#### SUPPLEMENTARY INFORMATION

#### to the article

## Nanostructured organosilicon luminophores and their application in highly efficient plastic scintillators

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#### 1. Experimental procedures for the synthesis of NOLs and their precursors.

Materials. Pentane solutions of tert-butyllithium (3.0 M), hexan solutions of n-butyllithium (1.6 and 2.5 M), N-bromosuccinimide (NBS), methyltrichlorosilane, dibromoethane, magnesium, *tetrakis*(triphenylphosphine)palladium (0) Pd(PPh<sub>3</sub>)<sub>4</sub>, 1,1'-*bis*(diphenylphosphino) ferrocene palladium(II) chloride Pd(dppf)Cl<sub>2</sub>, 1-bromo-4-methylbenzene, 1,4-dibromo-2,5dimethylbenzene, (4-bromophenyl)(trimethyl)silane, 4,4'-dibromobiphenyl, 4,7-dibromo-2,1,3benzothiadiazole, 4,7-bis(5-bromothiophen-2-yl)-2,1,3-benzothiadiazole, 1,2-dibromobenzene, 9,10-dibromoanthracene were obtained from Sigma-Aldrich Co. and used without further purification. 5-hexyl-2,2'-bithiophene was prepared according to the technique described earlier<sup>1</sup>. THF and diethyl ether were dried over CaH<sub>2</sub> and distilled from LiAlH<sub>4</sub>. Hexane was dried by distillation from CaH<sub>2</sub>. Toluene, hexane, diethyl ether and ethanol were distilled before use. The solvents were evaporated in vacuum under a pressure of up to 1 torr at 40 °C. All reactions were carried out in inert atmosphere. 2,2'-(9,9-didecyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (12) was synthesized according to a literature procedure<sup>2</sup>. 2-{5-[Methylbis(5'-hexyl-2,2'-bithienyl-5-yl)silyl]-2-thienyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13) was prepared by the technique described previously<sup>3</sup>.  $2-\{5'-[Methylbis(5'-hexyl-2,2'$ bithienyl-5-yl)silyl]-2,2'-bithien-5-yl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (21) was prepared by the technique described previously<sup>4</sup>. [[2,2'-bithien-5-yl(methyl)silanediyl]bis(2,2'bithiene-5',5-divl)]bis[bis(5'-hexyl-2,2'-bithien-5-yl)(methyl)silane] (22) was prepared by the technique described previously<sup>5</sup>.

Unless otherwise stated, all glassware before the reactions was dried in a dry box at 150 °C for 2 hours, assembled while hot, and cooled in a stream of argon.



**4-bromo-2,4',5-trimethylbiphenyl (8).** A solution of 26.74 g (0.156 mol) of 1-bromo-4methylbenzene in 150 mL of anhydrous THF was added dropwise to a suspension of 3.94 g (0.164 mol) of magnesium in 30 mL of THF. The Grignard reagent was refluxed for 1 h, cooled to 20°C and was added dropwise to a suspension of Pd(dppf)Cl<sub>2</sub> (1.50 g, 2.1 mmol) in a solution of 1,4-dibromo-2,5-dimethylbenzene (37.15 g, 0.14 mol) in 200 mL of anhydrous THF, while the temperature was kept between 0 and 10 °C. Then cooling was removed and stirring was continued for 8 h at room temperature. Afterward it was poured into 200 mL of ice water and extracted twice with freshly distilled diethyl ether. The organic phase was separated, washed with water, dried over sodium sulfate, and evaporated. The product was purified by distillation in vacuum (0.2 mBar, 127-130 °C) to give pure 4-bromo-2,4',5-trimethylbiphenyl (8) as a colorless liquid (24.55g, 63%). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 2.23 (s, 3 H), . 2.40 (s, 3 H), 2.42 (s, 3 H), 7.10 (s, 1 H), 7.20 (d, J = 8.5 Hz, 2 H), 7.25 (d, J = 8.5 Hz, 2 H), 7.45 (s, 1H). Anal. Calcd. for C<sub>15</sub>H<sub>15</sub>Br (%): C, 65.47; H, 5.49; Br, 29.04. Found (%):C, 65.56; H, 5.54; Br, 29.07.



**Trimethyl(2',4'',5'-trimethyl-1,1':4',1''-terphenyl-4-yl)silane (9)** was synthesized according to the procedure described for compound **(8)** from 22.44 g (0.098 mol) of (4-bromophenyl)(trimethyl)silane, 24.5 g (0.089 mol) of compound **8**, 2.57  $\Gamma$  (0.107 mol) of magnesium and 1 g (1.4 mmol) of Pd(dppf)Cl<sub>2</sub> to give 30.54 g of crude product, containing 80%

of compound (9) (GPC). The product was purified by distillation in vacuum (0.16 mBar, 167-173 °C) to give pure compound (9) (22.96 g, 75 %). as white crystals ( $m_p = 98$  °C). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 0.32 (s, 9 H), 2.29 (s, 3H), 2.31 (s, 3H), 2.43 (s, 3H), 7.16 (s, 2H), 7.31 (d, 4H, J = 8.5 Hz), 7.37 (d, 2H, J = 8.0 Hz), 7.58 (d, 2H, J = 8.5 Hz).



**4-bromo-2',4'',5'-trimethyl-1,1':4',1''-terphenyl (10).** A solution of NBS (13.91 g, 78 mmol) in anhydrous DMF (50 mL) was slowly added dropwise in the dark to a solution of compound **9** (11.22 g, 32 mmol) in anhydrous DMF (200 mL) at 0 °C. Then cooling was removed and the mixture was stirred for 8 h at room temperature. After completion of the reaction, the precipitate was filtered and washed with water to give of pure compound **10** (10.52 g, 92%) as white crystals (m<sub>p</sub> = 137 °C). <sup>1</sup>H NMR (250 MHz, CCl<sub>4</sub>-DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 2.23 (s, 6H), 2.39 (s, 3H), 7.06 (s, 2H), 7.21 (s, 4H), 7.28 (d, 2H, J = 8.5 Hz), 7.58 (d, 2H, J = 8.5 Hz). Anal. Calcd. for C<sub>21</sub>H<sub>19</sub>Br (%): C, 71.80; H, 5.45; Br, 22.75. Found (%):C, 72.01; H, 5.59; Br, 22.49.



