Polymerization

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# Nanochannel-Promoted Polymerization of Substituted Acetylenes in Porous Coordination Polymers**

*Takashi Uemura, Ryo Kitaura, Yusuke Ohta, Masataka Nagaoka, and Susumu Kitagawa**

In recent years, there has been considerable interest in porous coordination polymers (PCPs) composed of transition-metal ions and bridging organic ligands because of their potential applications in many areas, including storage, separation, and exchange processes.[1] In contrast to conventional microporous materials such as zeolites and activated carbon materials, PCPs have pore surfaces that can be rationally designed and functionalized by their constituents.[1,2] The versatile pore features of PCPs, such as redox activity, Lewis acidity, basicity, hydrophobicity, chirality, result from the precise arrangement of transition metals and organic functional groups, and should be of key importance for the creation of unique nanosized reaction fields based on the PCP materials.[3] Thus, functionalized PCPs bearing specific interaction sites in/on nanochannels have been envisioned for useful catalytic applications in organic and polymer syntheses, which allow several advantages: 1) reaction acceleration; 2) regulated and controlled reactions (stereo- and regiocontrols); 3) substrate specificity. All of these properties are similar to those of enzyme reactions in biological systems. However, the use of PCP nanochannels with such remarkable effects has been very limited to date.[3]

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[*] Dr. T. Uemura, Dr. R. Kitaura,[+] Prof. Dr. S. Kitagawa
Department of Synthetic Chemistry and Biological Chemistry
Graduate School of Engineering
Kyoto University
Katsura, Nishikyo-ku, Kyoto 615-8510 (Japan)
Fax: (+81) 75-383-2732
E-mail: kitagawa@sbchem.kyoto-u.ac.jp

Y. Ohta, Prof. Dr. M. Nagaoka
Department of Complex Systems Science
Graduate School of Information Science
Nagoya University
Furo-chou, Chikusa-ku, Nagoya 464-8601 (Japan)

[+] Current address:
Department of Chemistry
Graduate School of Science
Nagoya University
Furo-chou, Chikusa-ku, Nagoya 464-8602 (Japan)

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Much attention has also been directed to the electronic and optical properties of poly(substituted acetylenes) for a wide range of applications such as conducting materials, nonlinear optics, polymer sensors, and components in molecular electronics.[4] In particular, the controlled polymerization of substituted acetylenes by using several types of catalysts (such as metal complexes, anions, cations, radicals) has been investigated with the aim of increasing catalytic activity, decreasing the formation of cyclic trimer by-products (substituted benzenes), and controlling the stereostructure (the *cis* and *trans* chain sequence) because the characteristic properties of poly(substituted acetylenes), such as conjugation length, supra-structures, and processability, can be precisely adjusted by changing the substituents and stereoregularity.[4,5] In addition, the design and understanding of well-defined nanostructures based on such π-conjugated polymers is one of the most challenging goals in contemporary polymer and solid-state sciences for their future application in the creation of nanosized molecule-based devices.[6]

Recently, we first demonstrated the use of PCP nanochannels as a field of polymerization,[7] which lead not only to a controlled reaction but also to new model systems for well-ordered single polymer chains in the nanochannel structures.[8] In this study, we have performed controlled and selective polymerizations of substituted acetylenes in one-dimensional specific nanochannels of $[Cu_2(pzdc)_2(L)]_n$ (**1**; pzdc = pyrazine-2,3-dicarboxylate, L = pillar ligands)[2b,9] with basic carboxylate oxygen atoms as catalytic interaction sites on the pore walls.

