

Supporting Information

Structural optimization of alkylbenzenes as graphene dispersants

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1. Material

Natural flake graphite (Z5F, Figure S1: SEM) was purchased from Ito graphite Co. Ltd. (Mie, Japan). *N*-methylpyrrolidone (NMP), tetrahydrofuran (THF), Magnesium, Iodine, Copper(I) iodide (CuI), 1,3-Bis(diphenylphosphino)propane]nickel(II) dichloride [NiCl₂(dppp)], and 1-bromooctane were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Bromobenzene, 1-bromobutane, 1-bromohexadecane, 1-bromonaphthalene, 9-bromophenanthrene, 1,4-dichlorobenzene, 1,3,5-trichlorobenzene, were purchased from Tokyo Chemical Industries Co., Ltd. (Tokyo, Japan). These materials were used without further purification.

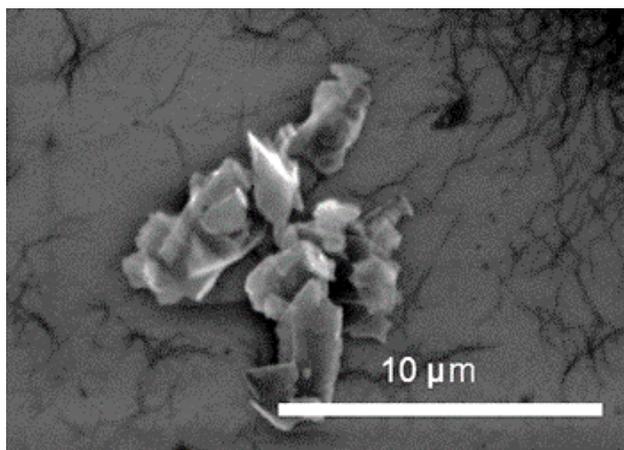


Figure S1. SEM image of natural flake graphite used in this research.

2. Experimental Section

2.1. Determination of Graphene Concentration Using Absorbance

Since the absorbance and the graphene concentration are proportional according to Lambert-Beer's law,¹ a calibration curve between the absorbance at 800 nm, where there is no influence of the dispersant and the graphene, and graphene concentration was prepared. First, the solvent of the graphene dispersion was removed in vacuo, and the weight of graphene was measured to calculate the original concentration of the graphene dispersion. In parallel, the same dispersion was diluted to five different concentrations, and the absorbances were measured by UV-Vis spectrometer. The obtained results were used to prepare the calibration curve. The results of UV-Vis measurement from 200 nm to 800 nm at five different concentrations and a calibration curve at 800 nm are shown in Figure S2 and S3.

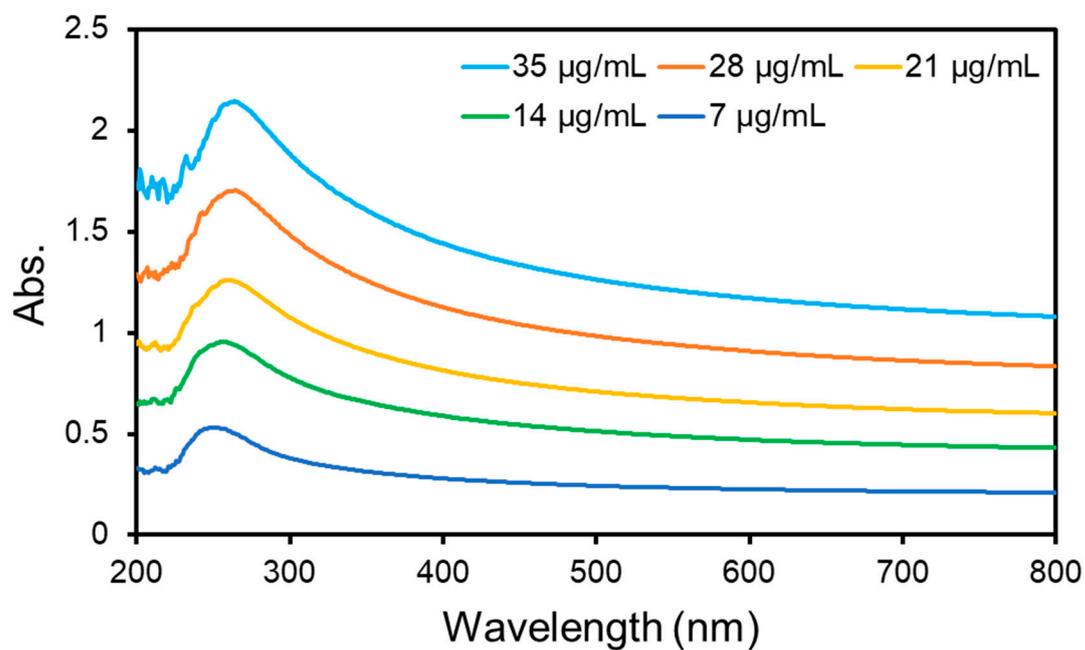


Fig. S2. UV-Vis spectra of 5 different concentrations of graphene dispersion.

