Incorporation of Fluorene-containing Pyridyl Ligand into Discrete Supramolecules *via* Coordination-Driven Self-Assembly[†]

Mi-Eun Moon, Joo-Yeon Park, Hwan Kyu Kim,[‡] and Ki-Whan Chi[*]

Department of Chemistry, University of Ulsan, Ulsan 680-749, Korea. [*]E-mail: kwchi@ulsan.ac.kr
[‡]Department of Chemistry, Korea University, Jochiwon, ChungNam 339-700, Korea
*Received June 7, 2007*

During the past decade, coordination-driven self-assembly with Pt[1] or Pd[2] acceptors has drawn much attention and been successfully applied for the production of various discrete 2-D or 3-D supramolecules. Well-matched pre-designed donors and metal-containing acceptors have provided discrete self-assembles in an almost quantitative yield. Exclusive production of discrete ensembles rather than oligomeric or polymeric structures has been unique and interesting outcome in that similar result can not be expected with other synthetic methodologies. This result could be ascribed to the fact that the coordination between metal and ligand is thermodynamically controlled and the formation of discrete entities favors in enthalpy over that of oligomeric forms. Thus, the right combination of donor and acceptor in the type of their reacting elements and bond angles was crucial for the effective production of discrete self-assemblies.[3] Most of the reactions required specific donor and acceptors with fixed-bond angles, and the shape of supramolecular product was decided by the fixed-bond angles used. Only a few flexible ligands in the presence of template molecules self-assembled into discrete entities.[4] Recently, ligands with variable bond angles were successfully applied without assistance of any template for the synthesis of discrete supramolecules *via* coordination-driven self-assembly.[5]

The important and challenging next question might be their applicability of self-assembled supramolecules. Some of their useful functions were reported as an optical sensor, reaction catalyst or molecular switch.[6] However, their known applicability to date is rather restricted and needs to be searched for further uses. In this sense, we are interested in the synthesis of discrete supramolecules containing a fluorene moiety since fluorene-based compounds are regarded as excellent fluorescent materials and often used as emitting materials in eletroluminescent devices.[7] Herein, we report the preparation of fluorene-substituted pyridyl ligand 1 (Scheme 1) then describe the non-templated self-assembly of this ligand into discrete supramolecules 2-3 upon reaction with platinum or palladium acceptors 4-5 (Scheme 2).

The synthesis of bidentate ligand 1 was achieved in a moderate yield (43%) by palladium-mediated coupling of commercially available 2,7-dibromofluorene with an excess

of 4-ethynyl pyridine using the reported conditions.[8] The self-assembly of supramolecules 2-3 was performed in NMR solvents for the facile monitor by NMR analysis. An acetone-d_6/D$_2$O solution of 1 and organoplatinum acceptor 4 was heated at 60 °C for 4 h. Anion exchange with KPF$_6$
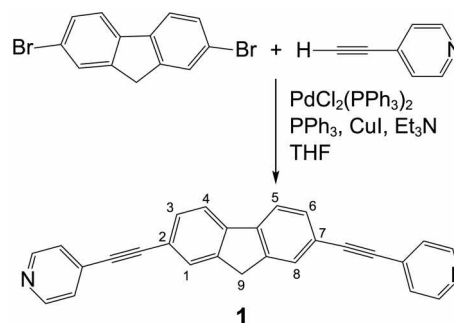
Scheme 1. Synthesis of Fluorene-containing Pyridyl Ligand 1.
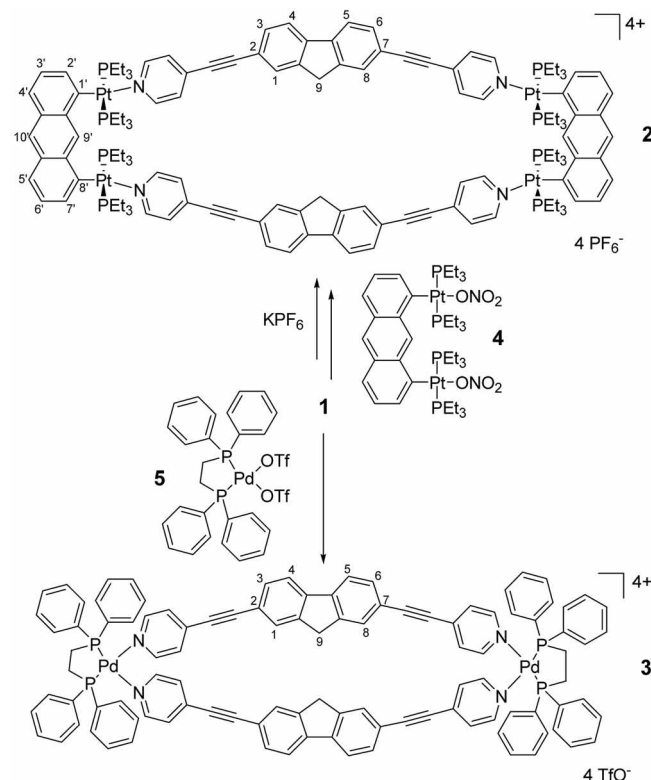
Scheme 2. Self-Assembly of Supramolecules 2 and 3.

