1,3-Dipolar Cycloaddition for the Generation of Nanostructured Semiconductors by Heated Probe Tips

Selma Bakbak,[†] Peter J. Leech,[†] Bradley E. Carson,[†] Shubham Saxena,[‡] William P. King,*[,‡] and Uwe H. F. Bunz*[,†]

School of Chemistry and Biochemistry and Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

Received July 15, 2006

Revised Manuscript Received August 12, 2006

The generation of nanostructured organic semiconductors is a critical technology in key areas that include device miniaturization, photovoltaics, photonic bandgap materials, and electronic circuitry.[1−5] Almost any area of high tech materials profits from the generation of nanostructures. An elegant way to generate nanostructures in soft materials is the use of heated atomic force microscope (AFM) cantilever tips, which allow the reversible or irreversible writing of nanostructures in thin films.[6] Simple ways of generating *organic* semiconductor nanostructures are rare and often rely on self-assembly processes such as ribbon or wire formation of substituted PPEs shown by Müllen and Rabe,[7] monolayer self-assembly and electron beam lithography.[8,9] Herein, we describe (a) the synthesis of conjugated fluorescent polymers by the thermal and Cu-catalyzed 1,3-dipolar cycloadditions of terminal diynes with aromatic diazides, the thermal reaction having been investigated by Szeimies and Huisgen long ago, and (b) fabrication of nanostructured organic semiconductors by nanoscale thermal processing of annealed diazide/dialkyne thin films with a heated AFM cantilever tip.[10,11]

The copper-catalyzed 1,3-dipolar cycloaddition, the so-called "Click" reaction, is an excellent tool towards novel materials as shown by Hawker and others.[12] However, the synthesis of conjugated polymers by 1,3-dipolar cycloadditions has been conspicuously absent and only one example has been reported.[13] Reaction of the diazides **1** with the diynes **2** in THF in the presence of copper sulfate and sodium ascorbate furnishes the polymers **3**−**6** in excellent yields as yellowish or off-white powders that precipitated out of solution, while the reaction of **7** with **2** generates the polymers **8** and **9** in excellent yields (Scheme 1, Table 1).[14−16]

The formed poly(arylenetriazolylene)s (PArT) are of moderate molecular weights ($<10^4$ Dalton) due to their relative lack of solubility in the THF−water mixture employed as reaction solvent**.** If the unsubstituted fluorenediazide **1** ($R_1 = H$) is used, a polymer with a significant fraction of insoluble material is isolated. However, most of the other PArTs are well soluble in chloroform or dichloromethane.

According to ^1H and ^{13}C NMR spectroscopy, the PArTs display regular 1,4-substitution around the triazole unit (Supporting Information). The PArTs are nonfluorescent in the solid state but blue fluorescent in solution. The quantum yield of emission of the soluble representatives is around 0.4 (quinine sulfate standard). Their absorption maxima is between 314 and 330 nm and the emission maxima are recorded between 370 and 379 nm, often accompanied by shoulders at 357−359 nm. The optical properties are practically independent of the molecular weight of the PArTs, suggesting that the used building blocks lead to species with localized HOMO and LUMO. A noteworthy observation is the red shift in emission upon addition of acid to the PArTs. Figure 1 shows the emission spectrum of polymer **5** upon protonation. It is surprising that the emission spectrum of **5** is narrow and structured but its absorption spectrum is broad and featureless. We speculate that **5** is conformationally unrestricted in the ground-state; i.e., the arylene units are twisted with respect to each other. In the excited state, the relaxed conformation is the planar one, similar to the case of the poly(*p*-phenyleneethynylene)s.[17] The conformational fixation into a planarized and well-defined excited state will lead to the observed vibronic progression, where a 0−1 transition in addition to the 0−0 transition is observed. We speculate that the excited state of the protonated polymer chain is not planarized, but twisted due to the interchain repulsion of the positive charges leading to a broader and unstructured emission spectrum.

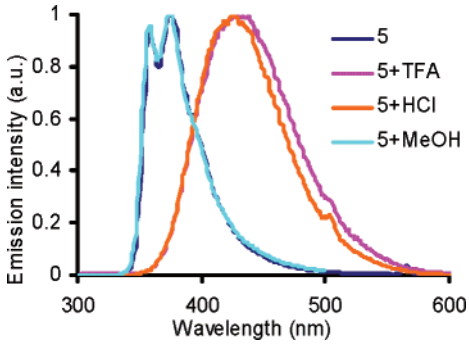


Figure 1. Emission spectra of **5** in chloroform and methanol and upon addition of acids in methanol.

