Angewandte
International Edition Chemie

DOI: 10.1002/anie.201000096

Micropatterning

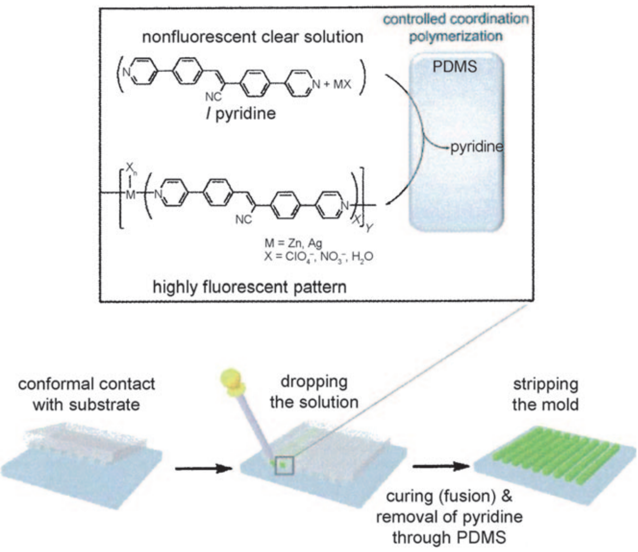
Micromolding of a Highly Fluorescent Reticular Coordination Polymer: Solvent-Mediated Reconfigurable Polymerization in a Soft Lithographic Mold**

*Youngmin You, Hoichang Yang, Jong Won Chung, Jong H. Kim, Yunoh Jung, and Soo Young Park**

Construction of ordered molecular superstructures is of central importance to the performance of photonic/electronic devices, in which molecular stacking modes contribute profoundly to charge carrier generation, carrier mobility,[1] and fluorescence emission[2] behavior. Although enormous efforts have been applied based on supramolecular approaches, the method often suffers from bare practicability in respect to spatial regularity and density, large area production, and reproducibility. Novel materials and innovative processing methods that favor high-fidelity superstructure formation are thus in great demand.

Coordination polymers have the fascinating benefits of versatility with respect to the range of possible combinatorial ensembles of metal and ligands,[3] easy implementation of the chemistry between metal and ligands,[4] and advanced functionalities afforded by metal and ligand interactions.[5] More importantly, coordination polymers can be designed to produce ordered supramolecular structures, the formation of which is driven by the coordination geometry around the metal ion.[6] Although reticular structures based on coordination geometry have been widely exploited,[7] the kinetically labile nature of coordination bonds is gaining increasing interest.[8] Lehn and co-workers recently demonstrated ligand exchange and reshuffling at a contact between two different coordination polymers.[9] Coordination polymerization, therefore, drives construction of the thermodynamically most-favored structure because lability permits sampling of several possible geometries through the reversible reorganization of coordination bonds. Therefore, it was envisioned that coordination polymerization may be employed for the reproducible construction of highly ordered molecular superstructures.

By taking advantage of the chemical reconfigurability of coordination polymers, we demonstrate herein a facile and efficient patterning method using a coordination polymer with a highly fluorescent reticular superstructure (Scheme 1). Preformed coordination polymers can be depolymerized in a strongly coordinating solvent, and then allowed to flow into microchannels by capillary forces. Inside the capillaries, controlled repolymerization is facilitated through selective absorption of the solvent by the mold, leading to the formation of a patterned coordination polymer. Patterning (that is, allocation and macroscale structural geometry) is implemented by a soft lithographic method, whilst the molecular superstructure is determined by the coordination geometry. The method of micromolding in capillaries (MIMIC)[10] was employed herein to enable the simultaneous patterning and formation of supramolecular structures by reconfigurable coordination polymerization. Micromolded coordination polymers were characterized by two-dimensional (2D) grazing-incidence X-ray diffraction (GIXD), which identified the three-dimensional (3D) reticular super-



Scheme 1. Structure of the coordination polymer and conceptual representation of the coordinative patterning by soft-lithography-driven coordination polymerization.

---

[*] Dr. Y. You, Dr. J. W. Chung, J. H. Kim, Y. Jung, Prof. Dr. S. Y. Park
Center for Supramolecular Optoelectronic Materials
WCU Hybrid Materials Program
and
Department of Materials Science and Engineering
Seoul National University
San 56-1, Shilim-dong, Gwanak-gu, Seoul 151-744 (Korea)
Fax: (+82) 2-886-8331
E-mail: parksy@snu.ac.kr
Homepage: http://csom.snu.ac.kr/
Prof. Dr. H. Yang
Department of Advanced Fiber Engineering, Inha University
253 Yonghyun-dong, Nam-gu, Incheon 402-751 (Korea)

[**] This work was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science, and Technology (CRI; RIAMIAM0209 (0417-20090011)), and the US department of Energy, Office of Science, Office of Basic Energy Sciences (DE-AC02-98CH10886).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201000096.

structure. This unique superstructure yielded bright fluorescence in the solid state. These results provide valuable tools for achieving high fidelity control in molecular superstructure fabrication and a reliable nanofabrication method. In particular, the solution processing used in this technique may facilitate fabrication of a broad array of devices that utilize coordination polymers.

