Supplementary Material (ESI) for Chemical Communications
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Supporting Information

Self-assembly of Tris(phenylisoxazolyl)benzene and its Asymmetric Induction of Supramolecular Chirality

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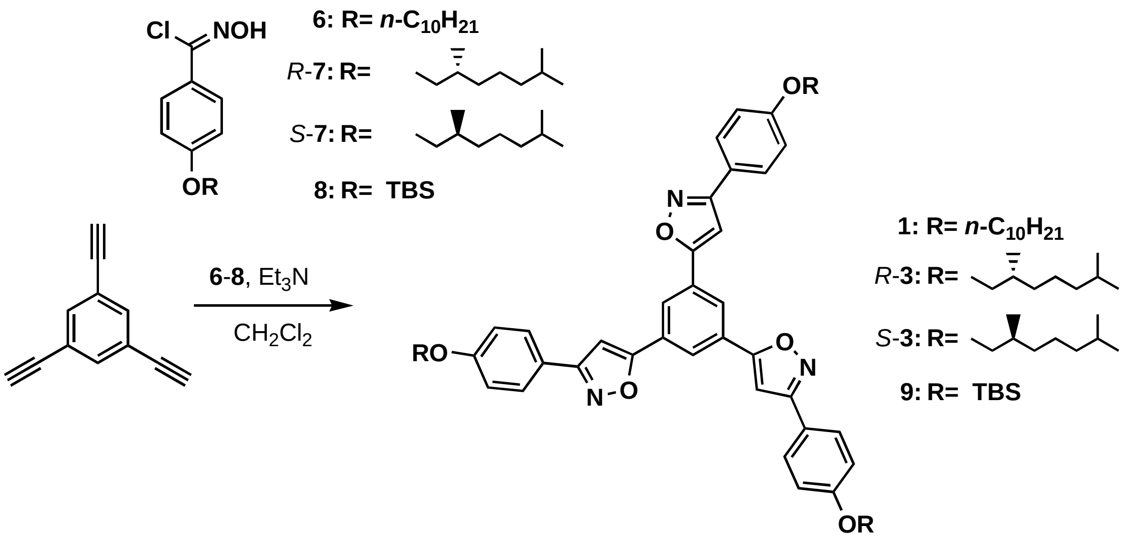
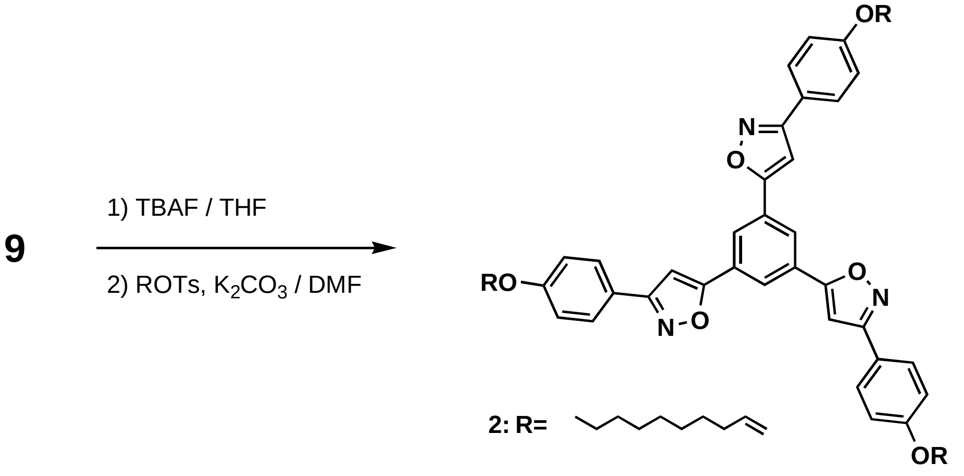
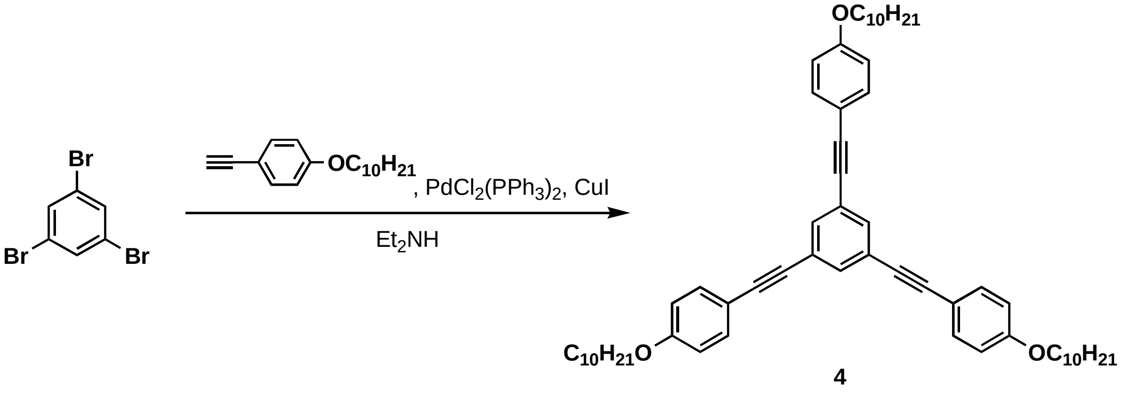
Synthetic schemes and procedures.



