Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Single-material organic solar cells with fully conjugated electron-donor alkoxy-substituted bithiophene units and electron-acceptor benzothiadiazole moieties alternating in the main chain

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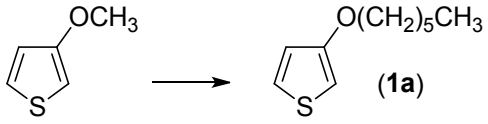
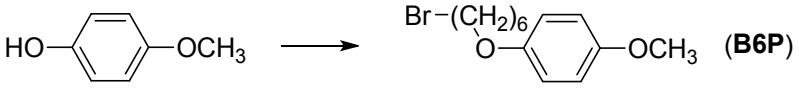
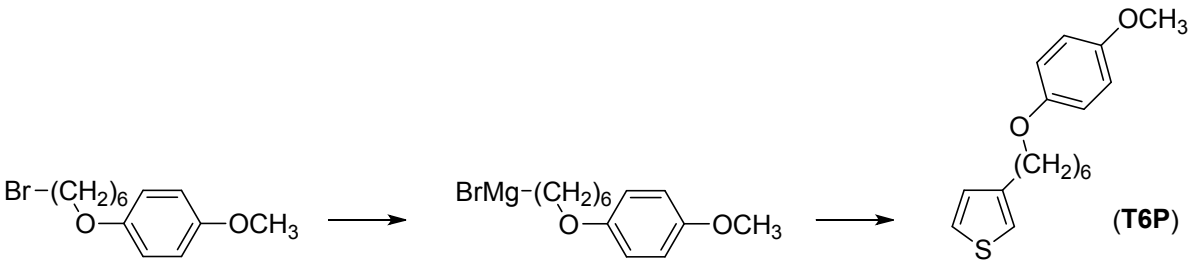
I. Monomers synthesis



3-Hexyloxythiophene (**1a**). To a three-necked flask containing a solution of 3-methoxythiophene (2.00 g, 17.4 mmol) in 16.8 ml of toluene, 1-hexanol (4.4 ml, 34.8 mmol) and *p*-toluenesulfonic acid monohydrate (0.60 g, 2.6 mmol) were sequentially added under stirring and inert atmosphere. The mixture was heated to 120°C for 20 h. After cooling, the reaction mixture was poured into water (150 ml) and extracted with CH_2Cl_2. The organic phase was washed with water, dried with Na_2SO_4 and the solvent removed by evaporation under reduced pressure. The crude product was finally purified by column chromatography on silica gel with cyclohexane/CH_2Cl_2 4:1 v/v as eluent to afford 2.21 g (68% yield) of **1a** as a colorless liquid. EI-MS m/z 184(M^+).
^{1}H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.17 (dd, ^3J = 5.2 Hz, ^4J = 3.2 Hz, 1H), 6.78 (dd, ^3J = 5.2 Hz, ^4J = 1.6 Hz, 1H), 6.22 (dd, , ^3J = 3.2 Hz, ^4J = 1.6 Hz 1H), 3.95 (t, 2H), 1.83-1.73 (m, 2H), 1.50-1.29 (m, 6H), 0.92 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.1, 124.5, 119.5, 96.9, 70.3, 31.6, 29.2, 25.7, 22.6, 14.0.

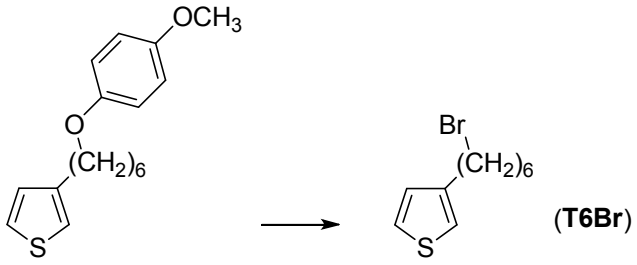


1-Bromo-6-(p-methoxy)phenoxyhexane (**B6P**). A solution of KOH (32.32 g, 0.58 mol) and *p*-methoxyphenol (49.46 g, 0.40 mol) in methanol (80 ml) was added in 90 min to a solution of 1,6-dibromohexane (200.0 g, 0.82 mol) in acetone (160 ml) and then heated at reflux under stirring for 1 h. After cooling to room temperature and removal of solid KBr by filtration, the solvent was evaporated under reduced pressure and the crude product was dissolved in Et_2O (100 ml), washed with NaOH 2% wt. and then with water. After drying on Na_2SO_4 and solvent evaporation at reduced pressure, the crude product was purified by fractional vacuum distillation (b.p. 52°-54°C at 0.5 mbar) in order to eliminate the excess of B6B to give 89.56 g (78% yield) of **B6P** as a white solid. EI-MS m/z 286(M^+).
^{1}H-NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 6.83 (s, 4H, aryl), 3.91 (t, 2H), 3.77 (s, 3H), 3.42 (t, 2H), 1.89 (m, 2H), 1.77 (m, 2H), 1.53-1.46 (m, 4H).



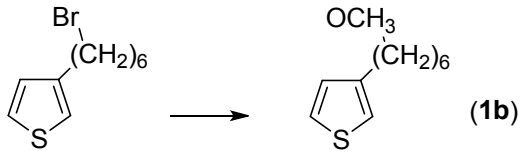
3-[6-(p-Methoxy)phenoxy]hexylthiophene **(T6P)**. To a three-necked flask, containing B6P (20.0 g, 0.07 mol) and Mg turnings (1.75 g, 0.07 mol), anh. Et_2O (150 ml) was added under nitrogen atmosphere and stirring. The reaction mixture was then heated to 35°C for 5 h. The so obtained

Grignard derivative of B6P was subsequently dropped via cannula to a second flask containing a suspension of 3-bromothiophene (9.62 g, 0.06 mol) and Ni(dppp)Cl_2 (0.056 g, 0.10 mmol) at –5/–8°C. The mixture was heated under reflux for 16 h and then poured into aq. HCl 2% (200 ml) followed by extraction with Et_2O. The organic phase was washed with water, dried on Na_2SO_4 and the solvent removed by evaporation under reduced pressure. The crude product was finally purified by crystallization from ligroin, followed by column chromatography on silica gel with hexane/Et_2O 97:3 v/v as eluent to obtain 8.49 g (42% yield) of **T6P** as a white solid. EI-MS m/z 290(M^+).
^{1}H-NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.24-7.22 (m, 1H), 6.94-6.90 (m, 2H), 6.82 (s, 4H), 3.90 (t, 2H), 3.76 (s, 3H), 2.64 (t, 2H), 1.82-1.70 (m, 2H), 1.70-1.58 (m, 2H), 1.54-1.38 (m, 4H).



