

Supporting Information for
“Large, Solution-Processable Graphene Quantum Dots as Light Absorbers for Photovoltaics”

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1. General Experimental Methods

All reactions were carried out under an argon atmosphere with dry solvent under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF), diethyl ether (Et₂O), toluene (PhMe), and dichloromethane (DCM) were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Unless otherwise noted, reagents as well as anhydrous benzene (PhH) were purchased from Aldrich and Alfa and were used as received. Reactions were monitored by thin-layer chromatography (TLC) carried on silica gel plates (F-254, 250 μ m, Dynamic Absorbents, Inc.) using ultraviolet (UV) light or KMnO₄ for visualization. Silica gel (particle size 0.032-0.063 mm) from Dynamic Absorbents, Inc. was used for flash and gravity column chromatography. NMR spectra were recorded on a Varian Inova (400 MHz) NMR spectrometers and calibrated using residual chloroform (δ H = 7.26 ppm, δ C = 77.0 ppm) and methanol (δ H = 3.31 ppm, δ C = 49.0 ppm) as internal references. Chemical shifts were reported in ppm δ . The following abbreviations are used to indicate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

Matrix-assisted laser desorption/ionization (MALDI) reflectron time-of-flight (MALDI-TOF) technique was used for mass analysis of the compounds, and recorded on Bruker Biflex III with Tetracyanoquinodimethane (TCNQ) as the matrix. Dynamic light scattering measurements were conducted with Zetasizer Nano-S (Malvern Instruments) at 20 °C, with toluene as solvent. Infrared spectra were taken by casting thin films of the compounds on KBr plates and dried prior to measurements. The solubility of the quantum dots was determined by mixing excess of quantum dots with solvents, followed by prolonged centrifugation. The weight of the solute in the supernatant was determined after the solvent was evaporated under vacuum, which compared with the total weight of the supernatant yielded the solubility.

To make nanocrystalline solar cells, TiO₂ nanocrystalline was synthesized following the literature procedure.¹ 7.2 g of Titanium(IV) isopropoxide (Sigma-Aldrich, 97%) in 6.0 g of isopropanol (Aldrich, 99.5%) was added dropwise to a mixture of 35 mL of acetic acid (Sigma-Aldrich, 99.7%) and 100 mL of deionized water while stirring at 0 °C. The resulting clear solution was heated to 80 °C for about 8 h until it was concentrated to 80 mL. Then it was transferred into an autoclave (Parr) and heated at 230 °C for 12 h. The upper layer clear solution in the autoclave was dumped, and the white cloudy suspension on the bottom was added 0.2 g of polyethylene glycol (MW 20000, Alfa Aesar). The suspension was then sonicated and concentrated to 0.14 g/mL to get a viscous paste. Three drops of this paste were deposited on a fluorine-doped stannic oxide glass (Hartford Glass, Hartford City, Indiana), which was masked by Scotch tape (3M) on four edges, and distributed uniformly on the plate by sliding a glass rod over the plate. After one minute, the tape was carefully removed and the film was dried in air at room temperature for 10 min, followed by heating to 450 °C at a rate of 5 °C/min and left at 450 °C for 30 min before cooling to 120 °C. The TiO₂ electrode was immersed in the solution of graphene quantum dots (5 mg graphene in a mixture of 10 mL of toluene, 10 mL of ethanol) while it was still hot (110-120 °C) and kept at 50 °C for 4 days. The stained TiO₂ electrode was then rinsed with acetonitrile and dried. Two strips of surlyn film were applied along the TiO₂ film and then a hot platinized counter electrode (110-120 °C) was clipped onto the top of TiO₂ working electrode to form the dye-sensitized solar cell. Three drops of electrolyte were added into the cell. The electrolyte solution was composed of 0.02M iodine, 0.04M lithium iodide,

with ethyl acetate/hexanes (1:4) to afford **S2** (1.4 g, 81%) as a brown solid: ^1H NMR (400 MHz, CDCl_3): δ = 7.31 (d, J = 8.4 Hz, 1H), 7.19 (d, J = 2.8 Hz, 1H), 6.51 (dd, J = 2.8, 8.8 Hz, 1H), 3.67 (br, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ = 146.25, 132.59, 126.05, 117.11, 116.47, 101.34.

1-bromo-3-(phenylethynyl)benzene 1-bromo-3-iodobenzene (2.26 g, 8 mmol), $\text{Pd}(\text{PPh}_3)_4$ (92 mg, 0.08 mmol), CuI (15.2 mg, 0.08 mmol) and piperidine (20 ml) were mixed together under argon atmosphere. The mixture was degassed by two “freeze-pump-thaw” cycles. Then phenylacetylene (817 mg, 8 mmol) was then added slowly. The reaction mixture was stirred for 4 h at room temperature. Then 2M aqueous NH_4Cl was added to quench the reaction. The mixture was extracted twice with dichloromethane, and the organic layer was washed twice with water and dried over Na_2SO_4 . After evaporating the solvent, the product was purified by column chromatography on silica gel with hexanes to afford 1-bromo-3-(phenylethynyl)benzene (2.0 g, 97%) as colorless oil: ^1H NMR (400 MHz, CDCl_3): δ = 7.70 (t, J = 1.6 Hz, 1H), 7.53 (m, 2H), 7.46 (m, 2H), 7.36 (m, 3H), 7.22 (t, J = 8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ = 134.29, 131.65, 131.35, 130.12, 129.75, 128.61, 128.39, 125.30, 122.73, 122.15, 90.66, 87.78.

3-(phenylethynyl)phenylboronic acid (S3) 1-bromo-3-(phenylethynyl)benzene (2.1 g, 8.2 mmol) was dissolved in anhydrous THF (10 ml) and cooled down to -78°C in a dry ice/acetone bath. $n\text{-BuLi}$ (9.8 mmol in 4 ml Hexanes) was slowly added into the reaction mixture under argon atmosphere. The resulting mixture was stirred for 1 h at -78°C , and then $\text{B}(\text{OMe})_3$ (1.37 mL, 12.3 mmol) was added. The reaction mixture was allowed to warm up to room temperature gradually. The reaction was quenched with 1 M HCl and extracted twice with ethyl acetate. The organic layer was washed twice with 10% HCl and dried over Na_2SO_4 . Evaporating the solvent afforded a white solid (1.9 g). The crude product was used in the following steps without further purification.

6-bromo-3'-(phenylethynyl)biphenyl-3-amine (S4) Freshly made 3-(phenylethynyl)phenylboronic acid (**S3**; 1.9 g), 4-bromo-3-iodoaniline (**S2**; 2.2 g, 7.4 mmol), $\text{Pd}(\text{PPh}_3)_4$ (170 mg, 0.15 mmol), toluene (20 mL), ethanol (5 mL) and 2M K_2CO_3 (10 mL) were mixed together. The resulting mixture was degassed by three “freeze-pump-thaw” cycles and then heated at 60°C and stirred for 3 d. After cooling, the reaction mixture was extracted twice with ethyl acetate. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The product was purified by column chromatography on silica gel with CH_2Cl_2 /hexanes (1:1) to afford **S4** (2.4 g, 94%) as a yellow waxy solid: ^1H NMR (400 MHz, CDCl_3): δ = 7.54 (m, 4H), 7.42-7.33 (m, 6H), 6.66 (d, J = 2.8 Hz, 1H), 6.56 (dd, J = 2.8, 8.4 Hz, 1H), 3.71 (br, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ = 145.72, 142.15, 141.44, 133.54, 132.29, 131.58, 130.56, 129.29, 128.31, 128.26, 127.89, 123.15, 122.91, 117.59, 115.79, 110.157, 89.53, 89.23.