A pillared-layer microporous compound, $[Cu_2(pzdc)_2(pyrazine)]_n$ (**1a**), with one-dimensional channels (4.0 × 6.0 Å$^2$) has basic surface oxygen atoms that act as specific adsorption sites for acetylene molecules (HC≡CH), as a consequence of a double hydrogen-bonding interaction.[2b] The HC≡CH molecule is strongly fixed in the confined nanochannel of **1a** (**1a**⊃HC≡CH), which results in electron delocalization between the hydrogen atoms of the HC≡CH molecule and the carboxylate oxygen atoms.[2b] In addition, as is often the case with metal oxides, abstraction of one proton per HC≡CH molecule has been realized on such Lewis base sites of solid surfaces, even at room temperature.[10] These facts inspired us to postulate that the introduction of more-acidic monosubstituted acetylenes (i.e., acetylenes bearing an electron-withdrawing substitution group) in the channels of **1** would produce reactive acetylide species by C–H bond dissociation, which would subsequently initiate anionic polymerization of the substituted acetylenes. Moreover, the narrow nanochannel structure would direct the selectivity towards a polymerization with *trans* addition because of the prohibitive steric demand for the formation of trisubstituted benzenes and *cis* polymers. Thus, we carried out the polymerization of methyl propiolate (MP) in the nanochannel of $[Cu_2(pzdc)_2(4,4'\text{-bipyridine})]_n$ (**1b**; channel size 8.2 × 6.0 Å$^2$). In this experiment, the reaction of neat MP with the sky-blue complex **1b** for 12 h at room temperature provided a dark-green powder composite (**1b**⊃polyMP).[11] In the solid-state UV/Vis reflection spectrum of **1b**⊃polyMP there is an additional absorption around 450 nm, which can be attributed to the π-conjugated polyMP (Figure 1 a). The resultant polyMP filled about 40 % of the void space of the nanochannel, as estimated by thermogravimetric analysis (TGA). The X-ray powder-diffraction (XRPD) pattern of **1b**⊃polyMP shows that the channel structure of **1b** in this composite is preserved during polymerization (Figure 1 b). A distinct change in the relative peak intensities and peak broadening after the polymerization are ascribed to the inclusion of the guest polyMP in the nanochannel of **1b** (Figure 1 b).[7,12] Moreover, a dramatic decrease in the capacity of **1b**⊃polyMP at 77 K to adsorb nitrogen compared with **1b** is consistent with the encapsulation of polyMP in the channels (Figure 1 c).[6b–d,12b]

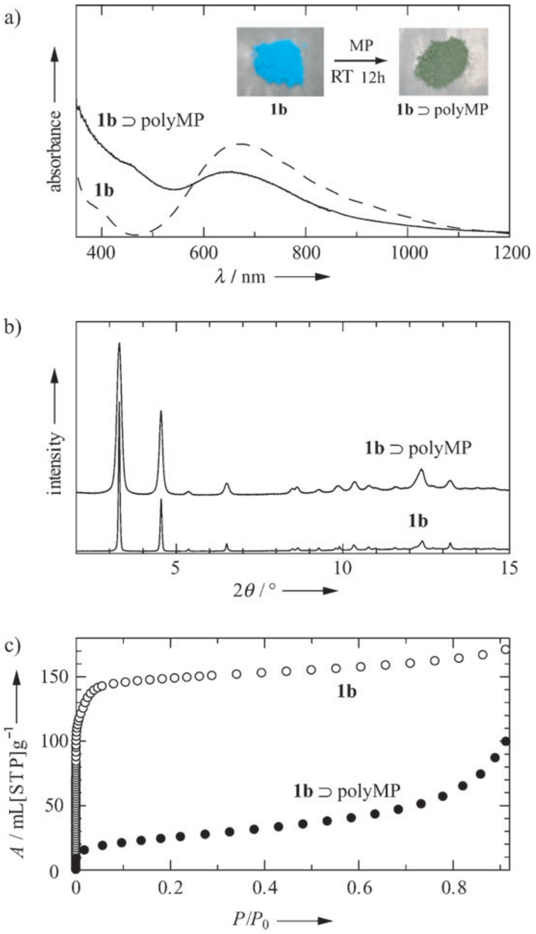

***Figure 1.*** a) Solid-state UV/Vis reflection spectra, b) XRPD patterns under reduced pressure, and c) $N_2$ adsorption isotherms at 77 K, for **1b** and **1b**⊃polyMP.

Accommodated polyMP was released from the host framework **1b** by extraction with *N*,*N*-dimethyl formamide (DMF) at 80 °C.[13] The extracted polymer exhibited a weight-average molecular weight ($\bar{M}_w$) and number-average molecular weight ($\bar{M}_n$) of 4800 and 850, respectively, as measured by gel permeation chromatography (GPC) in DMF with polystyrene standard. The IR spectrum of the polymer shows a characteristic peak pattern of polyMP and provides information on its stereostructure (Figure 2 a).[14] In the spectrum of the recovered polyMP, a peak around 700 cm$^{-1}$, which is specific to the *cis* form of polyMP, is hardly visible,[5c,14]