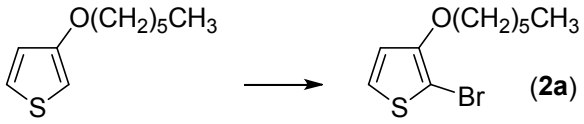
(**T6Br**)

3-(6-Bromohexyl)thiophene **(T6Br)**. A mixture of acetic anhydride (19.5 ml, 0.21 mol) and aq. HBr (48% wt.) (14.1 ml, 0.12 mol) was added to T6P (6.00 g, 0.021 mol) and the reaction mixture heated at 90°C for 24 h. After cooling and dilution with water, the mixture was extracted with petroleum ether, then washed with saturated aq. $NaHCO_3$ and finally with water to neutrality. After drying on Na_2SO_4 and solvent evaporation at reduced pressure, the crude product was purified by column chromatography on silica gel with cyclohexane as eluent to afford 3.92 g (77% yield) of **T6Br** as a colorless oil. EI-MS m/z 246(M^+).
^{1}H-NMR (400 MHz, $CDCl_3$, TMS/ppm): δ7.24-7.22 (m, 1H, 5-H), 6.94-6.90 (m, 2H), 3.40 (t, 2H), 2.63 (t, 2H), 1.90-1.82 (m, 2H), 1.68-1.60 (m, 2H), 1.50-1.32 (m, 4H).



(**1b**)

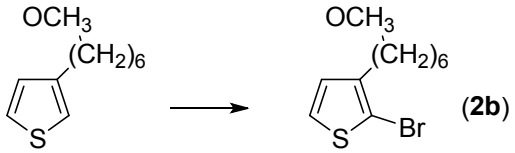
3-(6-Methoxyhexyl)thiophene **(1b)**. A 0.3 M solution of T6Br (3.83 g, 0.016 mol) in anh. MeOH (52 ml) was added to 16.4 ml of MeONa in MeOH (30% wt) under stirring and nitrogen atmosphere. The reaction mixture was refluxed for 4 h, then poured into water and extracted with Et_2O. The ethereal solution was dried on Na_2SO_4 and evaporated at reduced pressure obtaining 2.78 g (90% yield) of **1b** as a colorless liquid. EI-MS m/z 198(M^+).
^{1}H-NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.24-7.22 (m, 1H), 6.94-6.90 (m, 2H), 3.36 (t, 2H), 3.33 (s, 3H), 2.63 (t, 2H), 1.68-1.54 (m, 4H), 1.42-1.32 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): 143.1, 128.2, 125.1, 119.8, 72.8, 58.5, 30.5, 30.2, 29.6, 29.1, 26.0.



(**2a**)

2-Bromo-3-hexyloxythiophene (**2a**). N-Bromosuccinimide (NBS) (386 mg, 2.2 mmol) dissolved in 3 ml of N,N-dimethylformamide (DMF) was added in 1h to a solution of 3-hexyloxythiophene (**1a**) (400 mg, 2.2 mmol) in 3 ml of DMF at 0°C, under stirring and protection from light. The mixture was stirred for 24h at room temperature in the dark and then poured into water (50 ml) and extracted with Et_2O. After drying on Na_2SO_4 and solvent evaporation at reduced pressure, the crude product was purified by column chromatography on silica gel with cyclohexane/ethyl acetate 19:1 v/v as eluent to afford 560 mg (98% yield) of **2a** as a yellowish liquid. EI-MS m/z 264(M^+). *Caution! The product appears to be unstable, undergoing exothermic autopolymerization if stored in the absence of solvent even in the cold.*

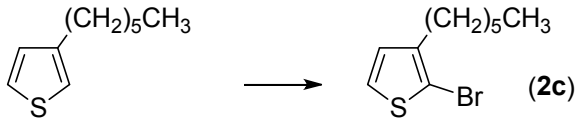
^{1}H-NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.18 (d, ^3J = 4 Hz, 1H), 6.78 (d, ^3J = 4 Hz, 1H), 4.03 (t, 2H), 1.79-1.71 (m, 2H), 1.50-1.32 (m, 6H), 0.91 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 124.1, 117.5, 91.6, 72.2, 31.5, 29.5, 25.5, 22.6, 14.0.



(**2b**)

2-Bromo-3-(6-methoxyhexyl)thiophene (**2b**). The same procedure described for **2a** was followed starting from 3-(6-methoxyhexyl)thiophene (**1b**) (262 mg, 1.32 mmol) and NBS (235 mg, 1.32 mmol) in DMF obtaining 325 mg (89% yield) of pure **2b** as a yellowish oil, without need of chromatographic purification. EI-MS m/z 276(M^+).

