

## Supporting Information

### Design and Development of Novel 2-D Oligomers for Electroactive Device Application

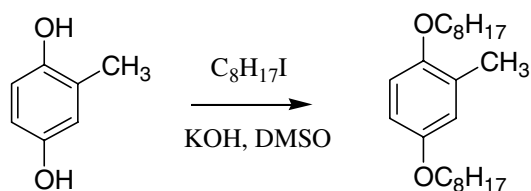
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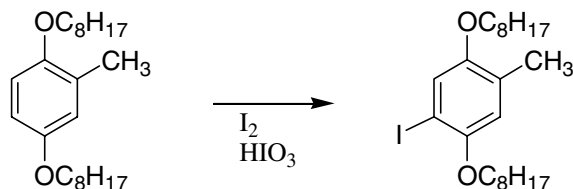
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### Synthesis

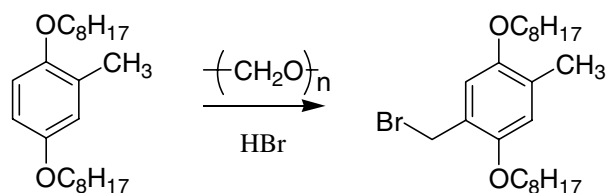


**1,4-Bis(octyloxy)-2-methylbenzene.** The following procedure was adapted from the literature<sup>1</sup>. To 200 mL of DMSO powdered KOH (44.8 g, 0.8 mole) was added and the solution was stirred for 5 min. Then 2-methylhydroquinone (12.41 g, 0.1 mole) was added followed immediately by octyl iodide (96 g, 0.4 mole). After stirring for 7 hours the reaction mixture was poured into water and extracted with dichloromethane (3 x 200 ml). The combined organic extracts were washed with water (5x100 ml) and filtered through cotton. The solvent was then removed by rotary evaporation and the product was purified by vacuum distillation (21g, yield 60%,  $b_{0.75}$  133-5°, lit.<sup>2</sup> mp 31°C). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 0.89 (t, J = 6.2 Hz, 6H, 2  $\times$  CH<sub>3</sub>); 1.15-1.57 (m, 20H, 10  $\times$  CH<sub>2</sub>); 1.69-1.79 (m, 4H, 2  $\times$  CH<sub>2</sub>CH<sub>2</sub>O); 2.20 (s, 3H, CH<sub>3</sub>); 3.89 (t, J = 6.5 Hz, 4H, 2  $\times$  CH<sub>2</sub>O); 6.62-6.76 (m, 3H, arom.).



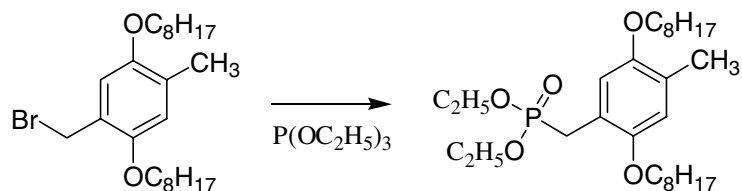
**1-Iodo-2,5-bis(octyloxy)-4-methylbenzene.** The following procedure was adapted from the

literature.<sup>3</sup> The mixture of 1,4-bis(octyloxy)-2-methylbenzene, (5.58 g, 16 mmol), I<sub>2</sub> (1.83 g, 7.2 mmol), HIO<sub>3</sub> (0.84 g, 4.8 mmol), 30% H<sub>2</sub>SO<sub>4</sub> (2.4 mL), and CCl<sub>4</sub> (3.2 mL) in acetic acid (15 mL) was heated for 7 hours at 70 °C. The reaction mixture was cooled with an ice bath. The precipitate was filtered off and washed with methanol and recrystallized twice from ethanol (crème color crystals). Yield 75%, 5.7 g, mp 51-2 °C. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>), δ(ppm): 0.89 (t, J = 6.8 Hz, 6H, 2 × CH<sub>3</sub>); 1.20-1.57 (m, 20H, 10 × CH<sub>2</sub>); 1.70-1.83 (m, 4H, 2 × CH<sub>2</sub>CH<sub>2</sub>O); 2.18 (s, 3H, CH<sub>3</sub>); 3.87 (t, J = 6.6 Hz, 2H, CH<sub>2</sub>O); 3.93 (t, J = 6.5 Hz, 2H, CH<sub>2</sub>O); 6.65 (s, 1H, arom.); 7.16 (s, 1H, arom.). IR (cm<sup>-1</sup>): 2962 (m), 2953 (m), 2940 (s), 2913 (s), 2865 (m), 2850 (s), 1670 (w), 1595 (w), 1495 (s), 1471 (s), 1453 (m), 1395 (m), 1382 (s), 1371 (s), 1279 (m), 1260 (m), 1213 (s), 1159 (w), 1127 (w), 1048 (s), 1033 (m), 1003 (m), 959 (w), 844 (s), 816 (m), 754 (w), 732 (m), 717 (m), 624 (w), 511 (w), 438 (w). MS (ES): m/z 474.2 (M<sup>+</sup>); high resolution MS: M<sup>+</sup> 474.1980 (obs); 474.1995 (calc).