Scheme S1.



Scheme S2.



Scheme S3.

1,3,5-Tris[3-(4-decyloxyphenyl)isoxazol-5-yl]benzene 1.

To a solution of 1,3,5-triethynylbenzene[1] (446 mg, 2.97 mmol), and **6** (3.20 g, 9.82 mmol) in CH_2Cl_2 (60 ml) was added triethyl amine (2.48 ml, 17.8 mmol). After stirred at room temperature for 48 h, the reaction mixture was concentrated in *vacuo*. The crude product was purified by column chromatography on silica gel ($CHCl_3$) and recrystallized from toluene solution to give desired product (2.32 g, 80 %) as a white solid. M.p. 132 ˚C; ^1H NMR (500 MHz, 10 mmol L^{-1}, $CDCl_3$): δ 8.30 (s, 3H), 7.82 (d, 6H, *J* = 8.9 Hz), 7.00 (d, 6H, *J* = 8.9 Hz), 6.97 (s, 3H), 4.02 (t, 6H, *J* = 6.7 Hz), 1.79-1.85 (m, 6H), 1.45-1.51 (m, 6H), 1.29-1.38 (m, 36H), 0.89 (t, 3H, *J* = 6.8 Hz); ^{13}C NMR (125 MHz, 10 mmol L^{-1}, $CDCl_3$): δ 168.1, 162.9, 160.9, 129.3, 128.3, 123.9, 120.9, 115.0, 98.8, 68.2, 31.9, 29.6x2, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1; IR (KBr) 3110, 2920, 2849, 1612, 1561, 1526, 1469, 1435, 1388, 1299, 1290, 1255, 1175, 1114, 1020 cm^{-1}; HRMS (FAB^+) calcd for $C_{63}H_{82}N_3O_6$ $[M+H]^+$ 976.6204, found 976.6183; Anal. Calcd for $C_{63}H_{81}N_3O_6$: C, 77.50; H, 8.36; N, 4.30. Found: C, 77.57; H, 8.33; N, 4.68.

11,3,5-Tris{3-[(R)-(–)-4-(3,7-Dimethyl)octyloxyphenyl]isoxazol-5-yl}benzene *R*-3.