Table 1. Substituent Key and Optical and Analytical Data for Polymers 3−6, 8, and 9

polymer	R^1	R^2	% yield	λ_{max}(abs) [nm]	λ_{max}(em) [nm]	F	M_n	PDI
3	H	dodecyl	92	322	358, 371	N/A	insoluble	
4	H	ethex	80	322	357, 370	0.41	1.9×10^3	2.1
5	dodecyl	dodecyl	92	329	359, 376	0.38	5.7×10^3	2.2
6	dodecyl	ethex	87	328	358, 375	0.48	8.7×10^3	5.8
8	N/A	dodecyl	86	314	379	N/A	insoluble	
9	N/A	ethex	88	314	379	0.48	5.1×10^3	5.5

What is the reason for (a) the molecular weight independence of the optical data and (b) the observed significant red shift upon protonation? Quantum chemical model calculations (SPARTAN B3LYP 6-31G**//6-31G**) on 1,4-diphenyl-1,2,3-triazole shed light on both issues: (a) The high band gap and the length independence of the optical properties are due to a distinct localization of the FMO on different parts of the molecule; the HOMO is predominantly located on the former alkyne and the LUMO is located on the former azide part of the cycloadduct. (b) Protonation in the 3-position of the triazole gives the most stable azaallylic imidazolinium type cation, which has a lower HOMO−LUMO gap and a more delocalized FMO.

* E-mail: (U.H.F.B) uwe.bunz@chemistry.gatech.edu; (W.P.K.) william.king@me.gatech.edu.

[†] School of Chemistry and Biochemistry, Georgia Institute of Technology.

[‡] Woodruff School of Mechanical Engineering, Georgia Institute of Technology.

10.1021/ma0615912 CCC: $33.50
Published on Web 08/29/2006

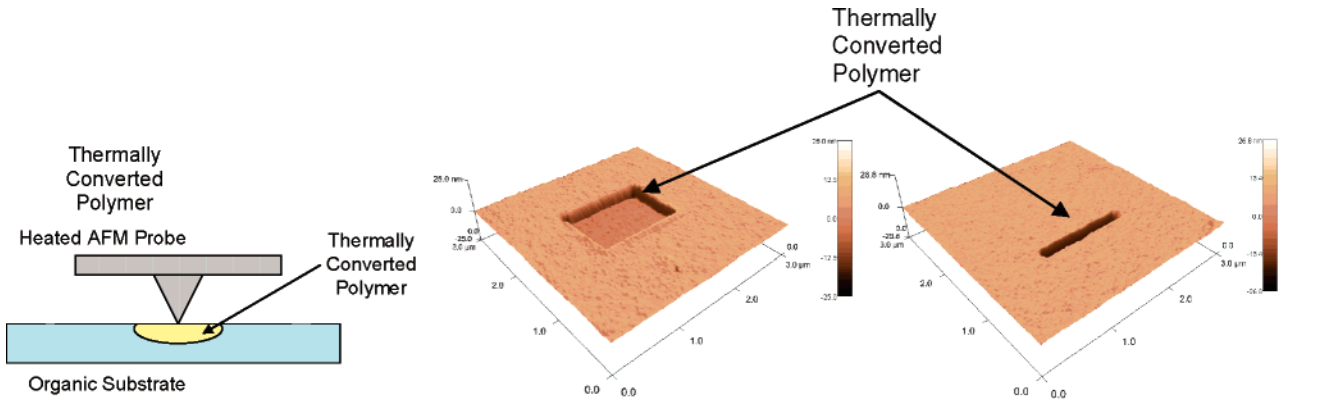
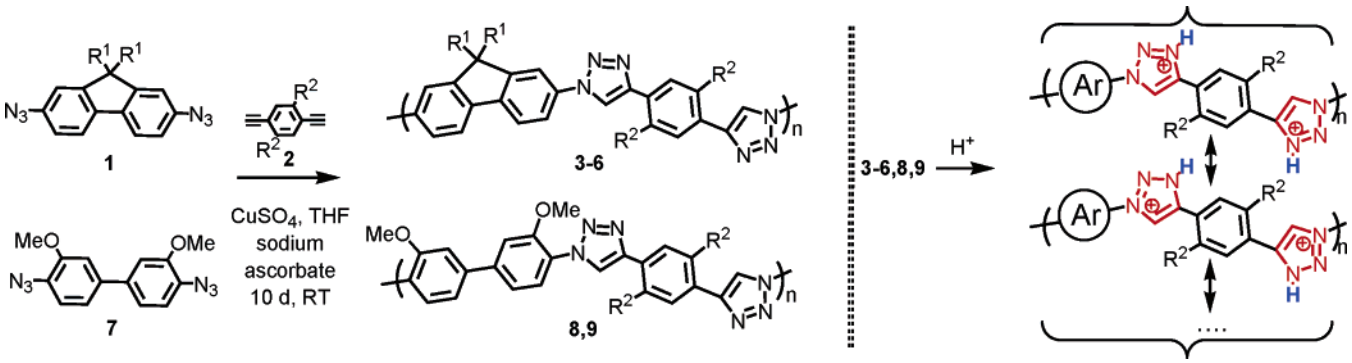


