Design of Coordination Polymer Gels as Stable Catalytic Systems

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Abstract: Here we report the first example of catalytic metallogels, which are formed irreversibly in dimethylsulfoxide via the creation of cross-linked, three-dimensional coordination polymer networks by using transition-metal ions with multiple sites available for coordination and multidentate ligands. Conformational flexibility of the ligands and slow formation of the coordination polymers apparently favor the gelation. These metallogels are stable in water and most organic solvents and can catalyze the oxidation of benzyl alcohol to benzaldehyde by using their Pd^{II} moieties as the catalytic centers. The best catalytic turnover of the metallogel is twice that of [Pd(OAc)$_2$] under similar reaction conditions.

Keywords: catalysis · gels · oxidation · palladium · polymers

Introduction

This paper reports the formation of coordination polymer gels ("metallogels") and their enhanced catalytic activity and remarkable stability. Gel materials[1–5] have presented many useful properties (e.g., phase transitions upon external stimuli[1, 6]) and applications (e.g., gel electrophoresis,[7] catalysts screening,[8] chemical sensing,[9] and as actuators[10]). Conventionally, one or a combination of four kinds of forces—ionic bonds, covalent bonds, hydrogen bonds, and hydrophobic interactions—leads to the formation of gels. Transition-metal-ligand bonds, however, have been less explored in terms of the design and construction of gel materials,[4, 5, 11, 12] despite their common usage for the formation of coordination polymers in crystal engineering.[13, 14] We have demonstrated recently that coordination of transition-metal ions to tetradentate ligands (Figure 1A) resulted in a remarkably stable metallogel, in which the tetradentate ligand **3** (Scheme 1) coordinates with $[Pd(en)(H_2O)_2]^{2+}$ (**5**) (en: ethylenediamine) to form a cross-linked coordination polymer network that traps dimethylsulfoxide (DMSO) in its interstitial spaces.[12] This metallogel is capable of "uptaking" neutral organic molecules from the aqueous phase.[12] This "uptake" process, resembling the uptake processes of alkanes in alkylotrophs,[15] causes the transfer of organic molecules from solution to the metal sites, and thus presents a system for designing catalytic metallogels that may mimic the function of alkylotrophs.[12] The immobilization of catalytic metal centers in a gel network can *inherently* prevent loss of metal ions into the solution phase,[12] and reduce contamination and bimolecular decomposition of catalysts. Additionally, the insolubility of metallogels in common solvents allows simple and easy separation or recovery of the catalyst.

We report herein the design and formation of a number of metallogels and their catalytic properties. Our results indicate that conformational flexibility of ligands and slow formation of coordination polymers favor the formation of metallogels. These metallogels are stable in water and most organic solvents except acetone, and can catalyze the oxidation of benzyl alcohol to benzaldehyde by using their Pd^{II} moieties as catalytic centers and air as the source of molecular oxygen. The gel-based Pd^{II} catalysts do not form Pd black; the best catalytic turnover of the metallogel is twice that of [Pd(OAc)$_2$]. To the best of our knowledge, this is the first example of catalytic metallogels.

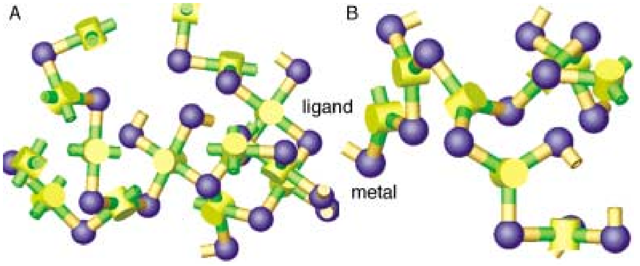

Figure 1. Three-dimensional networks of coordination polymers formed using a tetradentate ligand (A) or a tridentate ligand (B) to coordinate with a transition-metal ion (represented as blue balls) with two bonding sites available.