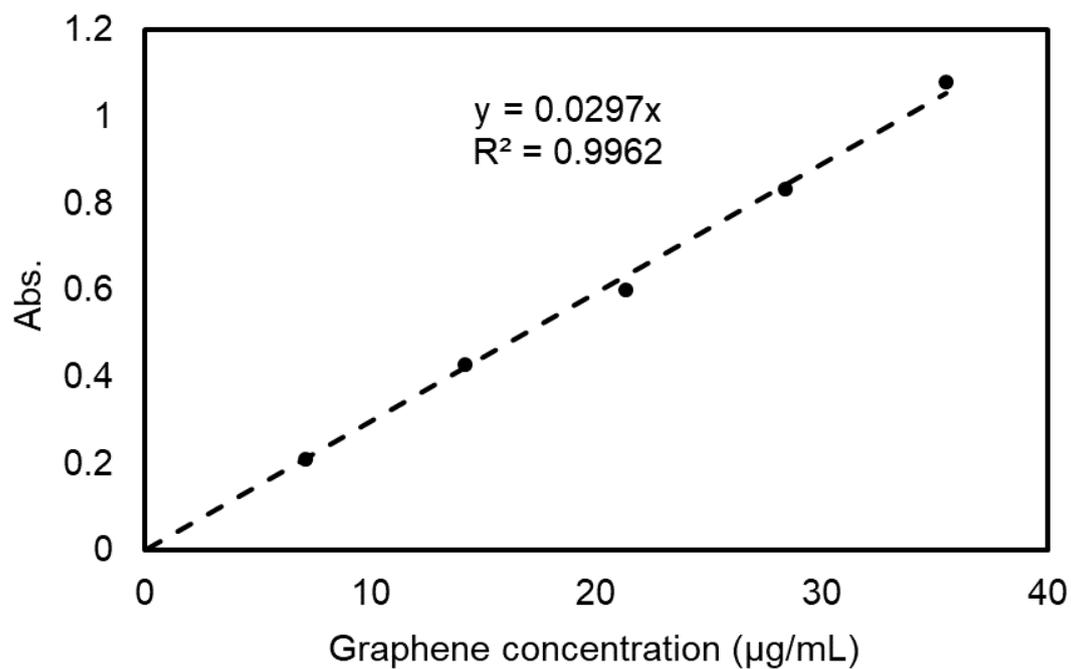


Fig. S3. Calibration curve of absorbance of graphene at 800 nm.

2.2. *Stability of the dispersion*

The dispersion was allowed to stand for several days, and the stability of the dispersion was examined. As a result, it was observed that only the dispersion using hexadecylbenzene aggregated on the upper part of the liquid.

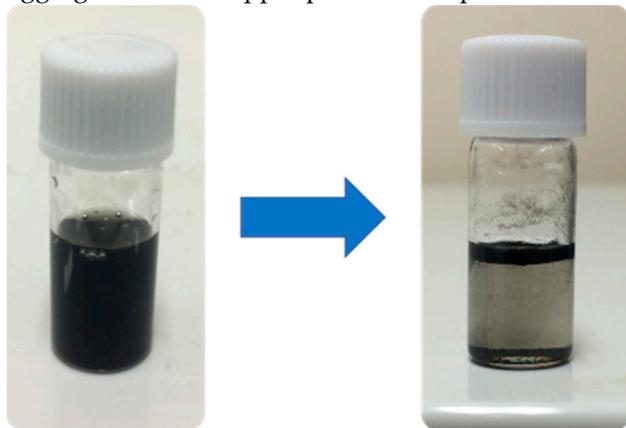


Fig. S4. Dispersion using hexadecylbenzene immediately after sonication (left) and after several days (right)

2.3. Recovery and reuse of dispersants

The recovered compound was analyzed by ^1H NMR (Figure S5).