2-bromo-5-iodo-3'-(phenylethynyl)biphenyl (S5) 6-bromo-3'-(phenylethynyl)biphenyl-3-amine (**S4**; 2.4 g, 6.9 mmol) and iodine (2.6 g, 10.4 mmol) were dissolved in dry benzene (35 mL) and cooled down to 5°C under argon atmosphere. $t\text{-butyl nitrite}$ (1.3 g, 12.5 mmol) was added dropwise over 30 min via a syringe. The resulting mixture was allowed to warm up to room temperature and stirred for 3 h. 1M NaOH (15 mL) was added to quench the reaction. The reaction mixture was extracted twice with ethyl acetate. The organic layers were combined and dried over Na_2SO_4 . After evaporating the solvent, the crude product was purified by column chromatography on silica gel with hexanes to afford **S5** (1.7 g, 54%) as a yellow waxy solid: ^1H NMR (400 MHz, CDCl_3): δ = 7.68 (d, J = 2.4 Hz, 1H), 7.54 (m, 5H), 7.42 (t, J = 7.6 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 7.35 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ = 143.75, 139.83,

139.68, 137.87, 134.66, 132.18, 131.63, 131.15, 129.12, 128.35, 128.15, 123.32, 123.05, 122.44, 92.33, 89.92, 88.90.

1,3,5-tris(3,7,11,15-tetramethylhexadecyl)benzene (S6) A mixture of 1,3,5-trichlorobenzene (1.21 g, 6.67 mmol) and NiCl₂(dppe) (51.8 mg, 0.1 mmol) in dry diethyl ether (10 mL) was stirred under argon atmosphere at 0°C. To this solution freshly made 3,7,11,15-tetramethylhexadecyl-1-magnesiumbromide (30 mmol in 30 mL dry diethyl ether) was slowly added. The resulting mixture was allowed to warm up to room temperature and stirred overnight. The mixture was refluxed for another 2 h before the reaction was quenched with ice/water. The organic phase was separated and dried over Na₂SO₄. After evaporating the solvent, the yellow crude product was purified by column chromatography on silica gel with hexanes to afford **S6** (yield: 92%) as colorless oil with 2,6,10,14-tetramethylhexadecane as byproduct (generated from excess 3,7,11,15-tetramethylhexadecyl-1-magnesiumbromide): ¹H NMR (400 MHz, CDCl₃): δ= 6.81 (s, 3H), 2.55 (m, 6H), 1.65-0.80 (m, 117H); ¹³C NMR (75 MHz, CDCl₃): δ= 143.04, 125.71, 39.43, 39.21, 39.12, 37.51, 37.45, 37.35, 33.58, 32.83, 32.74, 31.65, 28.02, 27.50, 24.86, 24.53, 22.76, 22.66, 19.80, 19.73.

2-bromo-1,3,5-tris(3,7,11,15-tetramethylhexadecyl)benzene (S7) 1,3,5-tris(3,7,11,15-tetramethylhexadecyl)benzene (**S6**; 5.87 mmol) was dissolved in CCl₄ (3.3 mL) under argon atmosphere. To this solution Br₂ (0.3 mL, 5.87 mmol) was added drop-wise over 30 min and the reaction mixture was stirred overnight at room temperature. The reaction was quenched with 1M NaOH and extracted twice with CH₂Cl₂. The organic phases were combined and dried over Na₂SO₄. After evaporating the solvent, the crude product was purified by column chromatography on silica gel with hexanes to give **S7** (yield: 95%) as colorless oil: ¹H NMR (400 MHz, CDCl₃): δ= 6.86 (s, 2H), 2.72 (m, 4H), 2.51 (m, 2H), 1.65-0.80 (m, 117H); ¹³C NMR (100 MHz, CDCl₃): δ= 142.73, 141.86, 127.72, 123.33, 39.39, 37.47, 37.41, 37.31, 37.24, 34.83, 33.01, 32.79, 31.60, 27.99, 27.50, 24.82, 24.49, 24.44, 22.73, 22.64, 19.77, 19.71.

trimethyl(2',4',6'-tris(3,7,11,15-tetramethylhexadecyl)biphenyl-4-yl)silane (S9) A round bottom flask was charged with 2-bromo-1,3,5-tris(3,7,11,15-tetramethylhexadecyl)benzene (**S7**; 3.60 g, 3.61 mmol), 4-(trimethylsilyl)phenylboronic acid (**S8**; 1.05 g, 5.41 mmol), Pd(OAc)₂ (20 mg, 0.09 mmol), 2-(2', 6'-dimethoxybiphenyl)-dicyclohexylphosphine (74 mg, 0.18 mmol), and K₃PO₄ (2.30 g, 10.8 mmol). Toluene (15 mL) was added via a syringe under argon atmosphere and the reaction mixture was stirred for 10 min at room temperature to allow the catalyst to be dissolved. Then the resulting mixture was heated to 80°C overnight. After cooling, the reaction solution was filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with hexanes to afford **S9** (yield: 94%) as colorless oil: ¹H NMR (400 MHz, CDCl₃): δ= 7.52 (d, J= 8 Hz, 2H), 7.16 (d, J= 8 Hz, 2H), 6.93 (s, 2H), 2.62 (m, 2H), 2.28 (m, 4H), 1.65-0.65 (m, 117H), 0.30 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ= 141.90, 141.24, 140.80, 138.44, 138.03, 132.72, 129.36, 126.37, 39.43, 39.19, 39.08, 38.97, 37.52, 37.47, 37.36, 37.07, 33.42, 32.82, 31.46, 28.02, 27.50, 24.87, 24.53, 22.77, 22.68, 19.81, 19.74, 19.42, 19.37, -0.974.

4,4,5,5-tetramethyl-2-(2',4',6'-tris(3,7,11,15-tetramethylhexadecyl)biphenyl-4-yl)-1,3,2-dioxaborolane (S10) trimethyl(2',4',6'-tris(3,7,11,15-tetramethylhexadecyl)biphenyl-4-yl)silane (**S9**; 1.54 g, 1.44 mmol) was dissolved in anhydrous dichloromethane (4.5 mL) under argon atmosphere. BBr₃ (433 mg, 1.73 mmol) was slowly added. The resulting solution was stirred for 5h at room temperature before water was added to quench the reaction. The reaction mixture was extracted twice with CH₂Cl₂ and

the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was dissolved in anhydrous CH₂Cl₂ (4.5 mL) again. Pinacol (340 mg, 2.88 mmol) was then added. The reaction mixture was stirred overnight under argon atmosphere. After evaporating the solvent, the crude product was purified by column chromatography on silica gel with CH₂Cl₂/hexanes (1:10) to afford **S10** (yield: 75%) as colorless oil: ¹H NMR (400 MHz, CDCl₃): δ= 7.81 (d, J= 7.4 Hz, 2H), 7.18 (d, J= 7.4 Hz, 2H), 6.91 (s, 2H), 2.60 (m, 2H), 2.26 (m, 4H), 1.65-0.68 (m, 129H); ¹³C NMR (100 MHz, CDCl₃): δ= 143.67, 141.94, 140.98, 138.29, 134.33, 129.40, 126.27, 83.67, 39.40, 39.06, 38.97, 37.49, 37.44, 37.33, 37.08, 34.69, 33.39, 32.81, 32.76, 31.62, 31.39, 27.99, 25.29, 24.96, 24.83, 24.51, 24.35, 22.74, 22.64, 19.78, 19.71, 19.35, 19.47, 14.14.