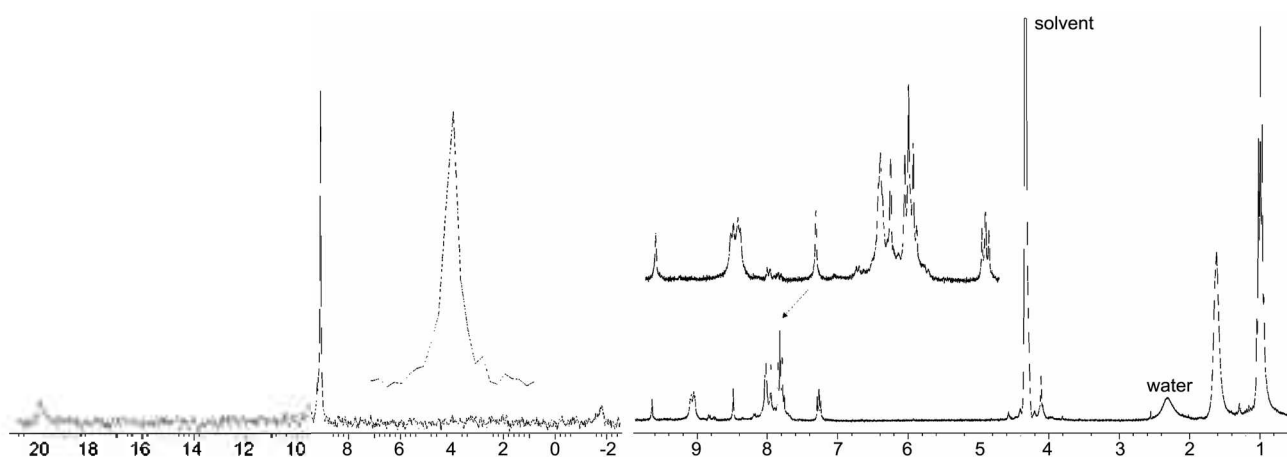[†]This paper is dedicated to Professor Sang Chul Shim on the occasion of his honorable retirement.

Figure 1. The $^{31}P\{^1H\}$ and ^1H NMR spectra of Supramolecule **2**.

facilitated isolation and purification of the [2+2] assembly **2** as a hexafluorophosphate salt in 94% yield.

The supramolecular product was characterized by electro-spray ionization mass spectrometry (ESI-MS), $^{31}P\{^1H\}$ and ^1H NMR. The $^{31}P\{^1H\}$ NMR spectrum of the [2+2] product **2** exhibited a single peak at 9.08 ppm (PCH$_2$CH$_3$) with concomitant ^{195}Pt satellites (Figure 1). Its upfield shift relative to **4** (15.33 ppm) is consistent with back donation from the platinum atoms upon pyridine coordination.[5b-e] One sharp singlet at 9.08 ppm is indicative of the predominant formation of one kind of product. A septet for the PF$_6^-$ counterions was centered at –143.1 ppm. In the ^1H NMR spectrum of **2**, the α-hydrogen nuclei of the pyridine rings experienced downfield shifts (*ca.* 0.5ppm) relative to **1**. (Figure 1) This is consistent with the loss of electron density upon coordination of the pyridine-N.[5b-e] A small amount of unidentified by-product was noticed in the ^1H NMR spectrum (8.83 ppm). Further critical evidence of **2** was obtained with ESI-MS analysis (Figure 2). Peaks corresponding to the successive loss of PF$_6^-$ ions were observed: [2-2PF$_6^-$]$^{2+}$ (*m/z* = 1552), [2-3PF$_6^-$]$^{3+}$ (*m/z* = 986) and [2-4PF$_6^-$]$^{4+}$ (*m/z* = 704). These peaks were all isotopically resolved and match the theoretical distributions well. And, satisfactory elemental analysis of **2** was obtained.