To a solution of 1,3,5-triethynylbenzene[1] (305 mg, 2.03 mmol), and *R*-**7** (2.20 g, 7.05 mmol) in CH_2Cl_2 (50 ml) was added triethylamine (2.8 ml, 20 mmol). After being stirred at room temperature for 48 h, the reaction mixture was concentrated in *vacuo*. The crude product was purified by column chromatography on silica gel ($CHCl_3$) and recrystallized from acetone solution to give desired product (675 mg, 34 %) as a white solid. M.p. 140 ˚C; $[\alpha]^{25}_{D}$ = +5.5 cm^3 g^{-1} dm^{-1} (*c* = 1 g cm^{-3} in chloroform); ^1H NMR (300 MHz, 10 mmol L^{-1}, $CDCl_3$): δ 8.31 (s, 3H), 7.82 (d, 6H, *J* = 9.0 Hz), 7.01 (d, 6H, *J* = 9.0 Hz), 6.99 (s, 3H), 4.00-4.12 (m, 6H), 1.82-1.90 (m, 3H), 1.48-1.71 (m, 9H), 1.14-1.37 (m, 18H), 0.97 (d, 9H, *J* = 6.6 Hz), 0.88 (d, 18H, *J* = 6.6 Hz); ^{13}C NMR (75 MHz, 10 mmol L^{-1}, $CDCl_3$): δ 168.1, 162.9, 160.8, 129.2, 128.2 123.9, 120.8, 114.9, 98.8, 66.5, 39.2, 37.3, 36.1, 29.8, 28.0, 24.7, 22.7, 22.6, 19.7; IR (KBr) 3111, 2953, 2925, 2869, 1613, 1561, 1527, 1464, 1435, 1385, 1296, 1252, 1178, 1117, 1051 cm^{-1}; HRMS (FAB^+) calcd for $C_{63}H_{82}N_3O_6$ $[M+H^+]$ 976.6204, found 976.6221; Anal. Calcd for $C_{63}H_{81}N_3O_6$: C, 77.50; H, 8.36; N, 4.30. Found: C, 77.15; H, 8.35; N, 4.20.

1,3,5-Tris{3-[(S)-(–)-4-(3,7-Dimethyl)octyloxyphenyl]isoxazol-5-yl}benzene *S*-3.

To a solution of 1,3,5-triethynylbenzene[1] (265 mg, 1.77 mmol), and *S*-**7** (1.82 mg, 5.84 mmol) in CH_2Cl_2 (20 ml) was added triethyl amine (2.5 ml, 18 mmol). After stirred at room temperature for 48 h, the reaction mixture was concentrated in *vacuo*. The crude product was purified by column chromatography on silica gel ($CHCl_3$) and recrystallized from toluene solution to give desired product (380 mg, 22 %) as a white solid. M.p. 140 ˚C; $[\alpha]^{25}_{D}$ = –5.9 cm^3 g^{-1} dm^{-1} (*c* = 0.2 g cm^{-3} in chloroform); ^1H NMR (300 MHz, 10 mmol L^{-1}, $CDCl_3$): δ 8.31 (s, 3H), 7.82 (d, 6H, *J* = 8.7 Hz), 7.01 (d, 6H, *J* = 8.7 Hz), 6.99 (s, 3H), 4.01-4.12 (m, 6H), 1.82-1.92 (m, 3H), 1.48-1.71

(m, 9H), 1.10-1.38 (m, 18H), 0.97 (d, 9H, *J* = 6.6 Hz), 0.88 (d, 18H, *J* = 6.6 Hz); ^{13}C NMR (75 MHz, 10 mmol L^{-1}, $CDCl_3$): δ 168.1, 162.9, 160.8, 129.3, 128.2, 123.9, 120.9, 115.0, 98.8, 66.5, 39.2, 37.3, 36.1, 29.9, 28.0, 24.7, 22.7, 22.6, 19.7; IR (KBr) 3111, 2953, 2925, 2869, 1613, 1561, 1527, 1464, 1436, 1385, 1296, 1252, 1177, 1116, 1051 cm^{-1}; HRMS (FAB$^+$) calcd for $C_{63}H_{82}N_3O_6$ [M+H]$^+$ 976.6204, found 976.6223; Anal. Calcd for $C_{63}H_{81}N_3O_6$: C, 77.50; H, 8.36; N, 4.30. Found: C, 77.69; H, 8.33; N, 4.23.

1,3,5-Tris{3-[4-(*tert*-Butyldimethylsilyl)oxyphenyl]isoxazol-5-yl}benzene 9.

