Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Knitting up 2,7-disubstituted Carbazole based oligomers through Supramolecular Interactions for their Application in Organic Thin Film Transistors

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All commercially available starting materials, reagents and solvents were used as supplied, unless otherwise stated, and were purchased from Acros Organics and Aldrich. All reactions were carried out under a dry nitrogen atmosphere and the temperatures were measured externally. Carbazole was recrystallized from toluene before use. *N*-Bromosuccinimide was recrystallized from water before use. For brominations using bromine no nitrogen was used to prevent contamination of the nitrogen line. DMF was dried over CaH_2 with stirring overnight followed by distillation under reduced pressure. THF and toluene were dried using sodium wire and benzophenone indicator. DCM was dried over calcium sulfate and distilled. Tetrabutylammonium bromide was used as the phase transfer catalyst (PTC). Reported yields are isolated yields. Purification of most intermediates and all final products was accomplished in most cases by gravity column chromatography, using silica gel. For qualitative purity tests of all intermediates and final products, a single spot (visualized using UV-light at 254 nm and 365 nm) was obtained. All materials were dried using a vacuum oven. Elemental analysis was used for quantitative purity checks of all final products. ^{1}H NMR spectra and ^{13}C NMR are reported in parts per million (PPM) relative to tetramethylsilane as an internal standard.

Synthesis of 1,4-bis(decyloxy)benzene (1).

A suspension of powdered KOH (24.0 g, 0.428 mol) and dry DMSO (120 mL) was stirred and degassed at room temperature for 60 min, and hydroquinone (5.51 g, 0.050 mol) and bromodecane (44.2 g, 0.200 mol) were added. The reaction mixture was then stirred for overnight at room temperature and finally poured into ice water (500 mL). The organic layer was collected and the aqueous layer was extracted with hexane (3 × 100 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated to give a yellow to brown oil. This oil was further dissolved in THF and on dropping this solution in methanol gave the white solid pure compound 1,4-bis(decyloxy)benzene (17.55 g, 90%).

^{1}H NMR (300 MHz, $CDCl_3$), δ(ppm): *δ* 6.83 (s, 4H, Ar-C<u>H</u>), 3.91 (m, 4H, the two –OC<u>H$_2$</u>), 1.79 (m, 4H, the two -OCH$_2$C<u>H$_2$</u>), 1.48 (m, 4H, the two -O(CH$_2$)$_2$C<u>H$_2$</u>), 1.29 (br, 24H, the two -O(CH$_2$)$_3$(C<u>H$_2$</u>)$_6$CH$_3$),0.88 (m, 6H; the two –O(CH$_2$)$_9$C<u>H$_3$</u>).

^{13}C NMR (300 MHz, $CDCl_3$) δ(ppm): *δ* 153.20, 115.39, 68.67, 31.90, 29.58, 29.42, 29.33, 26.07, 22.69, 14.12

Synthesis of 1,4-Bis(decyloxy)-2,5-diiodobenzene (2).

1,4-Bis-(decyloxy)benzene **[1]** (10 g, 0.0256 mol), KIO_3 (6.00 g, 0.0280 mol), and I_2 (3.30 g, 0.026 mol) were added to a stirred solution of acetic acid (90 mL), 96% H_2SO_4 (20 mL), and H_2O (20 mL). The reaction mixture was stirred at room temperature for 16 hour. The reaction mixture was filtered to get the crude product. It was dissolved in ethyl acetate (100 ml) and washed sequently with concentrated sodium sulphite solution (50%, 75 ml) and brine solution (75 ml). The organic layer was dried with $MgSO_4$ and concentrated to get a white solid product (2). It was further purified by dissolving in THF and re-precipitating it from methanol to get a white solid pure product (2), Yield (15.2 g, 92.4%)

^{1}H NMR (300 MHz, $CHCl_3$), δ(ppm): δ 7.18 (s, 2H, Ar-C<u>H</u>), 3.94 (m, 4H, the two –OC<u>H</u>$_2$),1.83 (m, 4H, the two -OCH$_2$C<u>H</u>$_2$), 1.48 (m, 4H, the two -O(CH$_2$)$_2$C<u>H</u>$_2$), 1.29 (br, 24H, the two -O(CH$_2$)$_3$(C<u>H</u>$_2$)$_6$CH$_3$), 0.88 (m, 6H, the two –O(CH$_2$)$_9$C<u>H</u>$_3$).

^{13}C NMR (300 MHz, $CHCl_3$), δ(ppm): δ 152.87, 122.79, 86.32, 70.37, 31.92, 29.57, 29.30, 29.16, 26.04, 22.70, 14.14

Synthesis of 4-(2,5-bisdecyloxy-4-iodophenyl)-2-methylbut-3-yn-2-ol (3)

To a degassed solution of dry Et_3N (45 mL) and THF (45 mL), 1,4-bis(decyloxy)-2,5-diiodobenzene[2] (10.0 g, 0.01557 mol), [$Pd(PPh_3)_4$] (0.150 mmol, 105 mg), and CuI (4.00 mmol, 762 mg) were added and the mixture degassed a second time. 2-methyl-3-butyn-2-ol (1.50 mL, 0.01557 mol) was then added and the reaction mixture degassed one last time, before allowing the whole to stir overnight at r.t. under Ar. The crude mixture was then filtered over celite, concentrated under vacuum and purified by CC EA/Hexane (20%) yielding [3] (4.2 gm, 45.6%) as a colorless viscous oil.

^{1}H NMR (300 MHz, $CHCl_3$), δ(ppm): δ 7.26 (s, 1H, Ar-CH), 6.81 (s, 1H, Ar-CH), 3.94 (m, 4H, the two –OC<u>H</u>$_2$), 1.79 (m, 4H, the two -OCH$_2$C<u>H</u>$_2$), 1.48 (m, 4H, the two -O(CH$_2$)$_2$C<u>H</u>$_2$), 1.28 (br, 24H, the two -O(CH$_2$)$_3$(C<u>H</u>$_2$)$_6$CH$_3$), 0.87 (m, 6H, the two –O(CH$_2$)$_9$C<u>H</u>$_3$).

