

Supporting Information for:

Electrical and electrochemical properties of lithium solvated electron solutions derived from 1,3,5-triphenylbenzenes

Andrey V. Lunchev¹, Kim Seng Tan¹, Andrew C. Grimsdale^{1*}, Rachid Yazami^{2*}.

1. *School of Materials Science and Engineering, Nanyang Technological University, Singapore, 50 Nanyang Avenue, Singapore 639798.*

2. *Energy Research Institute at Nanyang (ERIAN), Nanyang Technological University, 1 Cleantech Loop, CleanTech One 06-01, Singapore 637141*

*authors to whom correspondence should be addressed: acgrimsdale@ntu.edu.sg;

rachid@pmail.ntu.edu.sg

Synthetic procedures

General procedure for synthesis of 1,3,5-triphenylbenzene derivatives (1-4).

The synthesis was performed according to a literature procedure.[6] To a mixture of corresponding acetophenone and 100 ml of absolute ethanol, silicon tetrachloride (2.1 – 2.6 equivalents) was added in one portion at 0 °C under nitrogen. After the addition was completed and evolution of gaseous hydrogen chloride had finished, the reaction mixture was heated to 40 °C and stirred for 20 hours at this temperature. Then the reaction mixture was poured into ice-water. The resulting mixture was extracted twice with dichloromethane. The combined extracts were washed once with saturated NaCl solution, dried over anhydrous MgSO₄, and then concentrated. The crude product was purified either by recrystallization or by column chromatography.

1,3,5-triphenylbenzene (1, [TPB]). 4.0 g (33.3 mmol) of acetophenone, and 11.9 g (8.0 ml, 70.2 mmol, 2.1 eq.) of silicon tetrachloride were used. Purified via recrystallization from ethanol. Obtained 2.2 g (63% yield) of pale yellow crystals. ¹H-NMR (CDCl₃): δ= 7.41 (m, 3H), 7.50 (m, 6H), 7.72 (d, 6H, J = 7.33Hz), 7.80 (s, 3H). ¹³C-NMR (CDCl₃): δ= 125.21, 127.39, 127.57, 128.88, 141.18, 142.38

4,4''-dibutyl-5'-(4-butylphenyl)-1,1':3',1''-terphenyl (2, [C₄H₉TPB]). 4.0 g (22.8 mmol) of 1-(4-butylphenyl)ethan-1-one, and 8.9 g (6.0 ml, 52.3 mmol, 2.3 eq.) of silicon tetrachloride were used. Purified via column chromatography (hexane: dichloromethane 4:1). Obtained 3.1 g (86% yield) of a pale yellow waxy solid. ¹H-NMR (CDCl₃): δ= 0.96 (t, J = 7.33 Hz, 9H, CH₃), 1.41 (m, 6H, CH₂), 1.66 (m, 6H, CH₂), 2.68 (t, J = 7.58, 6H, Ar-CH₂), 7.29 (d, J = 8.34 Hz, 6H, Ar-H), 7.61 (d, J = 8.34 Hz, 6H, Ar-H), 7.74 (s, 3H, Ar-H). ¹³C-NMR (CDCl₃): δ= 13.99, 22.44, 33.67, 35.34, 124.62, 127.18, 128.89, 138.64, 142,17, 142,29

4,4''-dimethoxy-5'-(4-methoxyphenyl)-1,1':3',1''-terphenyl (3). 4.0 g (26.8 mmol) of 1-(4-methoxyphenyl)ethan-1-one, and 11.8 g (8.0 ml, 69.7 mmol, 2.6 eq.) of silicon tetrachloride were used. Purified via recrystallization from ethanol. Obtained 2.6 g (75% yield) of pale yellow crystals. ¹H-NMR (CDCl₃): δ= 3.87 (s, 9H, OCH₃), 7.01 (d, J = 8.59 Hz, 6H), 7.63 (d, J = 8.59 Hz, 6H), 7.66 (s, 3H). ¹³C-NMR (CDCl₃): δ= 55.39 (OCH₃), 114.27, 123.86, 128.37, 133.87, 141.85, 159.32.

