

Article

Electrorheological Effect of Gold Nanoparticles Coated with Fluorescent Mesogenic Groups Dispersed in Nematic Liquid Crystal

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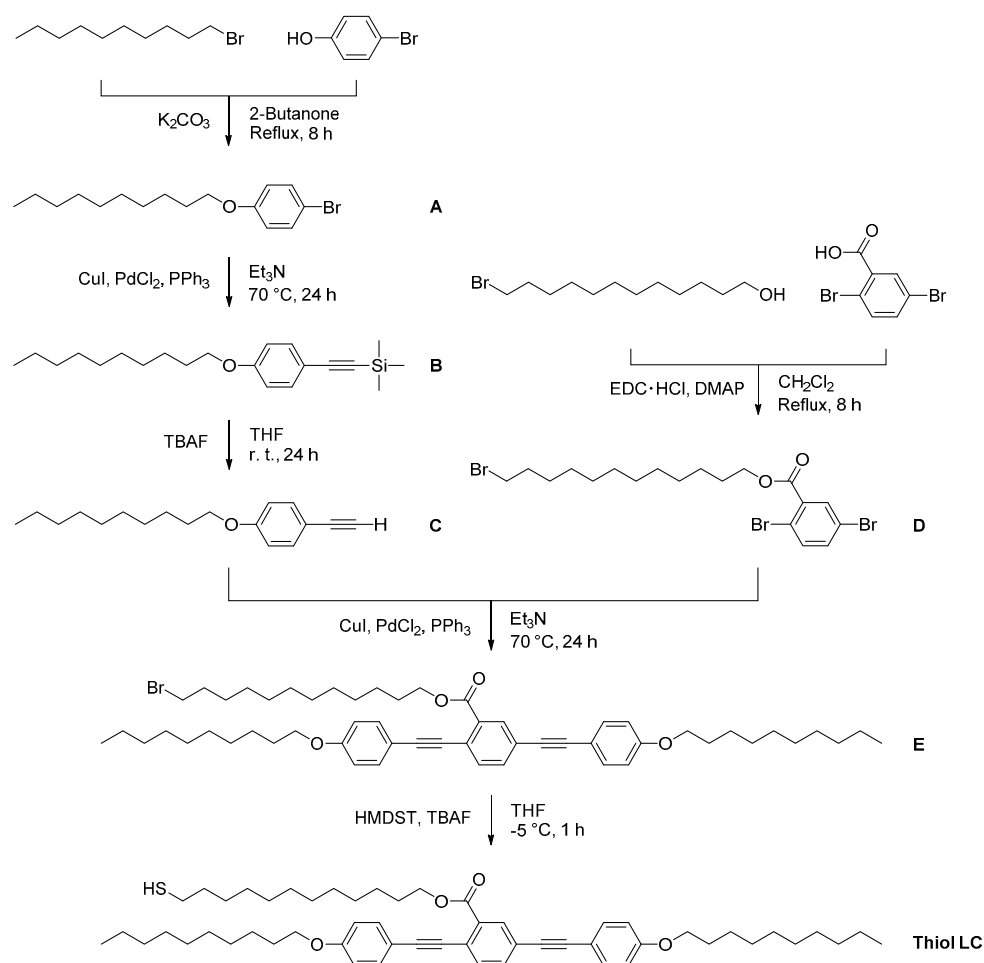


Figure S1. Synthetic route of the thiol LC used for coating the GNPs.

1-Bromo-4-(decyloxy)benzene A

A solution containing 4-bromophenol (5.34 g, 30.9 mmol), 1-bromodecane (8.78 g, 35.2 mmol), and potassium carbonate (6.02 g, 43.6 mmol) in 100 mL of 2-butanone was refluxed for 8 h. After removing the solid, the solvent was distilled off. The resulting crude was mixed with dichloromethane (100 mL), and the mixture was washed with water (3x100 mL) and saturated brine (100 mL). The organic phase was dried over Na₂SO₄. After evaporation of the solvent, the residue was purified by means of column chromatography (silica gel, hexane). As a result, 7.50 g of 1-bromo-4-(decyloxy)benzene was obtained as a transparent colorless liquid. (Yield : 78%)

¹H NMR (CDCl₃) : δ (ppm) 7.35 (d, *J* = 9.1 Hz, 2H), 6.77 (d, *J* = 9.1 Hz, 2H), 3.91 (t, *J* = 6.6 Hz, 2H), 1.81–1.71 (m, 2H), 1.48–1.38 (m, 2H), 1.38–1.21 (m, 12H), 0.88 (t, *J* = 7.0 Hz, 3H).