^{13}C NMR (300 MHz, $CHCl_3$), δ(ppm): δ 154.37, 151.76, 123.74, 116.16, 113.00, 98.58, 87.45, 70.11, 69.73, 65.75, 31.91, 31.42, 29.63, 29.57, 29.39, 29.32, 29.18, 26.06, 25.99, 22.69, 14.13

Synthesis of 4,4'-Dibromo-2-nitrobiphenyl (4)

4,4'-Dibromobiphenyl (20 g, 64 mmol), in 300 mL glacial acetic acid was heated (100 ^{o}C) to dissolve completely then 90 mL of fuming nitric acid was added drop wise for a period of 30 min. The resulting mixture was further stirred vigorously for 1 h at 100 ^{o}C to get a reddish brown precipitate. The reaction mixtures were cooled to room temperature and poured into ice cold water.

The precipitate was filtered and washed with excess of water then the obtained product was further purified by recrystallization from ethanol to get a yellow solid (20.30 g, 88.72%).

^{1}H NMR (300 MHz, $CDCl_3$), δ(ppm): δ 8.04 (d, J = 3 Hz, 1H), 7.76 (dd, J = 9 Hz, J = 3.0Hz 1H), 7.59 (d, J = 9.0 Hz, 2H), 7.29 (d, J = 9 Hz, 2H), 7.16 (d, J = 6 Hz, 2H).

^{13}C NMR (300 MHz, $CHCl_3$), δ(ppm): δ 149.26, 135.58, 135.30, 134.15, 133.04, 132.04, 129.42, 127.28, 123.08, 121.84

2,7-Dibromocarbazole (5)

Mixture of compound **[4]** (20 gm, 56.02 mmol) and triphenyl phosphine (36.73 gm, 140.05 mmol) were dissolved in 220 ml of dichlorobenzene and the reaction mixture was refluxed for 12 h. The excess dichlorobenzene ware removed by high vacuum distillation and the residue was purified by column chromatography (silica) using a mixture of hexane: ethyl acetate (7:3) to get a white solid (12.90 g, 70.87%).

^{1}H NMR (300 MHz, $CDCl_3$: DMSO, 3:1), δ(ppm): δ 10.59 (br, 1H), 7.63 (d, J = 8.7 Hz, 2H), 7.41 (d, J = 1.5 Hz, 2H), 7.08 (dd, J =1.8 Hz, J =8.4 Hz, 2H).

^{13}C NMR (300 MHz, $CHCl_3$), δ(ppm): δ 140.90, 122.09, 121.26, 121.17, 119.05,113.96

2,7-Dibromo-*N*-(2-ethylhexyl)carbazole (6)

2,7-Dibromocarbazole **[5]** (6.50 g, 0.0155 mol), Bu_4NBr (0.50 g) and 2-ethylhexyl bromide (25.0 g, 0.13 mol) were dissolved in toluene–DMSO (80:35 mL) under argon. Aq 50% NaOH (120 mL) was added and the reaction mixture was heated at 80 °C for 3 hr under vigorous stirring. The toluene–DMSO layer was separated and the aq NaOH layer was extracted with toluene (2 × 70 mL). The combined organic layers were washed with brine (2 × 100 mL) and dried ($MgSO_4$). The solvents were evaporated under vacuum (95 °C) and the yellow crystalline material obtained was dissolved in hot toluene (20 mL) and chromatographed on silica gel using toluene–heptane (1:1,

v/v) as eluent. The nicely separated fractions of the product **[6]** (5.65 gm, 70.2 %) were combined, evaporated, and crystallized from EtOH.

^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): *δ* 7.89 (d, *J* = 8.1 Hz, 2 H_{arom}), 7.52 (s, 2 H_{arom}), 7.36 (d, *J* = 6.9 Hz, 2 H_{arom}), 4.07 (m, 2 H, NCH_2), 2.04 (m, 1 H, =CH), 1.31 (m, 8 H, 4 × CH_2), 0.89 (t, *J* = 14.7 Hz, 6H, 2 × CH_3).

^{13}C NMR (300 MHz, $CDCl_3$) δ(ppm): *δ* 141.84, 122.52, 121.42, 121.24, 119.65, 112.30, 47.69, 39.14, 30.77, 28.54, 24.32, 23.03, 14.01, 10.89

Synthesis of 2,7-bis(2-methylbut-3-yn-2-ol)-9-(2-ethylhexyl)carbazole (7)

[6] (3.48 g, 6.70 mmol) was dissolved in triethylamine (15 ml) and THF (15 ml). This solution was degassed for 30 minutes and then [$Pd(PPh_3)_4$] (0.060 mmol, 70 mg), and CuI (0.25 mmol, 47.5 mg) were added and the mixture degassed a second time. 2-methyl-3-butyn-2-ol (1.68 ml, 20.1 mmol) was then added and the reaction mixture degassed one last time, before allowing the whole to stir overnight at r.t. under Ar. The crude mixture was then filtered over celite, concentrated under vacuum and purified by CC hexane/ethylacetate [(2/1) (v/v)] as an eluent (TLC R_f = 0.52). **[7]** (2.34 gm, 77.5 %) as a colorless viscous oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): *δ* 7.99 (s, 2H, Ar – H), 7.45 (d, 2H, Ar– H), 7.31 (d, 2H, Ar– H), 4.12 (d, 2H, – NCH_2–), 2.11 (m, 1H, – CH–), 2.11 (br, 1H, two – $(CH_3)_2$ –O<u>H</u>), 1.69 (s, 12 H, two -(C<u>H</u>$_3)_2$ –OH), 1.51–1.18 (s, br, 8H, – CH_2 –), 0.93–0.82 (s, br 6H, – CH_3).