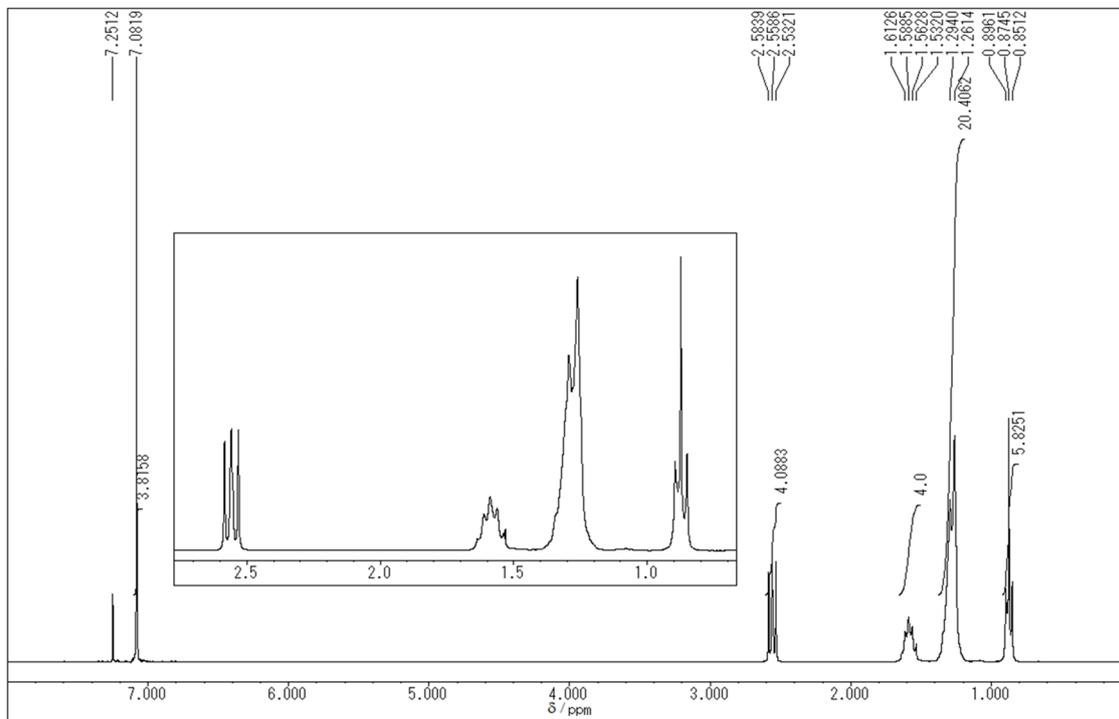


Fig. S5. ^1H NMR spectrum of 1,4-dioctylbenzene after recovery

2.4. General procedure for alkylation of arylbromide²

A dried round-bottom flask equipped with a magnetic stir bar was charged with magnesium (50 mmol), a small piece of iodine (0.13 mmol), and dry THF (50 mL) under Argon. To the solution, aryl bromide (48 mmol) was dropped slowly and stirred for 1 h to prepare the Grignard reagent. The Grignard reagent solution was added dropwise to a solution of alkyl halide (31 mmol) and CuI (0.82 mmol) in dry THF (5 mL) under Argon at room temperature. After completing the addition of the Grignard reagent, the reaction mixture was heated to reflux under Argon for 24 hours. After quenching with 1 M HCl aq., the mixture was extracted with hexane, and the organic layers were dried over MgSO_4 and the solvent was removed in vacuo. The crude residue was purified by silica gel column chromatography (hexane).

2.5. General procedure for alkylation of aryl dihalide³

A dried round-bottom flask equipped with a magnetic stir bar was charged with magnesium (48 mmol), a small piece of iodine (0.13 mmol), and dry THF under Argon. To the solution, bromooctane (40 mmol) was dropped slowly and stirred for 1 h to prepare the Grignard reagent. The Grignard reagent solution was added dropwise to a solution of aryl dihalide (20 mmol) and $\text{NiCl}_2(\text{dppp})$ (0.28 mmol) in dry THF under Argon at 0 °C. After completing the addition of the Grignard reagent, the reaction mixture was heated to room temperature under Argon for 24 hours. After quenching with 1 M HCl aq., the mixture was extracted with hexane, and the organic

layers were dried over MgSO_4 and the solvent was removed in vacuo. The crude residue was purified by Gel Permeation Chromatography (hexane).

