Supplementary Material for

Manipulation of Discrete Nanostructures by Selective Modulation of Noncovalent Forces

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Manipulation of Nanostructures by Selective Modulation of Noncovalent Forces

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1. Materials

All reagents were purchased from Kanto Chemical, Aldrich, Tokyo Chemical Industry (TCI), and Wako Pure Chemical Industries, and used as received without further purification unless otherwise noted. Compounds 1 (31), meso/rac-3 (16), 4 (32) and 1,1’-dichloroferrocene (33) were prepared according to reported procedures. For column chromatography, Silica Gel 60 N (particle size 63–210 \( \mu \text{m} \); silica; Kanto Chemical) or Aluminium oxide 90 standardized (alumina; Merck) was used.

2. General

Unless otherwise noted, \(^1\)H and \(^{13}\)C NMR spectra were recorded on a JEOL model NM-Excalibur 500 spectrometer, operating at 500 and 125 MHz, respectively, using as internal references non- or partially deuterated solvent residues. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed on an Applied Biosystems BioSpectrometry Workstation™ model Voyager-DE™ STR spectrometer with dithranol as a matrix. Electronic absorption spectra were recorded on a JASCO model V-670 UV/VIS/NIR spectrometer. Infrared (IR) spectra were recorded on a JASCO model FT/IR-6100 Fourier transform infrared spectrometer with an attenuated total reflection (ATR) equipment (ATR PRO450-S). Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out on an ALS/CHI619B Electrochemical Analyzer (BAS) using platinum working and counter electrodes and a reference silver-wire electrode RE-12 (EC FRONTIER). Prior to the measurements, sample solutions containing Bu\(_4\)NBF\(_4\) (0.1 M) as a supporting electrolyte were degassed by bubbling with Ar. A superconducting magnet (10 T) JASTEC model JMTF-10T100 with a horizontal bore of 100 mm was used for magnetic orientation. Polarizing optical microscopy (POM) was performed on an OLYMPUS model BX-51 polarizing optical microscope. Transmission electron micrographs (TEM) were recorded on a JEOL model JEM-14000 electron microscope operating at 120 kV. Samples were deposited on a specimen Cu grid covered with thin polymer and carbon support films manufactured by Okenshoji Co., Ltd. Tapping-mode atomic force microscopy (AFM) was performed in air at 25 °C on a SII NanoTechnology model.
NanoNavi S-image (scan range: 20 × 20 µm) with silicon cantilevers (SI-DF20S, SII NanoTechnology). For obtaining high-resolution tapping mode AFM images, a Bruker model NanoScope V with MultiMode 8 system equipped with A-Scanner (scan range: 0.4 × 0.4 µm) and silicon cantilevers (ScanAsyst-Fluid+, Bruker) was used in air at 25 °C. Dynamic light scattering (DLS) measurements were performed by a Malvern Zetasizer type µV light scattering spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on an ULVAC-PHI model PHI5000 VersaProbe. Small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) experiments were carried out at BL45XU in SPring-8 (Hyogo, Japan) (34) with an imaging plate area detector, a R-AXIS IV++ (Rigaku). Scattering vector \( q = 4\pi \sin(\theta)/\lambda \) and position of an incident X-ray beam on the detector were calibrated using several orders of layer reflections from silver behenate \( d = 58.380 \) Å, where \( 2\theta \) and \( \lambda \) are scattering angle and wavelength of the X-ray beam (1.0 Å), respectively. Unless otherwise noted, sample-to-detector distances for SAXS and WAXD measurements were 1.5 and 0.4 meters, respectively. Sample solutions for SAXS measurements were placed inside a 3-mm-thick metallic cell equipped with quartz windows. Scattering/diffraction images recorded were integrated along the Debye-Scherrer ring using the FIT2D software (35), affording one-dimensional intensity data.
3. Synthesis

![Chemical structure of Compound 2]