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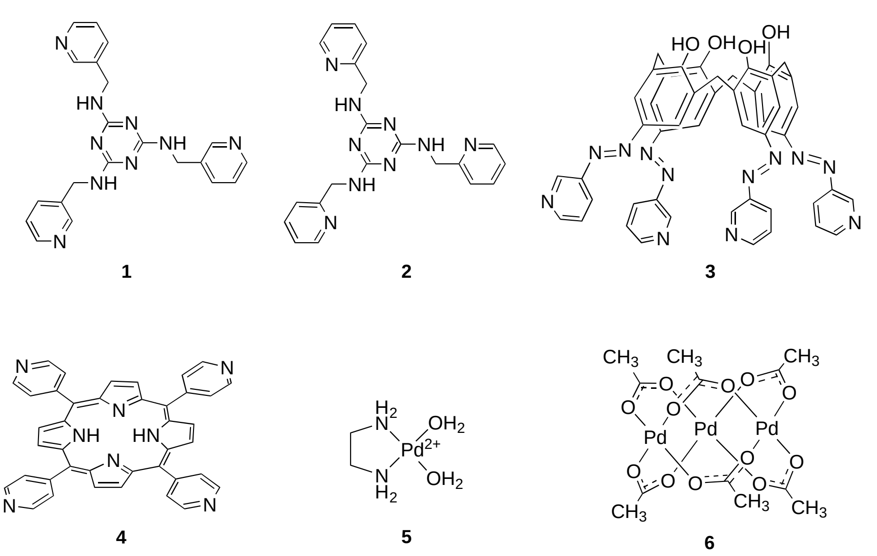

Scheme 1. Multidentate ligands **1**–**4** and metal complexes **5** and **6**.

Results and Discussion

Although precise prediction of gelation in an organic solvent[5, 16] remains a challenge,[3] coordination polymers tend to form metallogels[12] in appropriate solvents. According to our previous observations,[12] a cross-linked, three-dimensional network, generated by a proper combination of multidentate ligands and transition-metal ions that have multiple coordination sites, is important for forming the metallogels. Figure 1 illustrates two possible modes of cross-linking between the metal ions and the ligands that should allow the formation of metallogels. To further explore the structural and kinetic criteria for the formation of a metallogel, we evaluated combinations of transition-metal ions with several multidentate ligands illustrated in Scheme 1 (ligands **1**, **2**, **3**, and **4**) for making metallogels (Table 1). Based on others' works, in which $[Pd(en)]^{2+}$ acted as a linker to generate extended molecular structures,[13, 17] and our previous experience,[12] we chose $[Pd(en)(H_2O)_2](NO_3)_2$ (**5**) and $[Pd(OAc)_2]$ (**6**) as the sources of transition-metal ions.

We began with treating ligand **1** or **2** to **5** (molar ratio of metal/ligand = 3:2) in DMSO. Coordination occurred immediately after adding **5** to the solution of **1** or **2** in [D$_6$]DMSO; this was indicated by changes in ^{1}H NMR signals, and the peaks of protons on the pyridine rings and of the benzyl protons broadened upon addition (the broadness of the peaks interferes the observation of the supposed peak shifts upon coordination). Insoluble solids, however, precipitated from the solution without any gelation, which was partially due to inadequate solvent being trapped in the networks of coordination polymers (Table 1, entries 1 and 2).

Reasoning that rapid polymerization may hinder trapping of solvent molecules in the networks' interstitial spaces, we switched to $[Pd(OAc)_2]$ (**6**) instead. The slow dissociation of OAc^- from $[Pd(OAc)_2]$ can regulate the concentration of $[Pd(OAc)]^+$ in solution and provide a kinetically slower polymerization process that would assist solvent trapping. Treating ligand **1** with **6** formed a transparent metallogel A in solution in DMSO in 12 hours (Figure 2 and entry 4 in Table 1). The same procedure was applied to ligand **2**, but no metallogel was observed. The ^{1}H NMR spectra show broadening (less than that of other cases) and shifting of the peaks of the protons on the pyridine rings and benzyl positions, suggesting the formation of oligomer (entry 3 in Table 1). The short distances, between NHs and the Ns on the picolylamine rings of **2**, may only allow the formation of oligomers, which are inadequate for gelation.

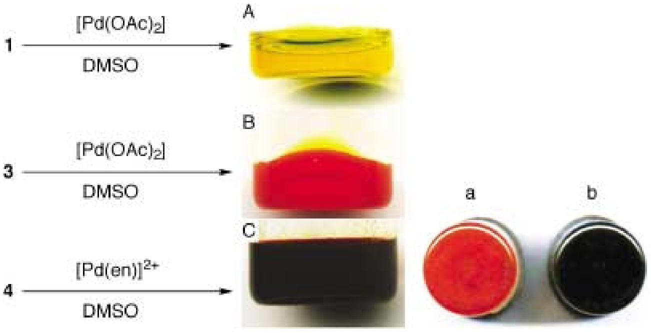

Figure 2. Formation of the metallogels by using Pd^{II} ions and ligands **1** (A), **3** (B), and **4** (C); the optical images of the reaction mixtures in the catalytic oxidation of benzyl alcohol after two hours (a) by using B as the catalyst (no palladium black formed) and (b) by using **6** as the catalyst (Pd black formed). The images were taken using a flatbed scanner with the vials containing metallogels or catalytic reaction mixtures.