2.6. General procedure for alkylation of aryl trihalide³

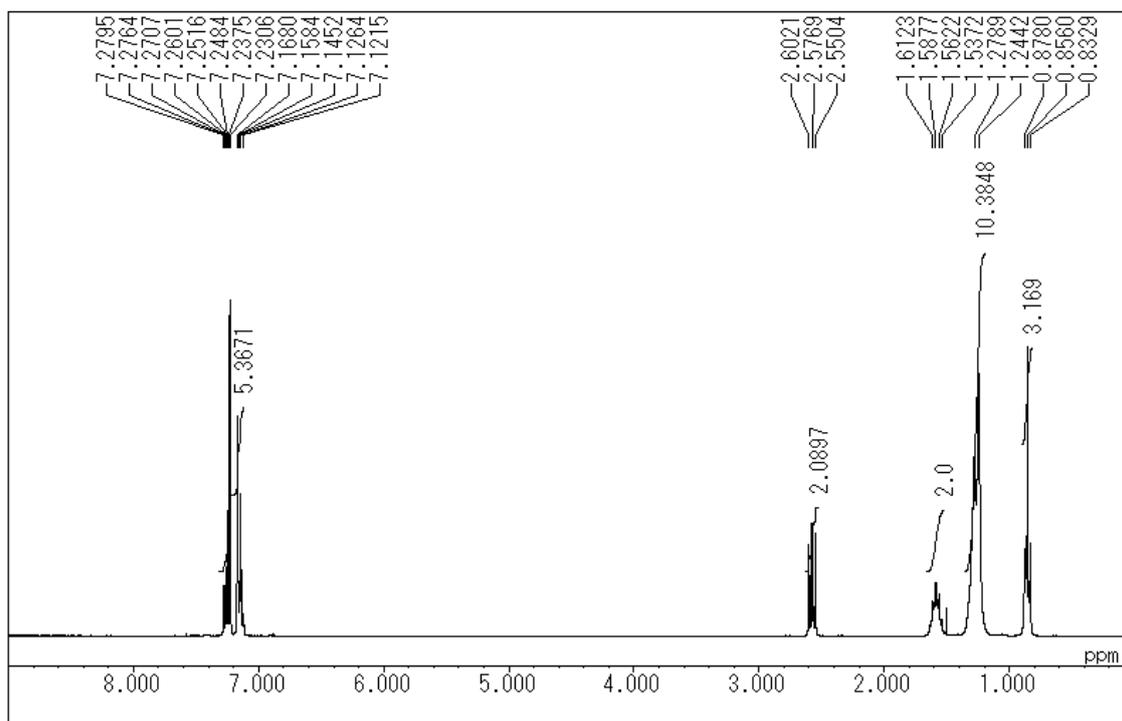
A dried round-bottom flask equipped with a magnetic stir bar was charged with magnesium (107 mmol), a small piece of iodine (0.31 mmol), and dry THF under Argon. To the solution, bromooctane (100 mmol) was dropped slowly and stirred for 1 h to prepare the Grignard reagent. The Grignard reagent solution was added dropwise to a solution of aryl trihalide (20 mmol) and $\text{NiCl}_2(\text{dppp})$ (0.25 mmol) in dry THF under Argon at 0 °C. After completing the addition of the Grignard reagent, the reaction mixture was heated to room temperature under Argon for 24 hours. After quenching with 1 M HCl aq., the mixture was extracted with hexane, and the organic layers were dried over MgSO_4 and the solvent was removed in vacuo. The crude residue was purified by Gel Permeation Chromatography (hexane).

3. Spectroscopic Characterization Data for Compounds:

Octylbenzene

Magnesium (1.22g, 50 mmol), iodine (34 mg, 0.13 mmol), bromobenzene (5.0 ml, 48 mmol), bromooctane (5.5 ml, 31 mmol), CuI (157 mg, 0.82 mmol). The product was obtained as a colorless liquid (5.29 g, 88%).