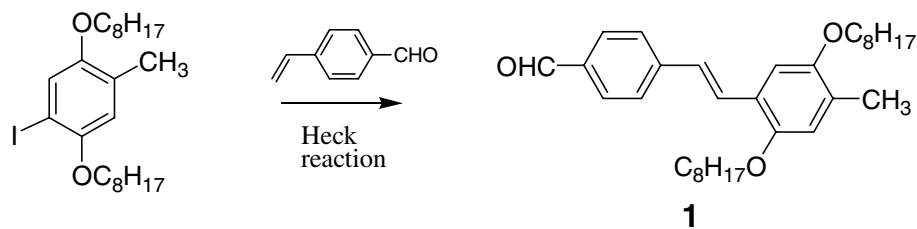


**1-(Bromomethyl)-2,5-bis(octyloxy)-4-methylbenzene.** The following procedure was adapted from the literature.<sup>4</sup> To a suspension of 1,4-bis(octyloxy)-2-methylbenzene, (7.42 g, 21.29 mmol) and paraformaldehyde (0.65 g, 21.82 mmol) in acetic acid (35 mL) hydrogen bromide (4.34 mL, 30 wt % in acetic acid) was added all at once. The mixture was then heated to 45 –48 °C with stirring for 2 hours. As the reaction proceeded, the suspension changed to a clear solution. After cooling to room temperature, the mixture was poured into the ice. The white precipitate was filtered off, dried and used for the next reaction (8.9 g, 95 % yield). For the analysis the product was recrystallized from chloroform/*i*-propanol, mp 56.7-57.3 °C. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>), δ (ppm): 0.89 (t, J = 6.4 Hz, 6H, 2 × CH<sub>3</sub>); 1.20-1.60 (m, 20H, 10 × CH<sub>2</sub>); 1.72-1.83 (m, 4H, 2 × CH<sub>2</sub>CH<sub>2</sub>O); 2.20 (s, 3H, CH<sub>3</sub>); 3.90 (t, J = 6.4 Hz, 2H, CH<sub>2</sub>O); 3.97 (t, J = 6.5 Hz, 2H, CH<sub>2</sub>O); 4.57 (s, 2H, CH<sub>2</sub>Br); 6.68 (s, 1H, arom.); 6.78 (s, 1H, arom.). IR (cm<sup>-1</sup>): 2953 (s), 2940 (s), 2919 (s), 2866 (m), 2853 (s), 1617 (w), 1589 (w), 1514 (s),

1505 (s), 1473 (s), 1456 (m), 1438 (m), 1407 (s), 1394 (s), 1379 (m), 1304 (m), 1263 (w), 1222 (s), 1208 (s), 1127 (m), 1079 (w), 1063 (w), 1045 (s), 1035 (s), 1004 (s), 946 (w), 900 (m), 889 (w), 873 (w), 857 (s), 841 (m), 758 (m), 731 (w), 719 9m), 698 (s), 667 (m), 562 (m), 497 (w), 445 (w). MS (CI):  $m/z$  440.10 ( $M^+$ , 98 % (calc. 440.23); 441.10 ( $M + H^+$ , 30%); 442.10 (81Br1; 12C41, 100%).

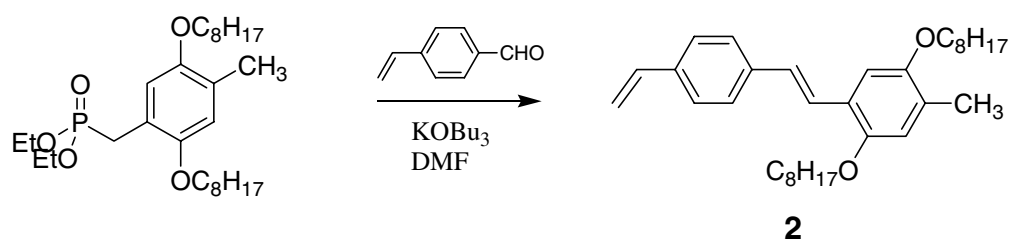


**1-(Diethylphosphonomethyl)-2,5-bis(octyloxy)-4-methylbenzene.** A mixture of 1-(bromomethyl)-2,5-bis(octyloxy)-4-methylbenzene (5.30g, 12 mmol) and triethyl phosphate (2.99 g, 18 mmol) was heated to 85 °C for 4 hours. After the mixture was cooled ethyl bromide and the excess of triethyl phosphate were distilled out under the vacuum. The white solid formed was recrystallized from ethanol. (Mp 38-38.5, yield 96%).  $^1H$  NMR (250 MHz,  $CDCl_3$ ),  $\delta$  (ppm): 0.89 (t,  $J = 6.8$  Hz, 6H,  $2 \times CH_3$ ); 1.25 (t,  $J = 7.1$  Hz, 6H,  $2 \times CH_3$ ); 1.20-1.57 (m, 20H,  $10 \times CH_2$ ); 1.70-1.80 (m, 4H,  $2 \times CH_2CH_2O$ ); 2.20 (s, 3H,  $CH_3$ ); 3.22 (d,  $J = 21.4$  Hz, 2H,  $CH_2P$ ); 3.90 (t,  $J = 6.4$  Hz, 4H,  $2 \times CH_2O$ ); 4.03 (quintet,  $J = 7.1$  Hz, 4H,  $2 \times CH_2$ ); 6.67 (s, 1H, arom.); 6.85 (s, 1H, arom.). MS (ES):  $m/z$  499.3 ( $M + H^+$ ).