^{13}C NMR (300 MHz, $CDCl_3$) δ(ppm): *δ* 141.05, 122.88, 122.42, 120.30,129.88, 112.39, 93.47, 83.37, 65.80, 47.59, 39.15, 31.59, 30.76, 28.56, 24.38, 23.06, 14.08, 10.96

Synthesis of 2,7-Diethynyl-9-(2-ethylhexyl)carbazole (8)

Sodium hydride (60 *wt* %, 1.55 g, 38.8 mmol) was added to a toluene solution (25 ml) of **[7]** (2.34 g, 5.42 mmol), and the mixture was heated to 100ºC with stirring for 2h. After the usual work up,

the product was purified with silica-gel chromatography using purified by CC hexane/ethylacetate [(2/1) (v/v)] as an eluent. (TLC R_f = 0.88). Pale-yellow viscous liquid was obtained in 74.2% yield (1.27 g).

^{1}H NMR (300.1 MHz, $CDCl_3$) δ(ppm): δ 8.22 (d, 2H, Ar – H), 7.61 (s, 2H, Ar– H), 7.34 (d, 2H, Ar– H), 4.16 (d, 2H, – NCH_2–), 3.08 (s, 2H, alkyne–H), 2.04 (m, 1H, – CH–), 1.51–1.18 (s, br, 8H, – CH_2–), 0.93–0.82 (s, br 6H, – CH_3).

^{13}C NMR (300 MHz, $CDCl_3$) δ(ppm): δ 141.00, 123.22, 122.78, 120.46, 119.32, 113.03, 84.92, 47.58, 39.24, 30.24, 30.85, 28.62, 24.36, 23.05, 14.02, 10.91

Synthesis of 4,4'-(4,4'-(9-(2-ethylhexyl)-8a,9-dihydro-4bH-carbazole-2,7-diyl)bis(ethyne-2,1-diyl)bis(2,5-bis(decyloxy)-4,1-phenylene))bis(2-methylbut-3-yn-2-ol) (9)

[8] (1.27 g, 3.89 mmol) was dissolved in triethylamine (15 ml) and THF (15 ml). This solution was degassed for 30 minutes and then [$Pd(PPh_3)_4$] (0.055 mmol, 65 mg), and CuI (0.22 mmol, 42.3 mg) were added and the mixture degassed a second time. **[3]** (4.65 gm, 7.78 mmol) was then added and the reaction mixture degassed one last time, before allowing the whole to stir overnight at r.t. under Ar. The crude mixture was then filtered over celite, concentrated under vacuum purified CC with hexane/EA [(5/1) (v/v)] as an eluent. The compound **[9]** is obtained as yellow solid (3.0 gm, 60.7%).

^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): δ 8.03 (d, 2H, Ar – H), 7.57 (s, 2H, Ar– H), 7.41 (d, 2H, Ar– H), 7.05 (s, 2H, Ar– H), 6.95 (s, 2H, Ar– H), 4.15 (d, 2H, – NCH_2–), 4.02 (m, 8H, the four – $OC\underline{H}_2$), 2.12 (br, 1H, two – $(CH_3)_2$ –O$\underline{H}$), 2.04 (m, 1H, – CH–), 1.51–1.18 (s, br, 8H, – CH_2–), 1.79 (m, 8H, the four -$OCH_2C\underline{H}_2$), 1.48 (m, 8H, the four -$O(CH_2)_2C\underline{H}_2$), 1.28 (br, 48H, the four-$O(CH_2)_3(C\underline{H}_2)_6CH_3$), 0.93–0.82 (s, br 6H, two – CH_3), 0.87 (m, 12H, the four –$O(CH_2)_9C\underline{H}_3$).

^{13}C NMR (300 MHz, $CDCl_3$) δ(ppm): δ 153.70, 153.58, 123.00, 122.58, 120.62, 120.33, 117.20, 116.79, 114.21, 113.21, 112.22, 99.21, 96.25, 85.77, 78.58, 69.68, 69.49, 65.79, 47.72, 39.25, 31.90, 31.47, 30.94, 29.68, 29.61, 29.44, 29.36, 28.69, 28.69, 26.06, 24.41, 23.09, 22.68, 14.10, 10.95

Synthesis of 2,7-bis((2,5-bis(decyloxy)-4-ethynylphenyl)ethynyl)-9-(2-ethylhexyl)-8a,9-dihydro-4bH-carbazole (10)

[9] (3.0 gm, 2.36 mmol) was dissolved in dry toluene and temperature of the reaction mixture is raised to 100 ^{o}C. At this stage, NaOH powder (1 gm, 25 mmol) is added and refluxed for 1 hour. The reaction mixture is cooled down and filtered to remove solid NaOH. The filtrate is evaporated and re-dissolved in EA and this organic layer is washed with water (acidified with HCl) and brine solution. The organic layer is dried over $MgSO_4$ and it is finally evaporated under vacuum. The remaining residue is dissolved in THF and re-precipitated from MeOH, two times to get reddish color compound **[10].** (1.80 gm, 52.7 %)

^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): δ 8.03 (d, 2H, Ar – H), 7.57 (s, 2H, Ar– H), 7.42 (d, 2H, Ar– H), 7.05 (s, 2H, Ar– H), 6.95 (s, 2H, Ar– H), 4.17 (d, 2H, $-NCH_2-$), 4.05 (m, 8H, the four $-OC\underline{H}_2$), 3.37 (s, 2H, two alkyne-H), 2.04 (m, 1H, – CH–), 1.51–1.18 (s, br, 8H, $-CH_2-$), 1.79 (m, 8H, the four $-OCH_2C\underline{H}_2$), 1.48 (m, 8H, the four $-O(CH_2)_2C\underline{H}_2$), 1.28 (br, 48H, the four $-O(CH_2)_3(C\underline{H}_2)_6CH_3$), 0.93–0.82 (br, 6H, two– CH_3), 0.87 (m, 12H, the four $-O(CH_2)_9C\underline{H}_3$).