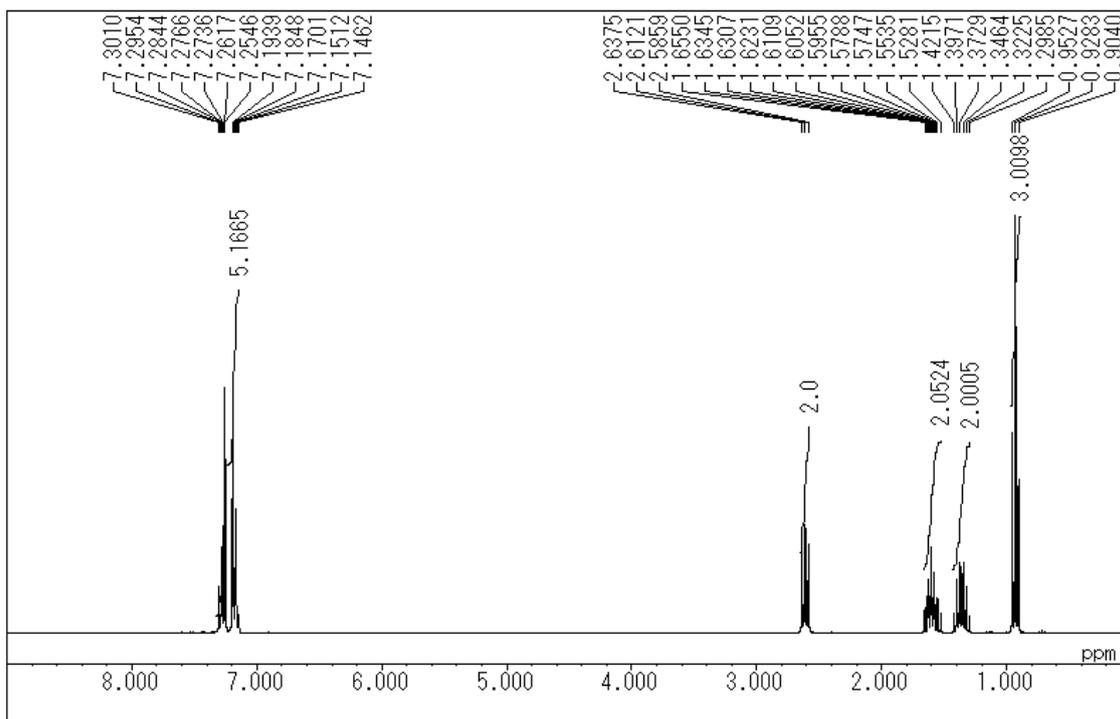
^1H NMR (400 MHz, solvent: CDCl_3 , scan: 16) δ 7.28-7.12 (m, 5H), 2.58 (t, $J = 10.3$ Hz, 2H), 1.62-1.54 (m, 2H), 1.28-1.25 (m, 10H), 0.86 (t, $J = 9.0$ Hz, 3H)⁴



Butylbenzene

Magnesium (1.26g, 52 mmol), iodine (34 mg, 0.13 mmol), bromobenzene (5.0 ml, 48 mmol), bromobutane (4.0 ml, 37 mmol), CuI (152 mg, 0.80 mmol). The product was obtained as a colorless liquid (4.15 g, 83%).

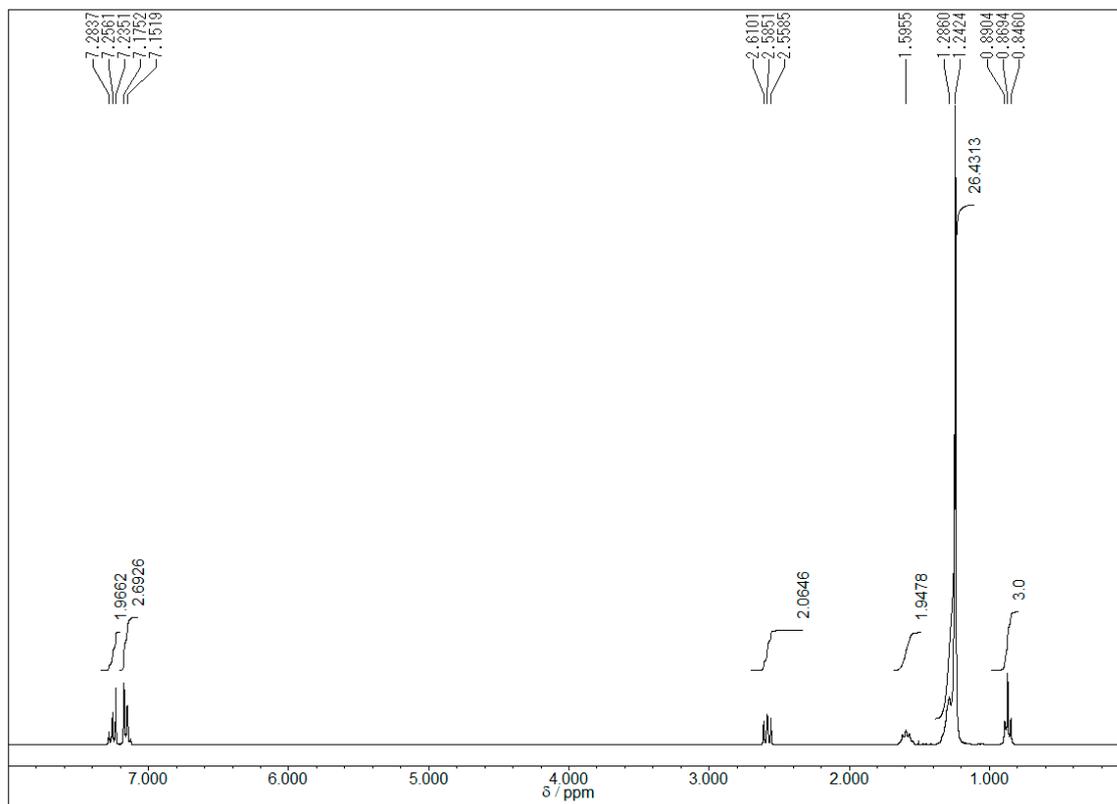
^1H NMR (400 MHz, solvent: CDCl_3 , scan: 16) δ 7.30-7.15 (m, 5H), 2.61 (t, $J = 10.3$ Hz, 2H), 1.66-1.53 (m, 2H), 1.42-1.30 (m, 2H), 0.93 (t, $J = 9.7$ Hz, 3H)²