A new aggregation-induced enhanced emission (AIEE)-type[11] bridging ligand, 4,4′-di(4-pyridyl)cyanostilbene, was readily synthesized in three steps and fully characterized using spectroscopic identification methods (see the Experimental Section). Coordination polymerization of the metal ion with this ligand was carried out by the slow diffusion of a metal ion solution ($Zn(ClO_4)_2{\cdot}6H_2O$ in MeOH, 5 mM) that was carefully layered over the top surface of a ligand solution ($CHCl_3$, 5 mM). The bilayer solution was left undisturbed for one day to give a yellow suspension, which was filtered, triturated, and thoroughly washed with $CHCl_3$ and MeOH to remove residual components. The polymer was almost insoluble in common organic solvents, precluding the use of common characterization methods, including GPC (DMF + LiBr or DMF + H_3PO_4), ^1H NMR, or viscometry. Instead, concurrent XPS peaks corresponding to Zn 2p, C 1s, and N 1s in the polymer powder indicated that zinc ions were successfully incorporated into the coordination polymer. Quantitative analysis of the XPS spectra afforded a ratio of zinc to ligand that was slightly larger than 1:2 (Supporting Information, Figure S1). This ratio implies that the polymer contained 2D or 3D alternating (zinc–ligand) backbone structures.[12] We conjecture that the weakly coordinating perchlorate ion allowed formation of this multidimensional structure. Powder XRD studies showed a set of diffractions with d spacings of 21.43, 15.35, and 10.88 Å (Supporting Information, Figure S2), which were consistent with the structure proposed by the XPS result. Fluorescence intensity of the coordination polymer powder decreased by a factor of about 10^{-2} with increasing temperature (Supporting Information, Figure S3), which reversibly recovered at room temperature, whereas the ligand powder showed no temperature-dependent change in fluorescence intensity.

The ligand was coordinated through the 4-pyridyl moiety, which was structurally equivalent to the pyridine solvent competing with the ligand for coordination to zinc. Therefore, depolymerization and repolymerization were expected when an excess of pyridine was added or removed, respectively. An aliquot of pyridine completely solvated the polymer powder to give a clear solution (ca. 10^2 mg mL^{-1}). ^1H NMR spectra of the polymer were taken in the presence and absence of [D$_5$]pyridine, which revealed appearance of displaced free ligands as [D$_5$]pyridine was added (Supporting Information, Figure S4). The fluorescent aggregates were recovered from the solution by evaporating the pyridine. Interestingly, during slow evaporation, the polymer tended to fuse (Supporting Information, Figure S5), which was similar to previous observations.[8m] The reassembly induced by removing pyridine solvent was indicative of the thermodynamic sampling of the coordination polymer. We combined the depolymerization and repolymerization method with the standard MIMIC method to achieve spatial patterning and supramolecular structure formation. Typically, 30 mg of the coordination polymer powder was dissolved in 200 μL pyridine. The solution was introduced into rectangular capillaries in conformal contact with a patterned poly(dimethylsiloxane) (PDMS, Sylgard 184, Dow Corning) mold and a glass substrate. The PDMS slowly swelled at the inner walls of the fully filled capillaries by the absorption of pyridine.[13] After polymerization, the mold was peeled from the substrate to yield patterned coordination polymer wires (4 μm × 2 μm width × height; Figure 1 a). The feature size and density of the patterns were governed by PDMS molds. The MIMIC method is versatile in that filling the capillary is rarely limited by the nature of the substrate.[14] During the reconfigurable coordination polymerization in the MIMIC mold, removal of pyridine was critical for the formation of ordered coordination structures.

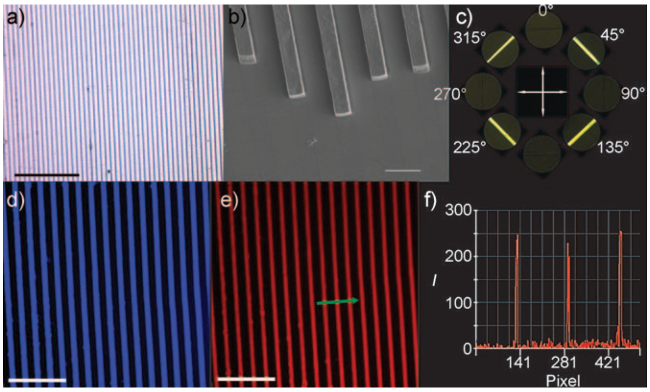


Figure 1. a) Optical microscopy (scale bar = 100 μm) and b) FE-SEM images (scale bar: 10 μm) of the patterns. c) Optical microscopy image of a single line pattern, collected under cross-polarized conditions. Rotation of a patterned wire showed birefringence at every 45 degree rotational interval with respect to the polarizer. d),e) Fluorescence images of the patterns obtained using an image restoration microscope (emission cut-off filters: 480 nm (d), 580 nm (e), scale bar: 40 μm). f) Fluorescence intensity profile along the green arrow indicated in (e).