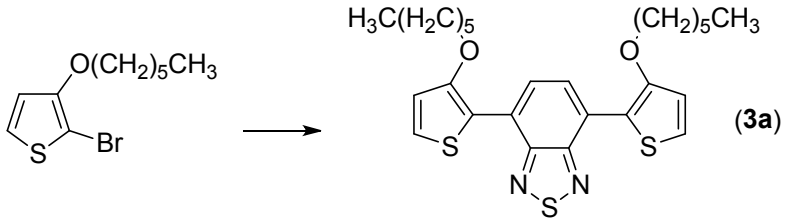
^{1}H-NMR (500 MHz, $CDCl_3$, TMS/ppm): δ 7.17 (d, ^3J = 4 Hz, 1H), 6.78 (d, ^3J = 4 Hz, 1H), 3.34 (t, 2H), 3.33 (s, 3H), 2.56 (t, 2H), 1.64-1.54 (m, 4H), 1.41-1.30 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$):141.8, 128.2, 125.2, 108.8, 72.8, 58.2, 29.7, 29.6, 29.3, 29.0, 25.9.



(**2c**)

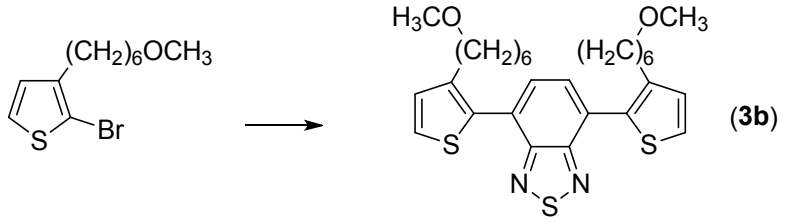
2-Bromo-3-hexylthiophene (**2c**). The same procedure described for **2a** was followed starting from 3-hexylthiophene (1.00 g, 0.006 mol) in 7 ml of DMF and NBS (1.06 g, 0.006 mol) dissolved in 7 ml of DMF. The crude product was purified by column chromatography on silica gel with cyclohexane as eluent to obtain 1.21 g (77% yield) of **2c** as a colorless liquid. EI-MS m/z 246(M^+).

^{1}H-NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.20 (d, ^3J = 4 Hz, 1H), 6.82 (d, ^3J = 4 Hz, 1H), 2.60 (t, 2H), 1.69-1.54 (m, 2H), 1.43-1.26 (m, 6H), 0.94 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 142.0, 128.2, 125.1, 108.8, 31.7, 29.7, 29.4, 29.0, 22.6, 14.1.



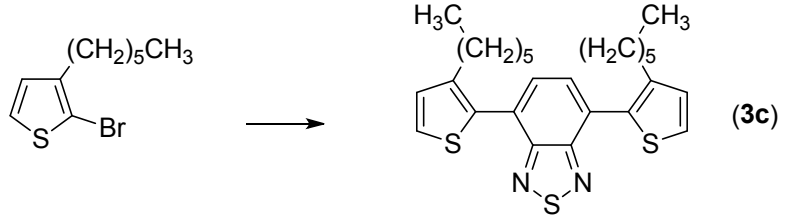
(**3a**)

4,7-Bis(3-hexyloxythiophen-2-yl)benzo[c][2,1,3]thiadiazole (**3a**). A mixture of 2-bromo-3-hexyloxythiophene (120 mg, 0.46 mmol), 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (106 mg, 0.27 mmol), $PdCl_2$dppf (19mg, 5% mol), $NaHCO_3$ (115 mg, 1.37mmol) in THF/water 2:1 v/v (4.5 ml) was kept under MW irradiation at 80°C for 30 min. The reaction mixture was cooled to room temperature and poured into water (100 ml), extracted with CH_2Cl_2 and finally washed with water. After drying (Na_2SO_4) and solvent evaporation at reduced pressure, the crude product was purified by flash chromatography with increasing amounts of CH_2Cl_2 in cyclohexane as eluent (85:15 v/v) to afford 106 mg (0.21 mmol, 56% yield) of **3a** as a dark red oil. EI-MS m/z 500(M^+).
^{1}H-NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 8.48 (s, 2H), 7.37 (d, ^3J = 4 Hz, 2H), 6.98 (d, ^3J = 4 Hz, 2H), 4.15 (t, 4H), 1.89-1.79 (m, 4H), 1.54-1.32 (m, 12H), 0.91 (t, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.8, 152.8, 127.1, 125.7, 124.1, 116,6, 115.9, 71.8, 31.5, 29.6, 25.8, 22.6, 14.0.



(**3b**)

4,7-Bis[3-(6-methoxyhexyl)thiophen-2-yl]benzo[c][2,1,3]thiadiazole (**3b**). The same procedure described for **3c** was followed starting from 2-bromo-3-(6-methoxyhexyl)thiophene (300 mg, 1.08 mmol) and 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (168 mg, 0.43 mmol) in toluene (6 ml). The crude product was purified by column chromatography on silica gel with cyclohexane/ethyl acetate 10:2 v/v as eluent to obtain 297 mg (0.56 mmol, 52% yield) of **3c** as a fluorescent orange oil. EI-MS m/z 528(M^+).
^{1}H-NMR (500 MHz, $CDCl_3$, TMS/ppm): δ 7.64 (s, 2H), 7.44 (d, ^3J = 4 Hz, 2H), 7.10 (d, ^3J = 4 Hz, 2H,), 3.32- 3.26 (m, 10H), 2.67 (t, 4H), 1.68-1.58 (m, 4H), 1.52-1.42 (m, 4H), 1.32-1.20 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): 154.3, 141.5, 132.2,129.9, 129.1,127.4, 125.9, 72.8, 58.5, 30.6, 29.7, 29.5, 29.4, 25.9.