To a solution of 1,3,5-triethynylbenzene[1] (338 mg, 2.25 mmol), and **8** (2.13 g, 7.45 mmol) in CH_2Cl_2 (40 ml) was added triethyl amine (1.88 ml, 13.5 mmol). After stirred at room temperature for 48 h, the reaction mixture was concentrated in *vacuo*. The crude product was purified by column chromatography on silica gel ($CHCl_3$) to give desired product (1.28 g, 63 %) as a white solid. M.p. 116-118 °C; ^{1}H NMR (300 MHz, 20 mmol L^{-1}, $CDCl_3$): δ 8.31 (s, 3H), 7.78 (d, 6H, *J* = 8.7 Hz), 6.98 (s, 3H), 6.96 (d, 6H, *J* = 8.7 Hz), 1.01 (s, 9H), 0.26 (s, 6H); ^{13}C NMR (75 MHz, 20 mmol L^{-1}, $CDCl_3$): δ 168.1, 163.0, 157.7, 129.2, 128.3, 124.0, 121.8, 120.7, 98.9, 25.6, 18.3, –4.4; IR (KBr) 2957, 2929, 2894, 2857, 1609, 1568, 1525, 1466, 1433, 1384, 1268, 1170, 1106, 1008 cm^{-1}; HRMS (FAB$^+$) calcd for $C_{51}H_{64}N_3O_6Si_3$ [M+H]$^+$ 898.4103, found 898.4123; Anal. Calcd for $C_{51}H_{63}N_3O_6Si_3$: C, 68.19; H, 7.07; N, 4.68. Found: C, 68.19; H, 7.16; N, 4.69.

1,3,5-Tris[3-(4-dec-9-enyloxyphenyl)isoxazol-5-yl]benzene 2.

To a solution of **9** (1.25 g, 1.50 mmol) in THF (15 ml) was added tetrabutyl ammonium fluoride (1.96 g, 7.50 mmol). After stirred at room temperature for 12 h, the reaction mixture was poured into aqueous NH_4Cl and extracted with EtOAc. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. Then, the crude product (510 mg) was dissolved in DMF (10 mL). 4-Dec-9-enyloxytoluene sulfonate[6] (1.09 g, 3.68 mmol) and K_2CO_3 (762 mg, 5.52 mmol) were added to the stirred solution. After refluxing for overnight, the reaction mixture was quenched with 1 N HCl. The resulting solution was extracted with EtOAc, dried over Na_2SO_4 and concentrated in *vacuo*. The crude product was purified by column chromatography on silica gel (5% AcOEt/hexane) and GPC to give desired product (304 mg, 31 %) as a white solid. M.p. 114 °C; ^{1}H NMR (300 MHz, 30 mmol L^{-1}, $CDCl_3$): δ 8.30 (s, 3H), 7.82 (d, 6H, *J* = 8.9 Hz), 7.00 (d, 6H, *J* = 8.9 Hz), 6.97 (s, 3H), 4.02 (t, 6H, *J* = 6.7 Hz), 1.79-1.85 (m, 6H), 1.45-1.51 (m, 6H), 1.29-1.38 (m, 36H), 0.89 (t, 3H, *J* = 6.8 Hz); ^{13}C NMR (75 MHz, 30 mmol L^{-1}, $CDCl_3$): δ 168.1, 162.9, 160.9, 129.3, 128.3, 123.9, 120.9, 115.0, 98.8, 68.2, 31.9, 29.6x2, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1; IR (KBr) 3115, 3074, 2924, 2851, 1639, 1612, 1562, 1526, 1466, 1436, 1387, 1295, 1251, 1176, 1115, 1020 cm^{-1}; HRMS (FAB$^+$) calcd for $C_{63}H_{76}N_3O_6$ [M+H]$^+$ 970.5734, found 970.5726; Anal. Calcd for $C_{63}H_{75}N_3O_6 \cdot 0.2CHCl_3$: C, 76.35; H, 7.62; N, 4.23. Found: C, 76.56; H, 7.74; N, 4.27.

1,3,5-Tris[(4-decyloxyphenyl)-1-ethynyl]benzene 5.