^{13}C NMR (300 MHz, $CDCl_3$) δ(ppm): δ 154.23, 153.48, 141.22, 123.02, 122.62, 120.56, 120.35, 117.87, 116.83, 114.88, 112.45, 112.26, 96.44, 93.37, 85.64, 82.29, 80.07, 69.68, 47.71, 39.26, 37.11, 31.91, 30.94, 30.05, 29.69, 29.60, 29.43, 29.35, 29.19, 28.69, 27.10, 26.05, 25.94, 24.41, 23.09, 22.69, 14.12, 14.10, 10.95

Synthesis of 3-(*N*-propargyl) uracil (11)

To a stirred solution of uracil (10 gm, 89.28 mmol) in dry acetonitrile was added 1,8-diazabicyclo[5.4.0]undec-7-ene, DBU (15 ml) and solution becomes clear. After this the clear solution was kept in ice bath and the propargyl bromide (80 *wt* % in toluene) (5.310 gm, 44.64 mmol) was added drop wise under nitrogen atmosphere. The reaction mixture was stirred overnight at room temperature. The acetonitrile was evaporated under vacuum and the remaining residue was dissolved in ethylacetate (100 ml) and washed with aq. (NH_4Cl) solution (5%, 80 ml). The organic phase was dried and concentrated and purified by CC with ethyl acetate as eluent (R_f = 0.50) to get white color compound **[11],** (5.25 gm, 43.2 %)

^{1}H NMR (300 MHz, $CDCl_3$: DMSO, 3:1) δ(ppm): δ 11.38 (s, -NH), 7.46 (d, J = 8.0 Hz, 1H, -NCH), 5.83 (d, J = 8.0Hz, 1H, -CH), 4.59 (s, J = 2.6 Hz, 2H, -CH_2), 2.50 (t, J = 2.5 Hz, 1H, =C-H)

^{13}C NMR (300 MHz, $CDCl_3$: DMSO, 3:1) δ(ppm): δ 164.04, 150.74, 143.30, 102.52, 75.38,

MS (EI): m/z 150.0 [M^+]

Synthesis of Tris(4-Iodophenyl)amine (12)

To a stirred solution of Triphenylamine (10 gm, 40 mmol) and KI (13.5 gm, 80 mmol) in 340 ml of acetic acid with 30 ml of distilled water at 80 ^oC was added KIO_3 (12 gm, 56 mmol). After stirring at 50 ^oC for 6 hr, the mixture was poured into distilled water to induce precipitation of crude product. The precipitates are filtered off and recrystallize with chloroform to give (22.8 gm, 69 %) of white product **[12]**.

^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): δ 7.54 (d, J = 8.8 Hz, 6H), 6.82 (d, J = 8.8 Hz, 6H)

^{13}C NMR (300 MHz, $CDCl_3$) δ(ppm): δ 146.57, 138.48, 126.08

Synthesis of 1,1'-(3,3'-(4,4'-(4-iodophenylazanediyl)bis(4,1-phenylene))bis(prop-2-yne-3,1-diyl))dipyrimidine-2,4(1H,3H)-dione, TPAU2 (13)

[12] (3 gm, 4.81 mmol), was dissolved in THF (10 ml) and TEA (10 ml). This solution was degassed and after adding [$Pd(PPh_3)_4$] (0.060 mmol, 70 mg), and CuI (0.25 mmol, 47.5 mg) the reaction mixture, was degassed second time. **[11]** (1.310 gm, 9.63 mmol) was introduced and reaction mixture was finally degassed third time and allowed to stir at 60 ^oC overnight under N_2 atmosphere. The reaction mixture was filtered through celite and purified CC with THF/hexane [(1/2) (v/v)] as an eluent. The compound **[13]** is obtained as bright yellow fluffy compound (0.88 gm, 27.4 %)

^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): *δ* 8.5 (s, 2H, two -NH), 7.79 (d, 2H, J = 8.7 two -NCH), *δ* 7.61 (d, J = 8.1, 2H), 7.36 (d, J = 8.7, 4 H), 7.57 (d, J = 8.7, 2H), 7.02 (d, J = 8.7, 4H), 6.87 (d, 2H, J = 8.7 two -CH), 5.81 (d, J = 2.4 Hz, 2H, two -CH_2), 4.79 (s, 2H, two -C= CH-)

^{13}C NMR (300 MHz, $CDCl_3$) δ(ppm): *δ* 160.80, 147.83, 144.82, 143.63, 140.14, 136.14, 130.69, 124.52, 120.95, 113.37, 100.26, 85.20, 84.56, 78.09, 35.40

Mass Spectra : FAB MS^+, M^+ 667.9 (Calculated 667.07)

Synthesis of 1,1',1'',1'''-(3,3',3'',3'''-(4,4',4'',4'''-(4,4'-(4,4'-(9-(2-ethylhexyl)-9H-carbazole-2,7-diyl)bis(ethyne-2,1-diyl)bis(2,5-didecyl-4,1-phenylene))bis(ethyne-2,1-diyl)bis(4,1-phenylene))bis(azanetriyl)tetrakis(4,1-phenylene))tetrakis(prop-2-yne-3,1-diyl))tetrauracil (CbzTPAU2)

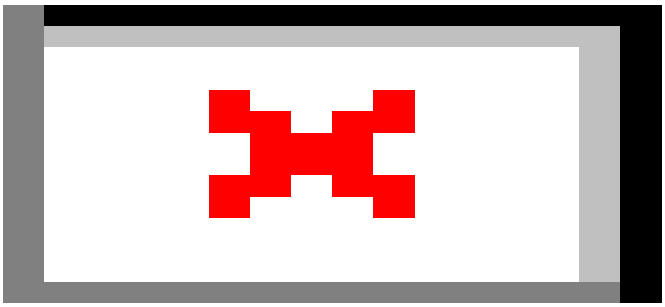
[13] (0.10 gm, 4.81 mmol), was dissolved in THF (6 ml) and TEA (6 ml). This solution was degassed and after adding [$Pd(PPh_3)_4$] (11 mg, 0.01 mmol) and CuI (1mg, 0.006 gm) the reaction mixture, was degassed second time. **[10]** (0.115 gm, 1.724 mmol) was introduced and reaction mixture was finally degassed third time and allowed to stir at 60 ^oC overnight under N_2 atmosphere. The reaction mixture was filtered through celite and purified by many precipitations from THF in