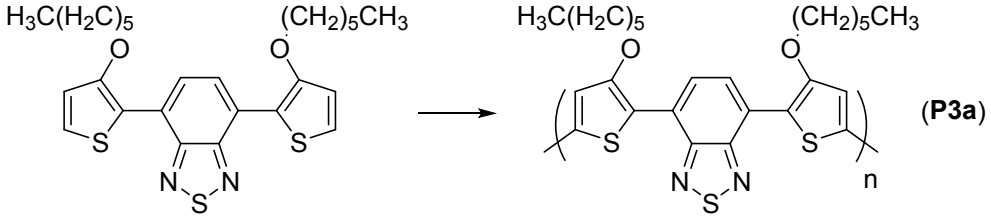
(**3c**)

4,7-Bis(3-hexylthiophen-2-yl)benzo[c][2,1,3]thiadiazole (**3c**). To a solution of 2-bromo-3-hexylthiophene (250 mg, 1.01 mmol) in 6.0 ml of degassed toluene, 2,1,3-benzo[c]thiadiazole-4,7-

bis(boronic acid pinacol ester) (157 mg, 0.40 mmol) was added, followed by the sequential addition of $Pd(PPh_3)_4$ (82 mg, 7% mol) and aq. 2M K_2CO_3 (5 ml), at room temperature under N_2 atmosphere. The mixture was vigorously stirred and degassed for 30 min and then heated under reflux (110°C) for 24h. After cooling, the mixture was treated with toluene and water, the organic layer dried on Na_2SO_4 and the solvent evaporated at reduced pressure. The crude product was finally purified by column chromatography on silica gel with increasing amounts of CH_2Cl_2 in cyclohexane as eluent (85:15 v/v) to afford 255 mg (0.54 mmol, 54% yield) of **3c** as a fluorescent yellow oil. EI-MS m/z 468(M^+).

^{1}H-NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.65 (s, 2H), 7.44 (d, ^3J = 4 Hz, 2H), 7.11 (d, ^3J = 4 Hz, 2H), 2.66 (t, 4H), 1.66-1.56 (m, 4H), 1.29-1.12 (m, 12H), 0.82 (t, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.3, 141.7, 132.2, 129.9, 129.2, 127.5, 125.9, 31.6, 30.7, 29.4, 29.1, 22.6, 14.0.

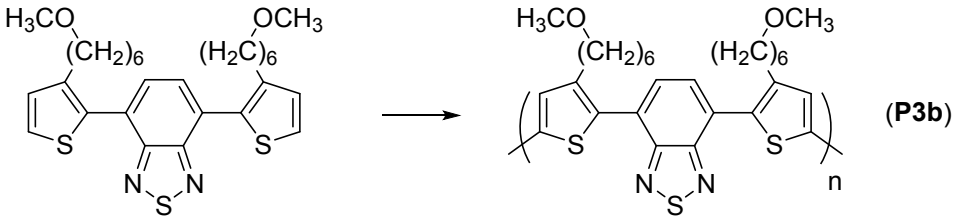
II. Polymers synthesis



(**P3a**)

Poly[4,7-bis(3-hexyloxythiophen-2-yl)benzo[c][2,1,3]thiadiazole] (**P3a**). To a three-necked flask containing a suspension of $FeCl_3$ (137 mg, 0.85 mmol) in anh. $CHCl_3$ (5 ml), a solution of **3a** (106mg, 0.21mmol) in anh. $CHCl_3$ (5 ml) was slowly added (20 min) under inert atmosphere at room temperature. The mixture was left under stirring for 24 h, turning from greenish to dark blue/black color. Then, 50 ml of THF and 100 ml of $CHCl_3$ were added and the mixture washed with 2% aq. HCl up to exhaustive extraction of iron (III) ion (negative essay with NH_4SCN). The organic phase was washed with water to neutrality, dried (Na_2SO_4) and concentrated to small volume. The crude product was finally treated with MeOH to give 0.102 g (0.21 mmol, 98% yield) of **P3a** as a dark blue solid.

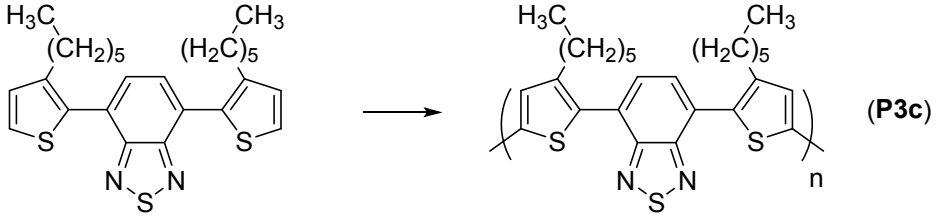
^{1}H-NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 8.55 (m) 7.00 (m), 4.25 (m), 1.90 (m), 1.64-1.18 (m), 0.97 (m).



(**P3b**)

Poly[4,7-bis[3-(6-methoxyhexyl)thiophen-2-yl]benzo[c][2,1,3]thiadiazole] (**P3b**). The same procedure described for **P3a** was followed starting from $FeCl_3$ (147 mg, 0.91 mmol) and **3b** (120 mg, 0.23 mmol) to give 96 mg (0.18 mmol, 79% yield) of **P3b** as a purple/black solid.

^{1}H-NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.71 (m), 6.98 (s), 3.31 (m), 2.72 (m), 1.72 (m), 1.52 (m), 1.46-1.22 (m).



(**P3c**)

Poly[4,7-bis(3-hexylthiophen-2-yl)benzo[c][2,1,3]thiadiazole] (**P3c**).The same procedure described for **P3a** was followed starting from $FeCl_3$ (138 mg, 0.85 mmol) in anh. $CHCl_3$ (5 ml) and **3c** (100 mg, 0.21 mmol) in anh. $CHCl_3$ (5 ml) to give 52 mg (0.11 mmol, 54% yield) of **P3c** as a dark red solid.

^{1}H-NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.65 (s), 6.92 (s), 2.64 (m), 1.70-1.06 (m), 0.90-0.84 (m).