# (4-bromophenyl)(methyl)bis(2',4'',5'-trimethyl-1,1':4',1''-terphenyl-4-yl)silane (11). A solution of 41.63 mmol tert-BuLi in 24.5 mL of pentane (3.0 M solution) was added dropwise

to a solution of compound **10** (7.31 g, 20.81 mmol) in 200 mL THF, while the temperature was kept between -50 and -40 °C. The cooling bath was then removed and the temperature was allowed to rise to 20 °C. The reaction mixture was cooled again to -75°C, and 2.81 mL (10.41 mmol) of (4-bromophenyl)(dichloro)methylsilane) was added. The solution was stirred at -75°C for 1 h. It was then poured into 500 mL of water and 1000 mL of diethyl ether. The organic layer was washed with water and dried over sodium sulfate. The solvent was evaporated in vacuum and the residue was dried at 1 Torr to give 8.47 g of crude product, containing 61% of compound **11** (GPC). This product was purified by a column chromatography on silica gel (eluent toluene – hexane 1:3) to give pure compound **11** (4.34 g, 62 %) as a colorless solid (m<sub>p</sub> = 103 °C). <sup>1</sup>H NMR (250 MHz, CCl<sub>4</sub>-DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 0.90 (s, 3H), 2.23 (s, 6H), 2.27 (s, 6H), 2.39 (s, 6H), 7.06 (d, 4H, J = 6.7 Hz), 7.19 (s, 8H), 7.35 (d, 4H, J = 7.3 Hz), 7.47 (d, 2H, J = 7.9 Hz), 7.56 (dd, 6 H, J<sub>1</sub> = 7.3 Hz, J<sub>2</sub> = 2.4 Hz). Anal. Calcd. for C<sub>49</sub>H<sub>45</sub>BrSi (%): C, 79.33; H, 6.11; Br, 10.77; Si, 3.79. Found (%):C, 79.41; H, 6.10; Br, 10.94; Si, 3.63.



[(9,9-didecyl-9H-fluorene-2,7-diyl)dibenzene-4,1-diyl]bis{methyl[bis(2',4'',5'-trimethyl-1,1':4',1''-terphenyl-4-yl)]silane} (1). Degassed solutions of compound 11 (1.06 g, 1.44 mmol) and compound 12 (0.50 g, 0.72 mmol) in toluene/ethanol mixture (20 ml / 20 ml), and a 2 Msolution of Na<sub>2</sub>CO<sub>3</sub> (2 mL) were added to Pd(PPh<sub>3</sub>)<sub>4</sub> (83 mg, 0.07 mmol). The reaction mixture was stirred under reflux for 26 h, and then it was cooled to room temperature and poured into

250 mL of water and 250 mL of toluene. The organic phase was separated, washed with water, dried over sodium sulfate and filtered. The solvent was evaporated in vacuum and the residue was dried at 1 Torr. The product was purified by a column chromatography on silica gel (eluent toluene – hexane 1:2) to give pure compound 1 (0.82 g, 65 %) as a colorless solid ( $m_p = 65 \text{ °C}$ ). Anal. Calcd. for C<sub>131</sub>H<sub>138</sub>Si<sub>2</sub> (%): C, 88.96; H, 7.86; Si, 3.18. Found (%): C, 88.83; H, 7.87; Si, 3.26. MS: m/z 1767  $[M]^+$  (63), 1752  $[M - CH_3]^+$  (51), 1484  $[M - Ph-Ph(Me)_2-Ph-Me]^+$  (63),  $1228 [M - 2(Ph-Ph(Me)_2-Ph-Me)]^+$  (80), 585  $[CH_3Si (Ph-Ph(Me)_2-Ph-Me)_2]^+$  (885). <sup>1</sup>H NMR (300 MHz, Chloroform-d)  $\delta$ : 7.80 (d,  ${}^{3}J$  = 8.0 Hz, 1H, H-C<sup>6</sup>), 7.76 (s, 4H, H-C<sup>9</sup> and H-C<sup>10</sup>), 7.69 (m<sup>\*</sup>,  ${}^{3}J \sim 8.0$  Hz, 4H, H-C<sup>14</sup>), 7.65 (dd,  ${}^{3}J = 8.0$ Hz;  ${}^{4}J = 1.5$ Hz, 1H, H-C<sup>5</sup>), 7.63 (d,  ${}^{4}J = 1.5$ Hz, 1H, H-C<sup>3</sup>) 7.44 (m<sup>\*</sup>,  ${}^{3}J \sim 8.0$  Hz, 4H, H-C<sup>15</sup>), 7.30 (m<sup>\*</sup>,  ${}^{3}J \sim 8.3$  Hz, 4H, H- $C^{24}$ ), 7.25 (m<sup>\*</sup>, <sup>3</sup>J ~ 8.3 Hz, 4H, H- $C^{25}$ ), 7.21 (br.s, 2H, H- $C^{22}$ ), 7.18 (br.s, 2H, H- $C^{19}$ ), 2.43 (s, 6H,  $H_3C^{39}$ ), 2.34 (s, 6H,  $H_3C^{37}$ ), 2.31 (s, 6H,  $H_3C^{38}$ ), 2.05 (m, 2H,  $H_2C^{27}$ ), 1.22 (m, 2H,  $H_2C^{35}$  ), 1.2 -1.03 (m, 12H,  $H_2C^{29,30,31,32,33,34}$ ), 0.99 (s, 3H,  $H_3C^{12}$  ), 0.81 (m\*, 3H,  $H_3C^{36}$  ), 0.73 (b.m<sup>\*\*</sup>, 2H, H<sub>2</sub>C<sup>28</sup>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  151.72, (C<sup>2</sup>), 142.80(C<sup>16</sup>), 142.54(C<sup>8</sup>),  $140.86(C^{20}), 140.46(C^{17}), 140.27(C^{7}), 139.81(C^{4}), 138.70(C^{23}), 136.38(C^{26}), 135.88(C^{10}),$  $135.07(C^{14})$ ,  $134.88(C^{11})$ ,  $134.23(C^{13})$ ,  $132.66(C^{21})$ ,  $132.55(C^{18})$ ,  $131.94(C^{19})$ ,  $131.84(C^{22})$ ,  $129.09(C^{24})$ , 128.79 and 128.78( $C^{15}$  or  $C^{25}$ ), 126.62( $C^{9}$ ), 126.06( $C^{5}$ ), 121.51( $C^{3}$ ), 120.07( $C^{6}$ ), 55.29( $C^{1}$ ), 40.50( $C^{27}$ ), 31.83( $C^{34}$ ), 30.04( $C^{29}$ ), 29.55 and 29.49( $C^{30}$  or  $C^{33}$ ), 29.24( $C^{31}$  and  $C^{32}$ ), 23.84(C<sup>28</sup>), 22.62(C<sup>35</sup>), 21.18(C<sup>39</sup>), 20.00 (C<sup>37</sup>), 19.96(C<sup>38</sup>), 14.08(C<sup>36</sup>), -3.09(C<sup>12</sup>). <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ: -11.09.

<sup>\*</sup> Due to second order effects.