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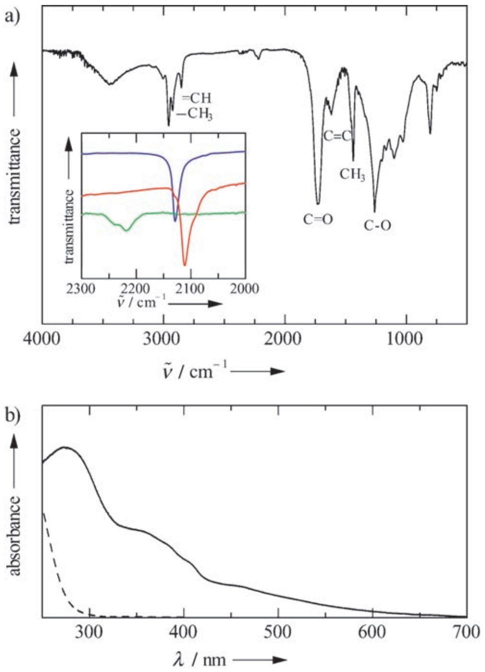

*Figure 2.* a) IR spectrum of polyMP prepared in **1b** shows characteristic bands of polyMP. Inset: IR spectra of neat MP (blue), MP in **1b** 5 min after the introduction of MP (red), and polyMP prepared in **1b** (green), in the region for stretching vibrations of substituted acetylenes. b) UV/Vis absorption spectra of polyMP prepared in **1b** (solid line) and monomer MP (dashed line) in chloroform.

whereas the presence of a band at 970 $cm^{-1}$ suggests that the *trans* geometry is dominant in this polymer.[5c,14] Electronic conjugation in the polyMP backbone is strongly dependent on its stereostructure, which has a considerable effect on color and band gap. The red–brown color of the recovered polyMP is characteristic of *trans* geometry, and a band at a longer wavelength (> 480 nm) in the absorption spectrum of the polymer also supports the dominance of the highly conjugated *trans* form of polyMP (Figure 2b).[5e,13,14]

The overall polymerization is characterized by the nanochannel-promoted polymerization in PCP (Figure 3a). In this reaction, acidic MP is adsorbed into the nanochannel and interacts with the basic oxygen atoms on the pore surface. As a consequence of the acid–base interaction, C–H bond dissociation of MP produces a reactive acetylide species that initiates regulated polymerization (*trans*-selective polymerization) in the narrow nanochannel. To explain this reaction mechanism, we have conducted IR measurements of neat MP, MP in the channel of **1b**, and polyMP prepared in **1b** in the region of the C≡C stretching of substituted acetylenes (inset in Figure 2a). Compared to the neat MP ($\tilde{\nu}_{C\equiv C} = 2129$ $cm^{-1}$), MP embedded in the nanochannel of **1b** shows a band at distinctly lower wavenumber (major and shoulder bands at 2111 and 2090 $cm^{-1}$, respectively), which is attributed to hydrogen bonding between the acetylene hydrogen atom of MP and the carboxylate oxygen atoms of the pore wall.[15] These shift values are found to be larger than that observed previously for $\mathbf{1a}\supset HC\equiv CH$, thus indicating the very strong interaction between those two moieties.[2b] Clear evidence of initiation in this polymerization was obtained from the spectrum of polyMP prepared in **1b**. Although the spectrum does not show the band around 2100–2130 $cm^{-1}$, a weak band appears at 2219 $cm^{-1}$, in the region of disubstituted acetylenes. This new band, which is absent in polyMP prepared by other methods, is assignable to the polymer terminal unit from the acetylide initiator. In addition to this spectral evidence, molecular-mechanics structure optimization by using a universal force field (UFF)[16] also reproduced a specific hydrogen-bonding interaction between the MP monomer and the carboxylate moiety of the host **1b** (Figure 3b). The $-C\equiv CH$ group of MP is clearly oriented towards the carboxylate oxygen atoms on the pore wall, and the acetylenic hydrogen atom and the oxygen atoms are close enough for an efficient hydrogen bonding (2.8 and 2.9 Å), which is consistent with the experimental results.