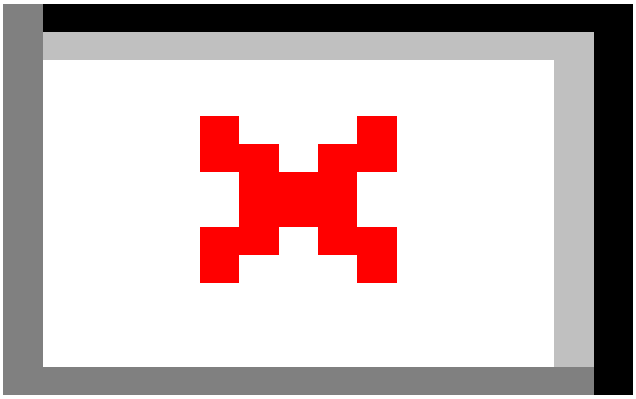
hexane. The compound **[13]** is obtained as bright red compound with brownish tinge (0.115 gm, 82.0 %)

^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): δ 8.0 (br, 4H, four -NH), 8.03 (d, 2H, J = 8.4, Ar – H), 7.61 (d, 4H, J = 9, four -NC<u>H</u>), 7.55 (d, J = 8.1, 4H, Ar-H), 7.53 (s, 2H, Ar-H), 7.42 (d, 2H, Ar-H), 7.36 (d, J = 8.7, 8H, Ar-H), 7.57 (d, J = 8.7, 4H, Ar-H), 7.02 (d, J = 8.7, 8H, Ar-H), 6.93 (d, 4H, J = 8.7, four -CH), 6.87 (s, 2H, Ar– H), 6.76 (s, 2H, Ar– H), 5.81 (d, 4H, J = 8.1 four -CH), 4.79 (s, 8H, four -C<u>H$_2$</u>), 4.17~4.05 (m, 10H, – NCH_2–, the four –OC<u>H$_2$</u>), 2.04 (m, 1H, – CH–), 1.51–1.18 (s, br, 8H, – CH_2–), 1.79 (m, 8H, the four -OCH_2C<u>H$_2$</u>), 1.48 (m, 8H, the four -$O(CH_2)_2C$<u>H$_2$</u>), 1.28 (br, 48H, the four -$O(CH_2)_3(C$<u>H$_2$</u>$)_6CH_3$), 1.31 (m, 8 H, 4 × CH_2), 0.89 (t, J = 14.7 Hz, 6H, 2 × CH_3), 0.93–0.82 (br, 6H, – CH_3), 0.87 (m, 12H, the four –$O(CH_2)_9C$<u>H$_3$</u>).

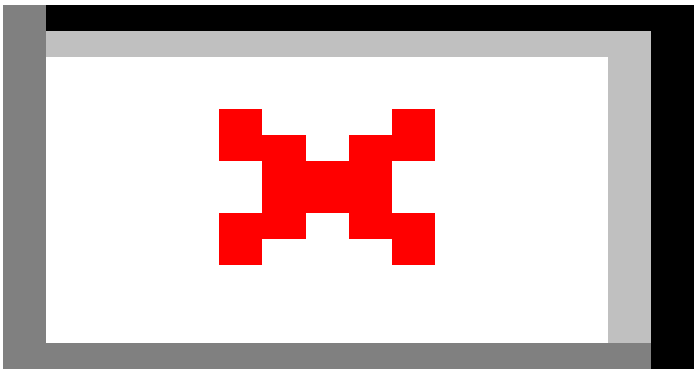
^{13}C NMR (300 MHz, $CDCl_3$) δ(ppm): δ 162.91, 150.14, 142.65, 138.69, 133.23, 133.09, 129.73, 127.07, 125.82, 123.49, 123.13, 102.74, 69.84, 69.68, 37.97, 31.89, 29.36, 26.06, 25.97, 22.69 14.11, (peaks in aliphatic region is missing possibly due to overlap)