Similarly, a nitromethane-*d$_3$* solution of **1** and organo-palladium acceptor **5** was heated 60 °C for 2 h to provide the
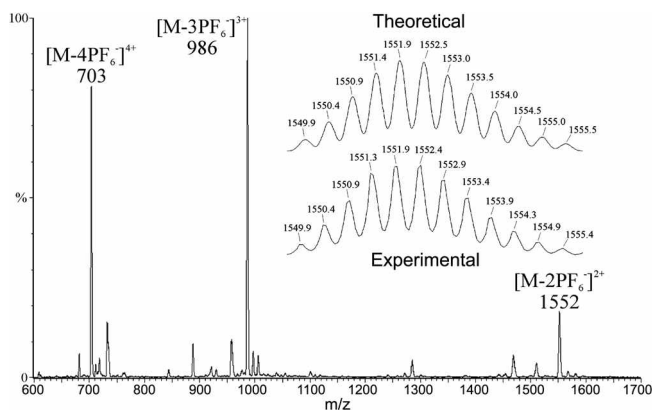
[2+2] assembly **3** as a triflate salt in 96% yield. The macro-cyclic structure of **3** was also characterized by ESI-MS, $^{31}P\{^1H\}$ and ^1H NMR. The $^{31}P\{^1H\}$ NMR spectrum of **3** exhibited a single peak at 68.85 ppm (Figure 3). The signal is shifted approximately 10.3 ppm upfield relative to **5** (79.18 ppm) due to back donation from the palladium centers.[5a] One sharp singlet in the $^{31}P\{^1H\}$ NMR is a good indication of the formation of one kind of product. Interest-ingly, the chemical shifts of the pyridyl hydrogen nuclei (in CD$_3$NO$_2$: H$_{\alpha\text{-Py}}$ 8.36 ppm, H$_{\beta\text{-Py}}$ 7.41 ppm) of **3** were almost unchanged relative to **1** (in CDCl$_3$+CD$_3$OD: H$_{\alpha\text{-Py}}$ 8.50 ppm, H$_{\beta\text{-Py}}$ 7.46 ppm). This is in contrast to the downfield shift these hydrogens normally show in pyridine-Pd based assemblies.[5a] However, similar unusual behavior was also observed in the self-assembled product between *cis*-(PEt$_3$)$_2$-Pt(ONO$_2$)$_2$ and a pyridyl-substituted diaza-crown ether.[9] In the [2+2] assembly **3**, electron donation from the *para*-substituted fluorene moiety must offset the loss of electron density that occurs upon coordination. ESI-MS analysis decisively supported the formation of **3** (Figure 4). The base peak corresponding to the intact macrocycle minus three TfO$^-$ counter ions, [3-3TfO$^-$]$^{3+}$ (*m/z* 631) was observed. This peak was isotopically resolved and is in excellent agreement with the theoretical distributions. Judging by isotopic distri-bution, the *m/z* 1021 peak was assigned to the half of the intact cycle minus one TfO$^-$ ion, [3/2-TfO$^-$]$^+$. Presumably macrocycle **3** readily undergo fragmentation into two halves under the electron-spray analysis conditions employed.[5a,b]

Both reactions gave one predominant species with few by-products evident in the ^{31}P and ^1H NMR spectra. Their sharp appearance suggests they are discrete species rather than oligomeric networks. In addition, no mass spectral evidence was found for any larger macrocycles. The applicability of supramolecules **2** and **3** are now being scrutinized.