For comparison, we also added **6** into the solution of ligand **3** in DMSO. The metallogel B (Figure 2 and entry 5 in Table 1) formed in six hours. The longer gelation time of B compared with D, formed by treating **5** with ligand **3**[12] (entry 7 in Table 1) under similar conditions, is consistent with the slower dissociation of $[Pd(OAc)_2]$.

Table 1. The conditions used for gelation.

	samples	ligand	metal ion	solvent	time [h]	solvent/gelator [molar ratio]	Pd^{II}/ligand	diameter of fibers in gel [nm]
1	polymer	**1**	**5**	DMSO	–	–	–	–
2	polymer	**2**	**5**	DMSO	–	–	–	–
3	oligomer	**2**	**6**	DMSO	–	–	–	–
4	Gel A	**1**	**6**	DMSO	12	270	1.3–1.5	20
5	Gel B	**3**	**6**	DMSO	6	950	2.0	70–120
6	Gel C	**4**	**5**	DMSO	1680	420	1.7–2.0	10
7[12]	Gel D	**3**	**5**	DMSO	4	1000	1.8–2.0	50

The physical properties of metallogel B are similar to those of the metallogel D[12] (entry 7 in Table 1). Gels (B and D) made from ligand **3** have a higher molar ratio of solvent and gelator (Table 1) than gel (A) made from ligand **1**. The cone shape and the conformational flexibility of calix[4]arene (**3**) may facilitate trapping solvent and contribute to the higher solvent content in the corresponding metallogels.

We used **4** as a new ligand to evaluate the structural requirements for forming metallogels. Unlike **3**, the porphyrin-based, tetradentate ligand **4** is rigid and planar, lacking the conformational flexibility and three-dimensional geometry. Reacting **5** and ligand **4** in DMSO formed the gel C (Figure 2 and entry 6 in Table 1) after ten weeks (**4** alone did not form a gel in DMSO under the same conditions). This process is much slower than the formation of D under similar conditions,[12] suggesting that the conformational freedom of the ligands also affects the kinetics of the gelation.

As shown in Figure 3, transmission electron microscopy (TEM) shows the fibrous structures in the metallogels. The fibers have diameters of $\approx$20 nm in gel A, 70– $\approx$120 nm in gel B, and $\approx$50 nm in gel D, which are all consistent with their transparency (the deep colors of gel B and gel C result from the absorption of the azocalixarene and the porphyrin-based ligands, respectively). Finer fibers ($\approx$10 nm) are present in gel C, with the coexistence of colloids. The fibers in all the metallogels display open cellular structures, as typically observed in gels.

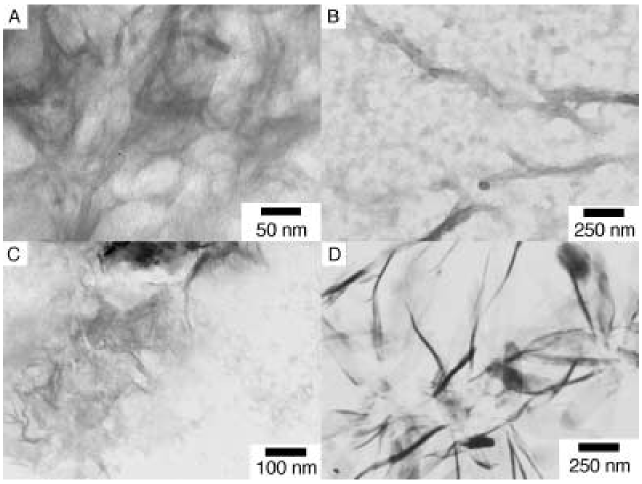

Figure 3. Transmission electron micrographs (TEM) of the metallogels (the gels were dried on Cu meshes prior to being coated with carbon) made from **1** and **6** (A), **3** and **6** (B), **4** and **5** (C), and **3** and **5** (D).