**Benzaldehyde, 4-[2-[2,5-bis(octyloxy)-4-methylphenyl]ethenyl], 1.** To a solution of 1-iodo-2,5-bis(octyloxy)-4-methylbenzene, (4.74 g, 10 mmol), tri-*o*-tolylphosphine (609 mg, 2 mmol) and 4-vinylbenzaldehyde (1.45 g, 11 mmol) in 25-30 mL of dry DMF, tributylamine (1.85 g, 10 mmol) was added under nitrogen. The mixture was heated and  $Pd(OAc)_2$  (90 mg, 0.4 mmol) was then added. The

resulting mixture was stirred at ~85 °C overnight under a nitrogen atmosphere. After having been cooled to room temperature, the mixture was poured into 1M HCl (~150 mL) and extracted with ethyl ether (3 × 60 ml). After drying with MgSO<sub>4</sub> and removing the solvent the crude product was crystallized from chloroform - methanol mixture to give 4.14 g (86%) of bright yellow solid. For analysis **1** was recrystallized from chloroform methanol mixture, mp 44.5-46 °C. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>), δ (ppm): 0.89 (t, J = 6.2 Hz, 6H, 2 × CH<sub>3</sub>); 1.20-1.59 (m, 20H, 10 × CH<sub>2</sub>); 1.76-1.92 (m, 4H, 2 × CH<sub>2</sub>CH<sub>2</sub>O); 2.25 (s, 3H, CH<sub>3</sub>); 3.98 (t, J = 6.4 Hz, 4H, 2 × CH<sub>2</sub>O); 6.75 (s, 1H, arom.); 7.04 (s, 1H, arom.); 7.11 (d, J = 16.3 Hz, 1H, H<sub>vinyl</sub>); 7.62 (d, J = 16.3 Hz, 1H, H<sub>vinyl</sub>); 7.65 (d, J = 8.1 Hz, 2H, arom.); 7.85 (d, J = 8.1 Hz, 2H, arom.); 9.98 (s, 1H, CHO). IR (cm<sup>-1</sup>): 3046 (w), 2955 (s), 2935 (s), 2918 (s), 2898 (sh.), 2864 (sh.), 2852 (s), 2717 (w), 1701 (s), 1598 (s), 1574 (w), 1565 (m), 1512 (s), 1502 (m), 1475 (s), 1468 (s), 1455 (w), 1439 (w), 1421 (w), 1411 (w), 1391 (s), 1374 (w), 1336 (w), 1320 (w), 1305 (w), 1289 (w), 1277 (w), 1260 (w), 1249 (w), 1215 (s), 1191 (sh.), 1169 (m), 1127 (w), 1104 (w), 1063 (sh.), 1049 (s), 1036 (m), 1004 (m), 964 (s), 865 (w), 845 (s), 808 (m), 765 (w), 727 (w), 718 (m), 513 (m). MS (CI): m/z 478.2 (M<sup>+</sup>).

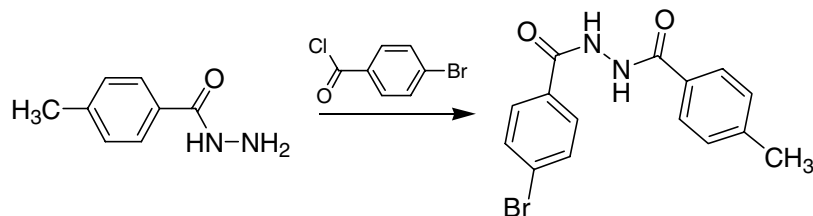


**1-Ethenyl-4-[2-[2,5-bis(octyloxy)-4-methylphenyl]ethenyl]benzene, 2.** To 4-vinylbenzaldehyde<sup>5</sup> (0.89 g, 6.7 mmol) and 1-(diethylphosphonomethyl)-2,5-bis(octyloxy)-4-methylbenzene (3.34 g, 6.7 mmol) in 10 ml of dry DMF potassium *tert*-butoxide (1.88 g, 16.75 mmol) in 20 ml of DMF was added dropwise under nitrogen. The mixture was heated for seven hours at ~ 85 °C then the solution was cooled to room temperature and poured into ~ 250 ml of water acidified with HCl. After extraction of the mixture with chloroform (~ 200 ml) the organic part was separated and washed with water five times, dried over MgSO<sub>4</sub> and the solvent was evaporated. The residue was purified by

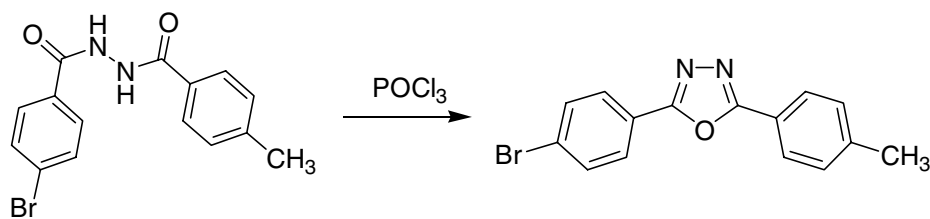
column chromatography using chloroform:hexane mixture (10:1  $\rightarrow$  4:1) as an eluent to yield 0.96 g (30%) of **2**.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 0.85-0.96 (m, 6H,  $2 \times \text{CH}_3$ ); 1.14-1.60 (m, 20H,  $10 \times \text{CH}_2$ ); 1.74-1.90 (m, 4H,  $2 \times \text{CH}_2\text{CH}_2\text{O}$ ); 2.23 (s, 3H,  $\text{CH}_3$ ); 3.96 (t,  $J = 6.2$  Hz, 2H,  $\text{CH}_2\text{O}$ ); 3.98 (t,  $J = 6.3$  Hz, 2H,  $\text{CH}_2\text{O}$ ); 5.23 (d,  $J = 10.8$  Hz, 1H,  $\text{H}_{\text{vinyl}}$ ); 5.75 (d,  $J = 17.6$  Hz, 1H,  $\text{H}_{\text{vinyl}}$ ); 6.71 (dd,  $J_1 = 17.6$ ,  $J_2 = 10.8$  Hz, 1H,  $\text{H}_{\text{vinyl}}$ ); 6.72 (s, 1H, arom.); 7.03 (s, 1H, arom.); 7.04 (d,  $J = 16.4$  Hz, 1H,  $\text{H}_{\text{vinyl}}$ ); 7.39 (d,  $J = 8.1$  Hz, 2H, arom.); 7.45 (d,  $J = 16.4$  Hz, 1H,  $\text{H}_{\text{vinyl}}$ ); 7.48 (d,  $J = 8.1$  Hz, 2H, arom.). MS (ES):  $m/z$  476.3 ( $\text{M}^+$ ).