Compound S11 4,4,5,5-tetramethyl-2-(2',4',6'-tris(3,7,11,15-tetramethylhexadecyl)biphenyl-4-yl)-1,3,2-dioxaborolane (**S10**; 827 mg, 0.74 mmol), 2-bromo-5-iodo-3'-(phenylethynyl)biphenyl (**S5**; 313 mg, 0.68 mmol), Pd(PPh₃)₄ (40 mg, 0.035 mmol), toluene (5 mL), ethanol (2 mL) and 2M aqueous K₂CO₃ (2.5 mL) were mixed together. The resulting mixture was degassed via three "freeze-pump-thaw" cycles and then heated at 80°C and stirred overnight. After cooling, the reaction mixture was extracted twice with ethyl acetate and dried over Na₂SO₄. After evaporating the solvent, the crude product was purified by column chromatography on silica gel with CH₂Cl₂/hexanes (1:20) to afford **S11** (830 mg, 92%) as yellow oil: ¹H NMR (400 MHz, CDCl₃): δ= 7.75 (d, J= 8.4 Hz, 1H), 7.65 (m, 4H), 7.60-7.50 (m, 4H), 7.45 (m, 2H), 7.35(m, 3H), 7.26 (d, J= 6.8 Hz, 2H), 6.94 (s, 2H), 2.61 (m, 2H), 2.31 (m, 4H), 1.70-0.60 (m, 117H); ¹³C NMR (100 MHz, CDCl₃): δ= 142.16, 142.10, 141.32, 141.24, 140.43, 140.19, 137.71, 137.57, 133.49, 132.47, 131.65, 130.85, 130.65, 129.61, 129.46, 128.33, 128.05, 127.43, 126.42, 126.33, 123.25, 123.22, 121.35, 89.73, 89.19, 39.39, 39.10, 39.04, 39.01, 38.97, 37.46, 37.40, 37.36, 37.31, 37.04, 33.39, 32.80, 32.73, 31.46, 27.98, 24.82, 24.47, 24.35, 22.74, 22.65, 19.76, 19.69, 19.62, 19.35, 19.47.

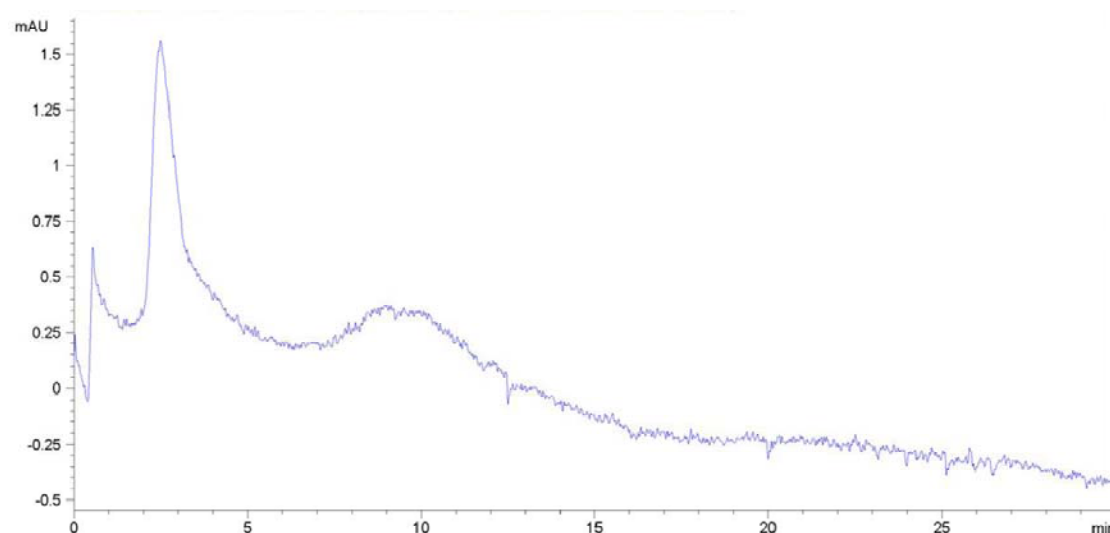
Compound S12 Compound **S11** (275mg, 0.21 mmol) was dissolved in anhydrous THF (2 mL) under argon atmosphere and cooled down to -78°C in a dry ice/acetone bath. *n*-BuLi (0.25 mmol in 0.1 mL hexanes) was added slowly into the reaction mixture resulting a yellow solution. The reaction mixture was stirred for 1h at -78°C, and then B(*i*-Pr)₃ (0.46 mL, 2 mmol) was added. The resulting mixture was allowed to warm up to room temperature gradually overnight. The reaction was quenched with 1 M HCl and extracted twice with ethyl acetate. The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The crude boronic acid (yield: 60%, estimated from ¹H NMR) was used directly without further purification. The fresh made boronic acid(0.13 mmol, 4 equiv), 1,3,5-triiodobenzene (14.6 mg, 0.032 mmol, 1 equiv), Pd(PPh₃)₄ (3 mg, 0.0025 mmol), toluene (1 mL) and 2M K₂CO₃ (0.5 mL) were mixed together. The resulting mixture was degassed by three "freeze-pump-thaw" cycles and then heated at 80°C and stirred overnight. After cooling, the reaction was extracted twice with dichloromethane and dried over Na₂SO₄. After evaporating the solvent, the product was purified by column chromatography on silica gel with CH₂Cl₂/hexanes (1:10) to afford **S12** (102 mg, 84%): ¹H NMR (400 MHz, CDCl₃): δ= 7.73 (d, J= 1.6 Hz, 3H), 7.70 (d, J= 8 Hz, 6H), 7.65 (dd, J= 1.6, 8 Hz, 3H), 7.60 (s, 3H), 7.55 (m, 6H), 7.48 (d, J= 8 Hz, 3H), 7.40-7.30 (m, 12H), 7.26 (d, J= 8 Hz, 6H), 7.04 (d, J= 8 Hz, 3H), 7.00 (d, J= 8 Hz, 3H), 6.95 (s, 9H), 2.62 (m, 6H), 2.33 (m, 12H), 1.70-0.65 (m, 351H); ¹³C NMR (100 MHz, CDCl₃): δ= 142.06, 141.98, 141.32, 140.73, 140.40, 140.15, 140.01, 139.76, 139.26, 139.02, 138.25, 137.92, 132.71, 131.62, 131.14, 130.71, 130.48, 129.98, 128.84, 128.33, 127.95, 126.45, 126.37, 123.34, 123.24, 89.60, 89.50, 39.36, 39.06, 37.42, 37.30, 37.14, 33.40, 32.79, 31.47, 29.71, 27.96, 24.80, 24.46, 24.35, 22.72, 22.63, 19.74, 19.68, 19.47, 19.40. HR-MS (MALDI-TOF) calculated. for C₂₈₂H₄₂₆ 3816.34 [M⁺] found 3816.80.