<sup>\*\*</sup> Due to restricted rotation



(biphenyl-4,4'-diyldithiene-5,2-diyl)bis[bis(5'-hexyl-2,2'-bithiophen-5-yl)(methyl)silane] (2). The reaction was carried out according to the procedure described above for 1. A Suzuki coupling reaction was carried out between 2-{5-[Methylbis(5'-hexyl-2,2'-bithienyl-5-yl)silyl]-2thienyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13) (9.4 g, 12.5 mmol) and 4.4'dibromobiphenyl (14) (1.63 g, 5.21 mmol) in degassed toluene/ethanol mixture 100 ml / 15 ml) at the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (700 mg, 0.63 mmol) and 2M aq. Na<sub>2</sub>CO<sub>3</sub> (19 ml, 37 mmol). The crude product was purified by a column chromatography on silica gel (eluent - hexane : toluene, 5:1) to give pure 2 as a slightly green solid ( $m_p = 83$  °C). Yield: 6.88 g (94%). Anal. Calcd. for C<sub>78</sub>H<sub>86</sub>S<sub>10</sub>Si<sub>2</sub> (%): C, 66.90; H, 6.19 S, 22.90; Si, 4.01. Found (%): C, 66.77; H, 6.20; S, 22.63; Si, 4.07. MS: m/z, 1385  $[M - CH_3]^+$  (6), 1149  $[M - 2T - Hex]^+$  (29), 541  $[CH_3Si (2T - Hex)_2]^+$ (155). <sup>1</sup>H NMR (300 MHz, Chloroform-d)  $\delta$  : 7.71 (m\* ("d"), <sup>3</sup>J ~ 8.4 Hz, 2H, H-C<sup>21</sup>), 7.62 (m\* ("d"),  ${}^{3}J \sim 8.4$  Hz, 2H, H-C<sup>22</sup>), 7.46 (d,  ${}^{3}J = 3.5$  Hz, 1H, H-C<sup>18</sup>), 7.41 (d,  ${}^{3}J = 3.5$  Hz, 1H, H-C<sup>17</sup>), 7.32 (d,  ${}^{3}J = 3.5$  Hz, 2H, H-C<sup>13</sup>), 7.21 (d,  ${}^{3}J = 3.5$  Hz, 1H, H-C<sup>12</sup>), 7.03 (d,  ${}^{3}J = 3.6$  Hz, 1H, H- $C^{9}$ ), 6.68 (br.d,  ${}^{3}J \sim 3.6$  Hz, 1H, H-C<sup>8</sup>), 2.79 (br.t,  ${}^{3}J \sim 7.6$  Hz, 4H, H<sub>2</sub>C<sup>6</sup>), 1.68 (br.p,  ${}^{3}J \sim 7$ Hz, 4H,  $H_2C^5$ ), 1.37 (m, 4H,  $H_2C^4$ ) 1.34 – 1.26 (m, 8H,  $H_2C^3$ ,  $H_2C^2$ ), 0.97 (s, 3H), 0.90 (m\* ("t"), <sup>3</sup>J ~ 6.7 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  : 151.20 (C<sup>19</sup>), 145.92 (C<sup>7</sup>), 145.15 (C<sup>11</sup>), 139.63  $(C^{23})$ , 138.13  $(C^{17})$ , 137.80 $(C^{13})$ , 134.58  $(C^{16})$ , 134.34  $(C^{10})$ , 133.22  $(C^{20})$ , 133.12  $(C^{14})$ , 127.21 (C<sup>22</sup>), 126.50 (C<sup>21</sup>), 124.82(C<sup>8</sup>), 124.64(C<sup>18</sup>), 124.36 (C<sup>12</sup>), 123.96 (C<sup>9</sup>), 31.54(C<sup>3</sup>), 31.51(C<sup>5</sup>),  $30.16(C^6)$ , 28.72 (C<sup>4</sup>), 22.55 (C<sup>2</sup>), 14.06 (C<sup>1</sup>), -0.12 (C<sup>15</sup>). <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>)  $\delta$ : -25.33.



(4-bromophenyl)(dichloro)methylsilane (16). A 2.5 M solution of *n*-butyllithium in hexane (68.00 mL, 0.170 mol) was added dropwise to a solution of 1.4-dibromobenzene (15) (40.00 g, 0.170 mol) in 800 mL of dry THF, while the temperature was kept between -50 and – -40 °C. The reaction mixture was stirred for 2 hours at –75 °C. An ether complex of MgBr<sub>2</sub> (freshly prepared from Mg (4.56 g, 0.190 mol) and dibromoethane (15.7 g, 0.181 mmol) in 20 mL of anhydrous ether) was added dropwise to the reaction mixture at -40°C, which was stirred then for 1.5 hours without a cooling bath. The Grignard reagent was added dropwise to the solution of freshly distilled methyltrichlorosilane (203 g, 1.36 mol) in THF (200 ml) while the temperature was kept between -55 °C and -50 °C. The temperature was then allowed to rise to r. t. for 4 hour and the stirring was continued for 2 hours at reflux. Afterwards the reaction mixture was cooled down to room temperature, washed with anhydrous hexane and filtered off on glass filter G4 under argon. The product was purified by distillation in vacuum (0.12 mBar, 58 °C) to give pure compound **16** (18.41 g, 40 %) as a colorless liquid. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 1.02 (s, 3H), 7.51-7.67 (AA'BB', C<sub>6</sub>H<sub>4</sub>Br, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 5.49; 126.86; 131.61; 132.24; 134.56. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 18.53.



(4-bromophenyl)[bis(5'-hexyl-2,2'-bithien-5-yl)]methylsilane (18). A 2.5 M solution of nbutyllithium (7.17 ml, 17.90 mmol) was added dropwise to a solution of 5-hexyl-2,2'bithiophene (17) (4.58 g, 18.30 mmol) in 140 mL THF, while the temperature was kept between -75 and -78 °C and then the solution was stirred at -78° C for 1 h. After that, 2.42 g (9.00 mmol) of compound (16) in 10 mL of THF was added. The solution was stirred at -78 °C for 30 min. It was then poured into 150 mL of water and 300 mL of diethyl ether. The organic layer was washed with water and dried over sodium sulfate. The solvent was evaporated in vacuum and the residue was dried at 1 Torr. The crude product was purified by a column chromatography on silica gel (eluent toluene – hexane 1:5) to give pure compound 18 as a slightly green liquid (4.40 g, 74 %). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>, δ, ppm): 0.84-0.93 (overlapped peaks, 9H), 1.25-1.42 (overlapped peaks, 12 H), 1.66 (m, 4H, M = 5, J = 7.3 Hz), 2.77 (t, 4H, J = 7.3 Hz), 6.66 (d, 2H, J = 3.7 Hz), 6.99 (d, 2H, J = 3.1 Hz), 7.16-7.20 (overlapped peaks, 4H), 7.44-7.59 (overlapped peaks, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ, ppm): -1.40; -14.07; 22.55; 28.71; 30.14; 31.52; 31.54; 123.93; 124.34; 124.83; 125.04; 131.19; 132.79; 134.25; 134.30, 136.27; 137.85; 145.12; 145.96. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>, δ, ppm): -20.19. Anal. Calcd. for C<sub>35</sub>H<sub>41</sub>BrS<sub>4</sub>Si (%): C, 60.23; H, 5.92; S, 18.38; Si, 4.02; Br, 11.45. Found (%): C, 60.24; H, 5.89; S, 18.27; Si, 3.94; Br, 11.53. MALDI-MS: *m/z* 696.86 [M<sup>+</sup>, calculated 696.10].