**1,4-Bis[2-[4-[2-[2,5-bis(octyloxy)-4-methylphenyl]ethenyl]phenyl] ethenyl]-2,5-dibromobenzene, 5.** NaH (216 mg, 9 mmol) was added to a solution of 2,5-bis(diethylphosphonomethyl)-1,4-dibromobenzene, **4**, (1.608 g, 3 mmol) in 10 ml of dry DME. After stirring the resulting mixture for 5 min compound **1** (2.782g, 6 mmol) in 20 ml of DME was added and the reaction mixture was heated for 7 hours at 80 – 85 °C. By the end of the reaction the bright yellow suspension turned into a clear brown solution. Then the solution was cooled to room temperature and poured into ~ 200 ml of water acidified with HCl. The brownish yellow color precipitate was filtered off and dried and the crude product was crystallized from chloroform methanol mixture to yield 2.87 g (81%) of bright yellow solid, mp 109-111 °C.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 0.83-0.96 (m, 12H,  $4 \times \text{CH}_3$ ); 1.24-1.62 (m, 40H,  $20 \times \text{CH}_2$ ); 1.74-1.90 (m, 8H,  $4 \times \text{CH}_2\text{CH}_2\text{O}$ ); 2.24 (s, 6H,  $2 \times \text{CH}_3$ ); 3.93-4.04 (m, 8H,  $4 \times \text{CH}_2\text{O}$ ); 6.73 (s, 2H, arom.); 7.05 (s, 2H, arom.); 7.06 (d,  $J = 16.1$  Hz, 2H,  $2 \times \text{H}_{\text{vinyl}}$ ); 7.07 (d,  $J = 16.3$  Hz, 2H,  $2 \times \text{H}_{\text{vinyl}}$ ); 7.38 (d,  $J = 16.1$  Hz, 2H,  $2 \times \text{H}_{\text{vinyl}}$ ); 7.51 (d,  $J = 16.3$  Hz, 2H,  $2 \times \text{H}_{\text{vinyl}}$ ); 7.54 (s, 8H, arom.); 7.89 (s, 2H, arom.). IR ( $\text{cm}^{-1}$ ): 3074 (w), 3046 (w), 3006 (w), 2950 (s), 2927 (sh.), 2919 (s), 2868 (sh.), 2852 (s), 1683 (w), 1623 (m), 1594 (m), 1573 (w), 1557 (w), 1513 (s), 1504 (s), 1468 (s), 1459 (s), 1411 (s), 1391 (s), 1372 (m), 1333 (m), 1312 (m), 1285 (m), 1276 (m), 1245 (m), 1207 (s), 1179 (m), 1125 (w), 1069 (m), 1052 (s), 1022 (m), 955 (s), 854 (s), 806 (m), 764 (w), 721 (w), 695 (w), 649 (w), 619 (w), 520 (m), 499 (w), 435 (w). MS (MALDI):  $m/z$  1182.43 ( $\text{M}^+$ ; calc: 1182.57);

1183.4, 1184.5, 1185.4, 1186.4, 1187. 4, 1188.4 (peaks from m/z 1182 to 1188 appear in the expected relative intensities for the molecular ions containing Br and C isotopes).

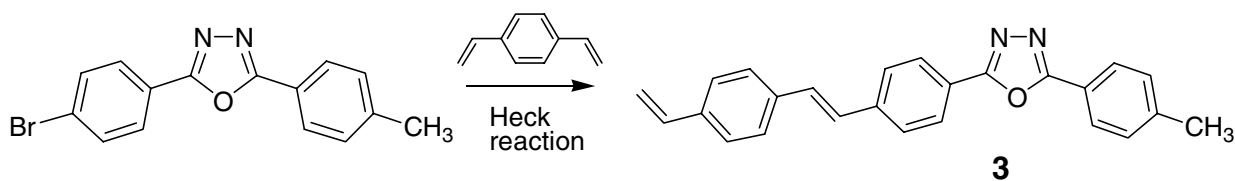


**N'-(4-bromobenzoyl)-4-methylbenzenecarbohydrazide.** The following procedure was previously described.<sup>6</sup> To a solution of 4-methylbenzoylhydrazide (6.843g, 45.56 mmol) in 70 ml of chloroform 4-bromobenzoyl chloride (10g, 45.56 mmol) dissolved in ~ 50 ml of chloroform was added dropwise at room temperature. The reaction mixture was stirred for two hours. The solid was collected by filtration, washed with water and methanol and dried to give 12.86 g of product (85 %, mp 128 °C (DSC 10 °C/min)). <sup>1</sup>H NMR (250 MHz, DMSO – d<sub>6</sub> , δ (ppm): 2.37 (s, 3H, CH<sub>3</sub>); 7.32 (d, J = 7.8 Hz, 2H, arom.); 7.70 (d, J = 8.6 Hz, 2H, arom.); 7.81 (d, J = 7.8 Hz, 2H, arom.); 7.85 (d, J = 8.6 Hz, 2H, arom.); 10.45 (s, 1H, NH); 10.57 (s, 1H, NH). IR (cm<sup>-1</sup>): 3355 (s), 3269 (s), 3093 (m), 3065 (m), 2912 (w), 2849 (w), 2547 (w), 1916 (w), 1680 (s), 1644 (s), 1612 (m), 1591 (s), 1570 (s), 1558 (s), 1503 (m), 1481 (s), 1427 (m), 1398 (m), 1372 (w), 1318 (s), 1302 (s), 1279 (s), 1211 (w), 1177 (M), 1128 (w), 1110 (m), 1010 (s), 920 (w), 869 (w), 852 (w), 840 (s), 833 (s), 815 (w), 805 (w), 792 (w), 757 (s), 748 (s), 739 (s), 680 (m), 583 (s), 547 (m), 497 (w), 473 (w), 464 (w). MS (CI): m/z 332.01 (M<sup>+</sup>); high resolution MS: M<sup>+</sup> 332.0145 (obs); 332.0160 (calc).