In conclusion, the coordination-driven self-assembly of **2** and **3** from fluorene-substituted pyridyl ligand **1** and platinum or palladium acceptors **4-5** has been described. The self-assembly provided [2+2] macrocyclic supramolecules exclusively. The result could be attributable to the favorable gain in enthalpy from the additional dative bond in the closed ring, and the preference in entropy for smaller cyclic
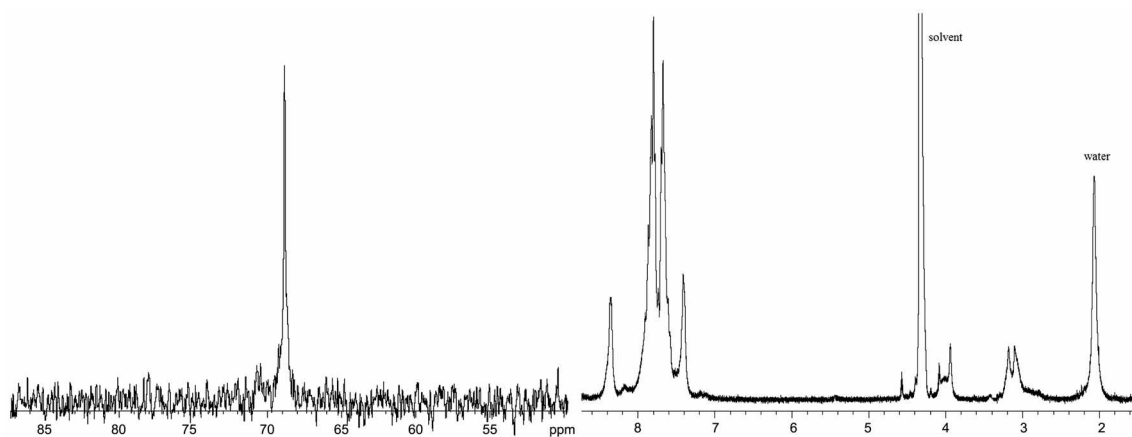

Figure 2. The ESI-MS spectrum of Supramolecule **2**.

Figure 3. The $^{31}P\{^1H\}$ and ^1H NMR spectra of Supramolecule **3**.
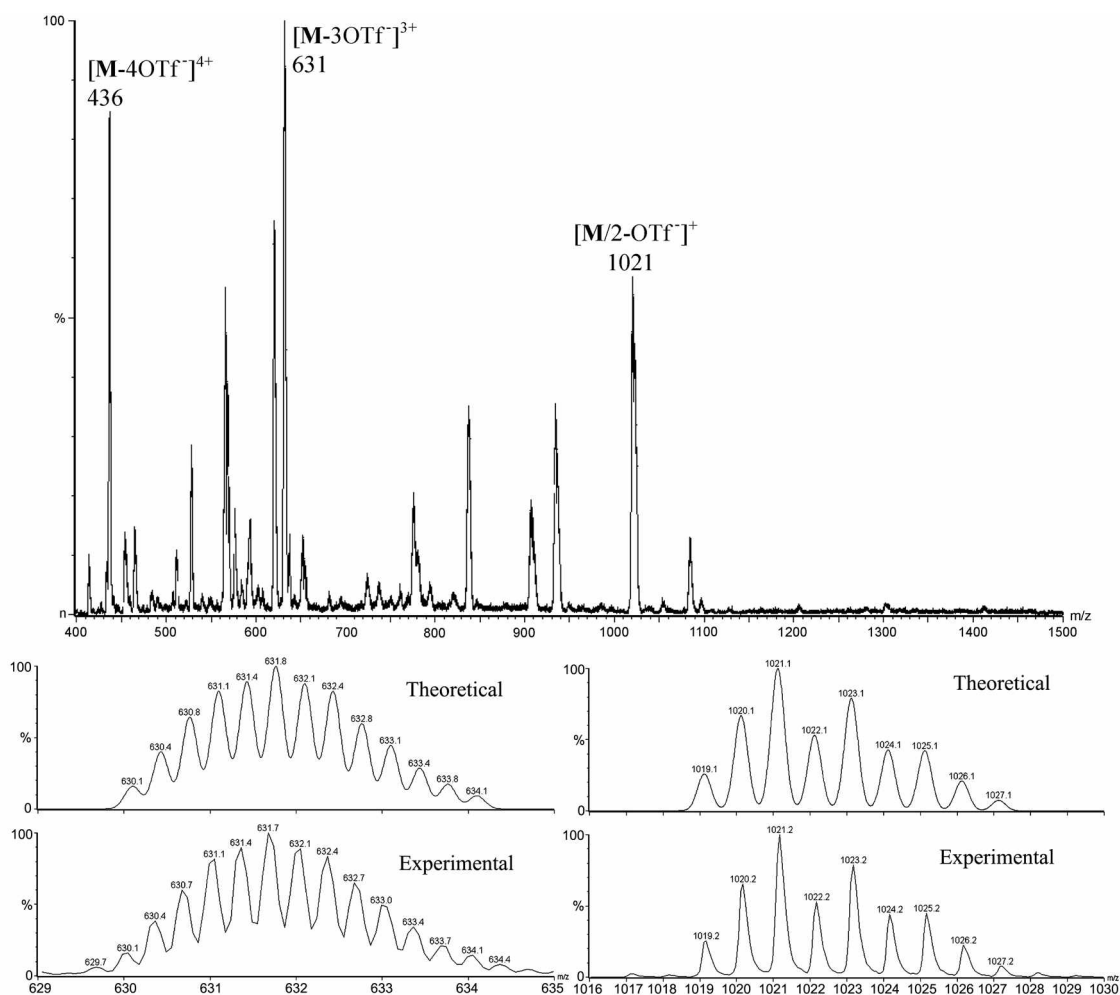