Hexadecylbenzene

Magnesium (1.26g, 52 mmol), iodine (32 mg, 0.13 mmol), bromobenzene (5.0 ml, 48 mmol), bromohexadecane (12 ml, 39 mmol), CuI (163 mg, 0.85 mmol). The product was obtained as a colorless liquid (6.01 g, 88%).

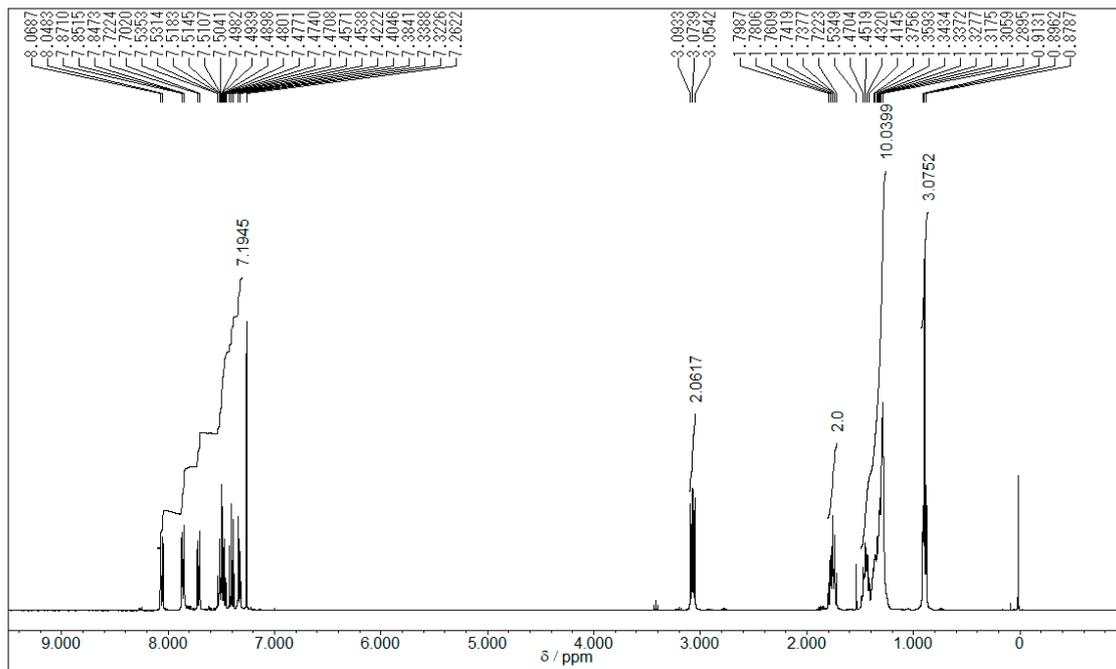
^1H NMR (400 MHz, solvent: CDCl_3 , scan: 16) δ 7.28-7.15 (m, 5H), 2.59 (t, $J = 10.3$ Hz, 2H), 1.61-1.57 (m, 2H), 1.28-1.24 (m, 26H), 0.87 (t, $J = 8.9$ Hz, 3H)⁵



Octylnaphthalene

Magnesium (1.20g, 49 mmol), iodine (44 mg, 0.17 mmol), bromonaphthlene (7.0 ml, 50 mmol), bromooctane (6.5 ml, 37 mmol), CuI (154 mg, 0.80 mmol). The product was obtained as a colorless liquid (5.00 g, 54%).