**2-(4-Bromophenyl)-5-(4-methylphenyl)-1,3,4-oxadiazole.** N'-(4-bromobenzoyl)-4-methylbenzene carbohydrazide (9 g, 27.11 mmol) in 120 ml POCl<sub>3</sub> was refluxed under nitrogen for 5 hours. The excess of POCl<sub>3</sub> was then distilled out and the residue was poured into water. The white precipitate

obtained was collected by filtration and purified by recrystallization from chloroform / methanol to give product as flaky clear crystals (7.0 g, 82 %, mp 208 °C (DSC 5 °C/min)). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>), δ (ppm): 2.45 (s, 3H, CH<sub>3</sub>); 7.34 (d, J = 7.9 Hz, 2H, arom.); 7.68 (d, J = 8.2 Hz, 2H, arom.); 8.01 (d, J = 7.9 Hz, 2H, arom.); 8.02 (d, J = 8.2 Hz, 2H, arom.). IR (cm<sup>-1</sup>): 3085 (w), 3047 (w), 3025 (w), 2912 (w), 2852 (w), 1921 (w), 1668 (w), 1614 (w), 1602 (s), 1579 (m), 1557 (m), 1543 (w), 1526 (w), 1496 (s), 1478 (s), 1453 (m), 1417 (m), 1400 (m), 1375 (w), 1354 (w), 1312 (w), 1300 (w), 1292 (w), 1280 (w), 1271 (w), 1183 (w), 1120 (w), 1099 (m), 1079 (s), 1067 (m), 1020 (w), 1010 (s), 992 (w), 965 (m), 834 (s), 736 (s), 699 (w), 627 (w), 532 (w), 497 (s), 461 (m), 420 (w). MS (CI): m/z 314.00 (M<sup>+</sup>); 313.9, 314.9, 315.9, 316.9; high resolution MS: M<sup>+</sup> 314.0040 (obs); 314.0055 (calc).

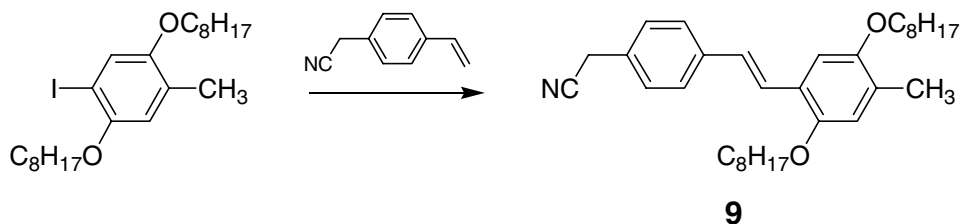


**2-(4-Methylphenyl)-5-{4-[(E)-2(vinylphenyl)ethenyl]phenyl}-1,3,4-oxadiazole, 3**, was synthesized from 2-(4-bromophenyl)-5-(4-methylphenyl)-1,3,4-oxadiazole (0.911 g, 2.9 mmol) and p-divinylbenzene (0.754 g, 5.8 mmol) by procedure described above for compound **1**. The reaction mixture was stirred at 65 °C for 8 hours. As the reaction proceeded, the yellow-green suspension was formed. After cooling to room temperature, the mixture was poured into the water. The precipitate was filtered off, rinsed with methanol and then dried. The solid was extracted with chloroform (~ 200 ml) to remove impurities. After filtering of undissolved particles (~0.220g) the solvent was evaporated to give 0.684 g of practically pure product (65 % yield). Mp 186.1 °C (DSC 5 °C/min). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>), δ (ppm): 2.46 (s, 3H, CH<sub>3</sub>); 5.29 (d, J = 10.7 Hz, 1H, H<sub>vinyl</sub>); 5.80 (d, J = 17.6 Hz, 1H, H<sub>vinyl</sub>); 6.73 (dd, J<sub>1</sub> = 17.6 Hz, J<sub>2</sub> = 10.7 Hz, 1H, H<sub>vinyl</sub>); 7.15 (d, J = 16.0 Hz, 1H, H<sub>vinyl</sub>); 7.24 (d, J = 16.0 Hz, 1H, H<sub>vinyl</sub>); 7.35 (d, J = 8.0 Hz, 2H, arom.); 7.44 (d, J = 8.3 Hz, 2H, arom.); 7.53 (d, J = 8.3 Hz, 2H, arom.); 7.67 (d, J = 8.3 Hz, 2H, arom.); 8.04 (d, J = 8.0 Hz, 2H, arom.); 8.13 (d, J = 8.3 Hz, 2H, arom.). IR (cm<sup>-1</sup>): 3081 (w), 3044 (w), 3019 (m), 3001 (w), 2984 (w), 2912 (w), 2855 (w), 2718 (w),