Figure 4. The ESI-MS spectrum of Supramolecule **3**.

ensembles. This work additionally supports the thermo-dynamically-controlled formation of discrete macrocycles over oligomeric networks, and confirms the effectiveness and versatility of coordination-driven self-assembly.

Experimental

Methods and Materials. The organometallic acceptors

4^{10} and 5^{11} were prepared as reported. All NMR spectra recorded on Varian Unity 300 spectrometer. ^1H, ^{13}C and $^{31}P\{^1H\}$ chemical shifts are reported relative to the residual protons of NMR solvents and an external, unlocked sample of H_3PO_4 (0.00 ppm) respectively. ESI mass spectra were recorded on a Micromass Quatto II Triple Quadrupole mass spectrometer with Micromass MassLynx operating system. Purified 4-ethynylpyridine was obtained by neutralization of

commercially available 4-ethynylpyridine hydrochloride and subsequent sublimation. THF and triethylamine were freshly distilled under nitrogen atmosphere prior to use. All the other reagent-grade chemicals were purchased and used without any further purification.

Preparation of Fluorene-containing Pyridyl Ligand 1.[8] To a THF (3.0 mL) solution of 2,7-dibromofluorene (97.2 mg, 0.30 mmol), 4-ethynylpyridine (92.7 mg, 0.90 mmol), bis(triphenylphosphine)palladium(II) dichloride (21.1 mg, 0.030 mmol), triphenyl phosphine (3.9 mg, 0.015 mmol) and copper(I) iodide (1.6 mg, 0.008 mmol) was added at room temperature triethylamine (0.13 mL, 0.90 mmol). The reaction mixture was stirred and heated at 60 °C under nitrogen atmosphere for 36 h. And solvents were removed at room temperature by blowing with nitrogen gas. The resulting crude products were partitioned with chloroform (50 mL) and saturated aqueous NaHCO₃ solution (15 mL). The separated organic phase was dried with anhydrous Na₂SO₄ and filtrated. Ligand **1** was purified by column chromatography (silica gel, 10-20% ethyl acetate/chloroform) and subsequent recrystallization.