Field-emission scanning electron microscope (FE-SEM) images showed that the outer surfaces of the patterns are nearly flawless, and grooves or shrinkages were minimal (Figure 1 b). Atomic force microscopy further characterized the well-defined pattern morphology (Supporting Information, Figure S6). The fabricated patterns showed strong alternative birefringence under cross-polarized illumination conditions, indicating that the patterns had a pronounced directional order (Figure 1 c). The MIMIC-fabricated coordination polymer patterns were highly fluorescent, and no background fluorescence emission was observed in the spaces between the patterns (Figure 1 d,e). Fluorescence mapping across the patterns revealed alternating on/off fluorescence signals (Figure 1 f).

2D GIXD measurements (incident beam angle = 0.5°) provided essential information about the polymer superstructure (Figure 2). Strong diffraction peaks were observed along both the out-of-plane and in-plane directions, indicating good ordering. A single series of Bragg peaks along the out-of-plane direction corresponded to the (00l) crystal planes, with d spacings of 21.13, 10.59, 6.14, 5.425, and 4.363 Å

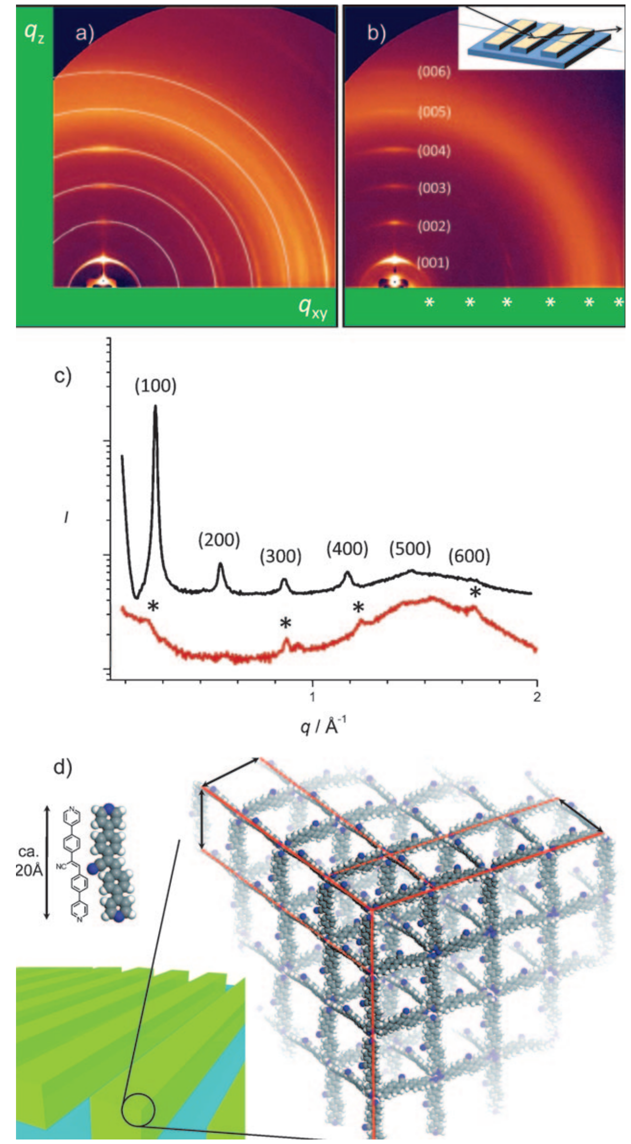


Figure 2. a,b) 2D GIXD of the cast region (a) and coordination polymer patterns (b). The peaks marked with an asterisk in (b) represent X-ray reflections of the (0*k*0) + (00*l*) planes.) c) 1D out-of-plane (black line) and in-plane (red line) X-ray profiles extracted from (b). d) Representation of the molecular superstructure of the patterns. Distances indicated by black arrows: 21.13 Å. Zinc atoms and counteranions are omitted for clarity.

(calculated peak positions at $q_z = 0.2974$, 0.5933, 0.8759, 1.1581, and 1.4402 Å^{-1} in Figure 2), which indicates the presence of periodic layers connected by vertically coordinated ligand pillars. In particular, the peak observed at 21.13 Å corresponds to the length of the ligand (determined quantum-chemically, optimized using B3LYP/6-31G**). In-plane *d* spacings of (0*k*0) were identified at the same positions as those of the out-of plane peaks. Therefore, the entire coordinated polymer framework assumed a primitive cubic structure along the primary axes. The 2D GIXD results, together with the XPS and powder XRD results, led us to conclude that the molecular superstructure was composed of a cubic structure in which ligands and zinc ions occupied rods and connecting points, respectively (Figure 2d).