1-Decyloxy-4-[(trimethylsilyl)ethynyl]benzene B

1-Bromo-4-(decyloxy)benzene obtained (5.08 g, 16.2 mmol) was dissolved in 100 mL of dry triethylamine. CuI(I) (0.168 g, 0.882 mmol), PdCl₂(II) (0.156 g, 0.879 mmol), PPh₃ (0.444 g, 1.69 mmol), and trimethylsilyl acetylene (3.27 g, 33.2 mmol) were added and the resulting mixture was stirred at 70 °C under Ar atmosphere for 24 h. After removing the solid, the solvent was distilled off. The resulting crude was mixed with dichloromethane (100 mL), and the mixture was washed with water (3x100 mL) and saturated brine (100 mL). The organic phase was dried over Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, hexane:dichloromethane=9:1). As a result, 4.46 g of 1-decyloxy-4-[(trimethylsilyl)ethynyl]benzene was obtained as a light-yellow liquid. (Yield : 83%)

¹H NMR (CDCl₃) : δ (ppm) 7.38 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.94 (t, *J* = 6.6 Hz, 2H), 1.81–1.71 (m, 2H), 1.48–1.38 (m, 2H), 1.38–1.19 (m, 12H), 0.88 (t, *J* = 6.6 Hz, 3H), 0.23 (s, 9H).

1-(Decyloxy)-4-ethynylbenzene C

1-Decyloxy-4-[(trimethylsilyl)ethynyl]benzene obtained (4.46 g, 13.5 mmol) was dissolved in dry THF, and then 13.5 mL of tetra-*n*-butylammonium fluoride in THF (1.00 M) was added. After stirring at r.t. for 24 h, dichloromethane (100 mL) was poured into the resulting mixture, and washed with water (100 mL). The organic phase was dried over Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, hexane:dichloromethane=9:1). As a result, 3.20 g of 1-(decyloxy)-4-ethynylbenzene was obtained as a light-yellow liquid. (Yield : 92%)

¹H NMR (CDCl₃) : δ (ppm) 7.41 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 3.95 (t, *J* = 6.6 Hz, 2H), 2.99 (s, 1H), 1.82–1.71 (m, 2H), 1.48–1.38 (m, 2H), 1.38–1.20 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 3H).

12-Bromododecyl 2,5-dibromobenzoate D

1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC · HCl, 6.94 g, 36.1 mmol) was added slowly to a stirred solution of 2,5-dibromobenzoic acid (5.03 g, 17.9 mmol), 12-bromo-1-dodecanol (6.17 g, 23.3 mmol) and *N,N*-dimethyl-4-aminopyridine (DMAP, 0.446 g,

3.65 mmol) in dry dichloromethane (100 mL). The mixture was refluxed for 8 h, and the reaction was quenched with a saturated ammonium chloride solution (100 mL). After dichloromethane (100 mL) was poured into the mixture, the organic layer was separated and washed with water (100 mL). The organic phase was dried over Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, hexane:dichloromethane=3:2). As a result, 5.70 g of 12-bromododecyl 2,5-dibromobenzoate as colorless crystals. (Yield : 60%)

¹H NMR (CDCl₃) : δ (ppm) 7.89 (d, *J* = 2.7 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.44 (dd, *J* = 8.6, 2.7 Hz, 1H), 4.33 (t, *J* = 6.6 Hz, 2H), 3.53 (t, *J* = 6.6 Hz, 2H), 1.81-1.72 (m, 4H), 1.48-1.37 (m, 4H), 1.37-1.23 (m, 12H).