**Compound 2.** To a THF solution (700 mL) of a mixture of 1 (31) (52.0 g, 163 mmol), 3-hydroxypyridine (13.0 g, 137 mmol), and 18-crown-6 ether (1.3 g, 50 mmol) was added K$_2$CO$_3$ (58.0 g, 421 mmol), and the resulting mixture was refluxed for 42 h under Ar. After being cooled to 25 °C, the reaction mixture was evaporated to dryness, and the residue was filtered through a plug of alumina with AcOEt/MeOH (9/1 v/v) as an eluent. The filtrate was evaporated to dryness under a reduced pressure, and the residue was chromatographed on silica gel with AcOEt/MeOH (9/1 v/v) as an eluent, to allow isolation of 2 as pale yellow oil in 55% yield (18.6 g, 77.1 mmol). 1H NMR (500 MHz, CDCl$_3$, TMS): $\delta$ (ppm) 8.34 (s, 1H), 8.22 (dd, $J = 3.7, 2.5$ Hz, 1H), 7.22–7.20 (m, 2H), 4.18 (t, $J = 4.6$ Hz, 2H), 3.88 (t, $J = 4.6$ Hz, 2H), 3.77–3.72 (m, 2H), 3.71–3.67 (m, 2H), 3.67–3.63 (m, 2H), 3.57–3.53 (m, 2H), 3.38 (s, 3H). 13C NMR (126 MHz, CDCl$_3$): $\delta$ (ppm) 154.66, 141.86, 137.80, 123.44, 120.83, 71.55, 70.50, 70.28, 70.21, 69.24, 67.40, 58.66. IR (ATR) $\nu_{\text{max}}$ 2878, 1586, 1575, 1475, 1426, 1351, 1266, 1231, 1188, 1061, 927, 852, 606 cm$^{-1}$. HRMS (MALDI-TOF MS) $m/z$ calcd. for C$_{12}$H$_{20}$NO$_4$ [M + H]+: $m/z = 242.1392$; found: 242.1398.

![Chemical structure of Compound FcL1]

**Compound FcL$_1$.** To a THF solution (100 mL) of 2 (5.37 g, 22.2 mmol) under Ar was added at $-78$ °C a hexane solution (8.5 mL) of BuLi (2.6 M, 22 mmol), and the mixture was stirred at the same temperature for 10 min, then 0 °C for 10 min, and again cooled to $-78$ °C. After triisopropyl borate (6.2 g, 33 mmol) was added, the reaction mixture was allowed to warm to 25 °C and stirred continuously for 30 min. Then, water (8 mL) was added to the resultant suspension, and the mixture was stirred at 25 °C for 30 min. To
this reaction mixture were successively added 3 (16) (1.35 g, 1.5 mmol, an isomeric mixture of its meso and racemic forms) and Cs₂CO₃ (5.9 g, 18 mmol). After being degassed by three freeze-pump-thaw cycles, PdCl₂(dppf)-CH₂Cl₂ (0.49 g, 0.60 mmol) was added further, and the resultant mixture was refluxed for 4 h. After being cooled to 25 °C, the reaction mixture was evaporated to dryness, and a waxy residue dissolved in CH₂Cl₂ was washed with water. An organic extract was dried over anhydrous Na₂SO₄, filtered off from insoluble fractions, and evaporated to dryness. Then, the residue was chromatographed on alumina followed by silica gel using CH₂Cl₂/MeOH (4/1 v/v) as an eluent, where a fraction containing the target compound was collected and evaporated to dryness. The residue was then subjected to recycling preparative HPLC (JAIGEL-SIL) with CH₂Cl₂/MeOH (4/1 v/v) as an eluent, to allow isolation of FcL₁ as red waxy solid in 55% yield (1.20 g, 0.83 mmol). ¹H NMR (500 MHz, CDCl₃, TMS): δ (ppm) 8.28 (s, 4H), 8.18 (d, J = 4.3 Hz, 4H), 7.40 (d, J = 8.5 Hz, 8H), 7.22 (d, J = 8.6 Hz, 8H), 7.13 (d, J = 4.9 Hz, 4H), 5.08 (br, 2H), 4.70 (d, J = 1.3 Hz, 4H), 4.17 (t, J = 4.9 Hz, 8H), 3.83 (t, J = 4.9 Hz, 8H), 3.70–3.67 (m, 8H), 3.66–3.63 (m, 8H), 3.62–3.59 (m, 8H), 3.52–3.49 (m, 8H), 3.33 (s, 12H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 151.65, 143.05, 137.11, 136.12, 135.84, 133.08, 129.17, 125.43, 123.84, 87.26, 71.83, 70.73, 70.60, 70.52, 69.93, 69.58, 68.54, 65.61, 58.97. IR (ATR) ν max 2873, 1608, 1588, 1531, 1496, 1465, 1408, 1350, 1315, 1281, 1251, 1230, 1198, 1101, 1048, 928, 822, 750, 729, 657, 592, 552, 533, 521, 509, 465, 434, 430, 408, 404 cm⁻¹. HRMS (MALDI-TOF MS) m/z calcd. for C₈₂H₉₄FeN₄O₁₆ [M⁺]: m/z = 1446.6014; found: 1446.5986.