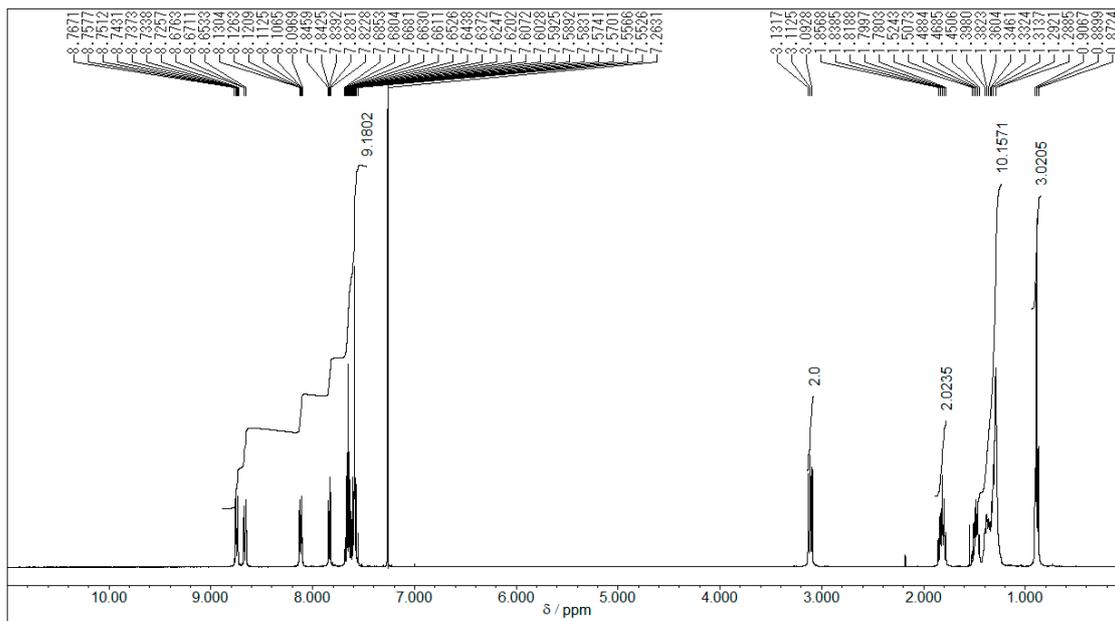
$^1\text{H NMR}$ (400 MHz, solvent: CDCl_3 , scan: 16) δ 8.07-7.26 (m, 7H), 3.07 (t, $J = 7.8$ Hz, 2H), 1.80-1.72 (m, 2H), 1.47-1.29 (m, 10H), 0.90 (t, $J = 6.9$ Hz, 3H) ⁶



Octylphenanthrene

Magnesium (597 mg, 25 mmol), iodine (34 mg, 0.13 mmol), bromonaphthlene (5.17 g, 20 mmol), bromooctane (3.5 ml, 20 mmol), CuI (200 mg, 1.1 mmol). The product was obtained as a white solid (2.56 g, 44%).

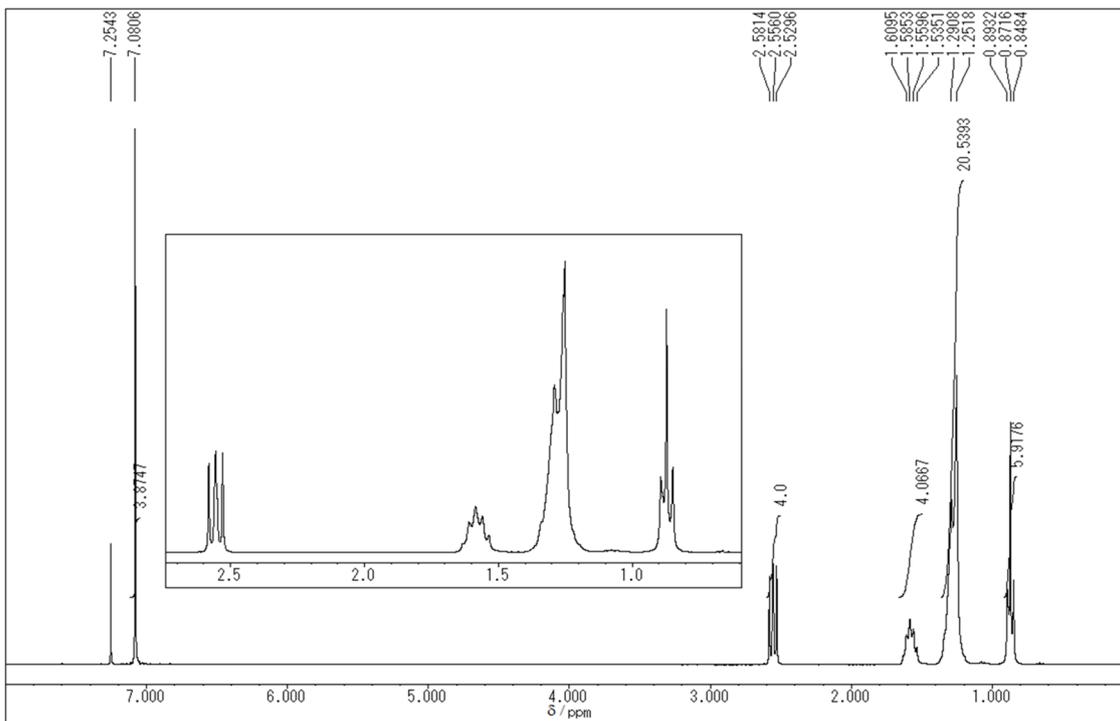
$^1\text{H NMR}$ (400 MHz, solvent: CDCl_3 , scan: 16) δ 8.77-7.26 (m, 9H), 3.11 (t, $J = 7.8$ Hz, 2H), 1.85-1.78 (m, 2H), 1.52-1.29 (m, 10H), 0.89 (t, $J = 6.9$ Hz, 3H)⁷