1: Yield 43%. Yellowish needle. Mp = 253-255 °C (dec.). ¹H NMR (CDCl₃ + CD₃OD, 300 MHz) δ 8.50 (dd, ^3J = 4.6 Hz, ^4J = 1.5 Hz, 4H, H$_{\alpha\text{-Py}}$), 7.80 (d, ^3J = 8.0 Hz, 2H, H$_{4,5}$), 7.73 (br s, 2H, H$_{1,8}$), 7.58 (dd, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 2H, H$_{3,6}$), 7.46 (dd, ^3J = 4.5 Hz, ^4J = 1.7 Hz, 4H, H$_{\beta\text{-Py}}$), 3.93 (s, 2H, H₉). ¹³C NMR (CDCl₃ + CD₃OD, 75 MHz) δ 149.6, 144.6, 142.8, 133.4, 131.8, 129.3, 126.7, 121.4, 121.2, 96.2 (acetylene C), 87.3 (acetylene C), 37.1 (C₉). HRMS C₂₇H₁₆N₂ requires M⁺ 368.13135. Found: M⁺ 368.13287.

Preparation of Self-assembly 2. Platinum acceptor **4** (5 μmol) and ligand **1** (5 μmol) were placed in a 1-dram vial. Acetone-d_6 (0.7 mL) and D₂O (0.4 mL) were added, and the vial was sealed with Teflon tape. The reaction mixture was heated in an oil bath at 60 °C for 4 h. Excess KPF₆ was added to precipitate the self-assembled product **2**, which was collected and washed with water then dried *in vacuo*.

2: Yield 94%. Yellowish solid. Mp = >300 °C (dec.). ¹H NMR (CD₃NO₂, 300 MHz) δ 9.64 (s, 2H, H₉·), 9.07 (m, 8H, H$_{\alpha\text{-Py}}$), 8.49 (s, 2H, H₁₀·), 8.02 (m, 8H, H$_{\beta\text{-Py}}$), 7.95 (s, 4H, H$_{1,8}$), 7.82 (m, 16H, H$_{2',4',5',7'}$ and H$_{3,4,5,6}$), 7.27 (t, ^3J = 7.4 Hz, 4H, H$_{3',6'}$), 4.11 (s, 4H, H₉), 1.61 (m, 48H, PCH₂), 0.99 (m, 72H, PCH₂C*H₃*); ³¹P{¹H} NMR (CD₃NO₂, 121 MHz) δ 9.08 (s, ¹⁹⁵Pt satellites ¹$J_{\text{Pt-P}}$ = 2646 Hz), −143.1 (septet, ¹$J_{\text{P-F}}$ = 707 Hz, PF₆⁻). Anal. Calcd. for C₁₃₀H₁₆₈F₂₄N₄P₁₂Pt₄: C, 45.99; H, 4.99; N, 1.65. Found: C, 45.83; H, 5.10; N, 1.67.

Preparation of Self-assembly 3. To a mixture of palladium acceptor **5** (5 μmol) and ligand **1** (5 μmol) was added CD₃NO₂ (0.9 mL) in a 1-dram vial. The vial was sealed with Teflon tape, and the reaction mixture was heated in an oil bath at 60 °C for 2 h. Solvents were evaporated by blowing with nitrogen gas and the remaining solid products were washed with diethyl ether. The self-assembled product **3** was finally dried *in vacuo*.

3: Yield 96%. Yellowish solid. Mp = >300 °C (dec.). ¹H NMR (CD₃NO₂, 300 MHz) δ 8.36 (br. s, 8H, H$_{\alpha\text{-Py}}$), 7.58-

7.94 (m, 52H, H$_{1,3\text{-}6,8}$ and Ph), 7.41 (br. s, 8H, H$_{\beta\text{-Py}}$), 3.94 (s, 4H, H₉), 3.14 (d, ^2J = 24.0 Hz, 8H, PCH₂); ³¹P{¹H} NMR (CD₃NO₂, 121 MHz) δ 68.85 (s). Anal. Calcd. for C₁₁₀H₈₀F₁₂N₄O₁₂P₄Pd₂S₄: C, 56.39; H, 3.44; N, 2.39. Found: C, 56.25; H, 3.41; N, 2.48.