**Compound 5.** A THF/Et₃N (1/1 v/v) solution (30 mL) of a mixture of 4 (32) (3.77 g, 6.73 mmol) and 4-ethynylpyridine (585 mg, 5.67 mmol) was bubbled for 15 min with Ar for deoxygenation. To this mixture were successively added PdCl₂(dppf)-CuI (81.2 mg, 99.4 µmol) and CuI (15.6 mg, 81.9 µmol), and the resultant mixture was refluxed for 20 h under Ar/H₂ (36). To this reaction mixture was added triisopropylsilylacetylene (0.69 mL, 9.5 mmol), and the resultant mixture was refluxed for 45 h. After being cooled to 25 °C, the reaction mixture was filtered through a plug of alumina with AcOEt as an eluent, and the filtrate was evaporated to dryness. The residue was
chromatographed on alumina with AcOEt/hexane (2/3 v/v) as an eluent, to allow isolation of 5 as pale yellow oil in 15% yield (709 mg, 1.04 mmol). 1H NMR (500 MHz, CDCl3): δ (ppm) 8.58 (d, J = 6.0 Hz, 2H), 7.35 (d, J = 6.0 Hz, 2H), 6.97 (s, 1H), 6.96 (s, 1H), 4.17 (t, J = 5.0 Hz, 2H), 4.14 (t, J = 5.0 Hz, 2H), 4.14 (t, J = 5.0 Hz, 2H), 3.89 (t, J = 5.0 Hz, 2H), 3.83 (t, J = 5.0 Hz, 2H), 3.79–3.76 (m, 2H), 3.73–3.70 (m, 2H), 3.66–3.59 (m, 8H), 3.54–3.51 (m, 2H), 3.50–3.48 (m, 2H), 3.35 (s, 3H), 3.33 (s, 3H), 1.12 (s, 21H).

13C NMR (126 MHz, CDCl3): δ (ppm) 154.07, 153.70, 149.67, 131.43, 125.35, 118.01, 117.28, 115.50, 112.81, 102.42, 97.57, 91.86, 90.40, 71.87, 71.85, 71.01, 70.86, 70.66, 70.62, 70.50, 69.66, 69.62, 69.49, 69.09, 58.94, 18.65, 11.27. IR (ATR) νmax 2939, 2864, 1591, 1501, 1457, 1407, 1351, 1275, 1218, 1108, 1063, 989, 952, 881, 866, 821, 752, 671, 604, 546, 516, 474, 456, 435, 421 cm–1. HRMS (MALDI-TOF MS) m/z calcd. for C38H57NOSi [M+H]+: m/z = 684.3932; found: 684.3912.

Powder A. To a dioxane suspension (1 mL) of a mixture of 3 (16) (90 mg, 0.10 mmol, an isomeric mixture of its meso and racemic forms), CuI (19 mg, 0.10 mmol), and NaI (60 mg, 0.40 mmol) was added trans-N,N′-dimethylcyclohexane-1,2-diamine (50 µL, 0.32 mmol), and the resultant mixture was refluxed for 22 h under Ar. To this mixture was added water (10 mL), and a precipitate formed was collected by filtration, washed with water and methanol, and then dried under a reduced pressure, to give a red powder composed of a crude mixture of 6 and 7 (powder A, 101 mg), which was used for the next reaction without further purification.

6: MS (MALDI-TOF MS) m/z calcd. for C34H22BrFeI3 [M]+: m/z = 945.74; found: 945.97.