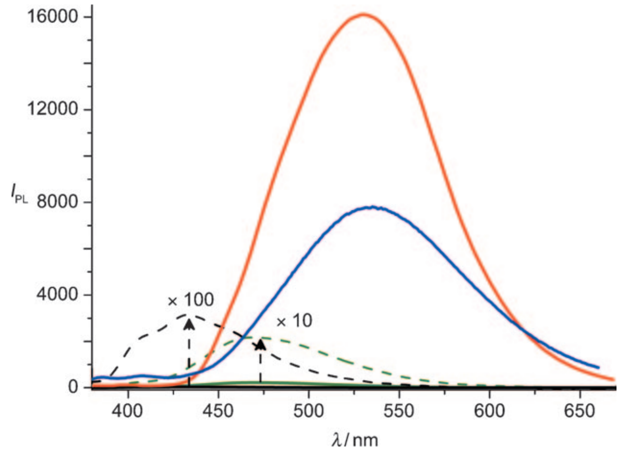


Figure 3. Photoluminescence spectra of the ligand solution (10 μM, CH_2Cl_2, black curve), its nanoparticle suspension (THF/water = 1:9 (v/v), 10 μM, green), and the Ag^I coordination polymer (blue) and Zn^{II} coordination polymer suspension (10 mg L^{-1}, $CHCl_3$, red). Magnifications shown as dashed lines.

Of interest was the large enhancement in fluorescence intensity that accompanied coordination polymerization (Figure 3). In contrast with the virtually nonfluorescent ligand solution (photoluminescence quantum yield, PLQY = 0.00086, CH_2Cl_2) and ligand nanoparticle suspension[11a] (PLQY = 0.0071, THF/water = 1:9 v/v) of ligand, the PLQY of the zinc coordination polymer increased to 0.61. An unusual enhancement of fluorescence by a factor of 700 was attributed to the cumulative effects of a suppressed nonfluorescent n–π* transition, locked intramolecular motion, and reduced interchromophoric contacts in the polymer structure, all of which arose from coordination interactions. In fact, both a bathochromic shift and an increase in fluorescence intensity, by a factor of 10, were observed when the ligand solution was treated with hydrochloric acid. Fluorescence of the coordination polymer also exhibited a positive slope in the Lippert–Mataga plot, which was not observed in the ligand solution (Supporting Information, Figure S7). This behavior, together with the diamagnetic character of zinc(II) ions, suggested that the coordination by the lone pair electrons on the pyridine promoted a new efficient fluorescence transition. Radiationless vibronic motions appear to be repressed by the coordination bond formation. Finally, the 3D cubic structure of the coordination polymer sufficiently separated the ligands, such that interchromophoric contacts were minimized. For comparison, we prepared a silver(I) coordination polymer that would be anticipated to be linear owing to the coordination geometry around the silver(I) center. Indeed, FE-SEM images of this polymer demonstrated the formation of nanobelts (Supporting Information, Figure S8) in which polymer chains were mutually aligned along their long axis. This alignment was expected to increase the interchromophoric contacts.[15] A smaller PLQY (0.33) of the silver(I) coordination polymer emphasized the importance of the 3D reticular superstructure in the zinc(II) coordination polymer in achieving high fluorescence efficiency.[16]

In summary, we have described a novel method for fabricating highly luminescent supramolecular patterns. The combined use of soft lithography and coordination polymerization permitted the control and synchronization over allocation, macroscale structural geometry, and interior superstructures. A reticular cubic structure was revealed by 2D GIXD, and the coordinative structure was investigated by various characterization methods. Owing to the cubic arrangement of the ligands involved in the coordination network, high intensity fluorescence was achieved without suffering from typical interchromophoric quenching. This approach holds a great potential for reliable nanoscopic fabrication that requires controlled integration of functional molecules.

Experimental Section

4-(4-(Cyanomethyl)phenyl)pyridine: Isopropanol (18 mL), (4-(cyanomethyl)phenyl)boronic acid (2.0 g, 12 mmol), and 2 M aqueous K_2CO_3 (24 mL) were added to a solution of 4-bromopyridine hydrochloride (2.0 g, 10 mmol) in toluene (18 mL). The solution was stirred for 30 min under a nitrogen atmosphere. After the addition of tetrakis(triphenylphosphine)palladium(0) (0.35 g, 0.30 mmol), the mixture was heated to reflux for 7 h. The cooled solution was poured onto water (200 mL) and extracted three times with ethyl acetate (200 mL). The combined organic layer was dried over magnesium sulfate and evaporated under vacuum. Finally, silica gel column chromatography (*n*-hexane/EtOAc = 1:2) yielded a white powder (1.9 g, 10 mmol) in a quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.83$ (s, 1 H), 7.47 (d, $J = 8.4$ Hz, 2 H), 7.50 (d, $J = 6.2$ Hz, 2 H), 7.66 (d, $J = 8.3$ Hz, 2 H), 8.68 ppm (d, $J = 6.2$ Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 23.63$, 117.65, 121.82, 127.99, 128.97, 131.16, 138.21, 147.83, 150.32 ppm; Elemental analysis (%) calcd for $C_{13}H_{10}N_2$: C 80.39, H 5.19, N 14.42; found: C 80.21, H 5.28, N 14.51.