12-Bromododecyl 2,5-bis[[4-(decyloxy)phenyl]ethynyl]benzoate E

12-Bromododecyl 2,5-dibromobenzoate obtained (2.94 g, 5.59 mmol) was dissolved in 100 mL of dry triethylamine. CuI(I) (0.111 g, 0.583 mmol), PdCl₂(II) (0.100 g, 0.562 mmol), PPh₃ (0.298 g, 1.13 mmol), and 1-(decyloxy)-4-ethynylbenzene (3.20 g, 12.4 mmol) were added and the resulting mixture was stirred at 70 °C under Ar atmosphere for 24 h. After removing the solid, the solvent was distilled off. The resulting crude was mixed with dichloromethane (100 mL), and the mixture was washed with water (3x100 mL) and saturated brine (100 mL). The organic phase was dried over Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, hexane:dichloromethane=7:3). As a result, 2.26 g of 12-bromododecyl 2,5-bis[[4-(decyloxy)phenyl]ethynyl]benzoate was obtained as a yellow liquid. (Yield : 45%)

¹H NMR (CDCl₃) : δ (ppm) 8.07 (s, 1H), 7.56 (s, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 9.1 Hz, 2H), 4.35 (t, *J* = 6.6 Hz, 2H), 3.96 (t, *J* = 6.6 Hz, 4H), 3.51 (t, *J* = 6.8 Hz, 2H), 1.83-1.69 (m, 8H), 1.50-1.38 (m, 8H), 1.38-1.18 (m, 36H), 0.87 (t, *J* = 6.6 Hz, 6H).

12-Mercaptododecyl 2,5-bis[[4-(decyloxy)phenyl]ethynyl]benzoate Thiol LC

12-Bromododecyl 2,5-bis[[4-(decyloxy)phenyl]ethynyl]benzoate obtained (2.02 g, 2.28 mmol) was dissolved in 20 mL of dry THF, and then bis(trimethylsilyl) sulfide (0.50 g, 2.80 mmol) and 3.50 mL of tetra-*n*-butylammonium fluoride in THF (1.00 M) was added. After stirring at -5 °C for 1 h, the reaction was quenched with a saturated ammonium chloride solution (100 mL). After dichloromethane (100 mL) was poured into the mixture, the organic layer was separated and washed with water (100 mL) and saturated brine (100 mL). The organic phase was dried over Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, hexane:dichloromethane=3:2). As a result, 5.70 g of 12-mercaptododecyl 2,5-bis[[4-(decyloxy)phenyl]ethynyl]benzoate was obtained as a yellow liquid. (Yield : 60%)

^1H NMR (CDCl_3) : δ (ppm) 8.08 (s, 1H), 7.57 (s, 2H), 7.49 (d, $J = 8.6$ Hz, 2H), 7.46 (d, $J = 8.6$ Hz, 2H), 6.87 (d, $J = 7.2$ Hz, 4H), 4.36 (t, $J = 6.6$ Hz, 2H), 3.96 (t, $J = 6.6$ Hz, 4H), 2.51 (q, $J = 7.4$ Hz, 2H), 1.83-1.73 (m, 6H), 1.64-1.54 (m, 2H), 1.50-1.39 (m, 4H), 1.39-1.19 (m, 41H), 0.88 (t, $J = 6.6$ Hz, 6H).

Figure S2. ^1H NMR spectrum of Thiol LC.