To a mixture of 1,3,5-tribromobenzene (800 mg, 2.54 mmol), (4-decyloxyphenyl)ethyne[7] (2.36 g, 8.66 mmol), and CuI (24 mg, 0.13 mmol) in Et_2NH (30 mL) was added $PdCl_2(PPh_3)_2$ (110 mg 0.157 mmol). After being stirred at 50 °C for 24 h, the reaction mixture was concentrated in *vacuo*. The crude product was purified by column chromatography on silica gel (10% AcOEt/hexane) to give desired product (1.24 g, 58 %) as a yellow solid. M.p. 43-44 ˚C; ^1H NMR (500 MHz, 10 mmol L^{-1}, $CDCl_3$): δ 7.57 (s, 3H), 7.45 (d, 6H, *J* = 8.9 Hz), 6.87 (d, 6H, *J* = 8.9 Hz), 3.97 (t, 6H, *J* = 6.6 Hz), 1.76-1.82 (m, 6H), 1.43-1.47 (m, 6H), 1.28-1.34 (m, 36H), 0.89 (t, 3H, *J* = 6.8 Hz); ^{13}C NMR (125 MHz, 10 mmol L^{-1}, $CDCl_3$): δ 159.5, 133.4, 133.1, 124.3, 114.7, 114.6, 90.5, 86.7, 68.1, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1; IR (KBr) 3043, 2921, 2851, 2209, 1606, 1577, 1508, 1468, 1389, 1293, 1248, 1171, 1107, 1024 cm^{-1}**;** HRMS (FAB^+) calcd for $C_{60}H_{79}O_3$ $[M+H]^+$ 847.6029, found 847.6021; Anal. Calcd for $C_{60}H_{78}O_3$: C, 85.06; H, 9.28. Found: C, 85.02; H, 9.28.

Figure S1. Pictures of gels of **1** in a) acetone, b) DMF, and c) ethyl acetate.

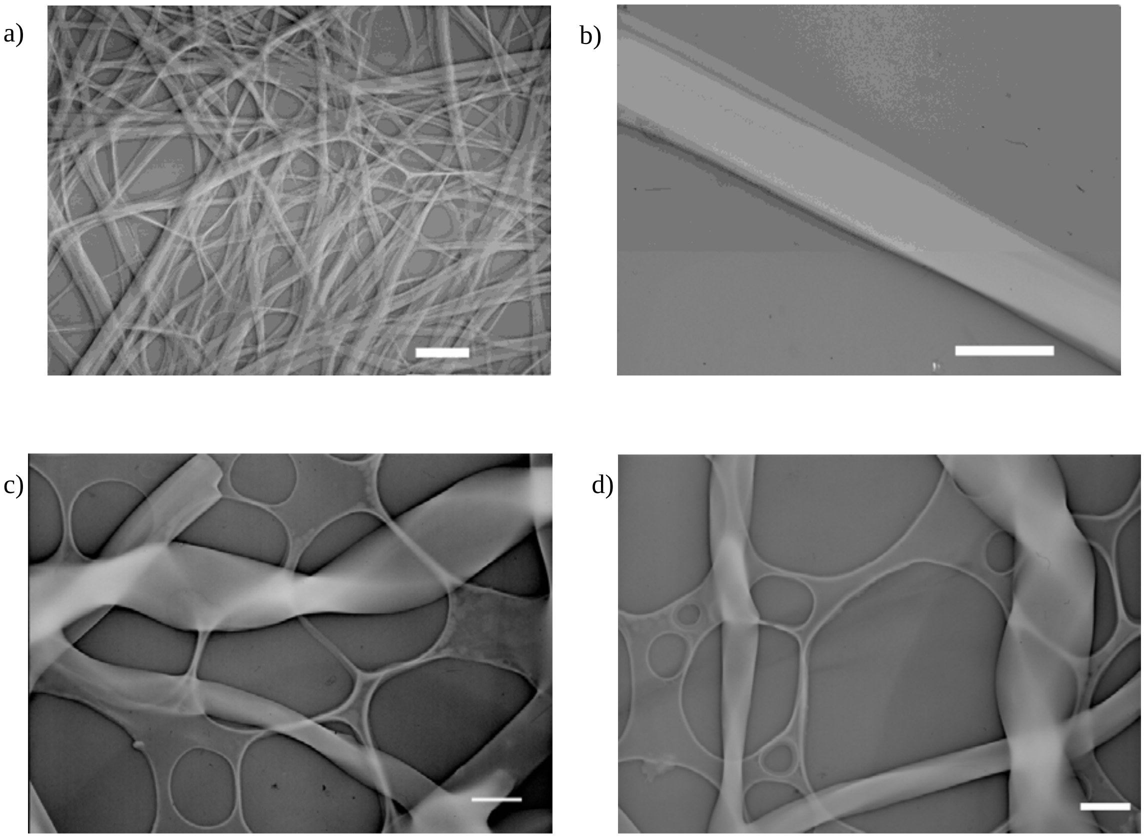


Figure S2*.* TEM images of xerogels of **1** (a and b) and **2** (c and d). The bars represent a) 1 µm, b) 200 nm, c) 1 µm, and d) 1 µm. The obtained sample was measured with a JEM-2010 (JEOL) transmission electron microscope. The accelerating voltage was 200 kV.