In a control experiment, MP was treated with sodium benzoate as a discrete model catalyst at room temperature and the mixture was left for one month, which gave only a trace amount of product. An increase in the reaction temperature to 70 °C resulted in a small quantity of yellow oily mixture (< 5 %) of cyclic trisubstituted benzenes as the major products and less-conjugated polyMP of *cis* geometry as a minor product, which contrasts with the result obtained in the nanochannels of **1b**. Our polymerization system with PCP is of considerable interest owing to several significant features

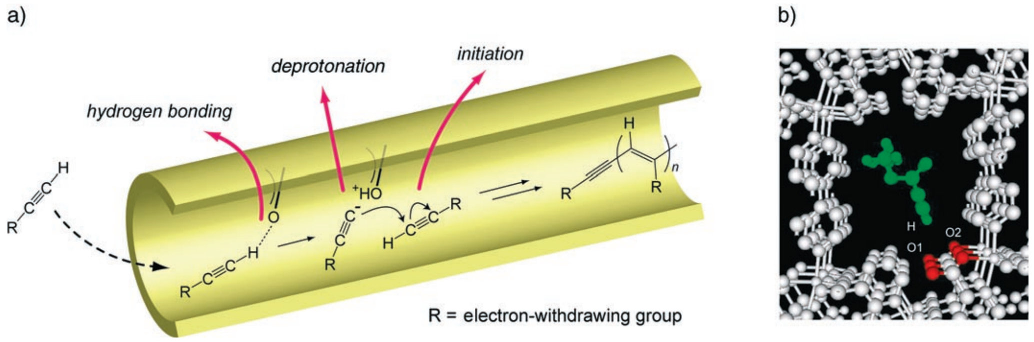

*Figure 3.* a) Mechanism of the nanochannel-promoted polymerization of acidic acetylenes in porous coordination polymers. b) Optimized structure of MP (green) incorporated in a nanochannel of **1b**. The distances between the MP hydrogen atom and oxygen atoms (red) of the pzdc ligand are 2.9 (H–O1) and 2.8 Å (H–O2). Hydrogen atoms of the host are omitted for clarity.

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such as a dramatic acceleration of the polymerization, no production of trisubstituted benzenes as by-products, and *trans*-selective polymerization. In this case, the basic carboxylate oxygen atoms are precisely arranged at appropriate positions of the narrow nanochannels, which enables a strong interaction between the monomer and carboxylate group and results in *trans*-selective polymerization.

To elucidate this polymerization specific to the channel properties of PCPs, we examined the reaction of MP in channels of different sizes of **1** (**1a**, $4.0 \times 6.0$ Å$^2$; **1c**, L = 1,2-di(4-pyridyl)ethylene, $10.3 \times 6.0$ Å$^2$) and the reactivity in a nonfunctionalized channel (without basic surface carboxylate moiety) of $[Cu_2(tp)_2(tren)]_n$ (**2**, tp = terephthalate, tren = triethylenediamine, $7.5 \times 7.5$ Å$^2$).[17] The pillared-layer complex **1c** with large pores was newly synthesized for this experiment.[9a,18] As expected, the polymerization of MP proceeded only in the channel of **1c** ($\bar{M}_w = 2760$, $\bar{M}_n = 710$), which shows that the monomer recognizes precisely the channel size as well as the surface functionality of PCPs. Investigations with different acetylene monomers have revealed distinct monomer selectivity, which is in agreement with the proposed polymerization mechanism. The reaction of acidic monosubstituted acetylenes (cyanoacetylene and 2-ethynylpyridine) with **1b** yields the corresponding polyacetylenes in the same manner;[19,20] in contrast, neither less-acidic monosubstituted acetylenes (phenylacetylene and 1-hexyne) nor non-acidic disubstituted acetylene (tetrolic acid methyl ester) is polymerized in the channels of **1b**. This result indicates that the strong hydrogen-bonding interaction (acid–base) between the monomers and the channel surface is a key factor to this unique spontaneous polymerization.

In conclusion, we have demonstrated that truly designable PCPs with specific basic interaction sites in the nanochannels allow the highly accelerated, stereocontrolled, and monomer-selective polymerization of substituted acetylenes. This methodology should contribute to the development of PCP materials for their application as unique and attractive catalysts that are distinct from inorganic zeolites. In addition, precisely aligned PCP nanochannels filled with π-conjugated substituted polyacetylenes should be a promising new class of host–guest nanostructures for applications such as nanoscale electronics and for fundamental investigations of these polymers in the isolated, single-chain state.

## Experimental Section

**1**$\supset$polyMP: General polymerization procedure: In a pyrex reaction tube, **1b** (300 mg) was dried by evacuation at 110 °C for 5 h. After the vessel was filled with nitrogen, methyl propiolate (0.4 mL) was added and the reaction mixture was left at room temperature for 12 h. A thorough washing of the reaction mixture with $CHCl_3$ to remove unconverted monomer and surface polymer left the dark-green powder composite **1b**$\supset$polyMP.