III. ^{1}H-NMR and ^{13}C-NMR spectra

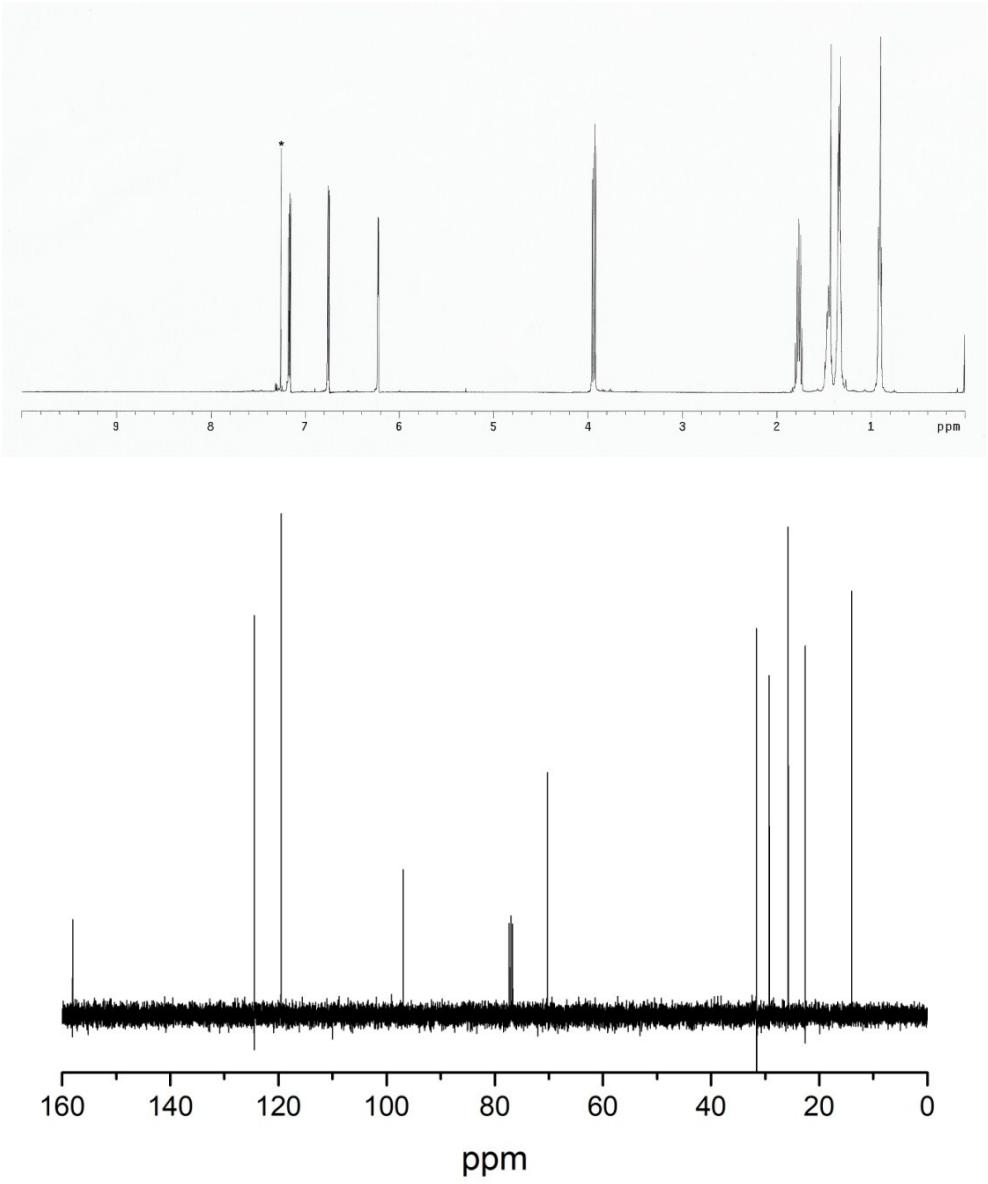


Figure S1. ^{1}H-NMR and ^{13}C-NMR spectra in $CDCl_3$ of **1a**.