Compound 2 In a round bottom flask equipped with a condenser, a mixture of compound **S12** (177 mg, 0.046 mmol), tetraphenylcyclopentadienones (214mg, 0.56 mmol) and diphenyl ether (1 mL) was heated to reflux under argon atmosphere for 17 h. After cooling, the reaction mixture was quenched with methanol (40 ml). The precipitate was filtered and purified by column chromatography on silica gel with CH₂Cl₂/hexanes (3:7) to afford **2** (85mg, 40%) as a white solid: ¹H NMR (400 MHz, CDCl₃): δ= 7.63 (m, 9H), 7.27 (m, 12H), 7.10-6.40 (m, 87H), 5.77 (d, J= 6.4 Hz, 3H), 5.63 (s, 3H), 5.19 (s, 3H), 2.63 (m, 6H), 2.35 (m, 12H), 1.70-0.60(m, 351H); ¹³C NMR (100 MHz, CDCl₃): δ= 142.18, 142.04, 141.21, 141.00, 140.68, 140.61, 140.52, 140.42, 140.31, 140.06, 139.72, 139.50, 138.62, 138.58, 137.90, 132.52, 131.69, 131.41, 131.06, 130.49, 130.19, 129.58, 129.50, 129.30, 129.22, 127.13, 126.96, 126.62, 126.50, 126.34, 125.83, 125.54, 125.30, 125.08, 124.67, 39.38, 39.09, 39.00, 37.46, 37.43, 37.30, 33.40, 32.81, 31.33, 29.70, 27.98, 24.81, 24.50, 22.74, 22.64, 19.77, 19.71, 19.52, 19.45. HR-MS (MALDI-TOF) calculated for C₃₆₆H₄₈₆ 4884.81 [M+H]⁺ found 4885.72.

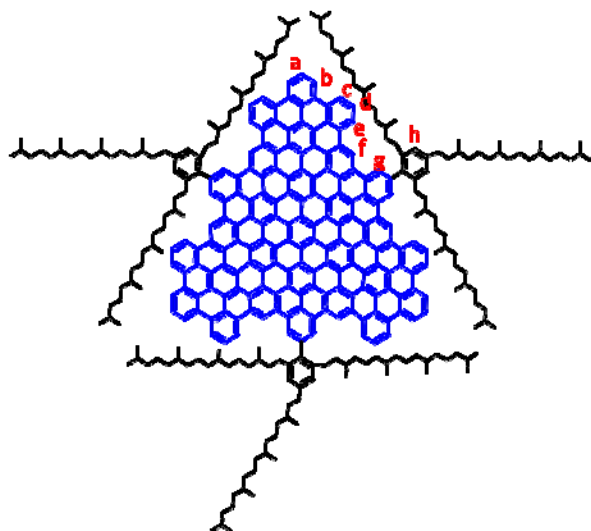
Compound 1 Compound **2** (20 mg, 0.0041 mmol) was dissolved in dry dichloromethane (10 mL). The solution was degassed via bubbling argon for 10min. Then FeCl₃ (144 mg, 0.88 mmol) in dry nitromethane (0.6 mL) was added slowly via a syringe. The resulting mixture was kept under argon flow during the entire reaction. After 3 h, the reaction was quenched with a large volume of methanol. The dark precipitate was collected and washed with methanol. The crude product was dissolved in CH₂Cl₂ (0.1 ml) again and precipitated in methanol (20 ml). The black precipitate was then collected and washed with methanol and dried in a vacuum to afford crude product **1** (17mg, 86%) as a black powder, which was subsequently purified with reverse-phase HPLC.

3. Isolation of **1** with Reverse-Phase HPLC

Graphene quantum dot **1** was purified with reverse-phase HPLC. An analytical chromatograph (Agilent 1100) is shown below. A tetrahydrofuran/dichloromethane mixture (50/50, v/v) was used as the eluent through a 4.6mm ID, 150 mm Agilent Zorbax 300SB-C18 column at a flow rate of 1.0 ml/min. The fraction between the 2nd and the 3rd minutes was collected for further analysis. The other fractions have not yet been identified.



4. Symmetry Analysis of C-H out-of-plane Bending Modes in Graphene Quantum Dot 1



We assume the graphene core is planar, and thus **1** has D_{3h} symmetry. The un-equivalent sets of aromatic C-H bonds are marked with letters from a to h. Within each set, the C-H bonds can be transformed from one another with the symmetry operations of the compound.

The normal vibrational modes of **1** involving C-H out-of-plane bending motion can be obtained with a standard method by analyzing the character of the symmetric transformations.⁴

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
χ_a	3	0	-1	-3	0	1
χ_{b-g}	6	0	0	-6	0	0

Thus the symmetry of the normal modes:

$\chi_a = A_2'' + E''$, $\chi_{b-g} = A_1'' + A_2'' + 2E''$, among which only modes with A_2'' symmetry are IR-active. Therefore we have 7 IR-active modes for bonds a - g.

The vibration of bonds h is analyzed with local symmetry (C_{2v}) due to the flexibility of the phenyl group, yielding three degenerate IR-active modes. Thus overall **1** should have no more than eight transitions in IR absorption due to the C-H out-of-plane bending motion, even considering the coupling among the un-equivalent sets, or coupling with other vibrations (which is however weak due to large energy difference).

The frequency of the eight normal modes can be estimated from the substitution pattern of the phenyl rings.⁵ We have 3 sets of isolated C-H bonds (f, g, h) with higher frequency (typically 850 ~ 910 cm⁻¹), and 5 sets of C-H bonds with neighboring C-H bonds (a, b, c, d, e) with lower frequency (typically 740 ~ 820 cm⁻¹).

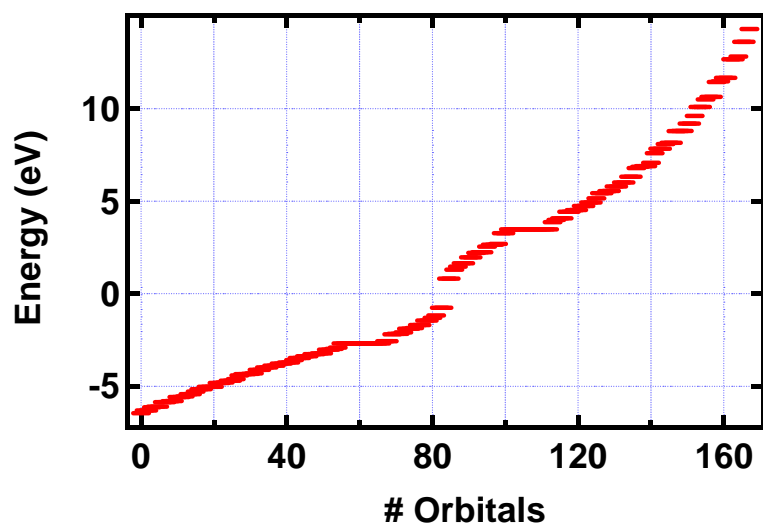
In our IR absorption spectrum, we observed 3 peaks in the higher- frequency group and 4 in the lower- frequency group. The fifth one in the lower- frequency group may be too weak or may overlap with other transitions. Thus the IR spectrum observed is consistent with that expected for structure **1**.

The simple absorption pattern also indicates that no significant amount of impurities is present in the quantum dots we obtained. Especially, no significant amount of chlorinated by-products is present, because C-Cl stretching is typically strong yet not seen in our spectrum. Presence of significant amount of chlorinated by-products would have led to a larger number of absorption peaks due to the reduced symmetry of the by-products.