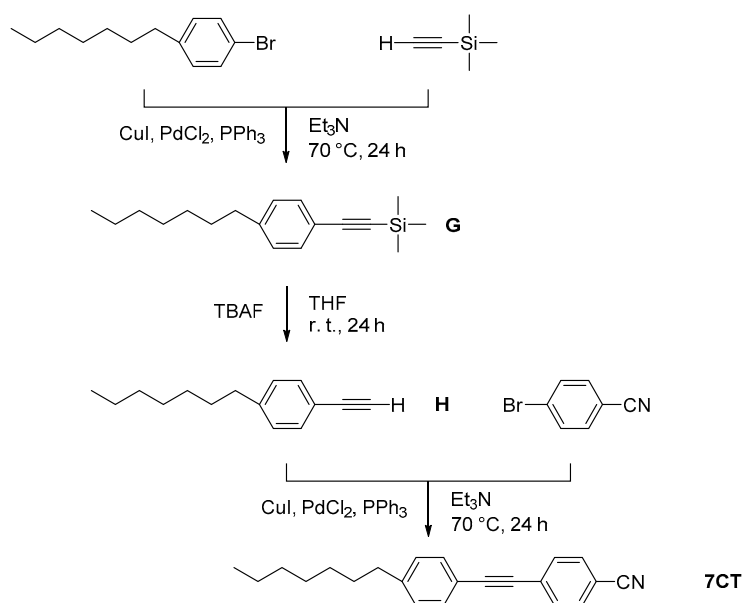
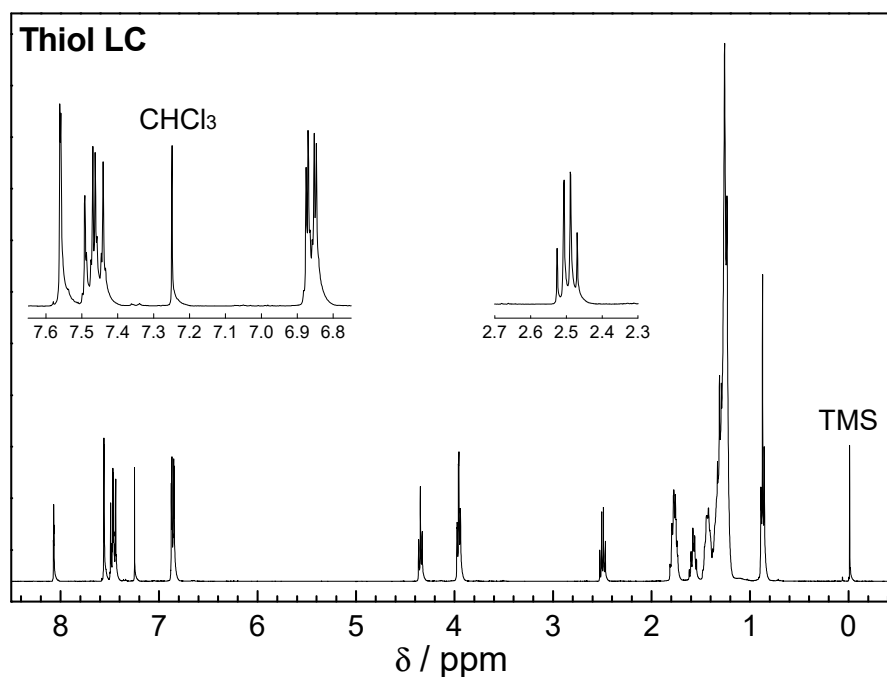


Figure S3. Synthetic route of the host nematic LC (7CT).

1-Heptyl-4-[(trimethylsilyl)ethynyl]benzene G

1-Bromo-4-heptylbenzene (5.08 g, 19.9 mmol) was dissolved in 100 mL of dry triethylamine. CuI(I) (0.210 g, 1.10 mmol), PdCl₂(II) (0.177 g, 0.998 mmol), PPh₃ (0.521 g, 1.99 mmol), and trimethylsilyl acetylene (3.87 g, 39.4 mmol) were added and the resulting mixture was stirred at 70 °C under Ar atmosphere for 24 h. After removing the solid, the solvent was distilled off. The resulting crude was mixed with dichloromethane (100 mL), and the mixture was washed with water (3x100 mL) and saturated brine (100 mL). The organic phase was dried over Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, hexane). As a result, 4.95 g of 1-heptyl-4-[(trimethylsilyl)ethynyl]benzene was obtained as a light-yellow liquid. (Yield : 91%)

¹H NMR (CDCl₃) : δ (ppm) 7.37 (d, *J* = 7.5 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 2.58 (t, *J* = 7.5 Hz, 2H), 1.63-1.53 (m, 2H), 1.34-1.19 (m, 8H), 0.87 (t, *J* = 7.0 Hz, 3H), 0.24 (s, 9H).

1-Ethynyl-4-heptylbenzene H

1-Heptyl-4-[(trimethylsilyl)ethynyl]benzene obtained (4.95 g, 18.2 mmol) was dissolved in dry THF, and then 18.2 mL of tetra-*n*-butylammonium fluoride in THF (1.00 M) was added. After stirring at r.t. for 24 h, dichloromethane (100 mL) was poured into the resulting mixture, and washed with water (100 mL) and saturated brine (100 mL). The organic phase was dried over Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, hexane). As a result, 3.07 g of 1-ethynyl-4-heptylbenzene was obtained as a light-yellow liquid. (Yield : 84%)

¹H NMR (CDCl₃) : δ (ppm) 7.41 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 3.03 (s, 1H), 2.60 (t, *J* = 7.7 Hz, 2H), 1.65-1.53 (m, 2H), 1.35-1.21 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H).