4-(4-Formylphenyl)pyridine: The same synthetic procedure used for 4-(4-(cyanomethyl)phenyl)pyridine was applied, except using (4-formylphenyl)boronic acid (2.0 g, 13 mmol) instead of (4-(cyanomethyl)phenyl)boronic acid. Yield = 84 % (1.4 g). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.59$ (d, $J = 6.2$ Hz, 2 H), 7.81 (d, $J = 8.3$ Hz, 2 H), 8.02 (d, $J = 8.2$ Hz, 2 H), 8.74 (d, $J = 6.2$ Hz, 2 H), 10.10 ppm (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 122.07$, 127.98, 130.65, 136.77, 144.04, 147.50, 150.38, 191.78 ppm; Elemental analysis (%) calcd for $C_{12}H_9NO$: C 78.67, H 4.95, N 7.65; found: C 78.49, H 5.09, N 7.68.

4,4′-Di(4-pyridyl)cyanostilbene: A mixture of 4-(4-(cyanomethyl)phenyl)pyridine (1.0 g, 5.2 mmol) and 4-(4-formylphenyl)pyridine (0.94 g, 5.2 mmol) and THF (1.0 mL) was stirred in *tert*-butanol (30 mL) at 50 °C for 1 h. Tetrabutylammonium hydroxide (TBAH) (1.0 M in methanol; 0.5 mL, 10 mol %) was added dropwise and stirred for an additional hour. The yellowish white precipitate was collected by filtration and washed with methanol. Silica gel column chromatography (*n*-hexane/EtOAc = 1:3) was carried out to give a beige powder (0.76 g, 2.1 mmol) in 41 % yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.56$ (m, 4 H), 7.67 (s, 1 H), 7.77 (m, 4 H), 7.84 (d, $J = 8.6$ Hz, 2 H), 8.05 (d, $J = 8.3$ Hz, 2 H), 8.71 ppm (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 112.00$, 117.86, 121.65, 121.67, 127.00, 127.79, 127.93, 128.66, 128.75, 130.35, 134.40, 135.13, 139.35, 140.44, 141.73, 147.20, 150.70 ppm; MS (FAB, glycerol): m/z calcd for $C_{25}H_{17}N_3$: 359.42; found: 359. Elemental analysis (%) calcd for $C_{25}H_{17}N_3$: C 83.54, H 4.77, N 11.69; found: C 83.53, H 4.79, N 11.68.

Procedures for the preparation of PDMS molds and the MIMIC technique using these molds have been reported elsewhere.[14] Absorption spectra were recorded with a SHIMAZU UV-1650PC over the range of 280–700 nm. Photoluminescence spectra were obtained using a Varian Cary Eclipse fluorescence spectrophotometer. Measurement of absolute photoluminescence quantum yields of the patterns was initially attempted using an instrument equipped with an integrated sphere; however, acquired values had large error ranges. Photoluminescence quantum yields (PLQYs) were calculated relatively using quinine sulfate (0.58; 0.1 M aq. H_2SO_4) and 9,10-diphenylanthracene (0.82; benzene) as standards. The polymer was thoroughly triturated and suspended in $CHCl_3$ (< 10 mg L^{-1}) for all optical measurement, otherwise mentioned. The photoluminescence measurements for organic suspensions were performed as described.[11a] X-ray photoelectron spectroscopy (XPS) was conducted using an AXIS, KRATOS with pelletized coordination polymer mounted on a SiO_2 substrate. 2D GIXD experiments were performed at the beam line X21 at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (Upton, NY, USA). The sample was mounted on a two-axis goniometer atop of an X-Z stage, and the scattered intensity was recorded by a 2D detector. The incident beam angle was about 0.5° for all the 2D GIXD patterns. The morphology of the patterned wires was observed in non-contact mode (scan rate and size were 0.2 Hz and 50×50 µm^2, respectively) by an XE-150 atomic force microscope (AFM), PSIA. An image restoration microscope (DeltaVision RT, AppliedPrecision) was used to record fluorescence images of the patterns. FE-SEM images were collected using a JSM-6330F (JEOL) instrument. Wide-angle X-ray diffractograms were acquired in reflection mode using nickel-filtered Cu KR radiation on a D8 Advance (Bruker) instrument equipped with a point detector operating at 40 kV and 40 mA.

Received: January 7, 2010
Published online: April 16, 2010

Keywords: coordination polymers · fluorescence · micromolding · nanostructures · soft lithography

---

[1] a) H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig, D. M. de Leeuw, *Nature* **1999**, *401*, 685 – 688; b) H. Yang, T. J. Shin, M.-M. Ling, K. Cho, C. Y. Ryu, Z. Bao, *J. Am. Chem. Soc.* **2005**, *127*, 11542 – 11543; c) S. E. Fritz, S. M. Martin, C. D. Frisbie, M. D. Ward, M. F. Toney, *J. Am. Chem. Soc.* **2004**, *126*, 4084 – 4085; d) D. H. Kim, Y. Jang, Y. D. Park, K. Cho, *Langmuir* **2005**, *21*, 3203 – 3206.