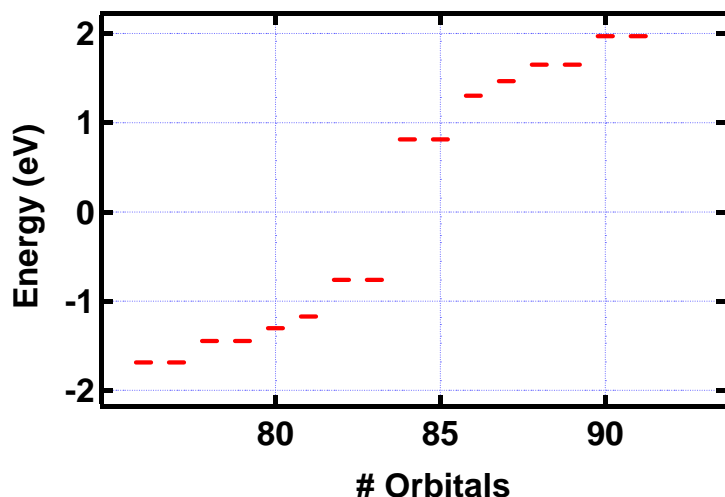
5. Tight-Binding Calculation of Electronic Levels in **1**

The electronic levels of **1** under one-electron approximation were calculated with a tight-bonding model.⁶ For the calculation we only considered the p_π orbitals of the carbon atoms, and diagonalized a 168 × 168 matrix to obtain the energy eigenvalues. For the calculation of the matrix elements, we assumed the molecule to be planar, and we only considered the nearest-neighbor coupling. The transfer integral and overlap integral were taken as -3.033 eV and 0.129, respectively, the values that reproduce *Ab initio* calculation results of graphite band structures.⁶ The difference between the interior bonds and those on the edges was ignored. *Ab initio* calculation of the electronic levels of **1** proved to be very difficult because of the large size of the graphene core.

The 168 one-electron eigenvalues we obtained are shown below, with the *x*-axis as the numbering of the molecular orbitals (from 0 to 167), and *y*-axis the energy eigenvalues relative to the work function of a bulk graphene (4.50 eV). Orbitals # 82 and 83 are the doubly-degenerate HOMO levels, and #84 and 85 the doubly-degenerate LUMO levels. The double degeneracy of the HOMO or LUMO levels is due to the symmetry of **1** (both belonging to E'' representation of D_{3h} group).



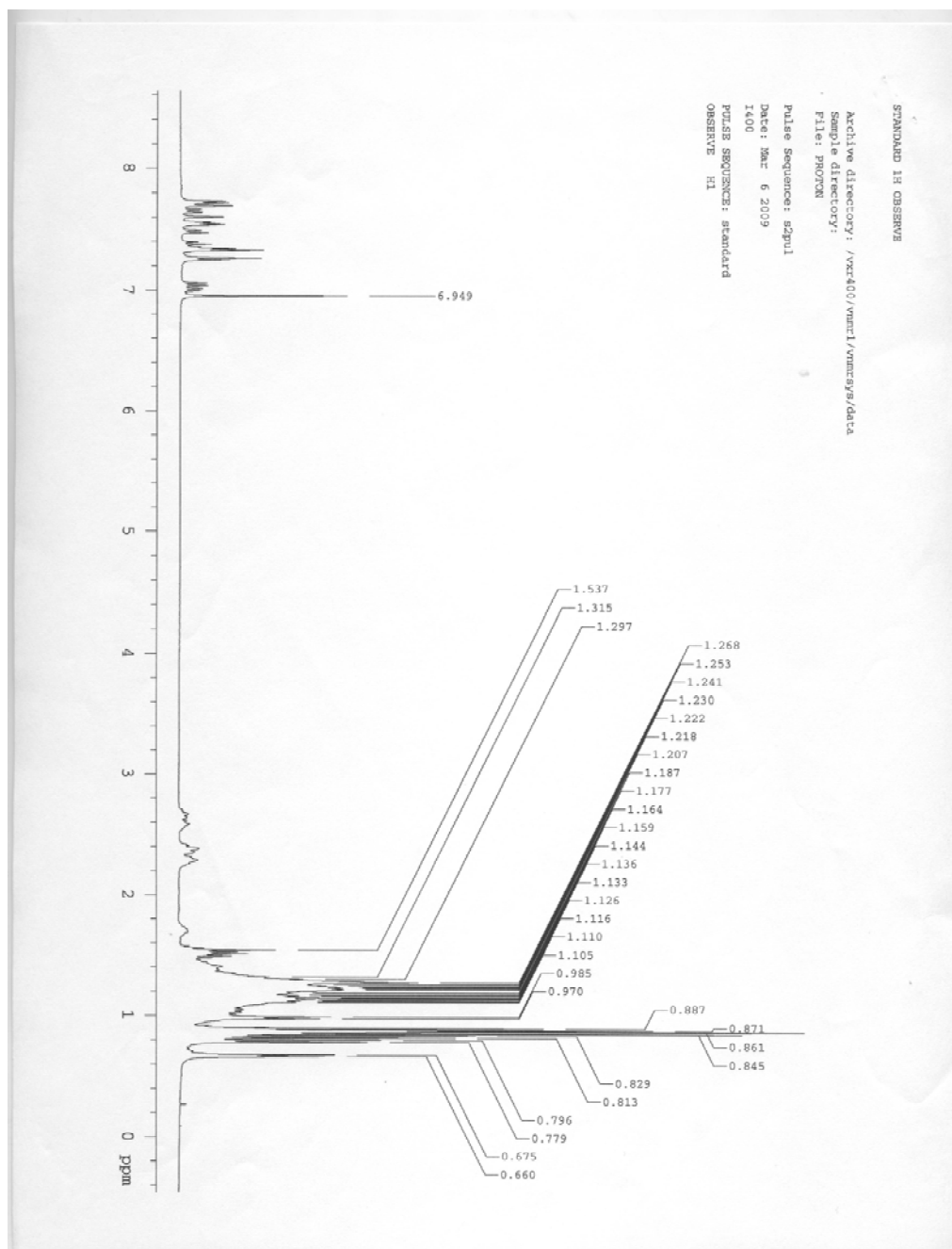
The following figure shows the zoom-in near the HOMO-LUMO levels, showing the HOMO levels as (-0.81) and the LUMO levels 0.73 eV, respectively. This leads to HOMO levels ~ 5.3 eV below vacuum and HUMO ~ 3.8 eV below vacuum. The calculated bandgap is ~ 1.5 eV, 0.1 eV larger than the experimentally determined one. This is remarkable considering the simplicity of the model. Under the one-electron approximation, the lowest excited states have quadruple degeneracy, which however is lifted by electron correlation. Therefore inclusion of electron correlation will lower the energy of the first excited state, and improve the accuracy of the calculation. In the calculation the interactions between σ bonds and π bonds were ignored. This is unlikely to cause significant error near the HOMO and LUMO levels because σ bonds are too far away in energy.



The experimental determination of the HOMO and LUMO levels of **1** with cyclic voltammetry was not successful either in solution or in solid films. In solution slow diffusion kinetics may be responsible for the failure. The solid films of **1** are not conductive enough so that no current was detected. This is a result of the three-dimensional enclosure of the graphene cores by the alkyl chains, which effectively decouples the graphene quantum dots electronically.