7: MS (MALDI-TOF MS) m/z calcd. for C34H22FeI4 [M]+: m/z = 993.72; found: 993.98.
Compound \( \text{FcL}_2 \). To a THF solution (6.4 mL) of 5 (317 mg, 0.463 mmol) was added a 1 M THF solution of TBAF (60 \( \mu \)L), and the mixture was stirred at 0 °C. After 1 h, the reaction mixture was filtrated through a plug of silica with AcOEt/MeOH (9/1 v/v) as an eluent. The filtrate was evaporated to dryness under a reduced pressure, powder A (\textit{vide ante}, 70.3 mg), THF (3.6 mL), and Et\(_3\)N (1.4 mL) were successively added to the residue. After being degassed by three freeze-pump-thaw cycles, PdCl\(_2\)(dpdf)·CH\(_2\)Cl\(_2\) (8.6 mg, 11 \( \mu \)mol) and CuI (3.7 mg, 19 \( \mu \)mol) were successively added to the mixture, and the resultant mixture was refluxed for 16 h under Ar/H\(_2\) (36). After being cooled to 25 °C, the reaction mixture was evaporated to dryness, and the residue was chromatographed on alumina followed by silica gel with CH\(_2\)Cl\(_2\)/MeOH (9/1 v/v) as an eluent, where a fraction containing the target compound was collected and evaporated to dryness. The residue was then subjected to recycling preparative GPC (JAIGEL-2H/2.5H) with CHCl\(_3\) as an eluent, followed by recycling preparative HPLC (JAIGEL-SIL) with CH\(_2\)Cl\(_2\)/MeOH (4/1 v/v) as an eluent, to allow isolation of \( \text{FcL}_2 \) as red waxy solid in 8.0 % yield (95.7 mg, 36.9 \( \mu \)mol). \(^1\)H NMR (500 MHz, CDCl\(_3\), TMS): \( \delta \) (ppm) 8.58 (d, \( J = 6.1 \) Hz, 8H), 7.38 (d, \( J = 8.6 \) Hz, 8H), 7.36 (d, \( J = 6.1 \) Hz, 8H), 7.20 (d, \( J = 8.0 \) Hz, 8H), 4.78 (s, 2H), 4.57 (s, 4H), 4.21 (t, \( J = 4.9 \) Hz, 8H), 4.16 (t, \( J = 4.9 \) Hz, 8H), 3.95 (t, \( J = 4.9 \) Hz, 8H), 3.93 (t, \( J = 4.9 \) Hz, 8H), 3.86–3.84 (m, 8H), 3.83–3.81 (m, 8H), 3.70–3.62 (m, 32H), 3.53–3.51 (m, 16H), 3.35 (s, 12H), 3.34 (s, 12H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta \) (ppm) 153.96, 153.39, 149.77, 137.24, 141.71, 131.48, 125.61, 120.93, 117.63, 117.59, 117.00, 116.95, 115.63, 112.58, 96.02, 92.07, 90.52, 87.07, 86.16, 71.91, 71.17, 71.12, 70.78, 70.73, 70.57, 69.75, 69.72, 69.62, 69.41, 67.20, 59.04, 58.98. IR (ATR) \( \nu_{\text{max}} \) 2872, 1590, 1529, 1503, 1488, 1453, 1411, 1352, 1280, 1218, 1098, 1058, 989, 947, 901, 822, 658, 540, 520, 510, 499, 483, 473, 457, 435, 420, 407 cm\(^{-1}\). HRMS (MALDI-TOF MS) \( m/z \) calcd. for C\(_{150}\)H\(_{166}\)Fe\(_4\)N\(_4\)O\(_{32}\) [M]: \( m/z = 2591.0835 \); found: 2591.0940.
1,1’-Dichloroferroacenium tetrafluoroborate, \((\text{Cl}_2\text{Fe}^+\text{BF}_4^-)\). To a \(\text{CH}_2\text{Cl}_2\) solution (20 mL) of 1,1’-dichloroferrocene (33) (500 mg, 2.0 mmol) was added AgBF_4 (370 mg, 1.9 mmol) under Ar, and the mixture was stirred at 25 °C for 30 min. The reaction mixture was filtered through Celite® to remove an insoluble fraction. Then, Et_2O (200 mL) was added to the filtrate under Ar to yield black crystalline solid, which was isolated by filtration to give \(\text{Cl}_2\text{Fe}^+\text{BF}_4^-\) in 61% yield (395 mg, 1.2 mmol). IR (ATR) \(\nu_{\text{max}}\) 3116, 3095, 1737, 1420, 1360, 1337, 1286, 1182, 1101, 1053, 1011, 910, 886, 853, 520, 472 cm\(^{-1}\). Anal: Calcd. for C_{10}H_8BCl_2F_4Fe: C, 35.15; H, 2.36. Found: C, 34.97; H, 2.53.
fig. S1. $^1$H NMR spectrum (500 MHz) of FeL in CDCl$_3$ at 22 °C.
fig. S2. $^{13}$C NMR spectrum (126 MHz) of FeL$_1$ in CDCl$_3$ at 22 °C.
**Fig. S3.** $^1$H NMR spectrum (500 MHz) of FcL$_2$ in CDCl$_3$ at 22 °C.
fig. S4. $^{13}$C NMR spectrum (126 MHz) of FeL$_2$ in CDCl$_3$ at 22 °C.
**fig. S5.** $^1$H NMR spectral change profiles of a CD$_3$CN solution of FeL$_1$ ([FeL$_1$] = 3.3 mM) upon heating from −40 to 60 °C.
**fig. S6.** $^1$H NMR spectral change profiles at 22 °C of a CD$_3$CN solution of FcL$_1$ ([FcL$_1$] = 4.0 mM) upon titration with AgBF$_4$. (A) $^1$H NMR spectra at [AgBF$_4$]/[FcL$_1$] = 0.0, 0.4, 1.0, 1.6, and 2.0. (B) Change in sum of the integral values of aromatic proton signals due to FcL$_1$ as a function of [AgBF$_4$]/[FcL$_1$], normalized by using tetrachloroethane as an internal reference.
4.2. Electronic Absorption Spectroscopy