All the above metallogels form irreversibly (i.e., the addition of DMSO will not dissolve them) and are stable and insoluble in common organic solvents (e.g., toluene, hexane, THF, and dichloromethane) and water over a long period of time (> one year) or at elevated temperatures (> 100 °C). The metallogels, when treated with large amounts of acetone, form precipitates, which do not gel again in DMSO or other solvents, and we used acetone to isolate the cross-linked coordination polymers ("dry gels"). Small-angle X-ray diffraction studies of those metallogels indicate the absence of mesophases (e.g., lamellar or columnar organizations) and suggest that these metallogels are analogues of the hydrogels formed by cross-linking of polyacrylamides.

The stability of the metallogels and their chemical resemblance to the reported catalytic systems[18, 19] prompted us to test the catalytic activity of the metallogels. We added the freshly prepared metallogels into pure benzyl alcohol (molar ratio of catalyst and substrate is $\approx$1:10^4), and introduced molecular oxygen by bubbling air into the reaction mixture. We monitored the conversion of benzyl alcohol into benzaldehyde, which did not affect the stability of the metallogels, by HPLC every ten minutes over two hours. Equal molar metal sites of corresponding dry gels were tested under the same reaction conditions. The catalytic turnovers of all the gels were calculated and compared with the catalytic turnovers of **5** or **6** under similar reaction conditions.

Figure 4a shows the turnovers of different catalysts after two hours of reaction. For the reactions involving [Pd(OAc)$^+$] moieties, the turnovers follow the order: B > A > **6** > dry A $\approx$ dry B. The catalytic turnover of A is more than twice that of the corresponding dry gel and $\approx$1.5 times that of **6**; the catalytic turnover of B is twice that of [Pd(OAc)$_2$], three

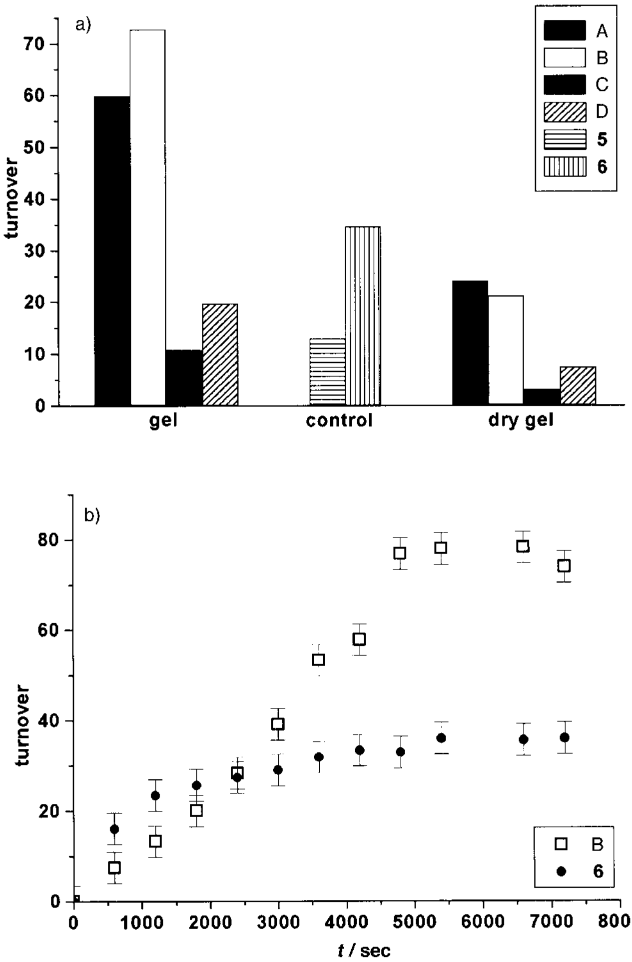

Figure 4. a) The catalytic turnovers (cumulative) for the oxidation of benzyl alcohol by air (1 atm) by using metallogels, their corresponding dry gels (formed by precipitating coordination polymers in acetone), and their corresponding transition-metal complexes as catalysts; b) The catalytic turnovers versus time of gel B and compound **6**.

times that of the corresponding dry gel, and four times that of similar systems[19] reported. Pyridine is not required in this oxidation reaction[19] since pyridine moieties are part of the polymer networks that form the gels. This eliminates the purification step of separating[19] pyridine from benzaldehyde.