4-[(4-Heptylphenyl)ethynyl]benzonitrile 7CT

4-Bromobenzonitrile (2.79 g, 15.3 mmol) was dissolved in 100 mL of dry triethylamine. CuI(I) (0.147 g, 0.772 mmol), PdCl₂(II) (0.136 g, 0.767 mmol), PPh₃ (0.416 g, 1.59 mmol), and 1-ethynyl-4-heptylbenzene obtained (3.07 g, 15.3 mmol) were added and the resulting mixture was stirred at 70 °C under Ar atmosphere for 24 h. After removing the solid, the solvent was distilled off. The resulting crude was mixed with dichloromethane (100 mL), and the mixture was washed with water (3x100 mL) and saturated brine (100 mL). The organic phase was dried over Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, hexane:dichloromethane=1:1). As a result, 4.09 g of 4-[(4-heptylphenyl)ethynyl]benzonitrile was obtained as a light-yellow liquid. (Yield : 89%)

¹H NMR (CDCl₃) : δ (ppm) 7.62 (d, *J* = 8.7 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 2.62 (t, *J* = 7.7 Hz, 2H), 1.67-1.56 (m, 2H), 1.37-1.20 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H).

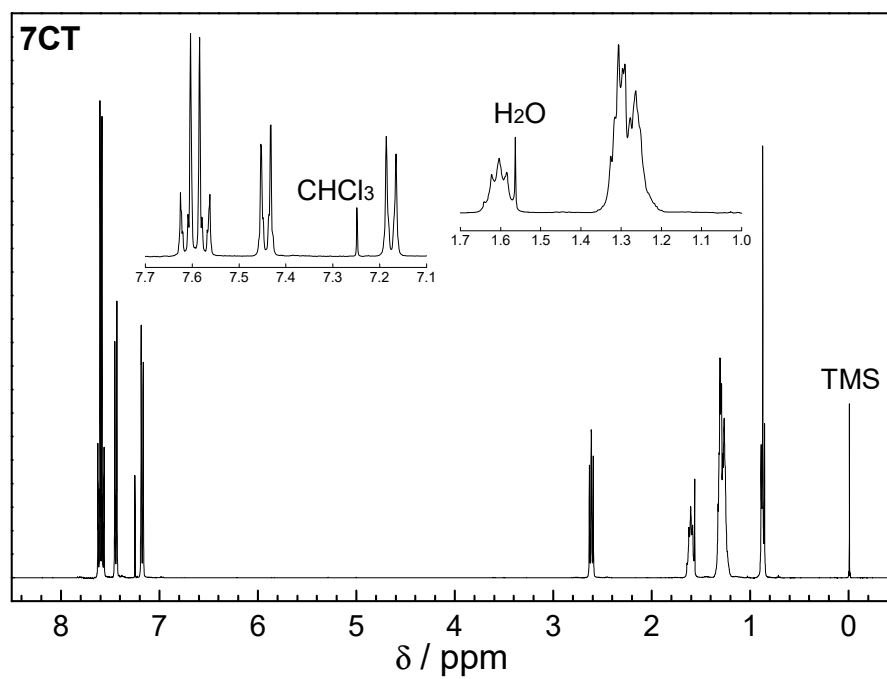


Figure S4. ^1H NMR spectrum of 7CT.

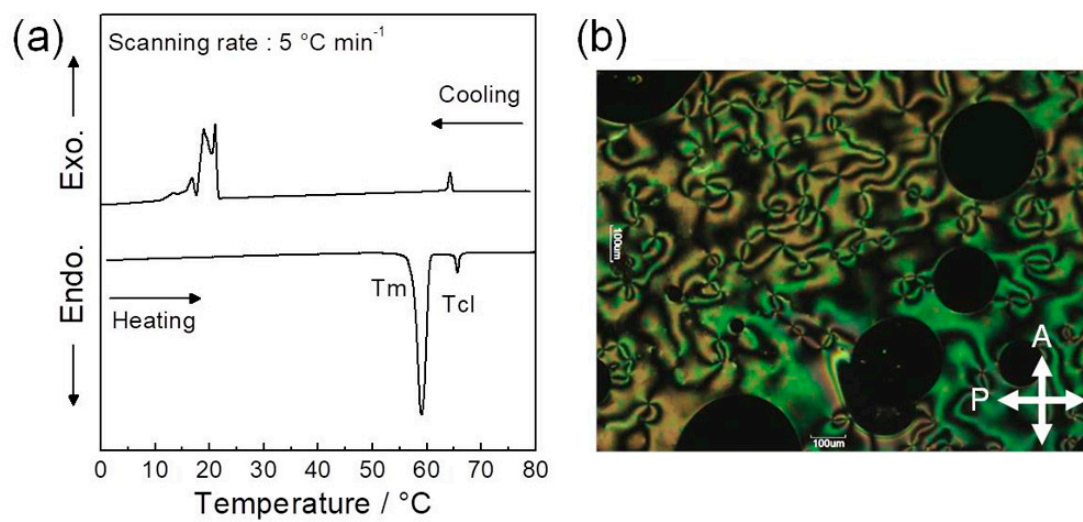


Figure S5. (a) DSC curves and (b) POM image of 7CT [1,2]. The image was taken at 63 $^\circ\text{C}$ on cooling.