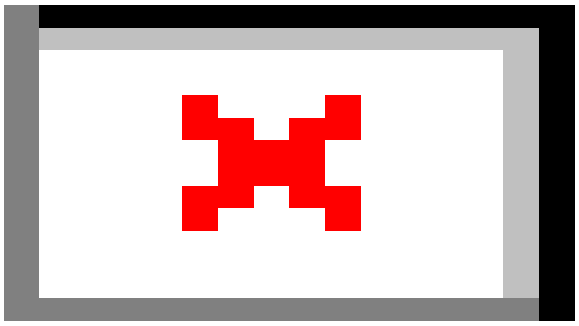
Mol. 1: ^{1}H-NMR and ^{13}C-NMR



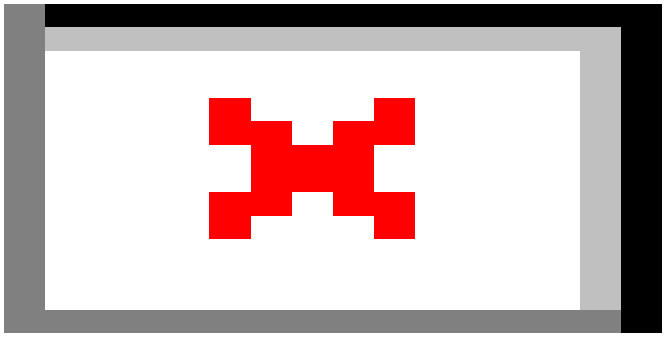


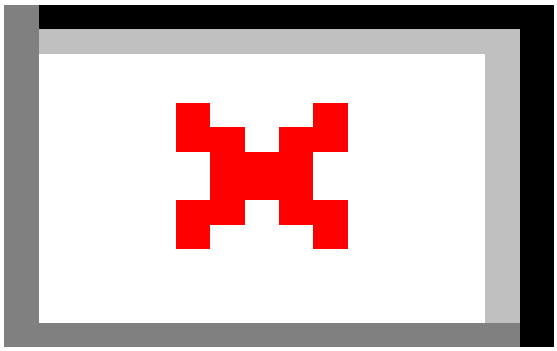
Mol. 2: ^{1}H-NMR and ^{13}C-NMR



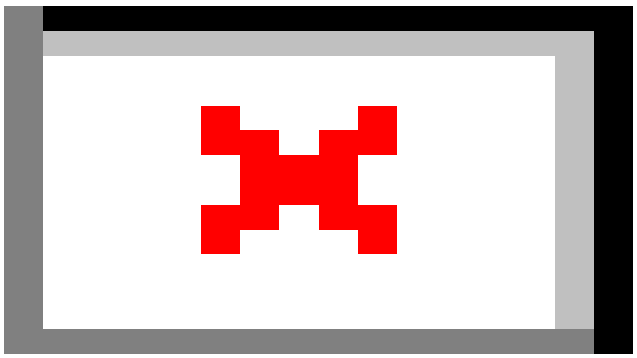


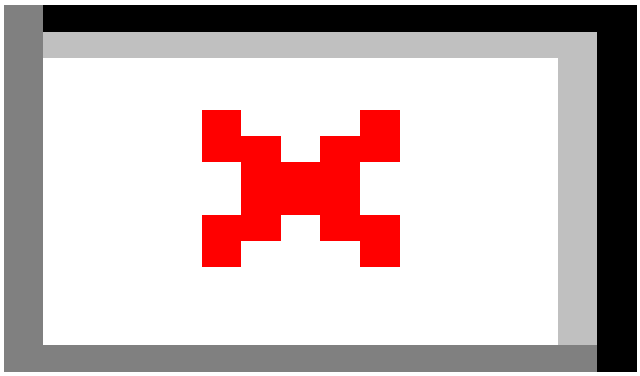
Mol. 3: ^{1}H-NMR and ^{13}C-NMR



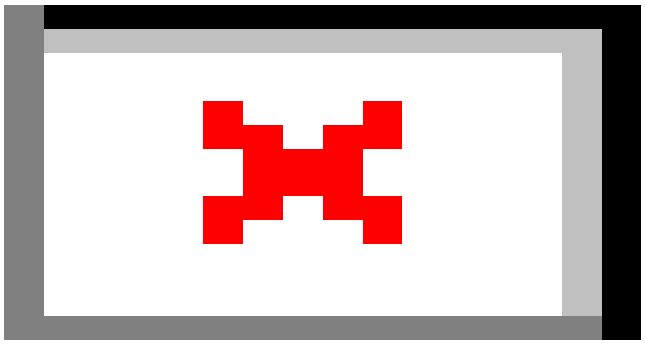


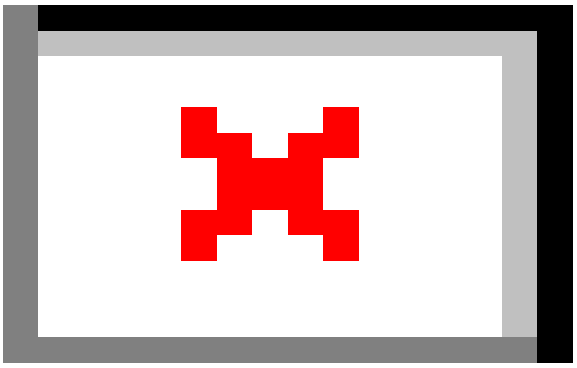
Mol. 4: ^{1}H-NMR and ^{13}C-NMR



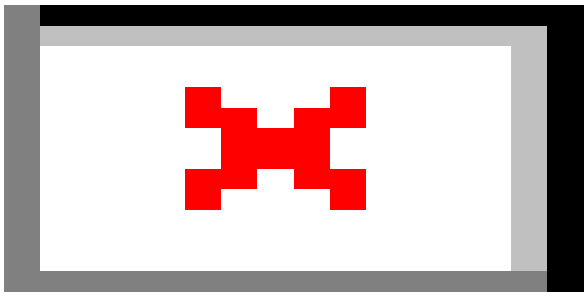


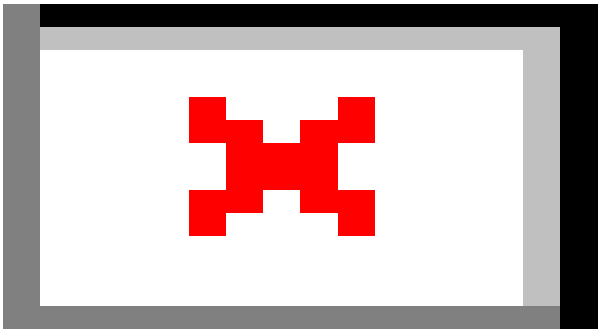
Mol. 5: ^{1}H-NMR and ^{13}C-NMR



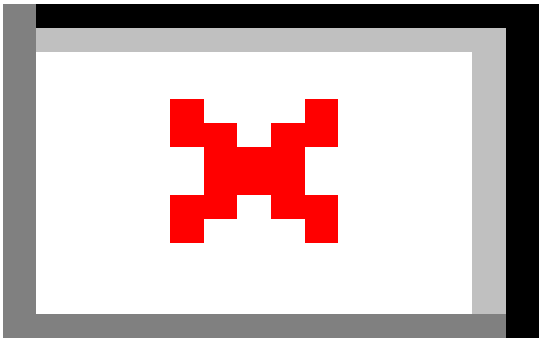


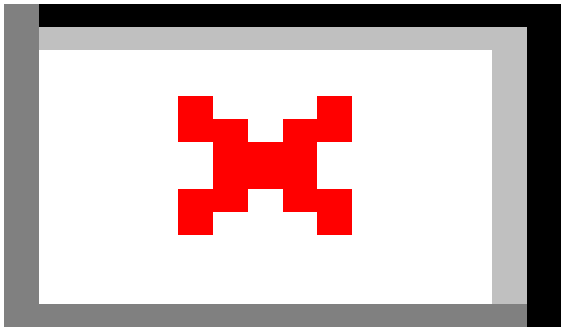
Mol. 6: ^{1}H-NMR and ^{13}C-NMR



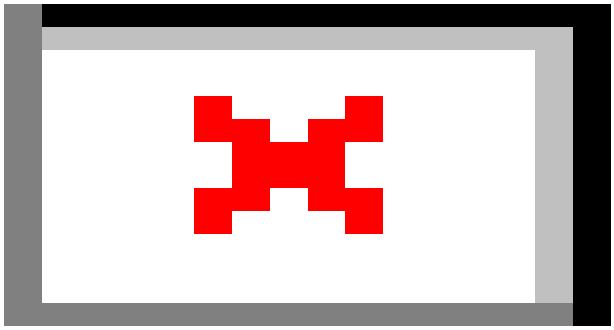


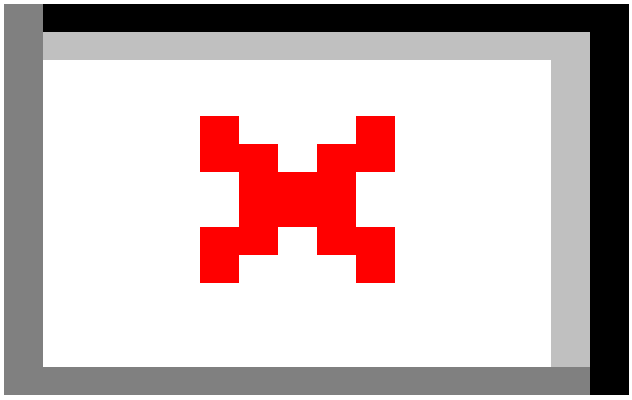
Mol. 7: ^{1}H-NMR and ^{13}C-NMR



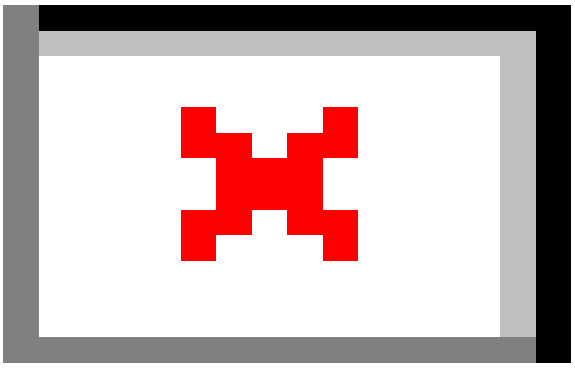


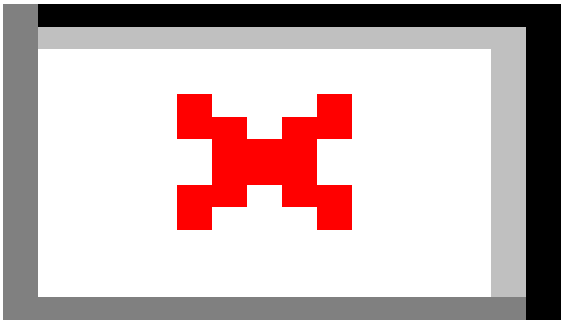
Mol. 8: ^{1}H-NMR and ^{13}C-NMR