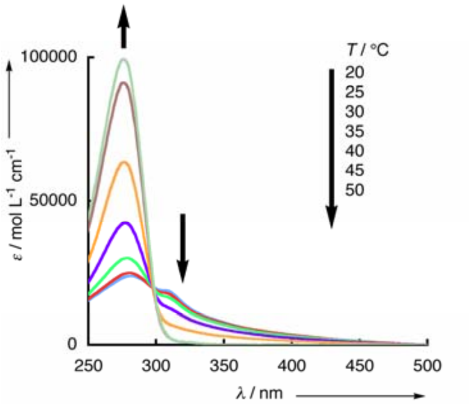


Figure S3*.* Temperature-dependent UV/Vis spectra of **1** (5.0×10^{-5} mol L^{-1}) in MCH.

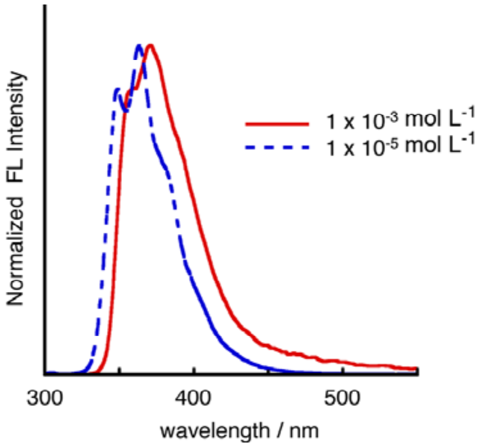


Figure S4*.* Fluorescence spectra (λ_{ex} = 278 nm) of **1** (1.0×10^{-5} and 1.0×10^{-3} mol L^{-1}) at 25 °C in MCH.

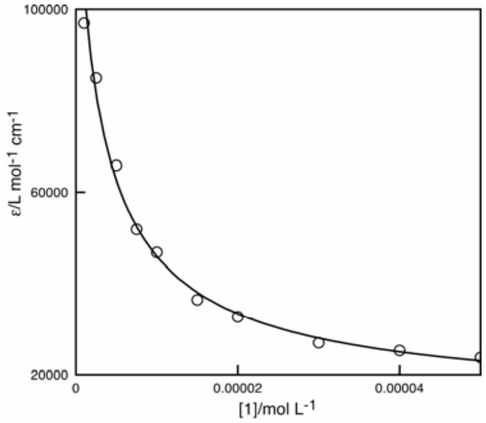


***Figure S5**.* Plots of the molar coefficient of **1** at 278 nm vs. the concentration of **1** in MCH, and the theoretical curve obtained by nonlinear least-squares regression analysis.

***Table S1**.* Gelation properties of **1–4**.

solvent	**1**	**2**	**3**	**4**
hexane	P	P	P	S
cyclohexane	pG	P	P	S
methylcyclohexane	G (35)	P	P	S
benzene	S	S	S	S
toluene	S	S	S	S
dichloromethane	S	S	S	S
chloroform	S	S	S	S
ether	G (18)	G (20)	P	S
acetone	G (8)	G (20)	P	S
ethyl acetate	G (8)	P	S	S
acetonitrile	I	P	P	I
ethanol	I	P	P	I
IPA	I	P	P	I
THF	S	S	S	S
DMF	G (10)	G (20)	P	S
DMSO	G (10)	G (20)	pG	P

[a] G: gel, pG: partial gelation, P: precipitation, S: solution, and I: insoluble
[b] P, I, and S are at [gelator] = 20 mg ml^{-1}.
[c] The critical gelation concentration (mg ml^{-1}) is showed in a parenthesis.

References

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[3] S. J. Lee, C. R. Park, J. Y. Chang, *Langmuir* **2004**, *20,* 9513-9519.