bis(5'-hexyl-2,2'-bithien-5-yl)(methyl)[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-

yl)phenyl|silane (19). A 1.6 M solution of butyllthium (1.41 ml, 2.3 mmol) in hexane was added dropwise to a solution of 18 (1.63 g, 2.3 mmol) in 60 ml of dry THF, while the temperature was kept between -70 and -78 °C. The reaction mixture was stirred for 60 min at -78 °C. Then 2isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.48 ml, 2.3 mmol) was added in one portion. The reaction mixture was stirred for 1 h at -78 °C, the cooling bath was removed, and the stirring was continued for 2 h. After completion of the reaction, 150 ml of freshly distilled diethyl ether and 75 mL of degassed water containing 2.3 ml of 1 N HCl were added. The organic phase was separated, washed with water, and dried over sodium sulphate. The solvent was evaporated and crude product was purified by column chromatography on silica gel (eluent toluene – hexane 1:5, then toluene) to give pure compound 19 (1.39 g, 82%) as a beige solid ( $m_p$ = 70 °C). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>, δ, ppm): 0.83-0.92 (overlapped peaks, 9H), 1.23-1.41 (overlapped peaks with maximum at 1.33 ppm, 24 H), 1.66 (m, 4H, M = 5, J = 7.3 Hz), 2.76 (t, 4H, J = 7.3 Hz), 6.64 (d, 2H, J = 3.7 Hz), 6.98 (d, 2H, J = 3.1 Hz), 7.14-7.21 (overlapped peaks, 4H), 7.62 (d, 2H, J = 7.9 Hz), 7.80 (d, 2H, J = 7.9 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): -1.37; 14.04; 22.53; 24.83; 28.69; 30.14; 31.50; 31.53; 83.83; 123.83; 124.31; 124.79; 133.43; 133.94; 134.04; 134.42; 137.74; 138.70; 144.89; 145.79. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>, δ, ppm): -20.51. Anal. Calcd. for C<sub>41</sub>H<sub>53</sub>BO<sub>2</sub>S<sub>4</sub>Si (%): C, 66.10; H, 7.17; S, 17.21; Si, 3.77. Found: C, 66.30; H, 7.34; S, 17.11; Si, 3.88. MALDI-MS: *m/z* 744.01 [M<sup>+</sup>, calculated 744.28].



[anthracene-9,10-diylbis(4,1-phenylene)]bis[bis(5'-hexyl-2,2'-bithien-5-yl)(methyl)silane] (3). The reaction was carried out according to the procedure described above for 1. A Suzuki coupling reaction was carried out between 19 (1.23 g, 1.66 mmol) and 9,10-dibromoanthracene (20) (0.23 g, 0.684 mmol) in degassed toluene/ethanol mixture (25 ml / 2.5 ml) at the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (96 mg, 0.083 mmol) and 2M aq. Na<sub>2</sub>CO<sub>3</sub> (2.5 ml, 5 mmol). The crude product was purified by a column chromatography on silica gel (eluent - hexane : toluene, 3:1) to give pure 3 as a light-yellow solid ( $m_p = 94$  °C). Yield: 0.94 g (97 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.87 (m<sup>†</sup>,  ${}^{3}J \approx 8.0$  Hz, 2H, H-C<sup>17</sup>), 7.71 (m<sup>\*</sup>, 2H, H-C<sup>22</sup>), 7.51 (m<sup>\*</sup>,  ${}^{3}J \approx 8.0$  Hz, 2H, H-C<sup>18</sup>), 7.36 (d,  ${}^{3}J = 3.5$  Hz, 2H, H-C<sup>13</sup>), 7.35 (m, 2H, H-C<sup>23</sup>), 7.25 (d,  ${}^{3}J = 3.5$  Hz, 2H, H-C<sup>12</sup>), 7.06 (d,  ${}^{3}J = 3.5$  Hz, 2H, H-C<sup>9</sup>), 6.69 (dt,  ${}^{3}J = 3.5$ ,  ${}^{4}J = 1.0$  Hz, 2H, H-C<sup>8</sup>), 2.79 (br.t,  ${}^{3}J \approx 7.6$  Hz, 4H,  $H_2C^6$ ), 1.67 (m,  ${}^{3}J \approx 7.5Hz$ , 4H,  $H_2C^5$ ), 1.37 (m, 4H,  $H_2C^4$ ), 1.34 – 1.26 (m, 8H,  $H_2C^3$  and  $H_2C^2$ ), 1.03 (s, 3H, H<sub>3</sub>C<sup>15</sup>), 0.89 (m\*,  ${}^{3}J \approx 6.9$  Hz, 3H, H<sub>3</sub>C<sup>1</sup>).  ${}^{13}$ C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 145.00( $C^{11}$ ), 140.80( $C^{19}$ ), 137.87( $C^{13}$ ), 136.89( $C^{20}$ ),  $145.89(C^7)$ ,  $134.72(C^{17}),$  $134.43(C^{10}), 134.42(C^{16}), 133.63(C^{14}), 130.96(C^{18}), 129.72(C^{21}), 126.94(C^{22}), 125.13(C^{23}), 125.13(C^{23$  $124.83(C^8)$ ,  $124.41(C^{12})$ ,  $123.92(C^9)$ ,  $31.55(C^3)$ ,  $31.54(C^5)$ ,  $30.17(C^6)$ ,  $28.72(C^4)$ ,  $22.56(C^2)$ , 14.05(C<sup>1</sup>), -1.13(C<sup>15</sup>). <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>, δ, ppm): -20.3. Anal. Calcd. for C<sub>84</sub>H<sub>90</sub>S<sub>8</sub>Si<sub>2</sub> (%): C, 71.44; H, 6.42; S, 18.16; Si, 3.98. Found (%): C, 71.31; H, 6.50; S, 17.82; Si, 3.82; MALDI-MS: *m/z* 1410.74 [M<sup>+</sup>, calculated 1411.43].