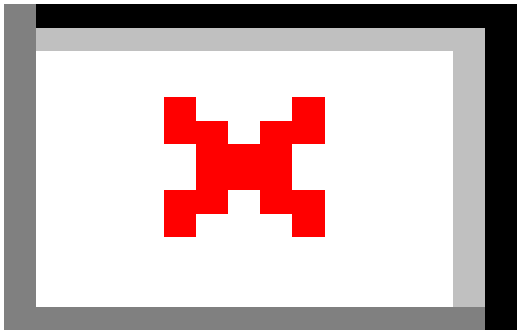


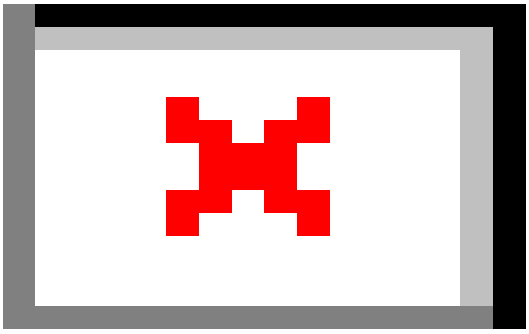
Mol. 9: ^{1}H-NMR and ^{13}C-NMR



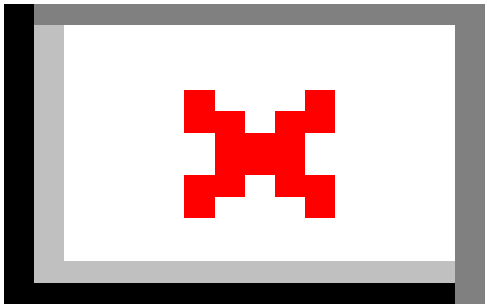


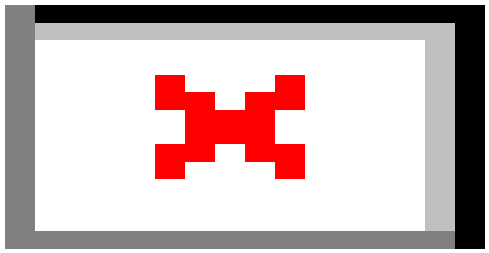
Mol. 10: ^{1}H-NMR and ^{13}C-NMR



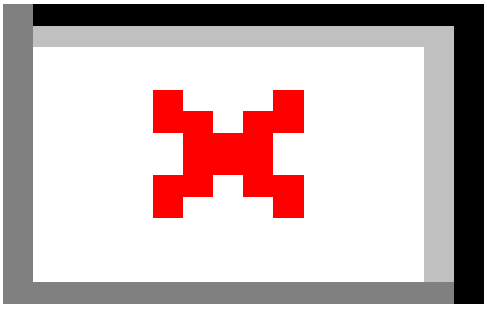


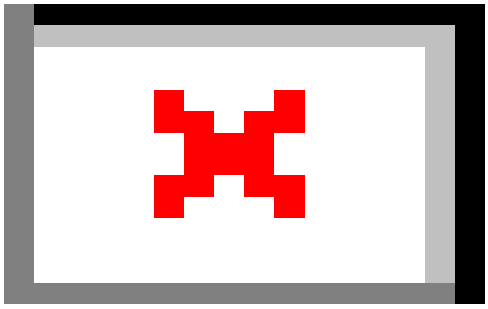
Mol. 11: ^{1}H-NMR and ^{13}C-NMR



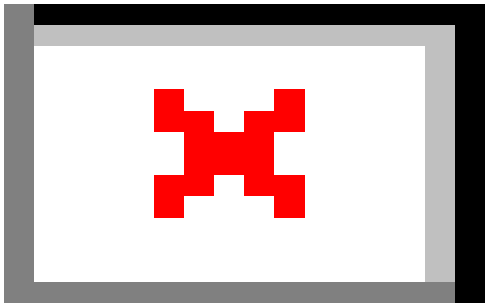


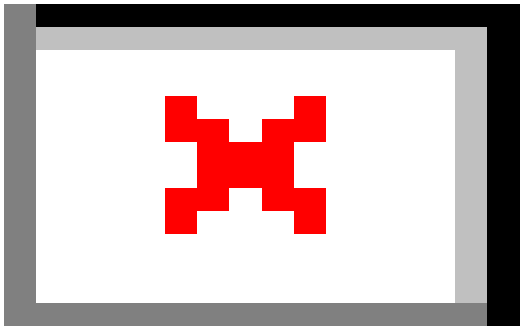
Mol. 12: ^{1}H-NMR and ^{13}C-NMR



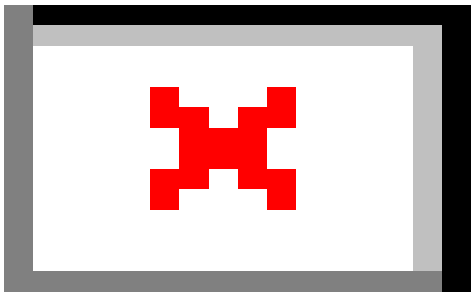


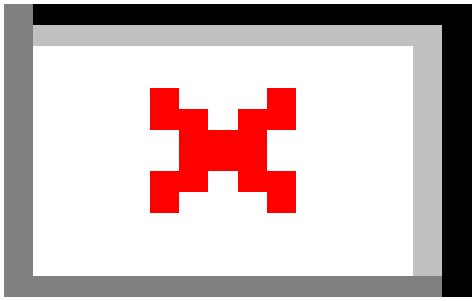
Mol. 13: ^{1}H-NMR and ^{13}C-NMR



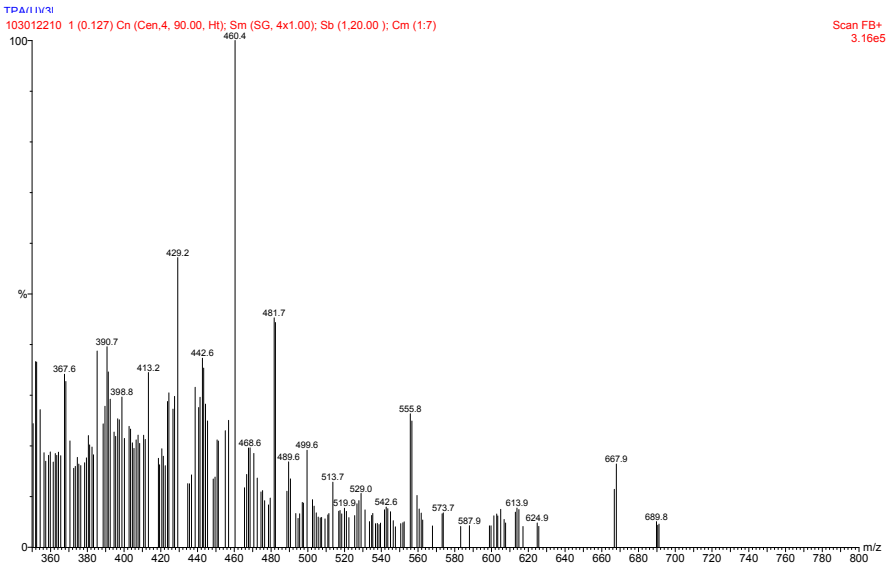


^{1}H NMR and ^{13}C NMR of CbzTPAU2





Mass Spectra of TPAU2 (13)



Mass Spectra of Mol 11

Organic Semiconductor	Charge Mobility	Current On/Off Ratio	Ref	
Poly(benzobisimidazobenzophenanthroline) (BBL) nanobelts	7×10^{-3} cm^2 V^{-1} s^{-1}	$\sim 1 \times 10^4$	1	