Recovery of polyMP: **1b**$\supset$polyMP (600 mg) was suspended in DMF (30 mL) and heated at 80 °C for two days. After the mixture had been filtered, the solvent of the filtrate was removed by evaporation and the filtrate poured into $Et_2O$. The resulting precipitate was collected by filtration, washed with $Et_2O$, and dried under reduced pressure to give red–brown polyMP (16 mg).

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[1] a) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629; b) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, *Acc. Chem. Res.* **2005**, *38*, 217; c) S. L. James, *Chem. Soc. Rev.* **2003**, *32*, 276; d) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior, M. J. Rosseinsky, *Acc. Chem. Res.* **2005**, *38*, 273; e) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334.

[2] a) S. Kitagawa, S. Noro, T. Nakamura, *Chem. Commun*, **2006**, 701; b) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, T. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe, Y. Mita, *Nature*, **2005**, *436*, 238; c) T. K. Maji, K. Uemura, H.-C. Chang, R. Matsuda, S. Kitagawa, *Angew. Chem.* **2004**, *116*, 3331; *Angew. Chem. Int. Ed.* **2004**, *43*, 3269; d) B. Chen, M. Eddaoudi, T. M. Reineke, J. W. Kampf, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 11559; e) R. Kitaura, G. Onoyama, H. Sakamoto, R. Matsuda, S. Noro, S. Kitagawa, *Angew. Chem.* **2004**, *116*, 2738; *Angew. Chem. Int. Ed.* **2004**, *43*, 2684; f) D. Bradshaw, T. J. Prior, E. J. Cussen, J. B. Claridge, M. J. Rosseinsky, *J. Am. Chem. Soc.* **2004**, *126*, 6106; g) B. Kesanli, W. Lin, *Coord. Chem. Rev.* **2003**, *246*, 305.

[3] a) C.-D. Wu, A. Hu, L. Zhang, W. Lin, *J. Am. Chem. Soc.* **2005**, *127*, 8940; b) M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151; c) H. J. Choi, M. P. Suh, *J. Am. Chem. Soc.* **2004**, *126*, 15844; d) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982; e) L. Pan, H. Liu, X. Lei, X. Huang, D. V. Olson, N. J. Turro, J. Li, *Angew. Chem.* **2003**, *115*, 560; *Angew. Chem. Int. Ed.* **2003**, *42*, 542.

[4] a) J. W. Y. Lam, B. Z. Tang, *Acc. Chem. Res.* **2005**, *38*, 745; b) K. J. S. Harrell, S. T. Nguyen in *Handbook of Advanced Electronic and Photonic Materials and Devices*, *Vol. 8*, Academic Press, San Diego, **2001**, pp. 131.

[5] a) C. I. Simionescu, V. Percec, *J. Polym. Sci. Polym. Symp.* **1980**, *67*, 43; b) T. Masuda, T. Higashimura, *Acc. Chem. Res.* **1984**, *17*, 51; c) M. Tabata, Y. Inaba, K. Yokota, Y. Nozaki, *J. Macromol. Sci. Part A* **1994**, *31*, 465; d) R. Nomura, J. Tabei, T. Masuda, *J. Am. Chem. Soc.* **2001**, *123*, 8430; e) K. Maeda, H. Goto, E. Yashima, *Macromolecules* **2001**, *34*, 1160; f) Y. Kishimoto, P. Eckerle, T. Miyatake, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1994**, *116*, 12131.

[6] For encapsulation of π-conjugated polymers and oligomers in ordered nanochannel structures, see: a) D. J. Cardin, *Adv. Mater.* **2002**, *14*, 553; b) C.-G. Wu, T. Bein, *Science* **1994**, *264*, 1757; c) A. G. Pattantyus-Abraham, M. O. Wolf, *Chem. Mater.* **2004**, *16*, 2180; d) V. S.-Y. Lin, D. R. Radu, M. K. Han, W. Deng, S. Kuroki, B. H. Shanks, M. Pruski, *J. Am. Chem. Soc.* **2002**, *124*, 9040; e) P. Sozzani, A. Comotti, S. Bracco, R. Simmonutti, *Angew. Chem.* **2004**, *116*, 2852; *Angew. Chem. Int. Ed.* **2004**, *43*, 2729; f) W. C. Molenkamp, M. Watanabe, H. Miyata, S. H. Tolbert, *J. Am. Chem. Soc.* **2004**, *126*, 4476.