[2] a) J. Kunzelman, M. Kinami, B. R. Crenshaw, J. D. Protasiewicz, C. Weder, *Adv. Mater.* **2008**, *20*, 119 – 122; b) Y. Sagara, T. Mutai, I. Yoshikawa, K. Araki, *J. Am. Chem. Soc.* **2007**, *129*, 1520 – 1521; c) J. Mizuguchi, N. Tanifuji, K. Kobayashi, *J. Phys. Chem. B* **2003**, *107*, 12635 – 12638; d) K. Ariga, Y. Terasaka, D. Sakai, H. Tsuji, J. Kikuchi, *J. Am. Chem. Soc.* **2000**, *122*, 7835 – 7836; e) T. Yamamoto, Y. Muramatsu, B. L. Lee, H. Kokubo, S. Sasaki, M. Hasegawa, T. Yagi, K. Kubota, *Chem. Mater.* **2003**, *15*, 4384 – 4393; f) Y. Mizobe, H. Ito, I. Hisaki, M. Miyata, Y. Hasegawa, N. Tohnai, *Chem. Commun.* **2006**, 2126 – 2128; g) T. Mutai, H. Satou, K. Araki, *Nat. Mater.* **2005**, *4*, 685 – 687; h) R. Davis, N. P. Rath, S. Das, *Chem. Commun.* **2004**, 74 – 75; i) Y. Zhao, H. Gao, Y. Fan, T. Zhou, Z. Su, Y. Liu, Y. Wang, *Adv. Mater.* **2009**, *21*, 19 – 28.

[3] a) S. Kitagawa, R. Kitaura, S.-i. Noro, *Angew. Chem.* **2004**, *116*, 2388 – 2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334 – 2375; b) J. M. Lehn, *Science* **2002**, *295*, 2400 – 2403; c) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629 – 1658.

[4] For examples: a) M. Shirakawa, N. Fujita, T. Tani, K. Kaneko, M. Ojima, A. Fujii, M. Ozaki, S. Shinkai, *Chem. Eur. J.* **2007**, *13*, 4155 – 4162; b) K. H. Park, K. Jang, S. U. Son, D. A. Sweigart, *J. Am. Chem. Soc.* **2006**, *128*, 8740 – 8741.

[5] a) O. Roubeau, A. Colin, V. Schmitt, R. Clérac, *Angew. Chem.* **2004**, *116*, 3345 – 3348; *Angew. Chem. Int. Ed.* **2004**, *43*, 3283 – 3286; b) K. Kuroiwa, T. Shibata, A. Takada, N. Nemoto, N. Kimizuka, *J. Am. Chem. Soc.* **2004**, *126*, 2016 – 2021; c) A.

Kishimura, T. Yamashita, T. Aida, *J. Am. Chem. Soc.* **2005**, *127*, 179 – 183; d) A. Y.-Y. Tam, K. M.-C. Wong, G. Wang, V. W.-W. Yam, *Chem. Commun.* **2007**, 2028 – 2030; e) W.-Y. Wong, X.-Z. Wang, Z. He, A. B. Djurii, C.-T. Yip, K.-Y. Cheung, H. Wang, C. S. K. Mak, W.-K. Chan, *Nat. Mater.* **2007**, *6*, 521 – 527; f) Y. Li, G. Xu, W.-Q. Zou, M.-S. Wang, F.-K. Zheng, M.-F. Wu, H.-Y. Zeng, G.-C. Guo, J.-S. Huang, *Inorg. Chem.* **2008**, *47*, 7945 – 7947; g) E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-García, V. Laukhin, *Nature* **2000**, *408*, 447 – 449; h) M. E. Itkis, X. Chi, A. W. Cordes, R. C. Haddon, *Science* **2002**, *296*, 1443 – 1445; i) S.-i. Ohkoshi, H. Tokoro, T. Hozumi, Y. Zhang, K. Hashimoto, C. Mathonière, I. Bord, G. Rombaut, M. Verelst, C. C. dit Moulin, F. Villain, *J. Am. Chem. Soc.* **2006**, *128*, 270 – 277; j) E.-Q. Gao, Y.-F. Yue, S.-Q. Bai, Z. He, C.-H. Yan, *J. Am. Chem. Soc.* **2004**, *126*, 1419 – 1429; k) S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita, S. Kitagawa, *J. Am. Chem. Soc.* **2007**, *129*, 2607 – 2614; l) K. M. L. Taylor, W. J. Rieter, W. Lin, *J. Am. Chem. Soc.* **2008**, *130*, 14358 – 14359.