1,4-Dioctylbenzene

Magnesium (1.16 g, 48 mmol), iodine (32 mg, 0.13 mmol), bromooctane (7.0 ml, 40 mmol), 1,4-dichlorobenzene (1.47 g, 20 mmol), NiCl₂(dppp) (154 mg, 0.28 mmol). The product was obtained as a colorless liquid (863 mg, 29%).

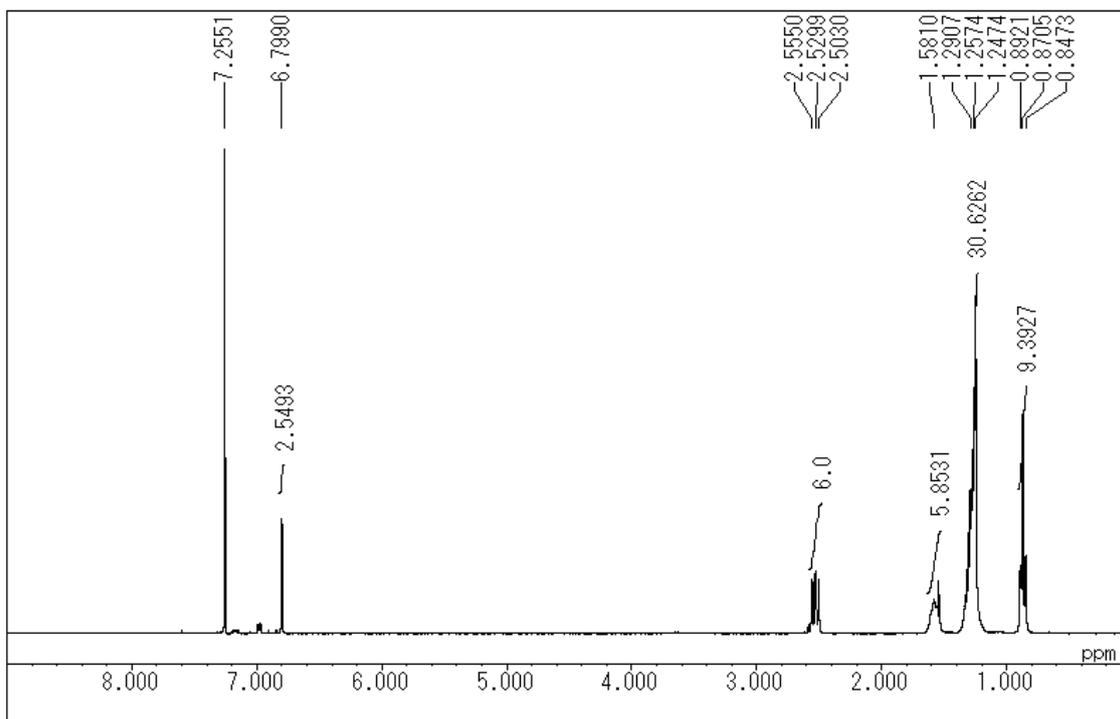
¹H NMR (400 MHz, solvent: CDCl₃, scan: 16) δ 7.08 (s, 4H), 2.56 (t, J = 10.4 Hz, 4H), 1.61-1.54 (m, 4H), 1.29-1.25 (m, 20H), 0.87 (t, J = 9.0 Hz, 6H)³



1,3,5-Trioctylbenzene

Magnesium (2.62g, 107 mmol), iodine (79 mg, 0.31 mmol), bromooctane (17.2 ml, 100 mmol), 1,3,5-trichlorobenzene (3.63 g, 20 mmol), NiCl₂(dppp) (135 mg, 0.25 mmol). The product was obtained as a colorless liquid (1.31 g, 16%).

¹H NMR (400 MHz, solvent: CDCl₃, scan: 16) δ 6.81 (s, 3H), 2.56 (t, J = 10.4 Hz, 6H), 1.61-1.57 (m, 6H), 1.30-1.25 (m, 30H), 0.88 (t, J = 9.0 Hz, 9H)⁸



Reference

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