![Changes in (A) electronic absorption spectrum and (B) absorbance at 437 nm of a MeCN solution of FcL₁ ([FcL₁] = 2.0 mM) at 20 °C upon titration with AgBF₄ ([AgBF₄]/[FcL₁] = 0.0, 1.0, 2.0, 3.0, and 4.0) in a 0.05-mm-thick sandwich-type quartz cell.](image)

**fig. S7.** Changes in (A) electronic absorption spectrum and (B) absorbance at 437 nm of a MeCN solution of FcL₁ ([FcL₁] = 2.0 mM) at 20 °C upon titration with AgBF₄ ([AgBF₄]/[FcL₁] = 0.0, 1.0, 2.0, 3.0, and 4.0) in a 0.05-mm-thick sandwich-type quartz cell.

4.3. Cyclic Voltammetry

![Cyclic voltammogram of FcL₁ (2 mM) in MeCN at 23 °C using TBABF₄ (0.1 M) as a supporting electrolyte (scan rate: 200 mV s⁻¹). An arrow indicates the scanning direction.](image)

**fig. S8.** Cyclic voltammogram of FcL₁ (2 mM) in MeCN at 23 °C using TBABF₄ (0.1 M) as a supporting electrolyte (scan rate: 200 mV s⁻¹). An arrow indicates the scanning direction.
4.4. Differential Pulse Voltammetry

**fig. S9.** Differential pulse voltammograms at 23 °C of (A) FeL₁ (2 mM) and (B) AgBF₄ in MeCN, using TBABF₄ (0.1 M) as a supporting electrolyte. Arrows indicate the scanning directions.

**fig. S10.** Differential pulse voltammograms at 23 °C of (A) FeNT₁ ([FeL₁] = 0.4 mM) in CH₂Cl₂/MeCN (4:1 v/v), (B) 1,1’-dichloroferrocene in CH₂Cl₂, and (C) bis(pentamethylcyclopentadienyl)iron(II) in CH₂Cl₂, using TBABF₄ (0.1 M) as a supporting electrolyte. Arrows indicate the scanning directions.
4.5. X-ray Photoelectron Spectroscopy

**fig. S11.** X-ray photoelectron spectra of an air-dried MeCN dispersion of FeNT$_1$ ([FeL$_1$] = 2.0 mM; [AgBF$_4$] = 4.0 mM) on a silicon substrate upon (A) survey scan and (B) high-resolution scan of the Fe 2p core level. By reference to typical XPS profiles of ferrocene derivatives (37, 38), two peaks centered at 719 and 707 eV are assignable to Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$, respectively, of the Fe(II) center of FeNT$_1$. 
4.6. Polarized Optical Microscopy

**fig. S12.** Optical micrographs (OM) and polarized optical micrographs (POM) of a film sample composed of one-dimensionally oriented FcNT$_1$ nanotubes. A MeCN dispersion of FcNT$_1$ ([FcL$_1$] = 2.0 mM; [AgBF$_4$] = 4.0 mM) was air-dried at 25 °C in a 10 T magnetic field generated by a superconducting magnet. Red arrows indicate the directions of a magnetic flux employed for the sample preparation.
4.7. X-ray Diffraction Analysis

**table S1.** Scattering vector \( q_{\text{obsd}} \) and \( d \)-spacing (\( d_{\text{obsd}} \)) values observed for a film sample composed of one-dimensionally oriented \( \text{FcNT}_1 \) nanotubes and calculated \( d \)-spacing (\( d_{\text{calcd}} \)) values for a 2D hexagonal lattice (lattice parameter \( a = 8.70 \text{ nm} \)). A MeCN dispersion of \( \text{FcNT}_1 \) ([\( \text{FcL}_1 \)] = 4.0 mM; [\( \text{AgBF}_4 \)] = 8.0 mM; [\( \text{TBAOTf} \)] = 8.0 mM) was air-dried at 25 °C in a 10 T magnetic field generated by a superconducting magnet.

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* A diffraction expected at \( d_{\text{calcd}} = 4.35 \text{ nm} \) (\( q_{\text{calcd}} = 1.44 \text{ nm}^{-1} \)) was not detected, probably because the form factor at \( q = 1.46 \text{ nm}^{-1} \) is minimal (see fig. S20 and table S2).