<sup>†</sup> Due to second order effects



1,4-bis(5'-[bis(5'-hexyl-2,2'-bithiophene-5-yl)(methyl)silyl]-2,2'-bithiophene-5-

yl)benzene (4). The reaction was carried out according to the procedure described above for 1. A Suzuki coupling reaction was carried out between 21 (1.12 g, 1.34 mmol) and 1,4dibromobenzene (15) (0.149 g, 0.63 mmol) in 30 ml of degassed toluene at the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (77 mg, 0.07 mmol) and 2M aq. Na<sub>2</sub>CO<sub>3</sub> (2.0 ml, 4 mmol). The crude product was purified by a column chromatography on silica gel (eluent - hexane - toluene, 3:1) to give pure 4 as yellow solid ( $m_p = 142$  °C). Yield: 0.47 g (50 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.58 (s, 2H, H-C<sup>25</sup>), 7.32 (d,  ${}^{3}J$  = 3.5 Hz, 1H,H-C<sup>17</sup>), 7.30 (d,  ${}^{3}J$  = 3.5 Hz, 2H, H-C<sup>13</sup>), 7.29 (d,  ${}^{3}J$  = 3.5 Hz, 1H, H-C<sup>18</sup>), 7.23 (d,  ${}^{3}J$  = 3.8 Hz, 1H, H-C<sup>22</sup>), 7.20 (d,  ${}^{3}J$  = 3.5 Hz, 2H, H-C<sup>12</sup>), 7.18 (d,  ${}^{3}J = 3.8$  Hz, 1H, H-C<sup>21</sup>), 7.02 (d,  ${}^{3}J = 3.6$  Hz, 2H, H-C<sup>9</sup>), 6.67 (dt,  ${}^{3}J = 3.6$ ,  ${}^{4}J = 1.0$  Hz, 2H, H- $C^{8}$ ), 2.77 (m<sup>+</sup>,  ${}^{3}J \sim 7.5$  Hz, 4H, H<sub>2</sub>C<sup>6</sup>), 1.66 (m, 4H, H<sub>2</sub>C<sup>5</sup>), 1.37 (m, 4H, H<sub>2</sub>C<sup>4</sup>), 1.34 - 1.26 (m, 8H,  $H_2C^3$  and  $H_2C^2$ ), 0.95 (s, 3H,  $H_3C^{15}$ ), 0.89 (m<sup>\*</sup>,  $^3J \sim 7.0$  Hz, 6H,  $H_3C^1$ ).  $^{13}C$  NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 145.96 (C<sup>7</sup>), 145.19 (C<sup>11</sup>), 144.34 (C<sup>19</sup>), 142.90 (C<sup>23</sup>), 137.85 (C<sup>17</sup>), 137.84 (C<sup>13</sup>), 136.42 (C<sup>20</sup>), 134.28 (C<sup>10</sup>), 134.25 (C<sup>16</sup>), 133.13 (C<sup>24</sup>), 132.88 (C<sup>14</sup>), 125.91 (C<sup>25</sup>), 125.24  $(C^{21}), 125.03 (C^{18}), 124.83 (C^{8}), 124.35 (C^{12}), 123.98 (C^{9}), 123.88 (C^{22}), 31.54 (C^{3}), 31.52 (C^{5}),$ 30.15 (C<sup>6</sup>), 28.72 (C<sup>4</sup>), 22.55 (C<sup>2</sup>), 14.07 (C<sup>1</sup>), -0.18 (C<sup>15</sup>). <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>, δ, ppm): -24.87. Anal. Calcd. for C<sub>80</sub>H<sub>86</sub>S<sub>12</sub>Si<sub>2</sub> (%): C, 64.55; H, 5.82; S, 25.85; Si, 3.77. Found (%): C, 64.50; H, 5.60; S, 25.55; Si, 3.50. MALDI-MS m/z 1473.52 [M - CH<sub>3</sub>]<sup>+</sup>; 1487.62 [M+Ag]<sup>+</sup>, calculated for  $[M+Ag]^+$  1488.29.

<sup>‡</sup> Due to second order effects



[{methyl[5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithien-5yl]silanediyl}bis(2,2'-bithiene-5',5-diyl)]bis[bis(5'-hexyl-2,2'-bithien-5-yl)(methyl)silane]

(23). A 1.6 M solution of butyllthium (0.41 ml, 0.7 mmol) in hexane was added dropwise to a solution of 22 (1.10 g, 0.7 mmol) in 35 ml of dry THF, while the temperature was kept between -70 and -75 °C. The reaction mixture was stirred for 60 min at -75 °C. Then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.14 ml, 0.7 mmol) was added in one portion. The reaction mixture was stirred for 1 h at -78 °C, the cooling bath was removed, and the stirring was continued for 2 h. After completion of the reaction, 150 ml of freshly distilled diethyl ether and 75 mL of degassed water containing 0.7 ml of 1 N HCl were added. The organic phase was separated, washed with water, and dried over sodium sulphate. The solvent was evaporated to give pure compound 23 (1.18 g, 98%) as a blue liquid. The product was used in the subsequent synthesis without further purification. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 0.87 (t, 12H, J = 6.7 Hz), 0.92 (s, 6H), 0.94 (s, 3H), 1.22-1.42 (overlapping peaks with maximum at 1.33 ppm, 24H), 1.65 (m, 8H, M = 5, J = 7.3 Hz), 2.76 (t, 8H, J = 7.3 Hz), 6.65 (4H, d, J = 3.7 Hz), 6.99 (4H, d, J = 3.7 Hz), 7,17 (4H, d, J = 3.7 Hz), 7.25-7.33 (overlapping peaks, 16H), 7.49 (1H, d, J = 3.7 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): -0.28; -0.21; 14.06; 22.54; 24.73;

28.69; 30.13; 31.50; 31.52; 84.16; 123.96; 124.34; 124.82; 125.56; 125.66; 125.70; 125.82; 132.85; 134.11; 134.26; 134.37; 134.70; 137.70; 137.83, 137.91; 137.94; 143.51; 143.88; 144.14; 144.34; 145.15; 145.93. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): -25.19; -25.40. Anal. Calcd. for C<sub>89</sub>H<sub>101</sub>BO<sub>2</sub>S<sub>14</sub>Si<sub>3</sub> (%): C, 61.20; H, 5.83; S, 25.70; Si, 4.82. Found (%): C, 61.20; H, 5.99; S, 25.56; Si, 4.61. MALDI-MS m/z 1852.70 [M + Ag]<sup>+</sup>, calculated 1853.24.