Figure 2. Local thermal writing into the organic substrate using a heated AFM cantilever tip. Left: Thermal writing process. Middle and right: Thermally induced writing using a conjugated polymer **6** made by click chemistry at the micrometer and submicrometer scale. The recessed regions are the locations where the heated AFM tip has scanned over the polymer film and locally induced cycloaddition.

Scheme 1. Copper Catalyzed Synthesis of 3−6, 8, and 9 and Resonance Structures of the Protonated Polymers



An exciting aspect of the in situ click chemistry is the potential for the formation of organic semiconductors in the solid state; thermal 1,3-dipolar cycloadditions are facile at enhanced temperatures.[10] Our capability for applying highly local heating from the tip of an AFM cantilever permits the formation of functional nanopatterns.[18] Monomers **1**, **2**, and **7** are crystalline. A solution containing didodecyldiazide **1** and bisethexyl-substituted diyne **2** (precursors for **6**) was spin-cast on a coverslip to give an 80 nm thick film that was preannealed at 170 °C for 1 h and formed a nontacky micrometer-thick polymer film. According to DSC, the 1,3-dipolar cycloaddition proceeds at this temperature. The cantilever tip was brought into contact with the film with a load force of ∼100 nN and heated. Precision calibration of the cantilever was possible[18] and in this case the tip temperature was near 225 °C. In one experiment, the probe rastered over a 1 μm square for 60 s, producing a lithographic mark 6 nm deep. Subsequent experiments showed that the lithographic mark could be as narrow as 160 nm (Figure 2). The lithographic marks were crisp and no residue or pileup was observed. No physical characteristics were observed that would be associated with simple polymer deformation, as the material exhibited a sharp, irreversible, and highly local transition when heated with the tip.

In conclusion, we have demonstrated that conjugated polymers form from azide and alkyne precursors under thermal and Cu-catalyzed conditions. Using a heated cantilever tip it is possible to write crisp nanoscale features into mixed diazide−diyne films after preannealing at 170 °C. The absence of tackiness and ripping makes these materials particularly attractive as novel organic semiconductors that can be easily thermally structured. At the moment, we are exploring the use of donor-substituted alkynes and acceptor-substituted diazides to make organic semiconductors with lower band gaps.

Acknowledgment. U.H.F.B., B.E.C., S.B., and P.J.L. thank the Department of Energy (DE-FG02-04ER46141) and the Georgia Institute of Technology for generous support; W.P.K. acknowledges an NSF CAREER Award (CTS-0238888).

Supporting Information Available: Text giving details for the synthesis and characterization of polymers **3**−**6** and **8** and **9** and details about the thermal probe technique, film making and annealing, heated cantilever AFM measurments, and quantum chemical calculations, schemes showing the synthesis of **3**, **7**−**10**, **12**, and **13**, and figures showing the absorption and emission spectra of **7**, **8**, **9**, **12**, and **13**, DSC data for **10**, AFM cantilevers, a plot of cantilever temperature calibration, and HOMO and LUMO structures of **M1** and **M2**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Janata, J.; Josowicz, M. *Nat. Mater.* **2003**, *2*, 19−24.
(2) (a) Wilson, J. N.; Bangcuyo, C. G.; Erdogan, B.; Myrick, M. L.; Bunz, U. H. F. *Macromolecules* **2003**, *36*, 1426−1428. (b) Song, L.; Bly, R. K.; Wilson, J. N.; Bakbak, S.; Park, J. O.; Srinivasarao, M.; Bunz, U. H. F. *Adv. Mater.* **2004**, *16*, 115−119. (c) Bunz, U. H. F. *Adv. Mater.* **2008**, *18*, 973−989.
(3) (a) Lovinger, A. J.; Rothberg, L. J. *J. Mater. Res.* **1996**, *11*, 1581−1592. (b) Horowitz, G. *J. Mater. Res.* **2004**, *19*, 1946−1962.
(4) Roberson, L. B.; Poggi, M. A.; Kowalik, J.; Smestad, G. P.; Bottomley, L. A.; Tolbert, L. M. *Coord. Chem. Rev.* **2004**, *248*, 1491−1499.
(5) (a) Dong, B.; Krutschke, M.; Zhang, X.; Chi, L. F.; Fuchs, H. *Small* **2005**, *1*, 520−524. (b) Li, G. F.; Martinez, C.; Semancik, S. *J. Am. Chem. Soc.* **2005**, *127*, 4903−4909.
(6) (a) Sheehan, P. E.; Whitman, L. J.; King, W. P.; Nelson, B. A. *Appl. Phys. Lett.* **2004**, *85*, 1589−1591. (b) King, W. P.; Goodson, K. E. *J. Heat Transfer* **2002**, *124*, 597. (c) Nelson, B. A.; King, W. P.; Gall, K. *Appl. Phys. Lett.* **2005**, *86*, Art.103108. (d) Yang, M.; Sheehan, P. E.; King, W. P.; Whitman, L. J. *J. Am. Chem. Soc.* **2006**, *128*, 6774−6775.