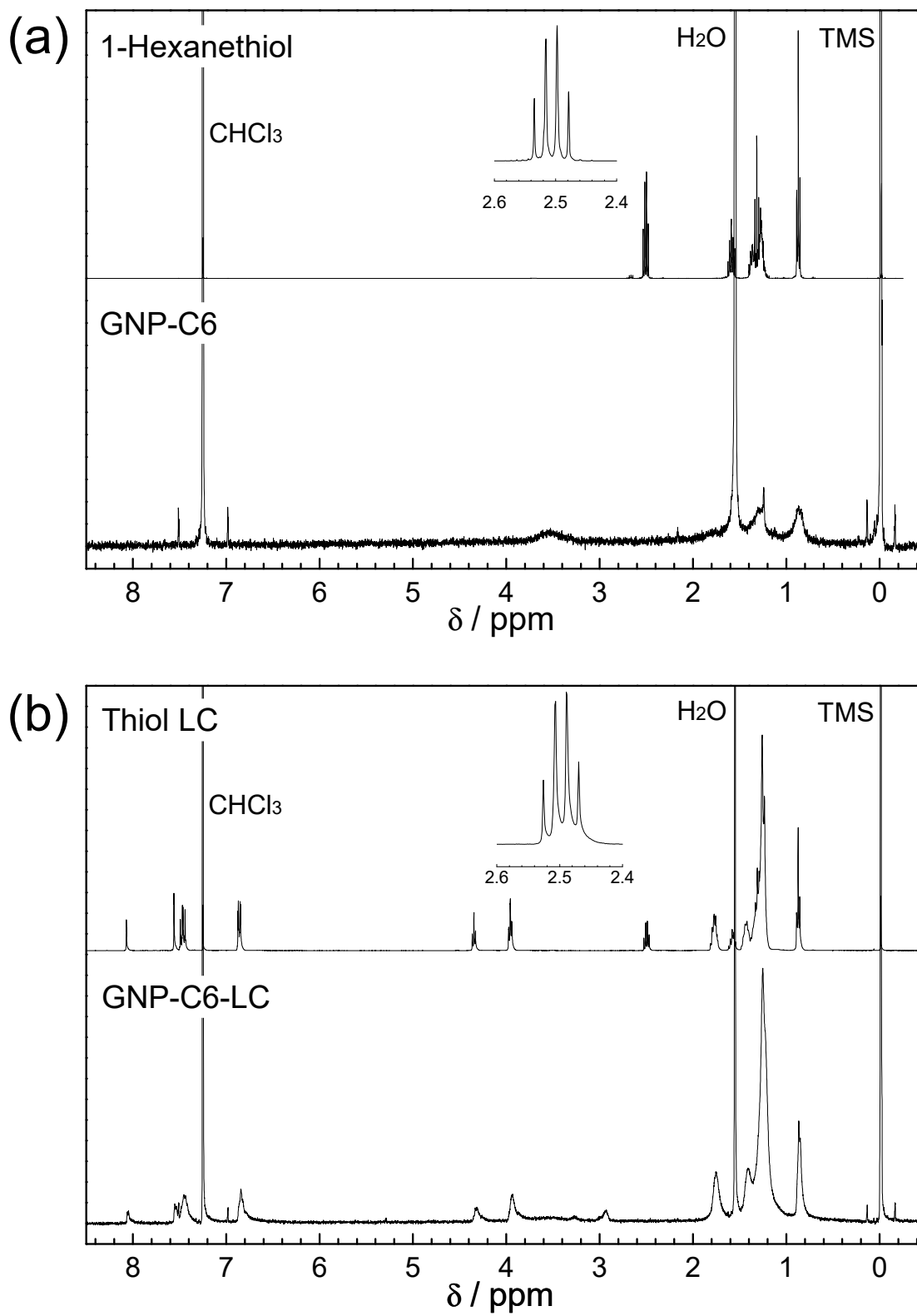


Figure S6. ¹H NMR spectra of (a) 1-hexanethiol and GNP-C6 and (b) Thiol LC and GNP-C6-LC.