1,4-bis(5'-{bis(5'-{bis(5'-hexyl-2,2'-bithiophen-5-yl)(methyl)silyl}-2,2'-bithiophene-5-

yl)(methyl)silyl]-2,2'-bithiophene-5-yl)benzene (5). The reaction was carried out according to the procedure described above for 1. A Suzuki coupling reaction was carried out between 23 (1.05 g, 0.60 mmol) and 1,4-dibromobenzene (15) (57 mg, 0.24 mmol) in 15 ml of degassed toluene at the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (35 mg, 0.03 mmol) and 2M aq. Na<sub>2</sub>CO<sub>3</sub> (0.9 ml, 1.8 mmol). The crude product was purified by a column chromatography on silica gel (eluent - hexane - toluene, 3:1) to give pure **5** as a yellow solid (m<sub>p</sub> = 117 °C). Yield: 0.34 g (43 %). <sup>1</sup>H NMR (300, MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.58 (s, 2H, H-C<sup>34</sup>), 7.32 (d, <sup>3</sup>J = 3.5 Hz, 1H, H-C<sup>26</sup>), 7.32-7.31(4H, H-C<sup>21</sup> and H-C<sup>22</sup>), 7.31-7.30 (5H, H-C<sup>17</sup>, H-C<sup>18</sup> and H-C<sup>27</sup>), 7.28 (d, <sup>3</sup>J = 3.5 Hz, 4H H-C<sup>13</sup>), 7.24 (d, <sup>3</sup>J = 3.8 Hz, 1H, H-C<sup>31</sup>), 7.18 (d, <sup>3</sup>J = 3.5 Hz, 5H, H-C<sup>12</sup> and , H-C<sup>30</sup>), 7.01 (d, <sup>3</sup>J = 3.6 Hz, 4H, H-C<sup>9</sup>), 6.66 (dt, <sup>3</sup>J = 3.6; <sup>4</sup>J = 1.0 Hz, 4H, H-C<sup>8</sup>), 2.77 (br.t, <sup>3</sup>J ≈ 7.5 Hz, 8H, H<sub>2</sub>C<sup>6</sup>), 1.68 (m, 8H, H<sub>2</sub>C<sup>5</sup>), 1.37 (m, 8H, H<sub>2</sub>C<sup>4</sup>), 1.34 – 1.26 (m, 16H, H<sub>2</sub>C<sup>3</sup> and H<sub>2</sub>C<sup>2</sup>) 0.96 (s,

3H, H<sub>3</sub>C<sup>24</sup>), 0.93 (s, 6H, H<sub>3</sub>C<sup>15</sup>), 0.88 (m\*<sup>§</sup>,  ${}^{3}J \approx 6.8$  Hz, 12H, H<sub>3</sub>C<sup>1</sup>).  ${}^{13}$ C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 145.95(C<sup>7</sup>), 145.20(C<sup>11</sup>), 144.50(C<sup>28</sup>), 144.19 and 143.93(C<sup>19</sup> or C<sup>20</sup>), 143.00(C<sup>32</sup>), 137.96(C<sup>22</sup> and C<sup>26</sup>), 137.83(C<sup>13</sup> and C<sup>17</sup>), 136.39(C<sup>29</sup>), 134.81(C<sup>16</sup>), 134.31(C<sup>10</sup>), 134.23(C<sup>23</sup>), 133.87(C<sup>25</sup>), 133.18(C<sup>33</sup>), 132.91(C<sup>14</sup>), 125.95(C<sup>34</sup>), 125.73(C<sup>18</sup>), 125.70(C<sup>21</sup>), 125.33(C<sup>30</sup>), 125.09(C<sup>27</sup>), 124.82(C<sup>8</sup>), 124.37(C<sup>12</sup>), 123.99(C<sup>9</sup>), 123.90(C<sup>31</sup>), 31.54(C<sup>3</sup>), 31.51(C<sup>5</sup>), 30.16(C<sup>6</sup>), 28.72(C<sup>4</sup>), 22.55(C<sup>2</sup>), 14.06(C<sup>1</sup>), -0.17(C<sup>15</sup>), -0.22(C<sup>24</sup>). <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): -25.2(Si-C<sup>24</sup>), -25.37(Si-C<sup>15</sup>). Anal. Calcd. for C<sub>80</sub>H<sub>86</sub>S<sub>12</sub>Si<sub>2</sub> (%): C, 62.31; H, 5.53; S, 27.08; Si, 5.08. Found (%): C, 62.22; H, 5.51; S, 26.91; Si, 4.94; MALDI-MS m/z 3421.28 [M<sup>+</sup>Ag]<sup>+</sup>, calculated 3422.41.



4,7-bis{5-[bis(5'-hexyl-2,2'-bithiophen-5-yl)(methyl)silyl]thiophen-2-yl}-2,1,3-

**benzothiadiazole (6).** The reaction was carried out according to the procedure described above for 1. A Suzuki coupling reaction was carried out between **13** (1.35 g, 1.80 mmol) and 4,7dibromo-2,1,3-benzothiadiazole **24** (220 mg, 0.75 mmol) in degassed toluene/ethanol mixture 30 ml / 3 ml) at the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (42 mg, 0.036 mmol) and 2M aq. Na<sub>2</sub>CO<sub>3</sub> (3 ml, 6.1 mmol). The crude product was purified by a column chromatography on silica gel (eluent hexane : toluene, 5:1) to give pure **6** as a dark yellow solid (m<sub>p</sub> = 49 °C). Yield: 0.84 g (81%). Anal. Calcd. for C<sub>72</sub>H<sub>80</sub>N<sub>2</sub>S<sub>11</sub>Si<sub>2</sub> (%): C, 62.56; H, 5.83, N 2,03, S, 25.52; Si, 4.06. Found (%):