4,4''-difluoro-5'-(4-fluorophenyl)-1,1':3',1''-terphenyl (4). 6.1 g (44.1 mmol) of 1-(4-fluorophenyl)ethan-1-one, and 11.8 g (12.0 ml, 104.6 mmol, 2.4 eq.) of silicon tetrachloride were used. Purified via recrystallization from ethanol. Obtained 3.4 g (63% yield) of pale yellow crystals. ¹H-NMR (CDCl₃): δ= 7.16 (m, 6H), 7.63 (m, 6H), 7.66 (m, 3H). ¹³C-NMR (CDCl₃): δ= 115.78 (d, J = 21.96 Hz, F-C-CH), 124.85, 128.89 (d, J = 8.78 Hz, F-C-CH-CH), 137.01, 141.54, 161.46, 163.91 (d, J = 246.63 Hz, F-C).

4,4''-diiodo-5'-(4-iodophenyl)-1,1':3',1''-terphenyl (7) 5.0 g (20.3 mmol) of 1-(4-iodophenyl)ethan-1-one, and 6.7 g (4.5 ml, 39.2 mmol, 1.9 eq.) of silicon tetrachloride were used. Purified via column chromatography (hexane: dichloromethane 4:1). Obtained 2.8 g (60% yield) of yellow crystals. ¹H-NMR (CDCl₃): δ= 7.33 (d, J = 8.34 Hz, 6H), 7.60 (s, 3H). ¹³C-NMR (CDCl₃): δ= 93.63, 124.93, 129.13, 138.03, 140.21, 141.61.

5'-(4-cyanophenyl)-[1,1':3',1''-terphenyl]-4,4''-dicyanitrile (5). A mixture of 4,4''-diiodo-5'-(4-iodophenyl)-1,1':3',1''-terphenyl (7, 5.5 g, 8.0 mmol), copper (I) cyanide (2.5 g, 27.6 mmol, 3.4 eq.)

and DMF (45 ml, freshly distilled from CaH₂) was refluxed under nitrogen for 24 hours. Then the reaction mixture was cooled down to 90 °C, and 100 ml of water together with 15 ml of 1,2-ethylenediamine was added. The mixture was extracted with DCM, the extract was dried over anhydrous MgSO₄ and then concentrated. Flash column chromatography (DCM) afforded 1.93 g (70% yield) of yellow crystals. ¹H-NMR (CDCl₃): δ= 7.74 – 7.84 (m, 12H + 3H). ¹³C-NMR (CDCl₃): δ= 111.95 (C-CN), 118.56 (CN), 126.37, 128.00, 132.86, 141.28, 144.56

4,4''-dinitro-5'-(4-nitrophenyl)-1,1':3',1''-terphenyl (6)

To a mixture of 4-nitroacetophenone (10.0g, 60.8mmol), and 30 ml of anhydrous ethanol, thionyl chloride (8.0 ml, 113.0 mmol) was added under nitrogen at room temperature. The rate of addition was adjusted in order not to allow the reaction temperature to increase above 50 °C. 4-nitroacetophenone became completely dissolved when all the thionyl chloride had been added, and after ca. 10 minutes the formation of a yellow precipitate was observed. The mixture was stirred at reflux for 12 hours, then cooled down to room temperature, and the yellow precipitate was separated and washed successively with ethanol, deionized water, diethyl ether, and ethanol. Recrystallization twice from dichloromethane gave 5.8 g of the product (65%). ¹H-NMR (DMSO-d₆): δ = 8.41 (6H, Ar-H), 8.30 (6H, Ar-H), 8.27 (3H, Ar-H) MALDI-TOF (%): 411.45 [M-NO] (46), 441.40 [M] (12), 465.05 [M+Na] (100)

Recovery of 1,3,5-triphenylbenzene (1) from Li_{2.0}TPB(THF)_{24.7}

In a glovebox, lithium (103.9 mg, 2.0 equivalents, 14.97mmol) was added to a mixture of triphenylbenzene (2.294g, 7.49 mmol) and 15ml of anhydrous THF. The bottle was sealed and the mixture stirred overnight. Then, the cap was replaced with a rubber seal, the bottle removed from the glovebox and connected to an argon line. A solution of iodine (1.95g, 7.81mmol) in THF (8 ml) was carefully added after cooling of the bottle with ice. After the solvent was evaporated, the mixture was redissolved in dichloromethane, washed with aqueous Na₂S₂O₃ solution, dried over MgSO₄, filtered, and evaporated. The resulting crude product was subject to NMR studies (see the Results and

Discussion section). The crude product was recrystallized from ethanol, giving 1,3,5-triphenylbenzene (1) (1.15 g, 50% recovery).

The crude residue recovered from $\text{Li}_{4.0}[\text{TPB}](\text{THF})_{24.7}$ was obtained in the same manner using 4 equivalents of iodine (3.95g, 15.8 mmol).