6. NMR Spectra of Selected Compounds

1) Compound S12



STANDARD 1H OBSERVE

Archive directory: /vxr400/vnmr1/vnmrsgs/data

Sample directory:

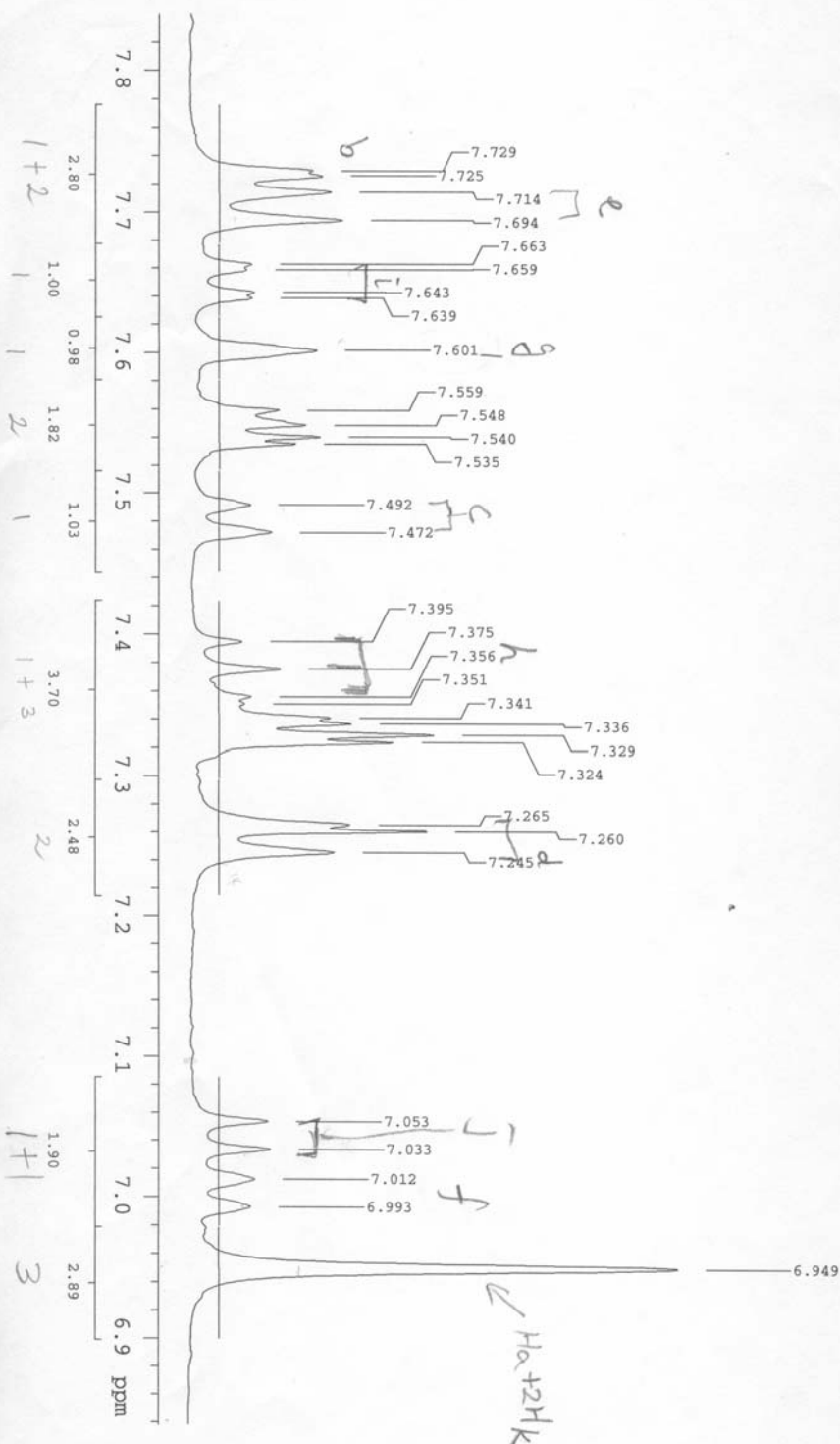
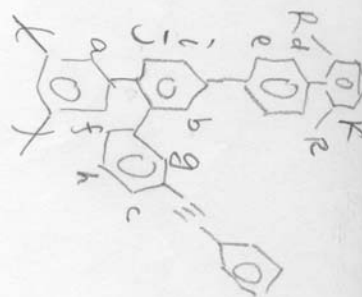
File: PROTON