The reactions involving **5** exhibited overall lower turnovers than the reactions involving **6**. This is likely to relate to the inherently low catalytic activity of $[Pd(en)]^{2+}$ centers in this type of reaction. Even in this case, the gels still showed higher (D) or comparable (C) catalytic activity than that of **5**.

We attribute the higher catalytic turnovers of metallogels to the superior stability of the catalysts under the reaction conditions. Since excess benzyl alcohol and O_2 were employed for all the experiments, the turnovers were dominated by the activity of the catalysts. As an example, Figure 4b plots the turnovers versus time of gel B and compound **6**. The turnover plot of **6** becomes flat at around 40 minutes, much earlier than that of the gel B. The loss of catalytic activity of **6** under these reaction conditions is probably due to the rapid decomposition of the catalyst. In fact, palladium black was observed after ten minutes until the end of the reaction (b, Figure 2). For **6**, the metallogel-based catalysts were stable, and no palladium black was observed (a, Figure 2). The turnover plot of B levels off starting at about two hours. This implies that the rate of the catalytic reaction is probably controlled by the diffusion of the substrates from surrounding media to the catalytic sites in the gel and the diffusion of the products from the gel to the surroundings. The saturation of the gel phase with benzaldehyde might be responsible for the plot leveling off. Although the overall catalytic turnovers of dry gels are the lowest, the dry gels don't form palladium black, which further confirms the immobility of Pd^{II} centers in the polymer networks. The lower catalytic activity of dry gels, compared with that of their corresponding gels and Pd^{II} complexes, is likely to relate respectively to: 1) lack of the metallogel's solution in the DMSO phase to deliver the reaction substrates to the metal sites; 2) relatively smaller surface area of the insoluble coordination polymers in this heterogeneous catalytic reaction.

Conclusion

In conclusion, we have demonstrated a simple method to construct the stable, catalytic metallogels from the coordination polymeric networks and an amphiphilic organic solvent. We also tested reusability of the metallogel (gel B); it indeed showed catalytic activity, but with lower turnover, which is possibly due to a small amount of benzaldehye remaining in the gel. We are currently designing and exploring better metallogels to overcome this problem. We believe that this metallogel approach offers a convenient path to explore and utilize otherwise (mostly) insoluble coordination polymers, which ultimately will lead to a gel system that integrates "uptake" and catalytic processes.

Experimental Section

Chemical reagents and solvents were used as received from commercial sources. We synthesized [1,3,5]triazine-based tridentate ligands **1**, **2**, and calix[4]rene-based tetradentate ligand **3**,[12] and purchased **4** from Aldrich.

Synthesis of 1 and 2: Cyanuric chloride (500 mg, 2.71 mmol) was added to an ice cold solution of 2-picolylamine (0.83 mL, 8.13 mmol) and *N,N*-diisopropylethylamine (DIEA, 1.43 mL, 8.13 mmol) in anhydrous THF (40 mL). The solution was stirred for five hours at 0 °C under nitrogen before it was warmed up to 25 °C and stirred for another five hours. Then the mixture was heated at reflux for two days, after which the solvent was removed under reduced pressure. The residue was redissolved in MeOH (40 mL). After filtration, the filtrate was collected and dried under reduced pressure, and the resulting yellow solid was purified by column chromatography, (silica, 10% MeOH/$CHCl_3$), and the final product (**1**) was obtained (368 mg, 34%).

^1H NMR (300 MHz, $[D_6]DMSO$, 298 K): $\delta = 4.49$ (s, 1H; CH_2), 4.62 (s, 1H; CH_2), 7.30 (t, 2H; pyridine), 7.81 (d, 1H; pyridine), 8.55 (d, 1H; pyridine); ^{13}C NMR (75 MHz, 298 K): $\delta = 166$, 160, 148, 136, 122, 121, 45.6; MS (FAB$^+$): m/z (%): 400 (100) $[M+H^+]$; elemental analysis calcd (%) for $C_{21}H_{21}N_9$: C 63.14, H 5.30, N 31.56; found: C 63.36, H 5.25, N 31.31.

Product **2** was synthesized (55%) using a similar procedure to that for making **1**.