[6] a) B. H. Northrop, H.-B. Yang, P. J. Stang, *Inorg. Chem.* **2008**, *47*, 11257 – 11268; b) C.-S. Lee, N. Kimizuka, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4922 – 4926; c) D. G. Kurth, N. Severin, J. P. Rabe, *Angew. Chem.* **2002**, *114*, 3833 – 3835; *Angew. Chem. Int. Ed.* **2002**, *41*, 3681 – 3683; d) M. Schütte, D. G. Kurth, M. R. Linford, H. Cölfen, H. Möhwald, *Angew. Chem.* **1998**, *110*, 3058 – 3061; *Angew. Chem. Int. Ed.* **1998**, *37*, 2891 – 2893; e) H. Krass, E. A. Plummer, J. M. Haider, P. R. Barker, N. W. Alcock, Z. Pikramenou, M. J. Hannon, D. G. Kurth, *Angew. Chem.* **2001**, *113*, 3980 – 3983; *Angew. Chem. Int. Ed.* **2001**, *40*, 3862 – 3865; f) C. Kaes, M. W. Hosseini, C. E. F. Rickard, B. W. Skelton, A. H. White, *Angew. Chem.* **1998**, *110*, 970 – 973; *Angew. Chem. Int. Ed.* **1998**, *37*, 920 – 922; g) Y. Yamanoi, Y. Sakamoto, T. Kusukawa, M. Fujita, S. Sakamoto, K. Yamaguchi, *J. Am. Chem. Soc.* **2001**, *123*, 980 – 981; h) L. Applegarth, N. Clark, A. C. Richardson, A. D. M. Parker, I. Radosavljevic-Evans, A. E. Goeta, J. A. K. Howard, J. W. Steed, *Chem. Commun.* **2005**, 5423 – 5425; i) U. Schlickum, R. Decker, F. Klappenberger, G. Zoppellaro, S. Klyatskaya, M. Ruben, I. Silanes, A. Arnau, K. Kern, H. Brune, J. V. Barth, *Nano. Lett.* **2007**, *7*, 3813 – 3817; j) F. Fages, *Angew. Chem.* **2006**, *118*, 1710 – 1712; *Angew. Chem. Int. Ed.* **2006**, *45*, 1680 – 1682; k) J. B. Beck, S. J. Rowan, *J. Am. Chem. Soc.* **2003**, *125*, 13922 – 13923; l) H.-J. Kim, W.-C. Zin, M. Lee, *J. Am. Chem. Soc.* **2004**, *126*, 7009 – 7014; m) J. M. J. Paulusse, D. J. M. van Beek, R. P. Sijbesma, *J. Am. Chem. Soc.* **2007**, *129*, 2392 – 2397; n) B. Xing, M.-F. Choi, Z. Zhou, B. Xu, *Langmuir* **2002**, *18*, 9654 – 9658.

[7] a) G. J. McManus, J. J. Perry IV, M. Perry, B. D. Wagner, M. J. Zaworotko, *J. Am. Chem. Soc.* **2007**, *129*, 9094 – 9101; b) R. Kitaura, S. Kitagawa, Y. Kubota, T. C. Kobayashi, K. Kindo, Y. Mita, A. Matsuo, M. Kobayashi, H.-C. Chang, T. C. Ozawa, M. Suzuki, M. Sakata, M. Takata, *Science* **2002**, *298*, 2358 – 2361; c) N. Sakai, S. Matile, *Angew. Chem.* **2008**, *120*, 9745 – 9749; *Angew. Chem. Int. Ed.* **2008**, *47*, 9603 – 9607; d) Q. Wei, S. L. James, *Chem. Commun.* **2005**, 1555 – 1556; e) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469 – 472; f) M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka, S. Kitagawa, *Angew. Chem.* **1997**, *109*, 1844 – 1846; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1725 – 1727; g) N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe, O. M. Yaghi, *Science* **2003**, *300*, 1127 – 1129; h) H. Hayashi, A. P. Côté, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Nat. Mater.* **2007**, *6*, 501 – 506; i) M. E. Kosal, J.-H. Chou, S. R. Wilson, K. S. Suslick, *Nat. Mater.* **2002**, *1*, 118 – 121; j) O. M. Yaghi, H. Li, T. L. Groy, *Inorg. Chem.* **1997**, *36*, 4292 – 4293; k) O.-S. Jung, Y. J. Kim, K. M. Kim, Y.-A. Lee, *J. Am. Chem. Soc.* **2002**, *124*, 7906 – 7907; l) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982 – 986; m) M. D. Allendorf, R. J. T. Houk, L. Andruszkiewicz, A. A. Talin, J. Pikarsky, A. Choudhury, K. A. Gall, P. J. Hesketh, *J. Am. Chem. Soc.* **2008**, *130*, 14404 – 14405; n) F. Nouar, J. F. Eubank, T. Bousquet, L. Wojtas, M. J. Zaworotko, M. Eddaoudi, *J. Am. Chem. Soc.* **2008**, *130*, 1833 – 1835; o) Y. Goto, H. Sato, S. Shinkai, K. Sada, *J. Am. Chem. Soc.* **2008**, *130*, 14354 – 14355; p) B. Chen, L. Wang, Y. Xiao, F. R. Fronczek, M. Xue, Y. Cui, G. Qian, *Angew. Chem.* **2009**, *121*, 508 – 511; *Angew. Chem. Int. Ed.* **2009**, *48*, 500 – 503; q) A. U. Czaja, N. Trukhan, U. Müller, *Chem. Soc. Rev.* **2009**, *38*, 1284 – 1293.