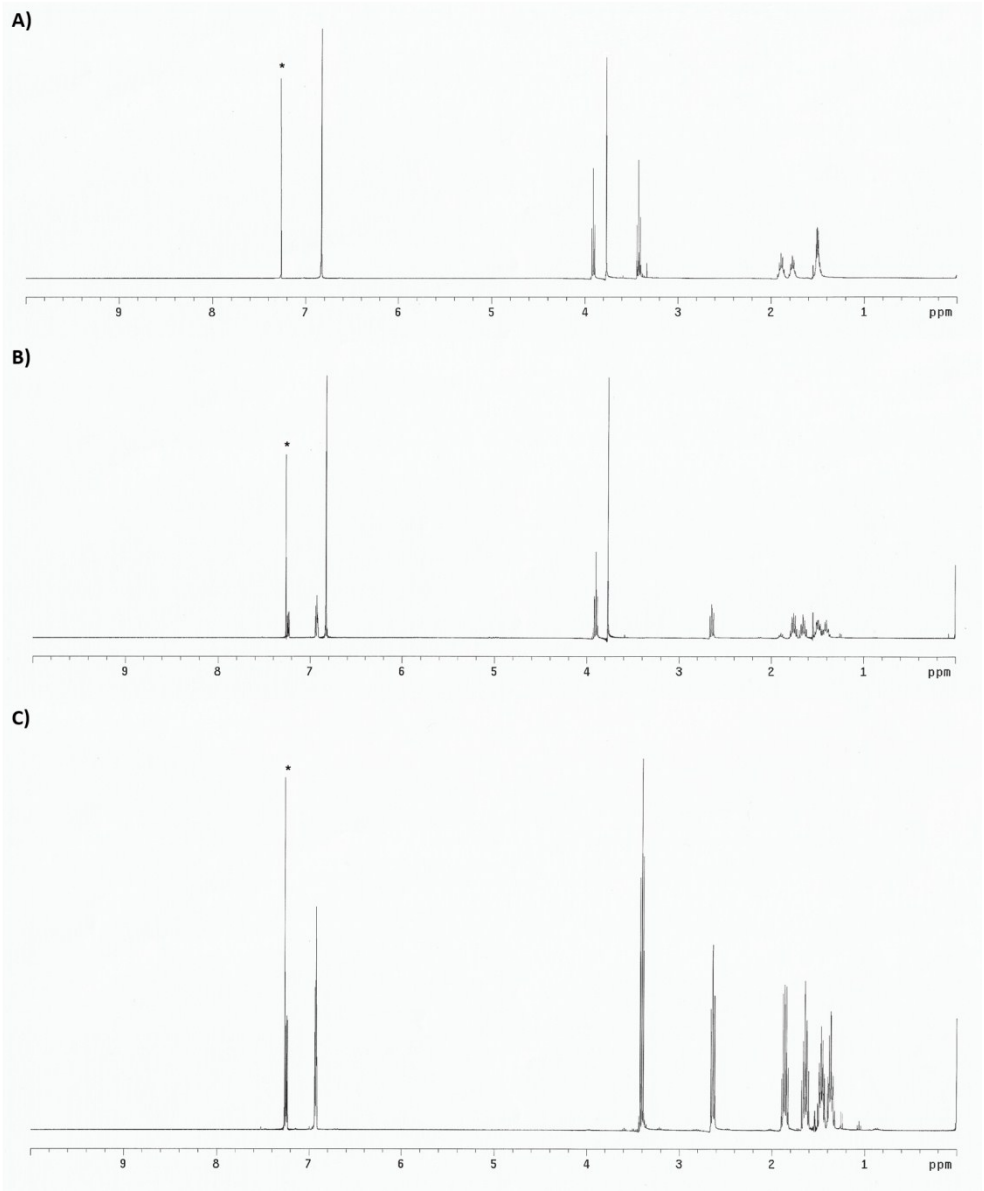


Figure S2. ^{1}H-NMR spectra in $CDCl_3$ of **B6P** (A), **T6P** (B)and (C) **T6Br** (C).

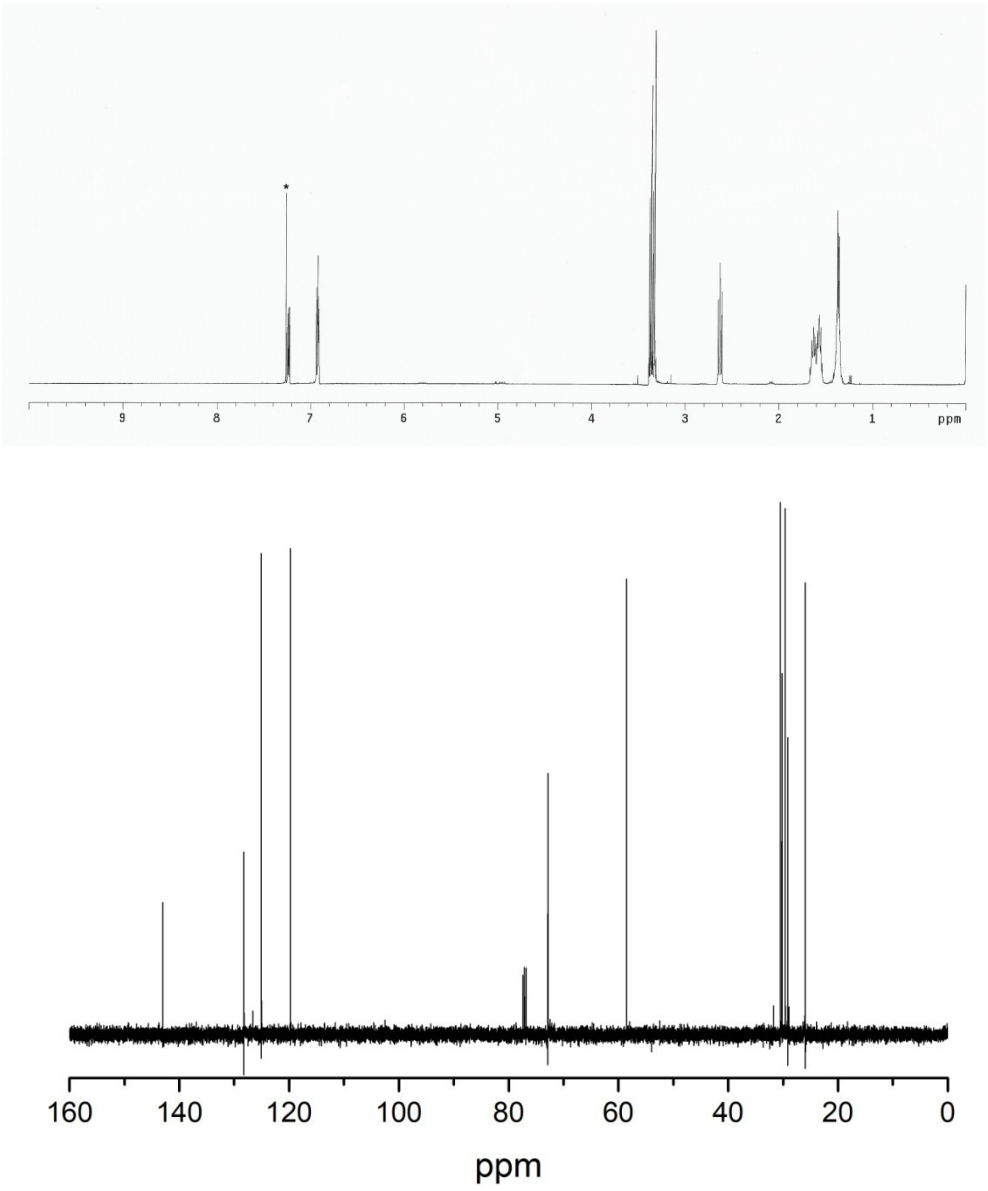


Figure S3. ^{1}H-NMR and ^{13}C-NMR spectra in $CDCl_3$ of **1b**.