<sup>§</sup> Due to second order effects

C, 62.78; H, 5.77; N 2,00, S, 25.52; Si, 3.97. MS: m/z 1381 [M]<sup>+</sup> (16), 1368 [M - CH<sub>3</sub>,]<sup>+</sup> (84), 1131 [M - 2T-Hex]<sup>+</sup> (32), 541 [CH<sub>3</sub>Si(2T-Hex)<sub>2</sub>]<sup>+</sup> (757). <sup>1</sup>H NMR (300 MHz, Chloroform-d)  $\delta$ : 8.22 (d, <sup>3</sup>*J* = 3.6 Hz, 1H, H-C<sup>18</sup>), 7.88 (s, 1H, H-C<sup>21</sup>), 7.50 (d, <sup>3</sup>*J* = 3.6 Hz, 1H, H-C<sup>17</sup>), 7.32 (d, <sup>3</sup>*J* = 3.5 Hz, 2H, H-C<sup>13</sup>), 7.20 (d, <sup>3</sup>*J* = 3.5 Hz, 2H, H-C<sup>12</sup>), 7.02 (d, <sup>3</sup>*J* = 3.6 Hz, 2H, H-C<sup>9</sup>), 6.66 (dt, <sup>3</sup>*J* = 3.6; <sup>4</sup>*J* = 1.0 Hz, 2H, H-C<sup>8</sup>), 2.70 (m\*,<sup>3</sup>*J*~7.5 Hz, 4H, H<sub>2</sub>C<sup>6</sup>), 1.66 (m, <sup>3</sup>*J*~7.5 Hz, 4H, H<sub>2</sub>C<sup>5</sup>), 1.37 (m, 4H, H<sub>2</sub>C<sup>4</sup>), 1.34 – 1.26 (m, 8H, H<sub>2</sub>C<sup>3</sup> and H<sub>2</sub>C<sup>2</sup>), 0.99 (s, 3H, H<sub>3</sub>C<sup>15</sup>), 0.88 (m\*, <sup>3</sup>*J* ~ 7Hz, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 152.49 (C<sup>22</sup>), 146.32(C<sup>19</sup>), 145.95(C<sup>7</sup>), 145.20(C<sup>11</sup>), 137.99(C1<sup>7</sup>), 137.90(C<sup>13</sup>), 136.71(C<sup>16</sup>), 134.32(C<sup>10</sup>), 132.93(C<sup>14</sup>), 128.94(C<sup>18</sup>), 126.20(C<sup>21</sup>), 125.96(C<sup>20</sup>), 124.83(C<sup>8</sup>), 124.39(C<sup>12</sup>), 123.98(C<sup>9</sup>), 31.55(C<sup>3</sup>), 31.52(C<sup>4</sup>), 30.16(C<sup>6</sup>), 28.72(C<sup>4</sup>), 22.55(C<sup>2</sup>), 14.07(C<sup>1</sup>), -0.10(C<sup>15</sup>). <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>)  $\delta$ : -25.13.



**4,7-bis**{**5'-[bis**(**5'-hexyl-2,2'-bithiophen-5-yl**)(**methyl**)**silyl**]-**2,2'-bithiophen-5-yl**}-**2,1,3-benzothiadiazole (7).** The reaction was carried out according to the procedure described above for 1. A Suzuki coupling reaction was carried out between **13** (1.34 g, 1.78 mmol) and 4,7-bis(5-bromothiophen-2-yl)-2,1,3-benzothiadiazole **25** (340 mg, 0.74 mmol) in degassed toluene/ethanol mixture 40 ml / 4 ml) at the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (42 mg, 0.036 mmol) and 2M aq. Na<sub>2</sub>CO<sub>3</sub> (3 ml, 6.1 mmol). The crude product was purified by a column chromatography on silica gel (eluent - hexane : toluene, 3:1) to give pure **7** as a dark red solid (m<sub>p</sub> = 115 °C). Yield: 0.71 g (62%). Anal. Calcd. for C<sub>80</sub>H<sub>84</sub>N<sub>2</sub>S<sub>13</sub>Si<sub>2</sub> (%): C, 62.13; H, 5.47, N 1,81, S, 26.95; Si, 3.63. Found (%): C, 62.14; H, 5.54; N 1,86, S, 26.89; Si, 3.64. MS: m/z 1545 [M]<sup>+</sup> (78), 1532 [M - CH<sub>3</sub>]<sup>+</sup> (273), 1297 [M - 2T-Hex]<sup>+</sup> (66), 541 [CH<sub>3</sub>Si (2T-Hex)<sub>2</sub>]<sup>+</sup> (941). <sup>1</sup>H NMR (300

MHz, Chloroform-d)  $\delta$ : 7.99 (d,  ${}^{3}J = 4.0$  Hz, 1H, H-C<sup>22</sup>), 7.78 (s, 1H, H-C<sup>26</sup>), 7.36 (d,  ${}^{3}J = 3.5$  Hz, 1H, H-C<sup>18</sup>), 7.33 (d,  ${}^{3}J = 3.5$  Hz, 1H, H-C<sup>17</sup>), 7.30 (d,  ${}^{3}J = 3.5$  Hz, 2H, H-C<sup>13</sup>), 7.26 (d,  ${}^{3}J = 3.9$  Hz, 1H, H-C<sup>21</sup>), 7.20 (d,  ${}^{3}J = 3.5$  Hz, 2H, H-C<sup>12</sup>), 7.02 (d,  ${}^{3}J = 3.6$  Hz, 2H, H-C<sup>9</sup>), 6.66 (dt,  ${}^{3}J = 3.6$ ;  ${}^{4}J = 0.9$  Hz, 2H, H-C<sup>8</sup>), 2.78 (m\*,  ${}^{3}J \sim 7.5$  Hz, 4H, H<sub>2</sub>C<sup>6</sup>), 1.67 (m,  ${}^{3}J \sim 7.5$  Hz, 4H, H<sub>2</sub>C<sup>5</sup>), 1.37 (m, 4H, H<sub>2</sub>C<sup>4</sup>), 1.34 – 1.26 (m, 8H, H<sub>2</sub>C<sup>3</sup> and H<sub>2</sub>C<sup>2</sup>), 0.95 (s, 3H, H<sub>3</sub>C<sup>15</sup>), 0.90 (m\*,  ${}^{3}J \sim 7.0$  Hz, 6H, H<sub>3</sub>C<sup>1</sup>).  ${}^{13}$ C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 152.33(C<sup>25</sup>), 145.97(C<sup>7</sup>), 145.21(C<sup>11</sup>), 144.21(C<sup>19</sup>), 138.46(C<sup>23</sup>), 138.36(C<sup>20</sup>), 137.92(C<sup>17</sup>), 137.87(C<sup>13</sup>), 134.69(C<sup>16</sup>), 134.27(C<sup>10</sup>), 132.83(C<sup>14</sup>), 128.25(C<sup>22</sup>), 125.42(C<sup>24</sup>), 125.36(C<sup>18</sup>), 125.13(C<sup>26</sup>), 125.08(C<sup>21</sup>), 124.83(C<sup>8</sup>), 124.37(C<sup>12</sup>), 123.99(C<sup>9</sup>), 31.55(C<sup>3</sup>), 31.52(C<sup>5</sup>), 30.16(C<sup>6</sup>), 28.72(C<sup>4</sup>), 22.56(C<sup>2</sup>), 14.08(C<sup>1</sup>), -0.18(C<sup>15</sup>).  ${}^{29}$ Si NMR (60 MHz, CDCl<sub>3</sub>)  $\delta$ : -25.37.