donor−acceptor (D−A) conjugated polymer based on bithiazole-thiazolothiazole	0.46 $cm^2 V^{-1} s^{-1}$	~1×10^5	2	
polyalkylthiophene	1.54×10^{-4} $cm^2 V^{-1} s^{-1}$	~1×10^1	3	
polyalkylthiophene	0.62 $cm^2 V^{-1} s^{-1}$	~1×10^1	4	
poly(3-hexylthiophene)	1.57×10^{-3} $cm^2 V^{-1} s^{-1}$	~1×10^3	5	
poly(p-phenyleneethynylene)	0.1 $cm^2 V^{-1} s^{-1}$	~1×10^3	6	
poly(3-octylthiophene)	0.62 $cm^2 V^{-1} s^{-1}$	~37	7	
single D−A conjugated polymer fibers	5.5 $cm^2 V^{-1} s^{-1}$	~1×10^5	8	
α,ω-dihexylquaterthiophene (DH4T)	10^{-4} $cm^2 V^{-1} s^{-1}$	10^2	9	
α,ω-dihexylquaterthiophene (DH4T)	10^{-2} $cm^2 V^{-1} s^{-1}$	10^4	10	
This work	0.167 $cm^2 V^{-1} s^{-1}$	~3.43×10^3	**This work**	

Table T1 Comparison of electrical performance of OTFTs as based on conventional Organic Semiconducting Materials with OTFTs as based on our Material (CbzTPAU2).

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