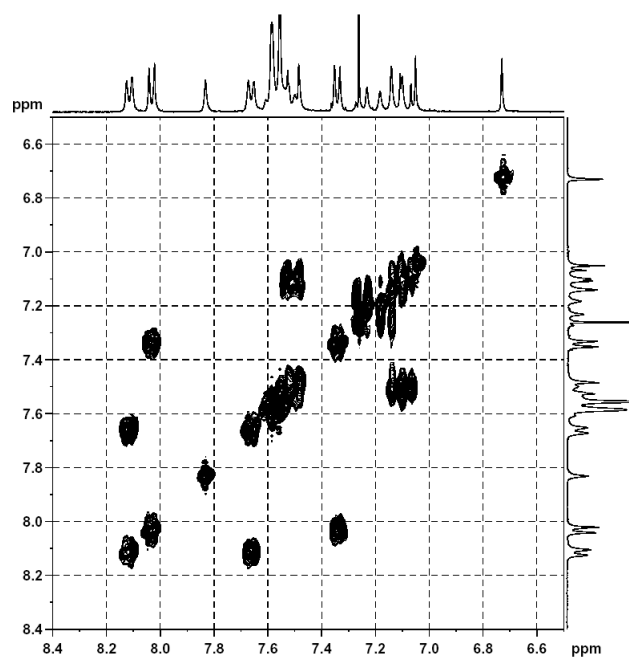
1922 (w), 1813 (w), 1671 (w), 1632 (m), 1609 (m), 1583 (m), 1573 (m), 1557 (m), 1551 (m), 1509 (m), 1496 (s), 1490 (s), 1458 (w), 1425 (m), 1418 (m), 1407 (m), 1373 (w), 1336 (w), 1312 (w), 1290 (w), 1272 (w), 1209 (w), 1184 (m), 1119 (m), 1102 (m), 1080 (s), 1015 (m), 992 (s), 970 (s), 965 (s), 956 (s), 908 (m), 899 (s), 845 (s), 828 (s), 752 (m), 735 (s), 722 (m), 704 (m), 638 (w), 616 (w), 540 (m), 527 (s), 505 (s), 407 (w). MS (MALDI):  $m/z$  364.27 ( $M^+$ ; calc: 364.16).

**1,2-dibromo-4,5-bis[(*E*)-2-(4-(*E*)-2-[4-methyl-2,5-bis(octyloxy)phenyl]ethenylphenyl)ethenyl]benzene, 7**, was synthesized from diethyl 4,5-dibromo-2-[(diethoxyphosphoryl)methyl]benzylphosphonate,<sup>7,8</sup> **6**, (113.4 mg, 0.209 mmol) and compound **1** (251.6 mg, 0.526 mmol) by procedure described above for compound **5**. After extraction of the mixture with chloroform the organic part was separated and washed with water several times, dried over  $MgSO_4$  and the solvent was evaporated. The residue was purified by column chromatography using chloroform:hexane mixture (2 : 1) as an eluent to yield 0.597 g (59 %) of bright yellow solid, mp 81-83 °C.  $^1H$  NMR (360 MHz,  $CDCl_3$ ),  $\delta$  (ppm): 0.84-0.92 (m, 12H,  $4 \times CH_3$ ); 1.24-1.56 (m, 40H,  $20 \times CH_2$ ); 1.77-1.88 (m, 8H,  $4 \times CH_2CH_2O$ ); 2.24 (s, 6H,  $2 \times CH_3$ ); 3.97 (t,  $J = 6.5$  Hz, 4H,  $2 \times CH_2O$ ); 3.99 (t,  $J = 6.1$  Hz, 4H,  $2 \times CH_2O$ ); 6.73 (s, 2H, arom.); 7.01 (d,  $J = 16.2$  Hz, 2H,  $2 \times H_{vinyl}$ ); 7.04 (s, 2H, arom.); 7.07 (d,  $J = 16.2$  Hz, 2H,  $2 \times H_{vinyl}$ ); 7.30 (d,  $J = 16.2$  Hz, 2H,  $2 \times H_{vinyl}$ ); 7.50 (d,  $J = 16.2$  Hz, 2H,  $2 \times H_{vinyl}$ ); 7.52 (dd,  $J_1 = 6.7$  Hz;  $J_2 = 9.3$  Hz, 8H, arom.); 7.83 (s, 2H, arom.). IR ( $cm^{-1}$ ): 3077 (w), 3047 (w), 2954 (s), 2918 (s), 2866 (s), 2850 (s), 1623 (w), 1594 (m), 1512 (s), 1503 (s), 1469 (s), 1454 (s), 1413 (s), 1390 (s), 1376 (w), 1363 (w), 1334 (m), 1314 (m), 1290 (w), 1278 (m), 1251 (m), 1207 (s), 1177 (m), 1124 (m), 1064 (m), 1074 (m), 1020 (m), 954 (s), 918 (m), 886 (w), 864 (w), 847 (s), 801 (m), 720 (w), 696 (w), 530 (m), 474 (w). MS (MALDI):  $m/z$  1182.57 ( $M^+$ ; calc: 1182.57); 1183.6, 1184.6, 1185.6, 1186.6, 1187.6 (peaks from  $m/z$  1182 to 1188 appear in the expected relative intensities for the molecular ions containing Br and C isotopes).