[8] a) P. K. Iyer, J. B. Beck, C. Weder, S. J. Rowan, *Chem. Commun.* **2005**, 319 – 321; b) Q. Ye, X.-S. Wang, H. Zhao, R.-G. Xiong, *Tetrahedron: Asymmetry* **2005**, *16*, 1595 – 1602; c) J. M. J. Paulusse, R. P. Sijbesma, *Angew. Chem.* **2004**, *116*, 4560 – 4562; *Angew. Chem. Int. Ed.* **2004**, *43*, 4460 – 4462; d) J. I. Garci'a, B. Lo'pez-Sa'nchez, J. A. Mayoral, *Org. Lett.* **2008**, *10*, 4995 – 4998; e) B. S. Luisi, K. D. Rowland, B. Moulton, *Chem. Commun.* **2007**, 2802 – 2804; f) B. Xing, M.-F. Choi, B. Xu, *Chem. Eur. J.* **2002**, *8*, 5028 – 5032; g) F. Camerel, R. Ziessel, B. Donnio, C. Bourgogne, D. Guillon, M. Schmutz, C. Iacovita, J.-P. Bucher, *Angew. Chem.* **2007**, *119*, 2713 – 2716; *Angew. Chem. Int. Ed.* **2007**, *46*, 2659 – 2662; h) H.-J. Kim, J.-H. Lee, M. Lee, *Angew. Chem.* **2005**, *117*, 5960 – 5964; *Angew. Chem. Int. Ed.* **2005**, *44*, 5810 – 5814; i) P. C. Andrews; P. C. Junk, M. Massi, M. Silberstein, *Chem. Commun.* **2006**, 3317 – 3319; P. C. Junk, M. Massi, M. Silberstein, *Chem. Commun.* **2006**, 3317 – 3319; j) H. Maeda, M. Hasegawa, T. Hashimoto, T. Kakimoto, S. Nishio, T. Nakanishi, *J. Am. Chem. Soc.* **2006**, *128*, 10024 – 10025; k) X. Sun, S. Dong, E. Wang, *J. Am. Chem. Soc.* **2005**, *127*, 13102 – 13103; l) M. Oh, C. L. Stern, C. A. Mirkin, *Inorg. Chem.* **2005**, *44*, 2647 – 2653; m) M. Oh, C. A. Mirkin, *Nature* **2005**, *438*, 651 – 654; n) M. Oh, C. A. Mirkin, *Angew. Chem.* **2006**, *118*, 5618 – 5620; *Angew. Chem. Int. Ed.* **2006**, *45*, 5492 – 5494; o) Y.-M. Jeon, J. Heo, C. A. Mirkin, *J. Am. Chem. Soc.* **2007**, *129*, 7480 – 7481; p) S. Jung, M. Oh, *Angew. Chem.* **2008**, *120*, 2079 – 2081; *Angew. Chem. Int. Ed.* **2008**, *47*, 2049 – 2051; q) Y.-M. Jeon, J. Heo, C. A. Mirkin, *Adv. Mater.* **2008**, *20*, 2105 – 2110 r) W. Cho, H. J. Lee, M. Oh, *J. Am. Chem. Soc.* **2008**, *130*, 16943 – 16946; s) H. J. Lee, W. Cho, S. Jung, M. Oh, *Adv. Mater.* **2009**, *21*, 674 – 677; t) E.-Y. Choi, C. Gao, H.-J. Lee, O-P. Kwon, S.-H. Lee, *Chem. Commun.* **2009**, 7563 – 7565; u) A. M. Spokoyny, D. Kim, A. Sumarein, C. A. Mirkin, *Chem. Soc. Rev.* **2009**, *38*, 1218 – 1227.

[9] C.-F. Chow, S. Fujii, J.-M. Lehn, *Angew. Chem.* **2007**, *119*, 5095 – 5098; *Angew. Chem. Int. Ed.* **2007**, *46*, 5007 – 5010.

[10] E. Kim, Y. Xia, G. M. Whitesides, *J. Am. Chem. Soc.* **1996**, *118*, 5722 – 5731.

[11] a) B.-K. An, S.-K. Kwon, S.-D. Jung, S. Y. Park, *J. Am. Chem. Soc.* **2002**, *124*, 14410 – 14415; b) B.-K. An, D.-S. Lee, J.-S. Lee, Y.-S. Park, H.-S. Song, S. Y. Park, *J. Am. Chem. Soc.* **2004**, *126*, 10232 – 10233; c) B.-K. An, S.-K. Kwon, S. Y. Park, *Angew. Chem.* **2007**, *119*, 2024 – 2028; *Angew. Chem. Int. Ed.* **2007**, *46*, 1978 – 1982.

[12] Theoretical constitutional metal-to-ligand ratios for perfect 1D linear, 2D sheet, and 3D jungle gym-like cubic structures are 1:1, 1:2, and 1:3, respectively, if chain ends are neglected.

[13] a) J. Lee, M. J. Kim, H. H. Lee, *Langmuir* **2006**, *22*, 2090 – 2095; b) J. N. Lee, C. Park, G. M. Whitesides, *Anal. Chem.* **2003**, *75*, 6544 – 6554.

[14] J. H. Kim, Y. Jung, J. W. Chung, B.-K. An, S. Y. Park, *Small* **2009**, *5*, 804 – 807.

[15] H.-J. Kim, E.-Y. Jung, L. Y. Jin, M. Lee, *Macromolecules* **2008**, *41*, 6066 – 6072.

[16] An insightful referee suggested that a heavy-atom effect contribution for silver may account for the relatively small PLQY.