Pulse Sequence: szpul

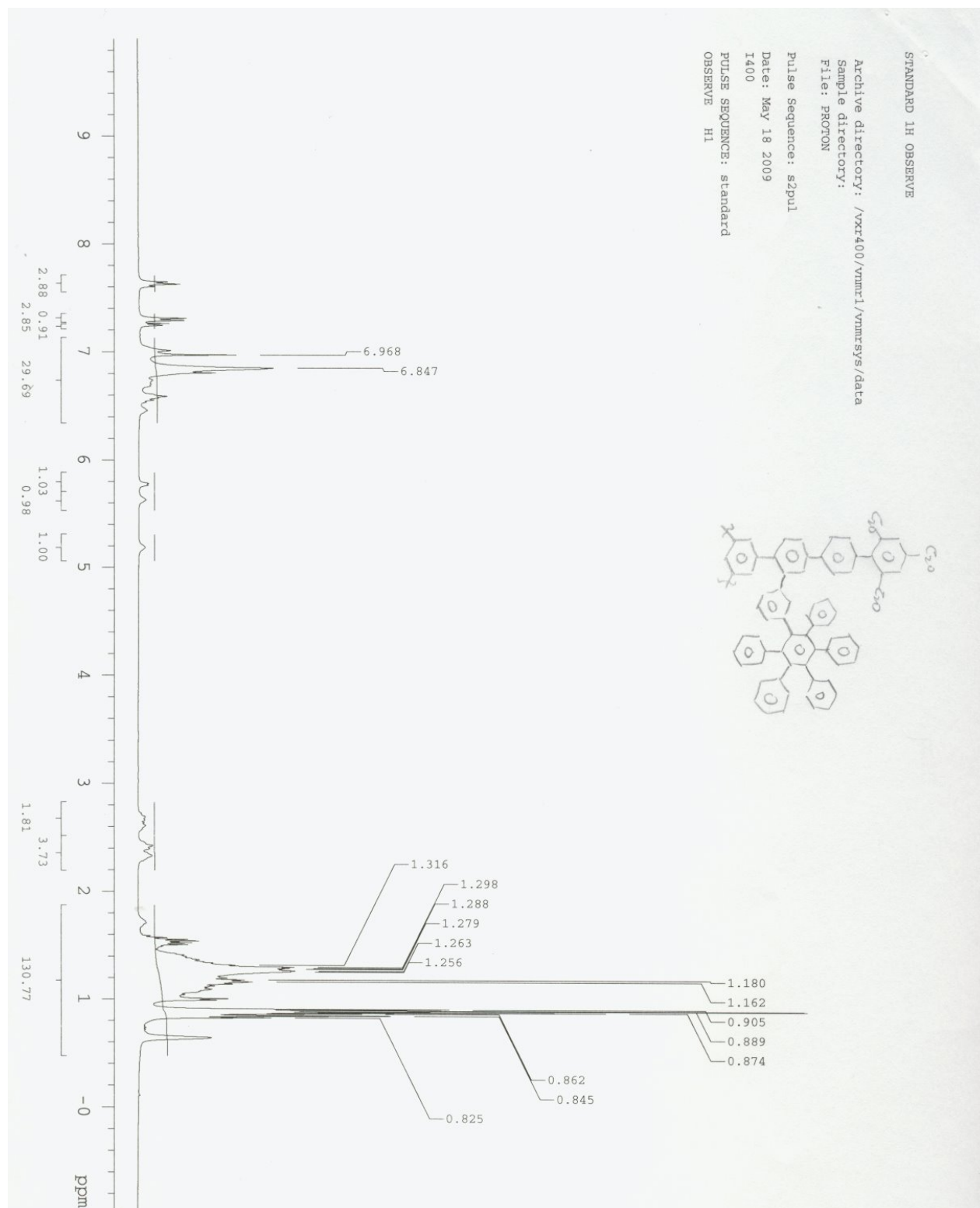
Date: Mar 6 2009

PULSE SEQUENCE: standard

OBSERVE H1



2) Compound 2



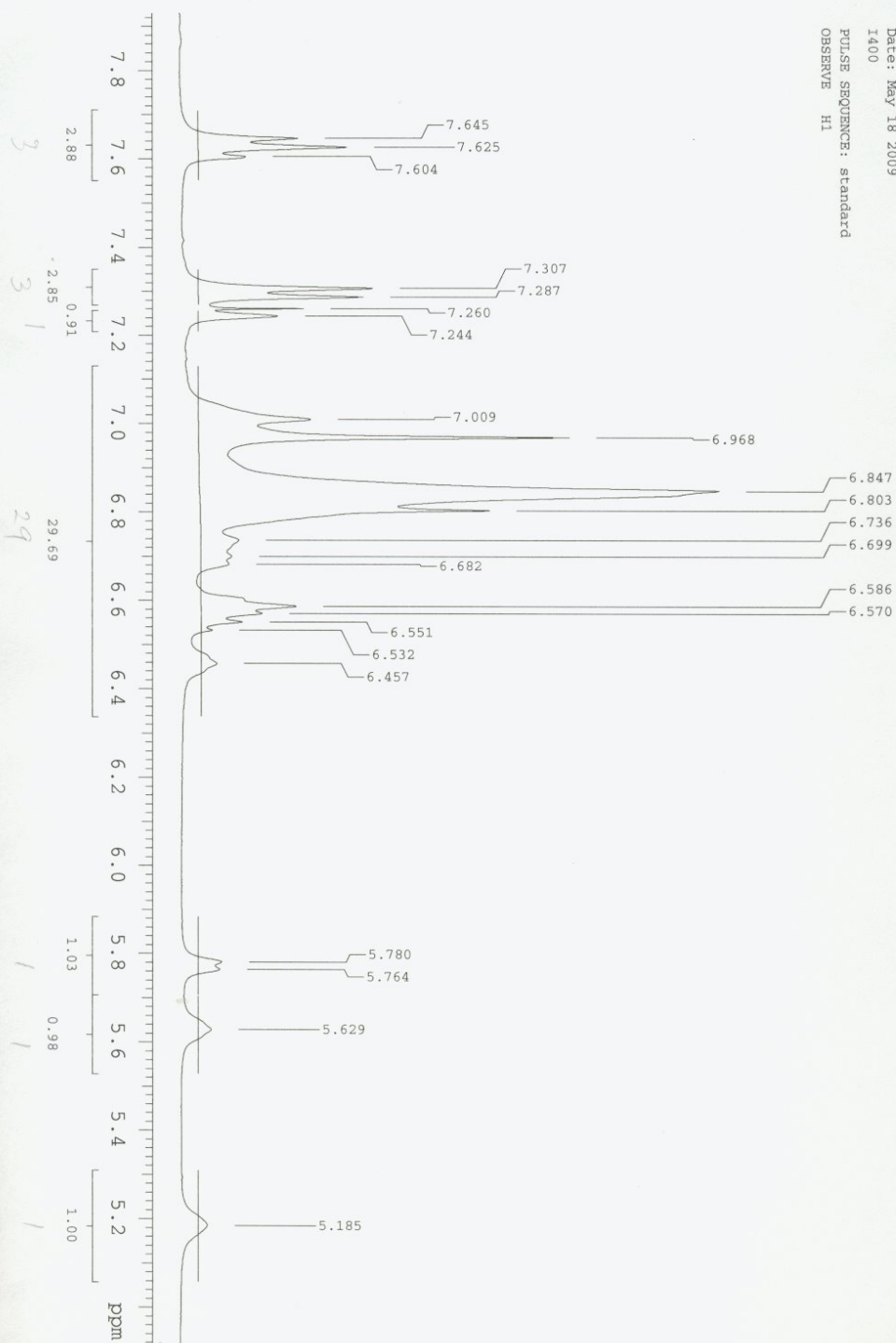
STANDARD 1H OBSERVE

Archive directory: /vxt400/vnmr1/vnmrSYS/data
 Sample directory:
 File: PROTON

Pulse Sequence: szpul

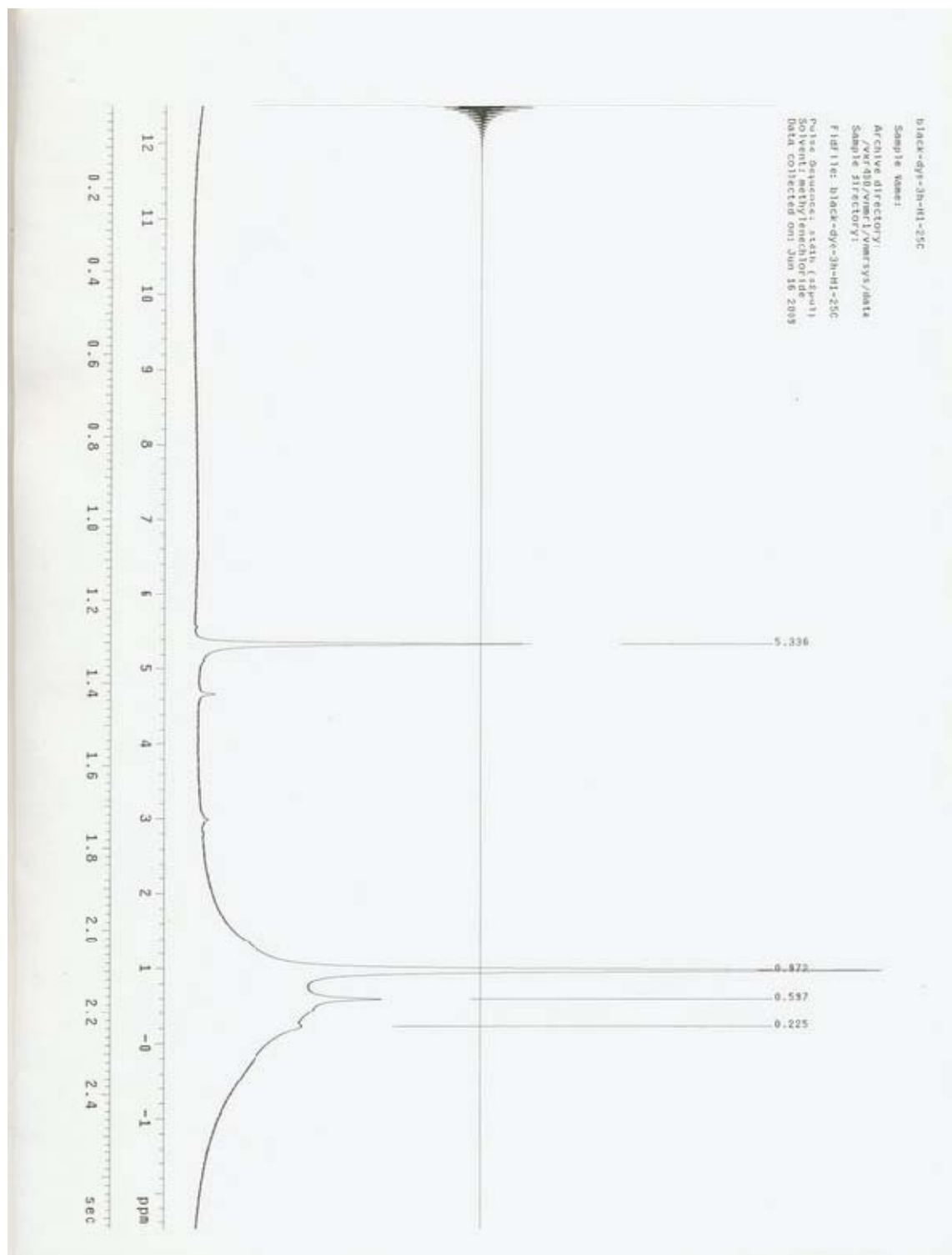
Date: May 18 2009
 1400

PULSE SEQUENCE: standard