#### 2. Analytical methods used.

**GPC analysis** was performed by means of a Shimadzu LC10A<sup>VP</sup> series chromatograph (Japan) equipped with an RID-10A<sup>VP</sup> refractometer and SPD-M10A<sup>VP</sup> diode matrix as detectors and a Phenomenex column (USA) with a size of  $7.8 \times 300 \text{ mm}^2$  filled with the Phenogel sorbent with a pour size of 500 Å; THF was used as the eluent.

For **thin layer chromatography (TLC)**, "Sorbfil" (Russia) TLC plates were used. In the case of **column chromatography**, silica gel 60 ("Merck") was taken.

<sup>1</sup>H NMR spectra were recorded at a "Bruker WP-250 SY" spectrometer, working at a frequency of 250.13 MHz and utilising the DMSO- $d_6$  signal (2.45 ppm) as the internal standard. <sup>13</sup>C and <sup>29</sup>Si NMR spectra were recorded using a "Bruker Avance II 300" spectrometer at 75 MHz and 60 MHz, respectively. In the case of <sup>1</sup>H NMR spectroscopy, the compounds to be analysed were taken in the form of 1% solutions in CCl<sub>4</sub>-DMSO- $d_6$  mixture. In the case of <sup>13</sup>C and <sup>29</sup>Si NMR spectroscopy, the compounds to be analysed were taken in the form of 5% solutions in CDCl<sub>3</sub>. The spectra were then processed on the computer using the ACD Labs software.

**Mass-spectra (MALDI)** were registered on the Autoflex II Bruker (resolution FWHM 18000), equipped with nitrogen laser (work wavelength 337 nm and time-of-flight mass-detector working in reflections mode. The accelerating voltage was 20 kV. Samples were applied to a polished stainless steel substrate. Spectrum was recorded in the positive ion mode. The resulting spectrum was the sum of 300 spectra obtained at different points of sample. 2,5-dihydroxybenzoic acid (DHB) (Acros, 99%) and  $\alpha$ -cyano-4-hydroxycinnamic acid (HCCA) (Acros, 99%) were used as matrices.

**Mass-spectrometry measurements** of compounds **3**, **4**, **5**, **18**, **19** were performed on the Micromass M@ldi<sup>TM</sup> MALDI-TOF MS instrument operating in the reflection mode. To prepare the samples separate solutions of the starting material and matrix in THF with concentrations of 1 mg/ml and a solution of salt (silver triflate) in deionized water at a concentration of 1 mg/ml were mixed and applied to a steel target (at  $\sim 2$  ul) to dry, volume ratio of 1:1:1. 2,5-dihydrobenzoic acid, 2-(4-hydroxyphenylazo) benzoic acid and 3-indolacrilic acid where used as the matrix substance. The standard laser operating frequency was 10 Hz. Standard spectra were regularly obtained by combining approximately 100 single laser shot spectra.

**Elemental analysis** of C, H elements was carried out using CHN automatic analyzer CE1106 (Italy). Experimental error is 0.30-0.50%. Analysis of Br element was carried by visual titration technique using Hg(NO<sub>3</sub>)<sub>2</sub> and diphenylcarbazone as indicator. The burning was done in the Sheninger flask using alkaline solution of hydrogen peroxide as an absorbent. Experimental error is 0.30-0.50%. Spectrophotometry technique was used for the Si analysis as described in reference<sup>6</sup>.

### 3. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of NOLs 1-7











**Figure S4.** <sup>13</sup>C NMR spectrum of **2** in CDCl<sub>3</sub> S20











Figure S8. <sup>13</sup>C NMR spectrum of 4 in CDCl<sub>3</sub>











Figure S11. <sup>1</sup>H NMR spectrum of 6 in CDCl<sub>3</sub>







Figure S13. <sup>1</sup>H NMR spectrum of 7 in CDCl<sub>3</sub>





#### 4. MS and MALDI-TOF spectra of NOLs (1-7)



Figure S15. MS spectrum of 1.



Figure S16. MS spectrum of 2.



Figure S17. MALDI-TOF spectrum of 3 (violet curve - calculated spectrum and red curve

#### experimental spectrum).



Figure S18. MALDI-TOF spectrum of 4 (violet curve - calculated spectrum and red curve

experimental spectrum).



Figure S19. MALDI-TOF spectrum of 5 (green curve - calculated spectrum and violete curve

experimental spectrum).



Figure S20. MS spectrum of 6.



Figure S21. MS spectrum of 7.

5. GPC curves of NOLs 1-7 and their precursors 11, 13, 18, 19, 21-23.



Figure S22. GPC curves of 1 (black curve) and 11 (red curve).



Figure S23. GPC curves of 2 (black curve) and 13 (red curve).



Figure S24. GPC-curves of 3 (black curve), 19 (red curve) and 18 (blue curve).



Figure S25. GPC-curves of 4 (black curve) and 21 (red curve).



Figure S26. GPC-curves of 5 (black curve), 23 (red curve) and 22 (blue curve).



Figure S27. GPC curves of 6 (black curve) and 13 (red curve).



Figure S28. GPC curves of 7 (black curve) and 13 (red curve).

6. A scheme and description of the measuring apparatus for scintillation characteristics



**Figure S29.** A scheme of the measuring apparatus for scintillation characteristics: 1 - impulse generator G5-78, 2 – digital oscilloscope Tektronix TDS5034, 3 – light-proof housing, 4 –  $\alpha$ -particles source <sup>239</sup>Pu, 5 – light-emitting diode, 6 – the sample under investigation, 7 – collimator of  $\alpha$ -particles, 8 – PMT2 (Hamamatsu R7400U-06), 9 – PMT1 (Hamamatsu R7400U-06), 10 – potential divider PMT2, 11 – electrical shield between PMT1 and PMT2, 12 – potential divider PMT1, 13 – high-voltage power supply for PMT2, 13 – high-voltage power supply for PMT1.

A scheme of the measuring apparatus for scintillation characteristics of the samples is shown on Figure S29. It consists from a light-proof housing (3), inside of which the following parts are placed: two photomultipliers (PMT) Hamamatsu R7400U-06 (8,9) with separate potential dividers (10, 12),  $\alpha$ -particles source <sup>239</sup>Pu (4) and light source (light-emitting diode KL107) (5), emitting in a green spectral range. The signals from PMTs were given to the digital oscilloscope (2) by two independent channels from PMT1 and PMT2, respectively. High voltage to the PMTs was supplied from high-voltage power sources BNV-16P (13,14) and it was controlled by digital voltmeter MXD 4660A. For output of one-electron signals in both PMTs, an impulse from the generator G5-78 (1) having the amplitude of 5V and duration of 50 ns was given to the light-emitting diode in the forward direction. For suppuration of the electrical interference from one channel to the other, the electrical shield (11) was mounted between the PMTs.

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