**fig. S13.** Azimuthal plots for XRD intensities of a film sample composed of one-dimensionally oriented \( \text{FcNT}_1 \) nanotubes in regard to the diffractions at \( q = (A) 0.83 \) (\( hkl = 100 \)), (B) 8.93 (\( d = 0.70 \text{ nm} \)), and (C) 17.9 nm\(^{-1} \) (\( d = 0.35 \text{ nm} \)). A MeCN dispersion of \( \text{FcNT}_1 \) ([\( \text{FcL}_1 \)] = 4.0 mM; [\( \text{AgBF}_4 \)] = 8.0 mM; [\( \text{TBAOTf} \)] = 8.0 mM) was air-dried at 25 °C in a 10 T magnetic field generated by a superconducting magnet.
4.8. Transmission Electron Microscopy

**fig. S14.** TEM micrographs of air-dried water/MeCN dispersions (negatively stained with uranyl acetate) of (A) FcNTₑ (prepared in MeCN; [FcL₁] = 2.0 mM; [AgBF₄] = 4.0 mM) and (B) FcNT₂ (prepared in MeCN; [FcL₂] = 5.0 mM; [AgBF₄] = 10 mM).

**fig. S15.** TEM micrographs of an air-dried CH₂Cl₂/MeCN (99.5:0.5 v/v) dispersion (negatively stained with uranyl acetate) of FcNT₁ ([FcL₁] = 10 µM) after mixing with oxidant Cl₂Fc⁺BF₄⁻ (1 equivalent to constituent FcL₁).
**fig. S16.** TEM micrographs (20 × 20 nm) of toroidal objects observed on the same grid as that in fig. S15. The average diameter (‘wall center-to-wall center’ distance) of these toroidal objects was calculated as 7.4 ± 0.4 nm by a “Radial_Profile” module in ImageJ program (39).
4.9. Atomic Force Microscopy

**fig. S17.** Tapping-mode AFM (A, C) height and (B, D) phase images of an air-dried CH$_2$Cl$_2$/MeCN (99.5:0.5 v/v) dispersion (spin-coated on a mica substrate) of FcNT$_1$ ([FcL$_1$] = 10 μM) after mixing with oxidant Cl$_2$Fc$^+$BF$_4^-$ (1 equivalent to constituent FcL$_4$) (A, B: 1 × 1 μm; C, D: 500 × 500 nm).
**fig. S18.** High-resolution tapping-mode AFM (A, D) height, (B, E) amplitude error, and (C, F) phase images (300 × 300 nm) of an air-dried CH$_2$Cl$_2$/MeCN (99.5:0.5 v/v) dispersion (spin-coated on a mica substrate) of FcNT$_1$ ([FcL$_1$] = 10 µM) after mixing with oxidant Cl$_2$Fc$^{+}$BF$_4^{-}$ (1 equivalent to constituent FcL$_1$) using (A to C) small (270 mV) and (D to F) large (500 mV) tapping amplitudes.
**fig. S19.** Tapping-mode AFM (A) height and (B) phase images of an air-dried CH₂Cl₂/MeCN (99.5:0.5 v/v) dispersion (spin-coated on a mica substrate) of Fe⁺L₁ (10 µM; oxidized with Cl₂Fc⁺BF₄⁻) after mixing with AgBF₄ (2 equivalent to Fe⁺L₁) (500 × 500 nm).
4.10. Models and Small-angle X-ray Scattering Analysis

Theories and Methods

For simulation and curve fitting of SAXS patterns, we used software SasView (40). The normalized form factor $P(q)$ of a hollow cylinder (“HollowCylinderModel” in SasView) is given by the following equations (41):

\begin{equation}
P(q) = \int_0^1 \Psi^2 \left[ q, R_{\text{outer}}(1 - x^2)^{1/2}, R_{\text{inner}}(1 - x^2)^{1/2} \right] \left[ \frac{\sin(qHx)}{qHx} \right]^2 dx
\end{equation}

\begin{equation}
\Psi(q, y, z) = \frac{2}{R_{\text{outer}}^2 - R_{\text{inner}}^2} \left[ \frac{R_{\text{outer}}^2 J_1(qy)}{qy} - \frac{R_{\text{inner}}^2 J_1(qz)}{qz} \right]
\end{equation}

where $q$ is scattering vector, $R_{\text{outer}}$ is outer radius, $R_{\text{inner}}$ is inner radius, $H$ is a half of cylinder length, and $J_1(a)$ is Bessel function of the first kind and first order.