^1H NMR (300 MHz, $[D_6]DMSO$, 298 K): $\delta = 4.48$ (d, 2H; CH_2), 7.40 (t, 1H; pyridine), 7.78 (d, 1H; pyridine), 8.50 (d, 1H; pyridine), 8.60 (d, 1H; pyridine); ^{13}C NMR (75 MHz, 298 K): $\delta = 166$, 149, 148, 136, 135, 123, 41; MS (FAB$^+$): m/z (%): 400 (100) $[M+H^+]$; elemental analysis calcd (%) for $C_{21}H_{21}N_9$: C 63.14, H 5.30, N 31.56; found: C 63.27, H 5.21, N 31.23.

General preparation of the metallogel: Sample gels were prepared by dissolving **1** (4.2 mg) and $[Pd(OAc)_2]$ (3.5 mg) in hot DMSO (0.2 mL) in sealed vials (1.5 × 5.0 cm). Once the solutions were homogeneous, they were allowed to cool down to room temperature in order to form the gels.

The measurement of the catalytic activity of the metallogel: The freshly prepared gel (0.006 mmol, based on Pd^{II}) was added into the benzyl alcohol (7 mL, 67 mmol) in a two-necked flask (20 mL). Atmospheric oxygen was bubbled into the flask, and the mixture was heated to 90 °C for two hours. Products were diluted with chloroform and were determined by TLC and HPLC. The control experiments using dry gel (crushed out by acetone) were carried out under the same conditions; the controls using **5** or **6** were also carried out under similar conditions, but with the addition of a small amount of pyridine or sodium acetate.[19]

Acknowledgements

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[1] F. Ilmain, T. Tanaka, E. Kokufuta, *Nature* **1991**, *349*, 400.
[2] M. Annaka, T. Tanaka, *Nature* **1992**, *355*, 430; *Synthesis, Characterization, and Theory of Polymeric Networks and Gels* (Ed.: S. M. Aharoni), Plenum, New York, **1992**; Y. Osada, H. Okuzaki, H. Hori, *Nature* **1992**, *355*, 242; R. Dagani, *Chem. Eng. News* **1997**, *75*, 26; S. Juodkazis, N. Mukai, R. Wakaki, A. Yamaguchi, S. Matsuo, H. Misawa, *Nature* **2000**, *408*, 178; T. Brotin, R. Utermohlen, F. Fages, H. Bouaslaurent, J. P. Desvergne, *J. Chem. Soc. Chem. Commun.* **1991**, 416; I. Furman, R. G. Weiss, *Langmuir* **1993**, *9*, 2084; L. D. Lu, R. G. Weiss, *Langmuir* **1995**, *11*, 3630; R. J. H. Hafkamp, M. C. Feiters, R. J. M. Nolte, *J. Org. Chem.* **1999**, *64*, 412; K. Yabuuchi, A. E. Rowan, R. J. M. Nolte, T. Kato, *Chem. Mater.* **2000**, *12*, 440.
[3] P. Terech, R. G. Weiss, *Chem. Rev.* **1997**, *97*, 3133.
[4] G. Mieden-Gundert, L. Klein, M. Fischer, F. Vogtle, K. Heuze, J. L. Pozzo, M. Vallier, F. Fages, *Angew. Chem.* **2001**, *113*, 3266; *Angew. Chem. Int. Ed.* **2001**, *40*, 3164.
[5] R. J. H. Hafkamp, B. P. A. Kokke, I. M. Danke, H. P. M. Geurts, A. E. Rowan, M. C. Feiters, R. J. M. Nolte, *Chem. Commun.* **1997**, 545.
[6] Y. Osada, J. P. Gong, *Adv. Mater.* **1998**, *10*, 827.

[7] E. Lai, B. W. Birren, *Electrophoresis of Large DNA Molecules: Theory and Applications,* Cold Spring Harbor, New York, **1990**; Y. H. Chu, J. K. Chen, G. M. Whitesides, *Anal. Chem.* **1993**, *65*, 1314.

[8] R. F. Harris, A. J. Nation, G. T. Copeland, S. J. Miller, *J. Am. Chem. Soc.* **2000**, *122*, 11270.

[9] J. H. Holtz, S. A. Asher, *Nature* **1997**, *389*, 829; T. Miyata, N. Asami, T. Uragami, *Nature* **1999**, *399*, 766; L. Liu, P. S. Li, S. A. Asher, *Nature* **1999**, *397*, 141; J. H. Holtz, J. S. W. Holtz, C. H. Munro, S. A. Asher, *Anal. Chem.* **1998**, *70*, 780.