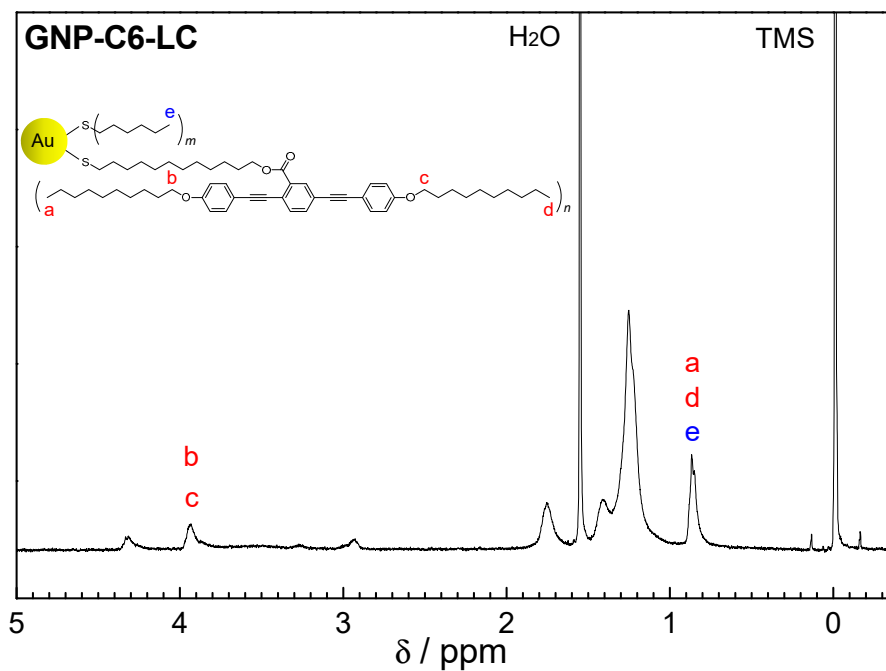


Figure S7. ^1H NMR spectrum of GNP-C6-LC.

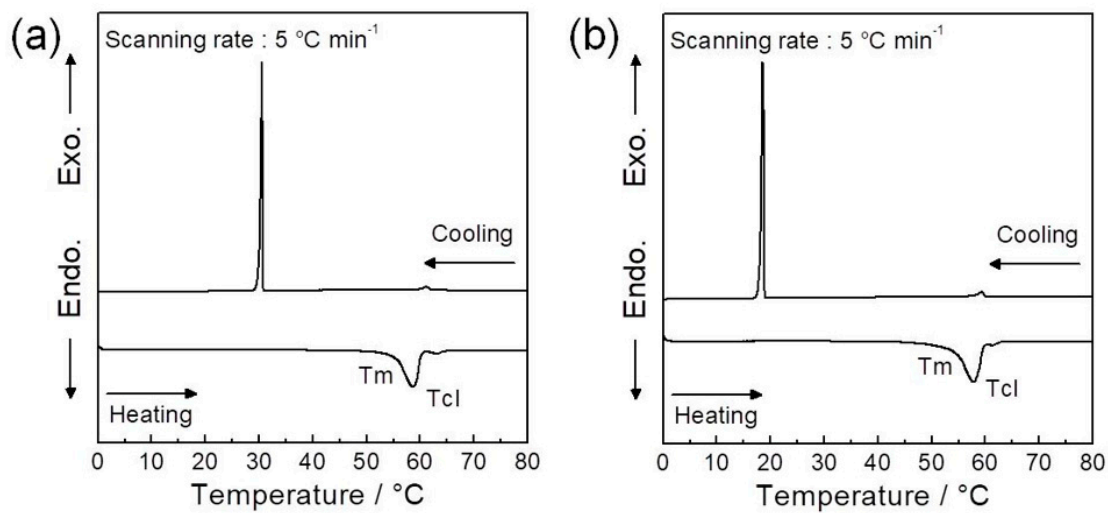


Figure S8. DSC curves of the composites consisting of 7CT and GNP-C6-LC ((a) 5 wt% and (b) 10 wt%).

References

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