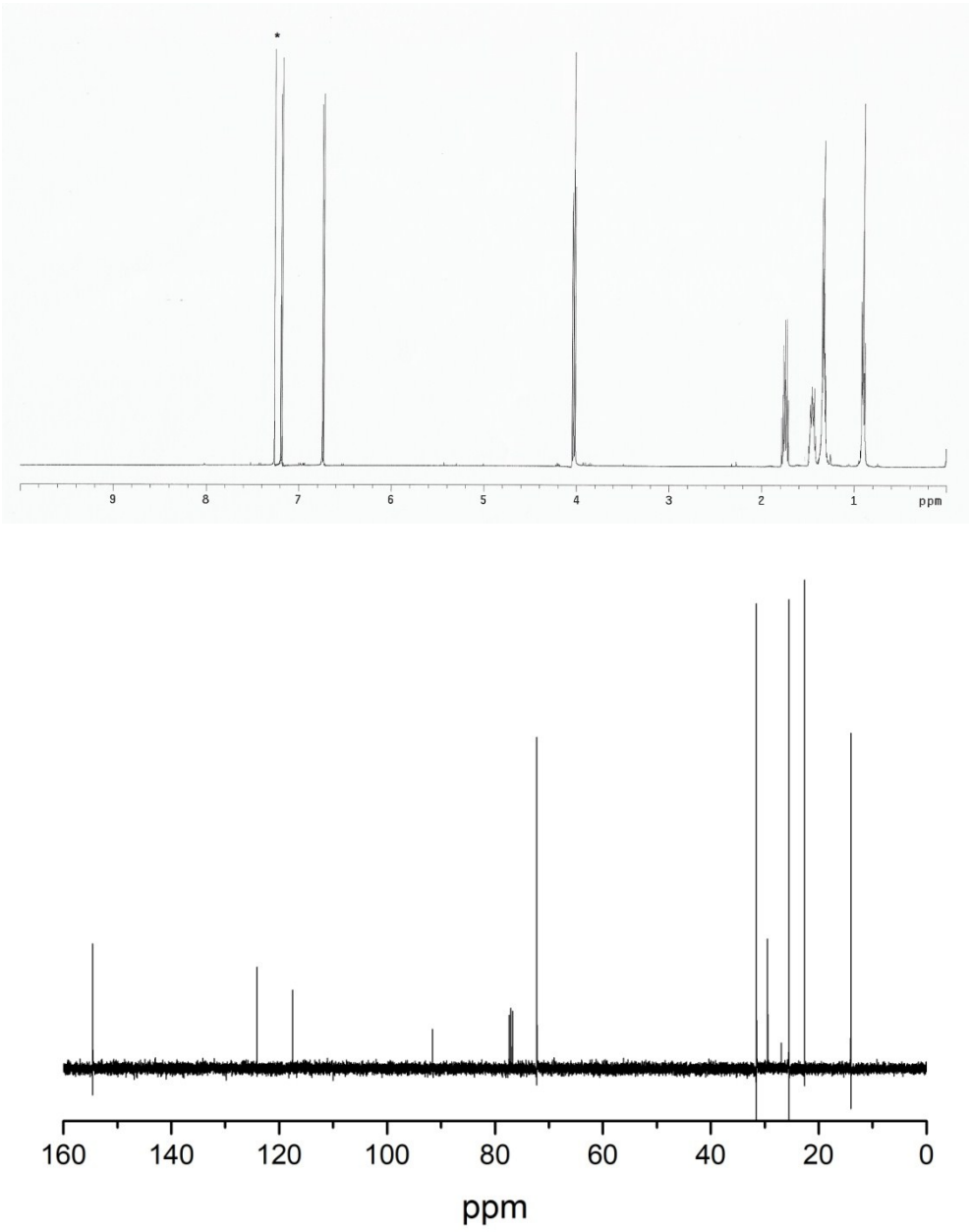


Figure S4. ^{1}H-NMR and ^{13}C-NMR spectra in $CDCl_3$ of **2a**.