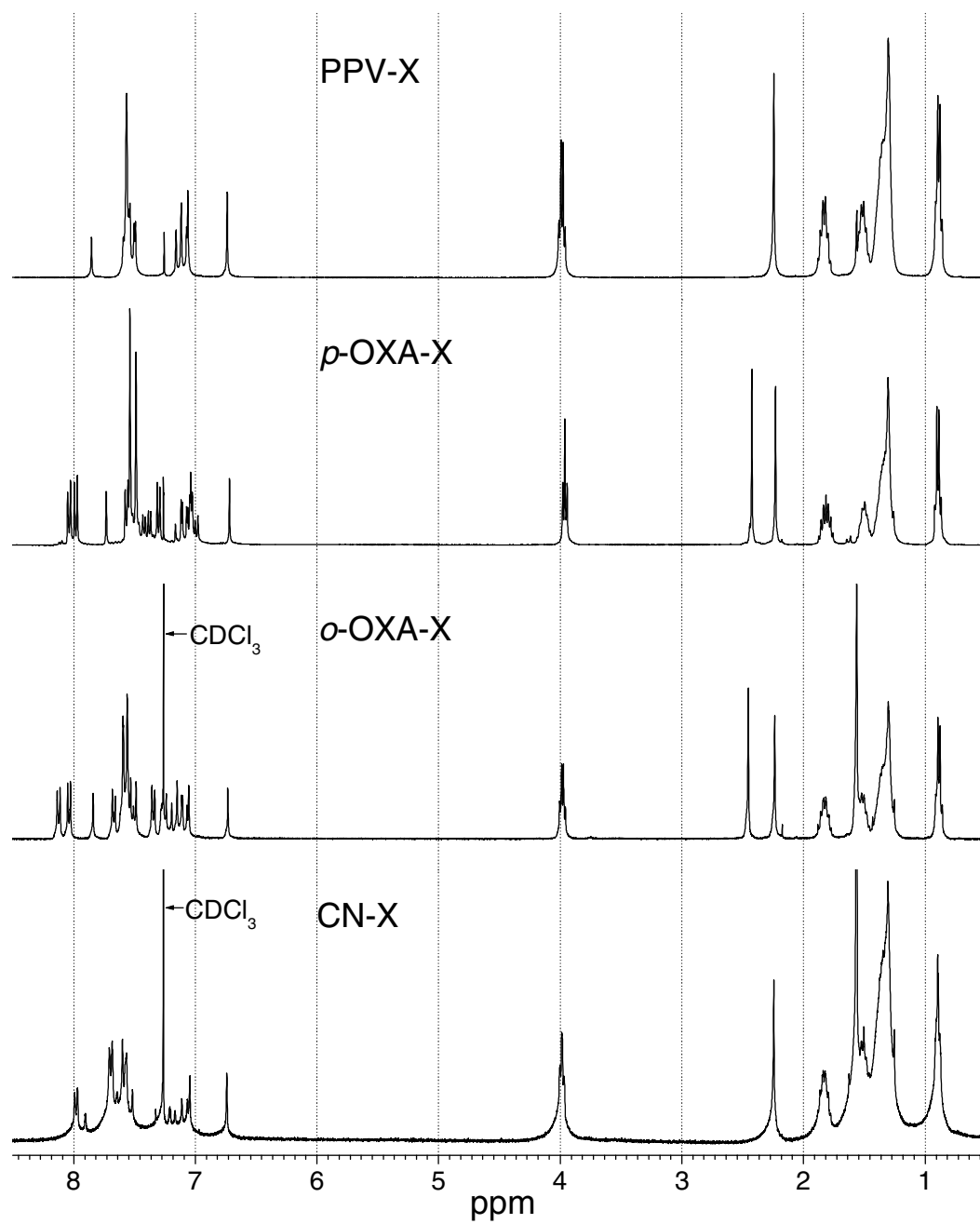




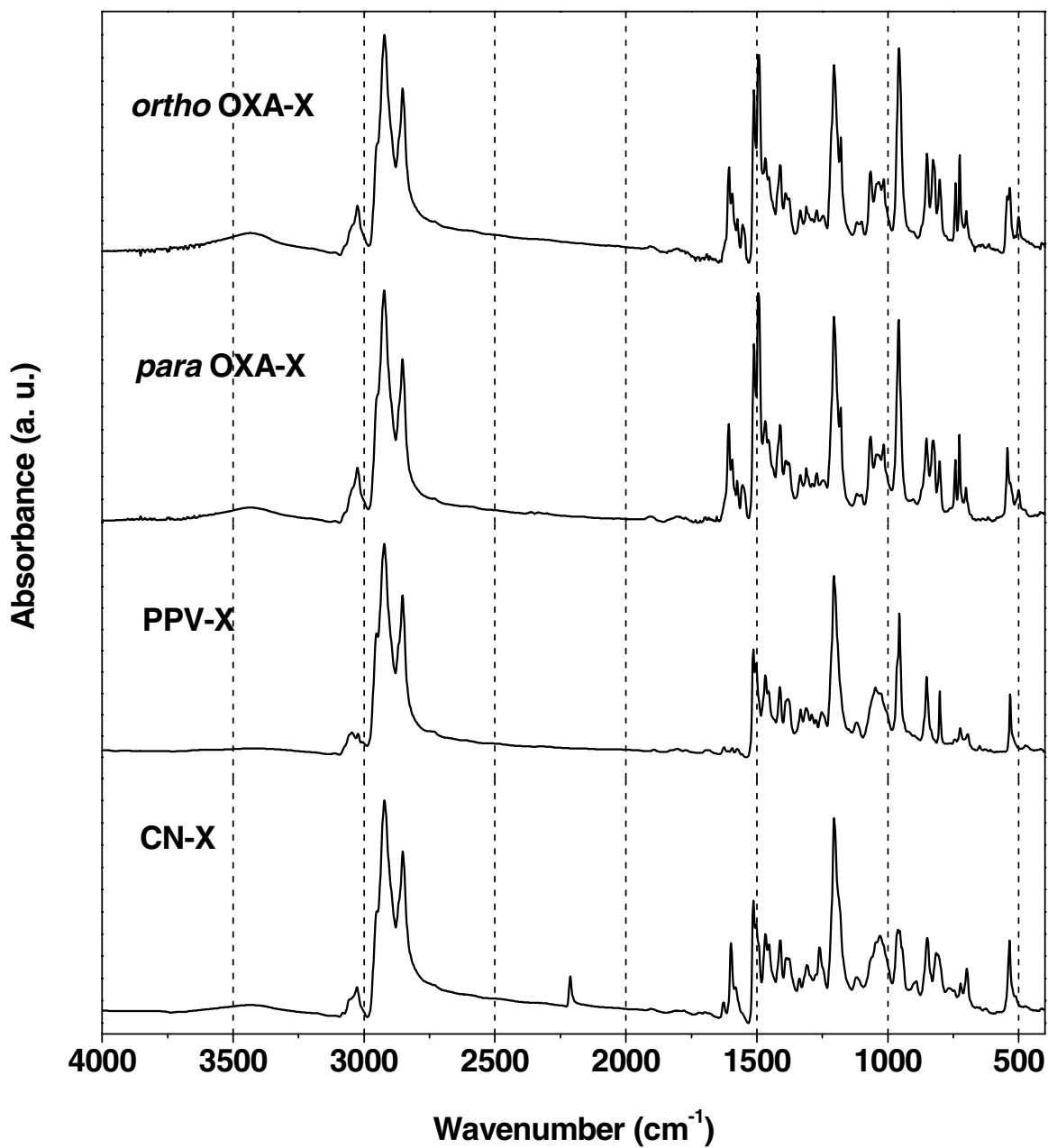
**2-(4-(*E*)-2-[4-methyl-2,5-bis(octyloxy)phenyl]ethenylphenyl)acetonitrile, 9**, was synthesized from 2-(4-vinylphenyl)acetonitrile<sup>9</sup> (1.995 g, 13.95 mmol) and 1-iodo-2,5-bis(octyloxy)-4-methylbenzene (4.40 g, 9.3 mmol) by procedure described above for compound **1**. The crude product was recrystallized from petroleum ether to yield 3.29 g (72%) of pure product, pale yellow crystals mp 68.5-69.5 °C. <sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>), (ppm): 0.88 (t, J = 6.9 Hz, 3H, CH<sub>3</sub>); 0.89 (t, J = 6.5 Hz, 3H, CH<sub>3</sub>); 1.20-1.60 (m, 20H, 10 × CH<sub>2</sub>); 1.70-1.83 (m, 4H, 2 × CH<sub>2</sub>CH<sub>2</sub>O); 2.23 (s, 3H, CH<sub>3</sub>); 3.76 (s, 2H, CH<sub>2</sub>CN); 3.97 (t, J = 6.4 Hz, 2H, OCH<sub>2</sub>); 3.98 (t, J = 6.3 Hz, 2H, OCH<sub>2</sub>); 6.73 (s, 1H, arom.); 7.02 (s, 1H, arom.); 7.04 (d, J = 16.8 Hz, 1H, H<sub>vinyl</sub>); 7.30 (d, J = 8.8 Hz, 2H, arom.); 7.47 (d, J = 16.8 Hz, 1H, H<sub>vinyl</sub>); 7.52 (d, J = 8.8 Hz, 2H, arom.). IR (cm<sup>-1</sup>): 3052 (w), 3026 (w), 2954 (s), 2940 (s), 2924 (s), 2898 (s), 2868 (s), 2853 (s), 2246 (w), 1629 (w), 1602 (w), 1515 (s), 1505 (s), 1492 (m), 1476 (s), 1463 (s), 1453 (m), 1439 (w), 1409 (s), 1393 (s), 1372 (w), 1339 (w), 1324 (w), 1314 (w), 1278 (w), 1262 (w), 1254 (w), 1205 (s), 1165 (w), 1127 (w), 1064 (m), 1045 (s), 1036 (m), 1019 (w), 1005 (m), 976 (s), 