[7] T. Uemura, K. Kitagawa, S. Horike, T. Kawamura, S. Kitagawa, M. Mizuno, K. Endo, *Chem. Commun.* **2005**, 5968.

[8] a) P. Sozzani, S. Bracco, A. Comotti, R. Simonutti, *Adv. Polym. Sci.* **2005**, *181*, 153; b) P. Sozzani, A. Comotti, S. Bracco, R. Simonutti, *Chem. Commun.* **2004**, 768; c) J. Lu, P. A. Mirau, A. E. Tonelli, *Prog. Polym. Sci.* **2002**, *27*, 357; d) K. A. Udachin,

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L. D. Wilson, J. A. Ripmeester, *J. Am. Chem. Soc.* **2000**, *122*, 12375.

[9] a) M. Kondo, T. Okubo, A. Asami, S. Noro, T. Yoshitomi, S. Kitagawa, T. Ishii, H. Matsuzaka, K. Seki, *Angew. Chem.* **1999**, *111*, 190; *Angew. Chem. Int. Ed.* **1999**, *38*, 140; b) R. Matsuda, R. Kitaura, Y. Kubota, T. C. Kobayashi, S. Horike, M. Takata, *J. Am. Chem. Soc.* **2004**, *126*, 14063.

[10] a) C. C. Chang, R. J. Kokes, *J. Am. Chem. Soc.* **1970**, *92*, 7517; b) C. C. Chang, R. J. Kokes, *J. Catal.* **1973**, *28*, 92; c) T. Z. Tabasaranskaya, A. A. Kadushin, *Kinet. Catal.* **1971**, *12*, 1334.

[11] Formation of trisubstituted benzenes is not observed in this polymerization system, which is confirmed by IR and $^1$H NMR spectroscopies.

[12] a) P.-S. E. Dai, J. H. Lunsford, *J. Catal.* **1980**, *64*, 173; b) K. Moller, T. Bein, R. X. Fischer, *Chem. Mater.* **1998**, *10*, 1841.

[13] The poly(alkyl propiolates) are thermally quite stable and do not show any conformation change upon heating, see: H. Nakako, R. Nomura, M. Tabata, T. Masuda, *Macromolecules* **1999**, *32*, 2861.

[14] C. I. Simionescu, V. Bulacovschi, M. Grovu-Ivanoiu, A. Stanciu, *J. Macromol. Sci. Chem. A* **1987**, *24*, 611.

[15] a) G. C. Pimentel, A. L. McClellan, *The Hydrogen Bond*, W. H. Freeman, San Francisco, **1960**; b) A. M. DeLaat, B. S. Ault, *J. Am. Chem. Soc.* **1987**, *109*, 4232.

[16] a) A. K. Rappé, C. J. Casewit, K. S. Colwell, W. A. Goddard III, W. M. Skiff, *J. Am. Chem. Soc.* **1992**, *114*, 10024; b) C. J. Casewit, K. S. Colwell, A. K. Rappé, *J. Am. Chem. Soc.* **1992**, *114*, 10035.

[17] a) K. Seki, Y. Mori, *J. Phys. Chem. B* **2002**, *106*, 1380; b) K. Seki, *Langmuir* **2002**, *18*, 2441.

[18] Crystal data for **1c**$\supset$6H$_2$O: $C_{24}H_{14}Cu_2N_6O_{14}$, $M_r = 737.50$, monoclinic, $P2_1/c$ (No. 14), $a = 4.7109(5)$, $b = 31.858(3)$, $c = 11.002(1)$ Å, $\beta = 96.008(8)°$, $V = 1642.0(3)$ Å$^3$, $Z = 4$, $R_1 = 0.027$, $R_w = 0.037$, $T = 298$ K. CCDC-295897 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[19] Poly(cyanoacetylene): IR (KBr): $\tilde{\nu} = 2203$, 1659, 1497, 1348, 1190 cm$^{-1}$; $M_w = 15800$, $M_n = 6700$ (polystyrene standard). Poly(2-ethynylpyridine): IR (KBr): $\tilde{\nu} = 1616$, 1588, 1466, 1132, 754 cm$^{-1}$; $M_w = 1400$, $M_n = 420$ (polystyrene standard).

[20] a) C. B. Gorman, R. W. Vest, T. U. Palovich, S. Serron, *Macromolecules* **1999**, *32*, 4157; b) S. Subramanyam, A. Blumstein, *Macromolecules* **1992**, *25*, 4058.

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