CDV

(7) (a) Samori, P.; Francke, V.; Müllen, K.; Rabe, J. P. *Chem.—Eur. J.* **1999**, *5*, 2312−2317. (b) Perahia, D.; Traiphol, R.; Bunz, U. H. F. *Macromolecules* **2001**, *34*, 151−155. (c) Yiang, Y. F.; Perahia, D.; Wang, Y. Q.; Bunz, U. H. F. *Macromolecules* **2006**, *39*, 4941−4944.
(8) (a) Dhirani, A. A.; Zehner, R. W.; Hsung, R. P.; Guyot-Sionnest, P.; Sita, L. R. *J. Am. Chem. Soc.* **1996**, *118*, 3319−3320. (b) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791−804.
(9) Angelopoulos, M. *IBM Res. Dev.* **2001**, *45*, 57−75.
(10) (a) Huisgen, R.; Knorr, R.; Moebius, L.; Szeimies, G. *Chem. Ber.* **1965**, *98*, 4014−4019. (b) Huisgen, R.; Szeimies, G.; Moebius, L. *Chem. Ber.* **1967**, *100*, 2494−2501.
(11) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem.* **2002**, *41*, 2596−2599.
(12) (a) Wooley, K. L.; Hawker, C. J. *Top. Curr. Chem.* **2005**, *245*, 287−305. (b) Helms, B.; Mynar, J. L.; Hawker, C. J.; Frechet, J. M. J. *J. Am. Chem. Soc.* **2004**, *126*, 15020−15021. (c) Englert, B. C.; Bakbak, S.; Bunz, U. H. F, *Macromolecules* **2005**, *38*, 5868−5877. (d) Binder, W. H.; Kluger, C. *Macromolecules* **2004**, *37*, 9321−9330. (e) Scheel, A. J.; Komber, H.; Voit, B. I. *Macromol. Rapid Commun.* **2004**, *25*, 1175−1180. (f) Parrish, B.; Breitenkamp, R. B.; Emrick, T. *J. Am. Chem. Soc.* **2005**, *127*, 7404−7410. (g) Tsarevsky, N. V.; Sumerlin, B. S.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 3558−3561.
(13) van Steenis, D. J. V. C.; David, O. R. P.; van Strijdonck, G. P. F.; van Maarseveen, J. H.; Reek, J. N. H. *Chem. Commun.* **2005**, 4333−4335.
(14) Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. *Angew. Chem.* **2005** *44*, 5188−5240.
(15) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605−1644. Bunz, U. H. F. *Adv. Polym. Sci.* **2005**, *177*, 1−52 and cited references.
(16) Diazides**1** and **7** were prepared from their diamines according to: Liu, Q.; Tor, Y. *Org. Lett.* **2003**, *5*, 2571−2572,.
(17) Sluch, M. I.; Godt, A.; Bunz, U. H. F.; Berg, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 6447−6448.
(18) (a) King, W. P.; Kenny, T. W.; Goodson, K. E.; Cross, G.; Despont, M.; Durig, U.; Rothuizen, H.; Binnig, G. K.; Vettiger, P. *Appl. Phys. Lett.* **2001**, *78*, 1300−1302. (b) King, W. P.; Kenny, T. W.; Goodson, K. E.; Cross, G. L. W.; Despont, M.; Durig, U.; Rothuizen, H.; Binnig, G.; Vettiger, P. *J. Microelectromech. Syst.* **2002**, *11*, 765−774. (c) Sheehan, P. E.; Whitman, L. J.; King, W. P.; Nelson, B. A. *Appl. Phys. Lett.* **2004**, *85*, 1589−1591.

MA0615912