 OBSERVE H1

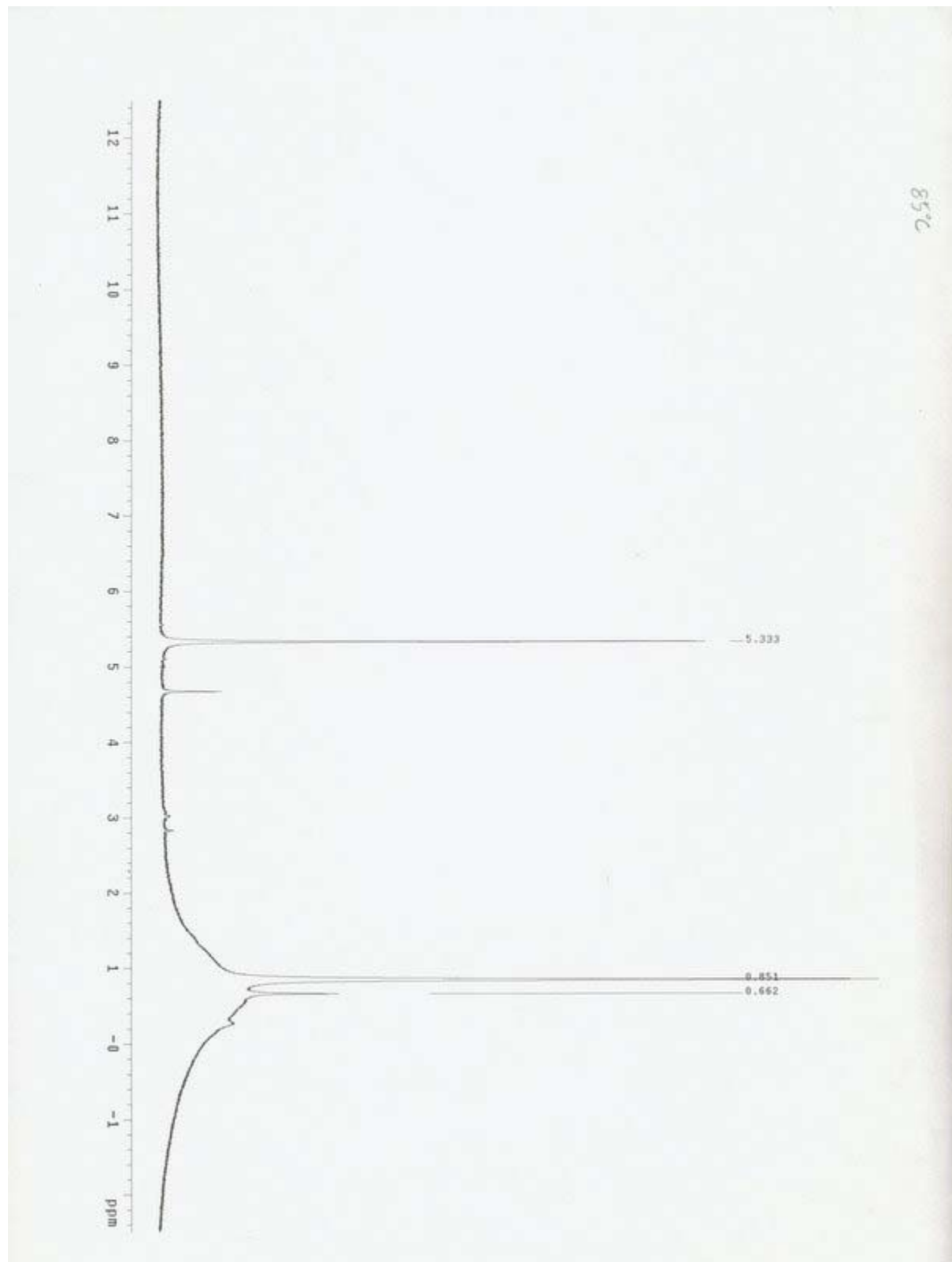


2) Compound 1

25 °C, in C₂D₂Cl₄, 400MHz

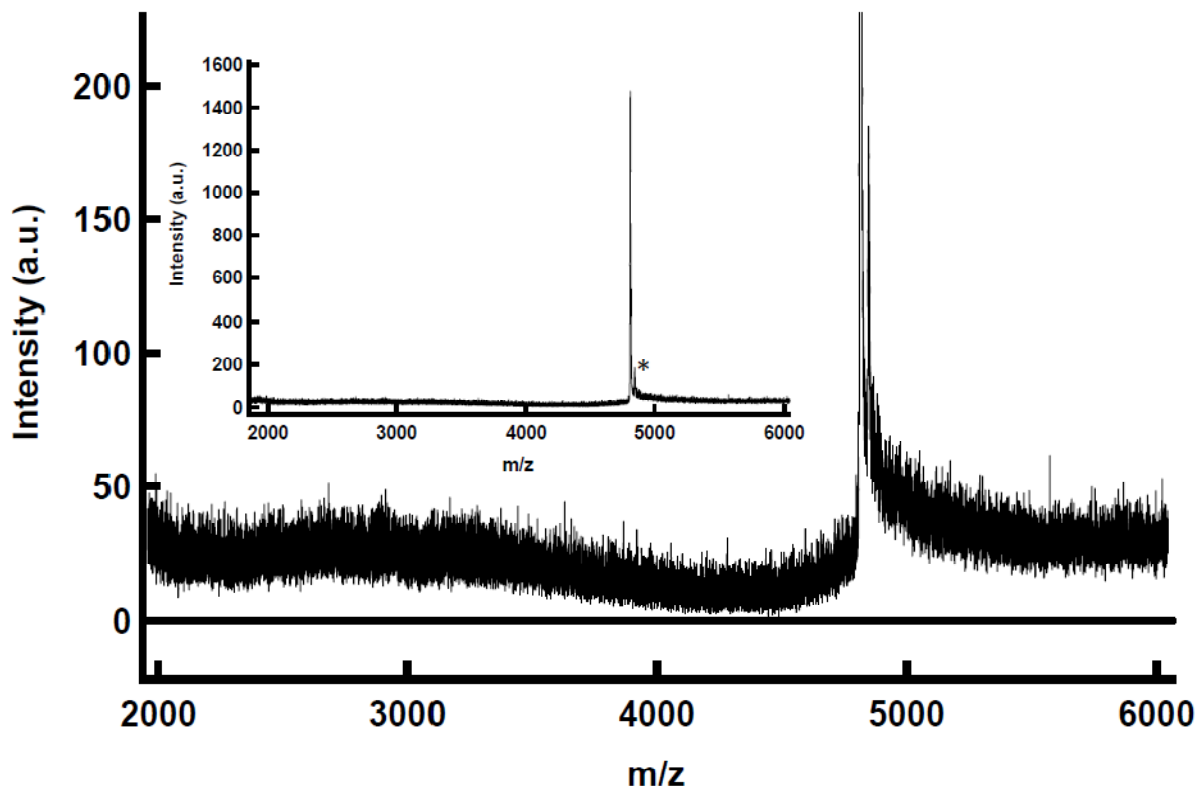


85 °C, in C₂D₂Cl₄, 400MHz



7. Amplified Baseline of MALDI-TOF Spectrum of 1

In the inset is the full spectrum shown in Fig. 3a. The baseline intensity is less than 2% of the main peak at $m/z = 4812$.



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