References

1. (a) Yang, H.-B.; Ghosh, K.; Northrop, B. H.; Stang, P. J. *Org. Lett.* **2007**, *9*, 1561. (b) Yang, H.-B.; Hawkridge, A. M.; Huang, S. D.; Das, N.; Bunge, S. D.; Muddiman, D. C.; Stang, P. J. *J. Am. Chem. Soc.* **2007**, *129*, 2120. (c) Mukherjee, P. S.; Das, N.; Kryschenko, Y. K.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 2464. (d) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972. (e) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (f) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502.
2. (a) Yamaguchi, T.; Tashiro, S.; Tominaga, M.; Kawano, M.; Ozeki, T.; Fujita, M. *Chem. Asian J.* **2007**, *2*, 468. (b) Ono, K.; Yoshizawa, M.; Kato, T.; Watanabe, K.; Fujita, M. *Angew. Chem. Int. Ed.* **2007**, *46*, 1803. (c) Suzuki, K.; Kawano, M.; Fujita, M. *Angew. Chem. Int. Ed.* **2007**, *46*, 2819. (d) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 371. (e) Fujita, M. *Chem. Soc. Rev.* **1998**, *6*, 417.
3. (a) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: New York, 1995. (b) Chambron, J.-C.; Dietrich-Buchecker, C.; Sauvage, J.-P. In *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Chair, E., Atwood, J. L., Davis, J. E. D., MacNicol, D. D., Vogtle, F., Eds.; Pergamon Press: Oxford, 1996; Vol 9, Chapter 2, p 43. (c) Uller, E.; Demleitner, I.; Bernt, I.; Saalfrank, R. W. *Synergistic Effect of Serendipity and Rational Design in Supramolecular Chemistry* in *Structure and Bonding*; Fujita, M., Ed.; Springer: Berlin, 2000; Vol 96, p 149.
4. (a) Ikeda, A.; Udzu, H.; Zhong, Z.; Shinkai, S.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **2001**, *123*, 3872. (b) Liu, H.-K.; Sun, W.-Y.; Ma, D.-J.; Yu, K.-B.; Tang, W.-X. *Chem. Commun.* **2000**, 591. (c) Hiraoka, S.; Kubota, Y.; Fujita, M. *Chem. Commun.* **2000**, 1509. (d) Hiraoka, S.; Fujita, M. *J. Am. Chem. Soc.* **1999**, *121*, 10239. (e) Fujita, M.; Nagao, S.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 1649.
5. (a) Moon, M.-E.; Lee, H. J.; Ko, B. S.; Chi, K.-W. *Bull. Korean Chem. Soc.* **2007**, *28*, 311. (b) Chi, K.-W.; Addicott, C.; Moon, M.-E.; Lee, H. J.; Yoon, S. C.; Stang, P. J. *J. Org. Chem.* **2006**, *71*, 6662. (c) Chi, K.-W.; Addicott, C.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 16569. (d) Chi, K.-W.; Addicott, C.; Kryschenko, Y. K.; Stang, P. J. *J. Org. Chem.* **2004**, *69*, 964. (e) Chi, K.-W.; Addicott, C.; Arif, A. M.; Das, N.; Stang, P. J. *J. Org. Chem.* **2003**, *68*, 9798.
6. (a) Resendiz, M. J. E.; Noveron, J. C.; Disteldorf, H.; Fischer, S.; Stang, P. J. *Org. Lett.* **2004**, *6*, 651. (b) Yoshizawa, M.; Tamura, M.; Fujita, M. *Science* **2006**, *312*, 251. (c) Nakabayashi, K.; Kawano, M.; Fujita, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 5322.
7. (a) Han, M.; Lee, S.; Jung, J.; Park, K.-M.; Kwon, S.-K.; Ko, J.; Lee, P. H.; Kang, Y. *Tetrahedron* **2006**, *62*, 9769. (b) Lie, X.-M.; He, C.; Huang, J. *Chem. Mater.* **2005**, *17*, 434. (c) Lee, C.-W.; Rhee, H.-W.; Kim, C.; Gong, M.-S. *Bull. Korean Chem. Soc.* **2000**, *21*, 701.
8. Thorand, S.; Krause, N. *J. Org. Chem.* **1998**, *63*, 8551.
9. Chi, K.-W.; Addicott, C.; Stang, P. J. *J. Org. Chem.* **2004**, *69*, 2910.
10. Kuehl, C. J.; Huang, S. D.; Stang, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 9634.
11. (a) Zhong, Z.; Ikeda, A.; Ayabe, M.; Shinkai, S.; Sakamoto, S.; Yamaguchi, K. *J. Org. Chem.* **2001**, *66*, 1002. (b) Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6273.