If the length of the hollow cylinder is long enough not to affect SAXS patterns, the infinite hollow cylinder model can be applied, in which the normalized form factor is given as follows (22, 23):

\begin{equation}
P(q) = \left[ \frac{J_0(qR)}{qR} \right]^2
\end{equation}

\begin{equation}
R = \frac{R_{\text{outer}} + R_{\text{inner}}}{2}
\end{equation}

where $J_0(a)$ is Bessel function of the first kind and zero order. In this model, $R$ is the parameter that determines oscillation patterns (positions of minima).
A Brief Summary of Results

According to the theory of Oster et al. (23) for hollow cylinders, the simulated SAXS pattern is sensitive to the cylinder diameter ($D$; ‘wall center-to-wall center’ distance) but insensitive to the wall thickness ($W$) and cylinder length ($L$).

For the purpose of utilizing SAXS data to elucidate the dimensional aspects of nanotubular FeNT$_1$ and FeNT$_2$, nonagonal, decagonal, and undecagonal macrocycles were constructed from FeL$_1$ and FeL$_2$ as cross-sectional molecular models for FeNT$_1$ and FeNT$_2$, respectively. Then, as shown in figs. S20 (FeL$_1$) and S22 (FeL$_2$), their diameters ($D$) were evaluated from the diameters ($D_{Ag}$ and $D_{Cp}$) of circles that path through all Ag(I) ions (for $D_{Ag}$) and all the centers of cyclopentadienyl rings (for $D_{Cp}$). Next, by using the $D$ values thus obtained, a set of their hollow cylinder models were constructed for SAXS simulation, where the wall thickness ($W$) and cylinder length ($L$) were fixed at 0.5 nm and 2 $\mu$m, respectively. These settings are reasonable considering the results of simulations for hollow cylinder models ($D = 7.5$ nm), where neither wall thickness ($W < 0.7$ nm) (fig. S24) nor cylinder length ($L > 20$ nm) (fig. S25) affects the positions of minima in the oscillation patterns.

Finally, oscillatory SAXS patterns simulated for the individual hollow cylinder models corresponding to the nanotubular molecular models with nonagonal (blue), decagonal (red), and undecagonal (purple) cross-sections [FeL$_1$ (fig. S21) and FeL$_2$ (fig. S23)] were obtained. As shown in tables S2 and S3, only when the hollow cylinder models adopt a decagonal cross-section, the positions of minima simulated nicely match those actually observed for the MeCN dispersions of FeNT$_1$ (fig. S21, black) and FeNT$_2$ (fig. S23, black).
**fig. S20.** Nonagonal, decagonal, and undecagonal macrocycles constructed from FcL₁ and Ag(I) ions as the cross-sectional models (upper) for the self-assembled nanotube (FcNT₁; decagonal) and their full-circle models (lower) that are allowed to pass through the geometrical centers of Ag(I) (blue) and Cp (cyclopentadienyl, red) corners. For constructing the models, following bond distances and angles were employed: Ag–Cp–Ag angle = 144 °, Ag···Cp distance = 1.19 nm (Cp···N distance [0.98 nm; molecular mechanics with the MMFF force field] + Ag···N distance [0.21 nm; relevant crystal structure data (19)]). The cross-sectional diameter (**D**) of each macrocycle was calculated by equation \( D = \frac{D_{Ag} + D_{Cp}}{2} \), where **D** is the cross-sectional diameter of each macrocycle; **D** is the diameter of the full circles based on the locations of Ag ions and Cp units, respectively. Counter anions and side chains are omitted for clarity.
**fig. S21.** SAXS pattern (black dots) observed at 25 °C for an MeCN dispersion of FcNT₁ ([FcL₁] = 8.0 mM; [AgBF₄] = 16 mM; sample-to-detector distance = 0.4 meters) and those simulated for hollow cylinder models with diameters (D; ‘wall center-to-wall center’ distances) of 6.8 nm (nonagonal, blue), 7.5 nm (decagonal, red), and 8.2 nm (undecagonal, purple), plotted against scattering vector \( q = 4\pi\sin\theta/\lambda \). Structural parameters \( W \) (wall thickness) and \( L \) (cylinder length) for the hollow cylinder models were fixed at 0.5 nm and 2 \( \mu \)m, respectively.

**table S2.** Scattering vector values (\( q \)) at scattering intensity minima in SAXS patterns simulated and observed for FcNT₁ (fig. S21).

