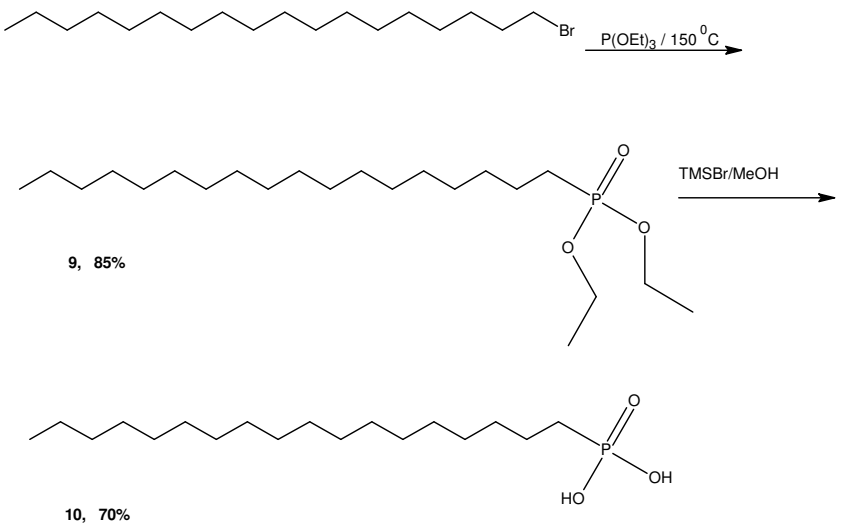


Scheme 1. Synthesis of 6-(2-bromo-2-methylpropanoyloxy)hexyl phosphonic acid.

In the same manner, the products **4** and **5**, prepared from 1,12-dibromododecane and the products **9**, and **10** are prepared from 1-bromooctadecane. The reaction of triethylphosphite with 1,12-dibromododecane gives the product **4**. Further treatment of product **4** with TMSBr in methanol followed by the same purification method as in the synthesis of product **3**, gave the product **5**. The reaction is shown in the Scheme 2. In the similar method, product **9** and **10** were synthesized using 1-bromooctadecane with the overall yield of about 70%. The reaction is shown in the Scheme 3.



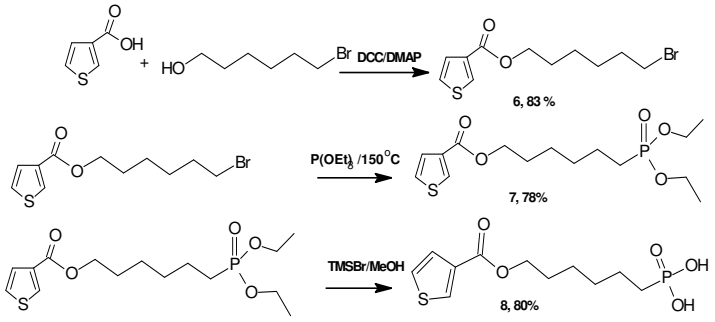
Scheme 2. Synthesis of dodecane di-phosphonic acid.



Scheme 3. Synthesis of octadecyl phosphonic acid.

The product **6** was synthesized by coupling reaction of 6-thiophene carboxylic acid and 1-bromo-6-hexanol with N,N-dimethylaminopyridine and dicyclohexylcarbodiimide (DMAP/DCC). After this reaction, the product **6** was purified by column chromatography using hexane/ethyl acetate (85/15) gives the yield of 83%. The product **7** was prepared in excellent yield by following the reaction of product **6** with triethyl phosphite and work up as described before. The 6-hexyl(3-thiophene carboxylic) phosphonite, **7**, was treated with TMSBr in dichloromethane for 18 h, after removing the unreacted TMSBr under vacuum, and stirred the

product with hot hexane several times, followed by filtration which gave pure product **8**. The overall reaction is shown in the Scheme 4.



Scheme 4. Synthesis of 6-(thiophene-3-carbonyloxy)hexyl phosphonic acid.

CONCLUSIONS

We have reported a straightforward and versatile route for the high yield synthesis of many phosphonic acid linkers to control both the ligating functionality, as well as the chain length of the alkyl spacers (5-10 carbons) between ligating and polymerizable groups. These derivatives have a potential application as tethers to the SC-NP surfaces that promote the efficient electron transfer. Further investigations on the applicability of these compounds along with developing other possible compounds of same application are underway.

ACKNOWLEDGEMENTS

Authors gratefully acknowledge the financial support and facilities of VSK University, Bellary.

REFERENCES

1. Crabtree, G.W.; Lewis, N.S. *Physics Today* **2007**, 60, 37.
2. Kamath, P.V. *J. Phys. Chem. C*. **2007**, 111, 2834.
3. Gratzel, M. *MRS. Bull*. **2005**, 30, 23.
4. Rajeshwar, K. *J. Appl. Elec. Chem.* **2007**, 37, 765.
5. Thompson, B.C.; Frechet, J.M.J. *Angew. Chem. Int. Ed*. **2008**, 47, 58.
6. Gunes, S.; Neugebauer, H.; Sariciftci, N.S. *Chem. Rev*. **2007**, 107, 1324.
7. Coackley, K.M.; McGhee, M.D. *Chem. Mat*. **2004**, 16, 4533.
8. Nozik, A.J. *Phys. E* **2002**, 14, 115.
9. Milliron, D.J.; Gur, I.; Alivisatos, A.P. *MRS. Bull*. **2005**, 30, 41.
10. Shallcross, R.C.; D'Ambruoso, G.D.; Korth, B.D.; Hall, Jr. H.K.; Zeng, Z.; Armstrong, N.R. *J. Am. Chem. Soc.* **2007**, 129, 11310.
11. Marrikar, F.S.; Brumbach, M.; Evans, D.H.; Lebrón-Paler, A.; Pemberton, J.E.; Wysocki, R.J.; Armstrong, N.R. *Lang*. **2007**, 23, 1530.
12. Marrikar, F.S.; Carter, C.; Kieltyka, K.; Robertson, J.W.F.; Williamson, C.; Simmonds, A.; Zangmeister, R.; Fritz, T.; Armstrong, N.R. *Lang*. **2007**, 23, 10395.
13. Liu, J.S.; Tanaka, T.; Sivula, K.; Alvisatos, A.P.; Frechet, J.M.J. *J. Am. Chem. Soc.* **2004**, 126, 6550.
14. Milliron, D.J.; Alivisatos, A.P.; Pitois, C.; Edder, C.; Frechet, J.M.J. *Adv. Mat*. **2003**, 15, 58.
15. Balazs, A.C.; Emrick, T.; Russell, T.P. *Sci*. **2006**, 314, 1107.
16. Sudeep, P.K.; Emrick, T. *Poly. Rev*. **2007**, 47, 155.
17. Zang, Q.L.; Russell, T.P.; Emrick, T. *Chem. Mat.* **2007**, 19, 3712.
18. Tangirala, R.; Revanur, R.; Russell, T.P.; Emrick, T. *Lang*. **2007**, 23, 965.