953 (w), 898 (w), 856 (m), 851 (m), 834 (w), 821 (w), 793 (w), 760 (w), 735 (w), 726 (w), 710 (m), 698 (m), 652 (w), 632 (w), 614 (w), 542 (w), 510 (w), 412 (w). MS (CI): m/z 489.35 (M<sup>+</sup>); high resolution MS: M<sup>+</sup> 489.3591 (obs); 489.3607 (calc).



**Figure S1.** 400 MHz  $^1\text{H}$ ,  $^1\text{H}$  COSY spectrum of *o*-OXA-X in  $\text{CDCl}_3$ .



**Figure S2.**  $^1\text{H}$  NMR (360 MHz) spectra of PPV-X, p-OXA-X, o-OXA-X and CN-X in  $\text{CDCl}_3$ .



**Figure S3.** IR spectra of *ortho* OXA-X, *para* OXA-X, PPV-X and CN-X in KBr pellets.

## REFERENCES

- (1) Johnstone, R. A. W.; Rose, M. E. *Tetrahedron* 1979, 35, 2169.
- (2) Kretzschmann, H.; Meier, H. *Journal Fur Praktische Chemie-Chemiker-Zeitung* 1994, 336, 247.
- (3) Bao, Z. N.; Chen, Y. M.; Cai, R. B.; Yu, L. P. *Macromolecules* 1993, 26, 5281.
- (4) Van der Made, A. W.; Van der Made, R. H. *Journal of Organic Chemistry* 1993, 58, 1262.
- (5) Niazimbetova, Z. I.; Menon, A.; Galvin, M. E.; Evans, D. H. *Journal of Electroanalytical Chemistry* 2002, 529, 43.
- (6) Peng, Z. H.; Bao, Z. N.; Galvin, M. E. *Advanced Materials* 1998, 10, 680.
- (7) Rivera, J. M.; Martin, T.; Rebek, J. *Journal of the American Chemical Society* 2001, 123, 5213.
- (8) Kimura, M.; Narikawa, H.; Ohta, K.; Hanabusa, K.; Shirai, H.; Kobayashi, N. *Chemistry of Materials* 2002, 14, 2711.
- (9) Wright, S. W.; McClure, L. D. *Organic Preparations and Procedures International* 1994, 26, 602.