<table>
<thead>
<tr>
<th>Order</th>
<th>Hollow Cylinder Models</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( D = 6.8 \text{ nm} ) (Nonagonal)</td>
<td>( D = 7.5 \text{ nm} ) (Decagonal)</td>
</tr>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>0.71</td>
<td>0.64</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>1.62</td>
<td>1.47</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt;</td>
<td>2.54</td>
<td>2.31</td>
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<td>4&lt;sup&gt;th&lt;/sup&gt;</td>
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<td>5&lt;sup&gt;th&lt;/sup&gt;</td>
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<td>6&lt;sup&gt;th&lt;/sup&gt;</td>
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<td>7&lt;sup&gt;th&lt;/sup&gt;</td>
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<td>8&lt;sup&gt;th&lt;/sup&gt;</td>
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</tr>
<tr>
<td>9&lt;sup&gt;th&lt;/sup&gt;</td>
<td>8.08</td>
<td>7.33</td>
</tr>
<tr>
<td>10&lt;sup&gt;th&lt;/sup&gt;</td>
<td>9.00</td>
<td>8.17</td>
</tr>
</tbody>
</table>
**fig. S22.** Nonagonal, decagonal, and undecagonal macrocycles constructed from FeL₂ and Ag(I) ions as the cross-sectional models (upper) for the self-assembled nanotube (FeNT₂; decagonal) and their full-circle models (lower) that are allowed to pass through the geometrical centers of Ag(I) (blue) and Cp (cyclopentadienyl, red) corners. For constructing the models, following bond distances and angles were employed: Ag–Cp–Ag angle = 144°, Ag···Cp distance = 2.13 nm (Cp···N distance [1.92 nm; molecular mechanics with the MMFF force field] + Ag···N distance [0.21 nm; relevant crystal structure data (J9)]). The cross-sectional diameter ($D$) of each macrocycle was calculated by equation ($D_{Ag} + D_{Cp})/2$, where $D_{Ag}$ and $D_{Cp}$ are diameters of the full circles based on the locations of Ag ions and Cp units, respectively. Counter anions and side chains are omitted for clarity.
**fig. S23.** SAXS pattern (black dots) observed at 25 °C for an MeCN dispersion of FcNT₂ ([FcL₂] = 5.0 mM; [AgBF₄] = 10 mM) and those simulated for hollow cylinder models with diameters ($D$, ‘wall center-to-wall center’ distance) of 12.1 nm (nonagonal, blue), 13.4 nm (decagonal, red), and 14.7 nm (undecagonal, purple), plotted against the scattering vector $q = 4\pi\sin\theta/\lambda$. Structural parameters $W$ (wall thickness) and $L$ (cylinder length) for the hollow cylinder models were fixed at 0.5 nm and 2 µm, respectively.

**table S3.** Scattering vector values ($q$) at scattering intensity minima in SAXS patterns simulated and observed for FcNT₂ (fig. S23).

<table>
<thead>
<tr>
<th>Order</th>
<th>Hollow Cylinder Models</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D = 12.1$ nm (Nonagonal)</td>
<td>$D = 13.4$ nm (Decagonal)</td>
</tr>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>0.40</td>
<td>0.36</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
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<td>0.83</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt;</td>
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<td>1.29</td>
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<td>1.76</td>
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<td>2.47</td>
<td>2.23</td>
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<td>4.57</td>
</tr>
</tbody>
</table>
**fig. S24.** SAXS patterns simulated for hollow cylinder models with wall thicknesses \((W)\) of 0.1 nm (green), 0.3 nm (orange), 0.5 nm (red), and 0.7 nm (purple), plotted against scattering vector \(q = 4\pi \sin \theta / \lambda\). Structural parameters \(D\) (diameter; ‘wall center-to-wall center’ distance) and \(L\) (cylinder length) for the hollow cylinder models were fixed at 7.5 nm and 2 \(\mu\)m, respectively.

**fig. S25.** SAXS patterns simulated for hollow cylinder models with cylinder lengths \((L)\) of 2 \(\mu\)m (red), 0.2 \(\mu\)m (orange), 0.02 \(\mu\)m (green), and 0.005 \(\mu\)m (blue), plotted against scattering vector \(q = 4\pi \sin \theta / \lambda\). Structural parameters \(D\) (diameter; ‘wall center-to-wall center’ distance) and \(W\) (wall thickness) for the hollow cylinder models were fixed at 7.5 nm and 0.5 nm, respectively.
**fig. S26.** SAXS patterns observed at 25 °C for MeCN dispersions of FeNT₁ ([FeL₁] = 4.0 mM; [AgBF₄] = 8 mM) in the absence (black) and presence (red) of TBAOTf (2 equivalents to constituent FeL₁), plotted against scattering vector $q = 4\pi\sin\theta/\lambda$. 
References and Notes


24. Materials and methods are available as supporting material on Science Online.