[10] R. Yoshida, K. Uchida, Y. Kaneko, K. Sakai, A. Kikuchi, Y. Sakurai, T. Okano, *Nature* **1995**, *374*, 240.

[11] J. S. Sohna, F. Fages, *Chem. Commun.* **1997**, 327.

[12] B. Xing, M.-F. Choi, B. Xu, *Chem. Commun.* **2002**, 362.

[13] M. Fujita, S. Nagao, M. Iida, K. Ogata, K. Ogura, *J. Am. Chem. Soc.* **1993**, *115*, 1574.

[14] P. J. Stang, D. H. Cao, K. Chen, G. M. Gray, D. C. Muddiman, R. D. Smith, *J. Am. Chem. Soc.* **1997**, *119*, 5163; H. Li, M. Eddaoudi, M. O'Keefe, O. M. Yaghi, *Nature* **1999**, *402*, 276; M. Albrecht, M. Lutz, A. L. Spek, G. van Koten, *Nature* **2000**, *406*, 970; N. Takeda, K. Umemoto, K. Yamaguchi, M. Fujita, *Nature* **1999**, *398*, 794; M. Fujita, N. Fujita, K. Ogura, K. Yamaguchi, *Nature* **1999**, *400*, 52; M. Fujita, F. Ibukuro, H. Hagihara, K. Ogura, *Nature* **1994**, *367*, 720.

[15] N. C. Neidhardt, J. L. Ingraham, M. Schaechter, *Physiology of the Bacterial Cell: A Molecular Approach*, 1st ed., Sinauer Associate, Sunderland, **1990**.

[16] M. Aoki, K. Murata, S. Shinkai, *Chem. Lett.* **1991**, 1715; J. van Esch, S. De Feyter, R. M. Kellogg, F. De Schryver, B. L. Feringa, *Chem. Eur. J.* **1997**, *3*, 1238; M. de Loos, J. van Esch, I. Stokroos, R. M. Kellogg, B. L. Feringa, *J. Am. Chem. Soc.* **1997**, *119*, 12675; D. J. Abdallah, S. A. Sirchio, R. G. Weiss, *Langmuir* **2000**, *16*, 7558; L. D. Lu, T. M. Cocker, R. E. Bachman, R. G. Weiss, *Langmuir* **2000**, *16*, 20; F. S. Schoonbeek, J. H. van Esch, R. Hulst, R. M. Kellogg, B. L. Feringa, *Chem. Eur. J.* **2000**, *6*, 2633; D. J. Abdallah, R. G. Weiss, *Chem. Mater.* **2000**, *12*, 406; J. Brinksma, B. L. Feringa, R. M. Kellogg, R. Vreeker, J. van Esch, *Langmuir* **2000**, *16*, 9249; E. Ostuni, P. Kamaras, R. G. Weiss, *Angew. Chem.* **1996**, *108*, 1423; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1324; D. J. Abdallah, R. G. Weiss, *Adv. Mater.* **2000**, *12*, 1237.

[17] P. J. Stang, D. H. Cao, *J. Am. Chem. Soc.* **1994**, *116*, 4981; M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151; B. Olenyuk, M. D. Levin, J. A. Whiteford, J. E. Shield, P. J. Stang, *J. Am. Chem. Soc.* **1999**, *121*, 10434; M. D. Levin, P. J. Stang, *J. Am. Chem. Soc.* **2000**, *122*, 7428; C. Muller, J. A. Whiteford, P. J. Stang, *J. Am. Chem. Soc.* **1998**, *120*, 9827; J. Manna, C. J. Kuehl, J. A. Whiteford, P. J. Stang, D. C. Muddiman, S. A. Hofstadler, R. D. Smith, *J. Am. Chem. Soc.* **1997**, *119*, 11611.

[18] S. R. Fix, J. L. Brice, S. S. Stahl, *Angew. Chem.* **2002**, *114*, 172; *Angew. Chem. Int. Ed.* **2002**, *41*, 164; B. A. Steinhoff, S. R. Fix, S. S. Stahl, *J. Am. Chem. Soc.* **2002**, *124*, 766; G. Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **2000**, *287*, 1636.

[19] T. Nishimura, T. Onoue, K. Ohe, S. Uemura, *Tetrahedron Lett.* **1998**, *39*, 6011.

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