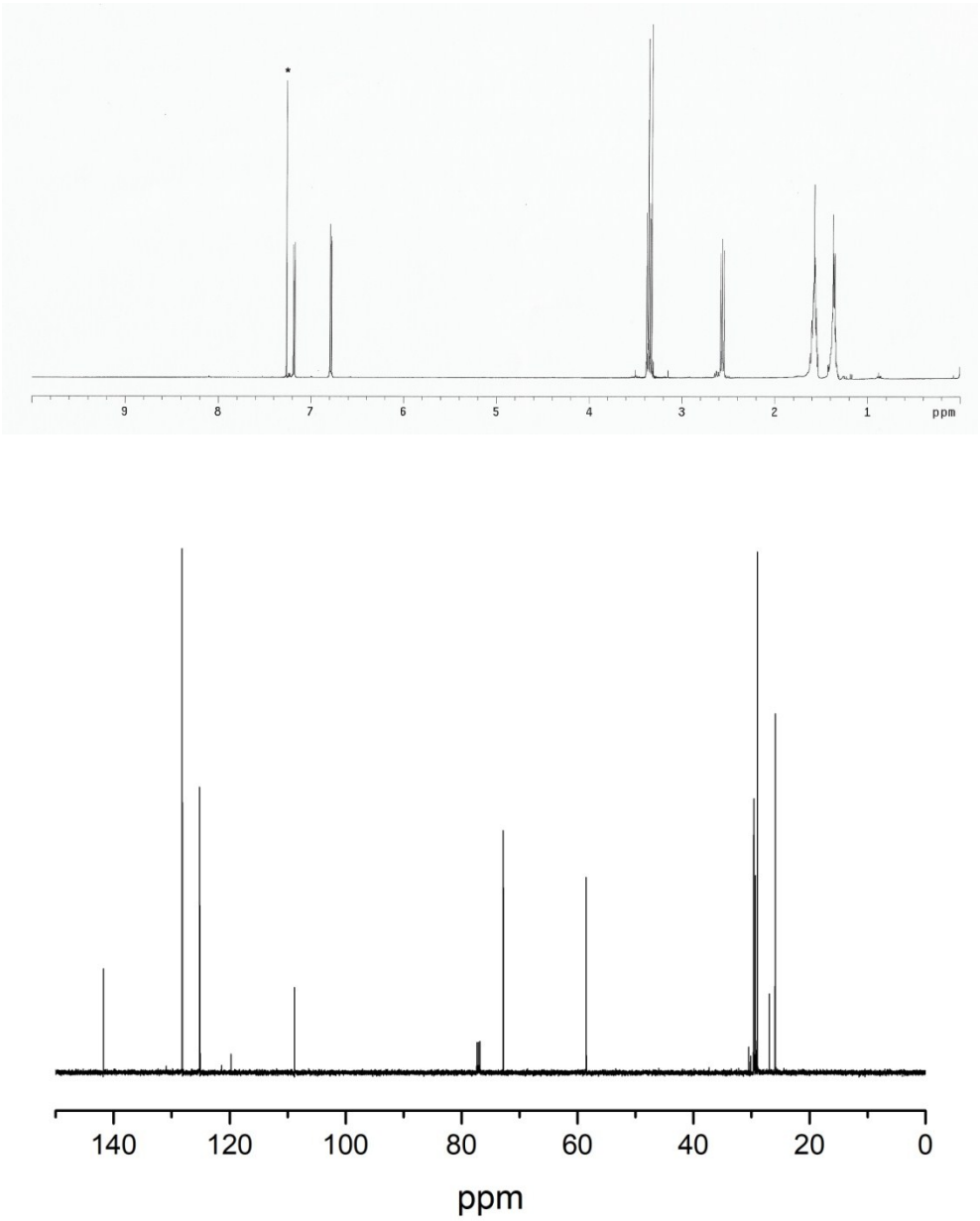


Figure S5. ^{1}H-NMR and ^{13}C-NMR spectra in $CDCl_3$ of **2b**.

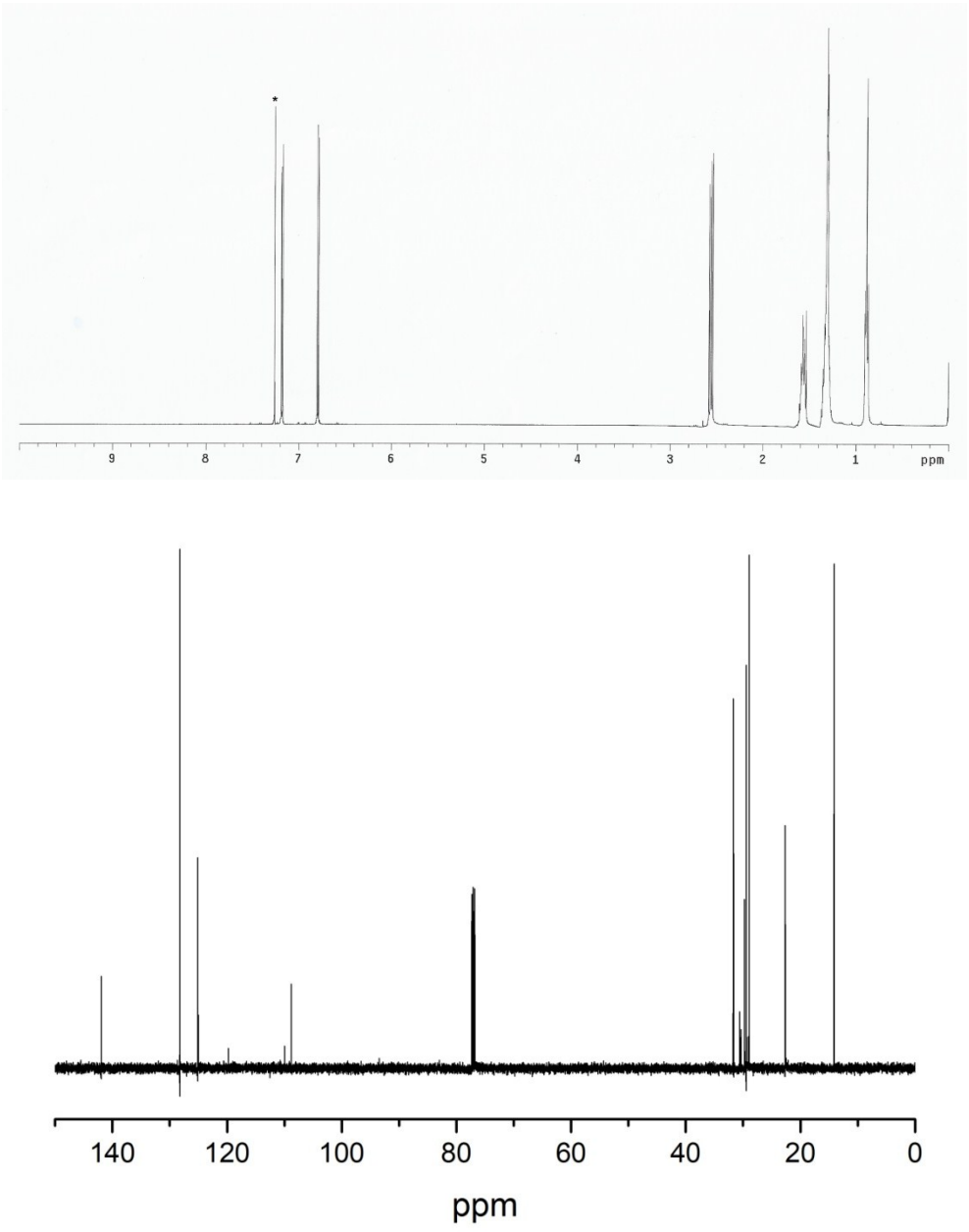


Figure S6. ^{1}H-NMR and ^{13}C-NMR spectra in $CDCl_3$ of **2c**.

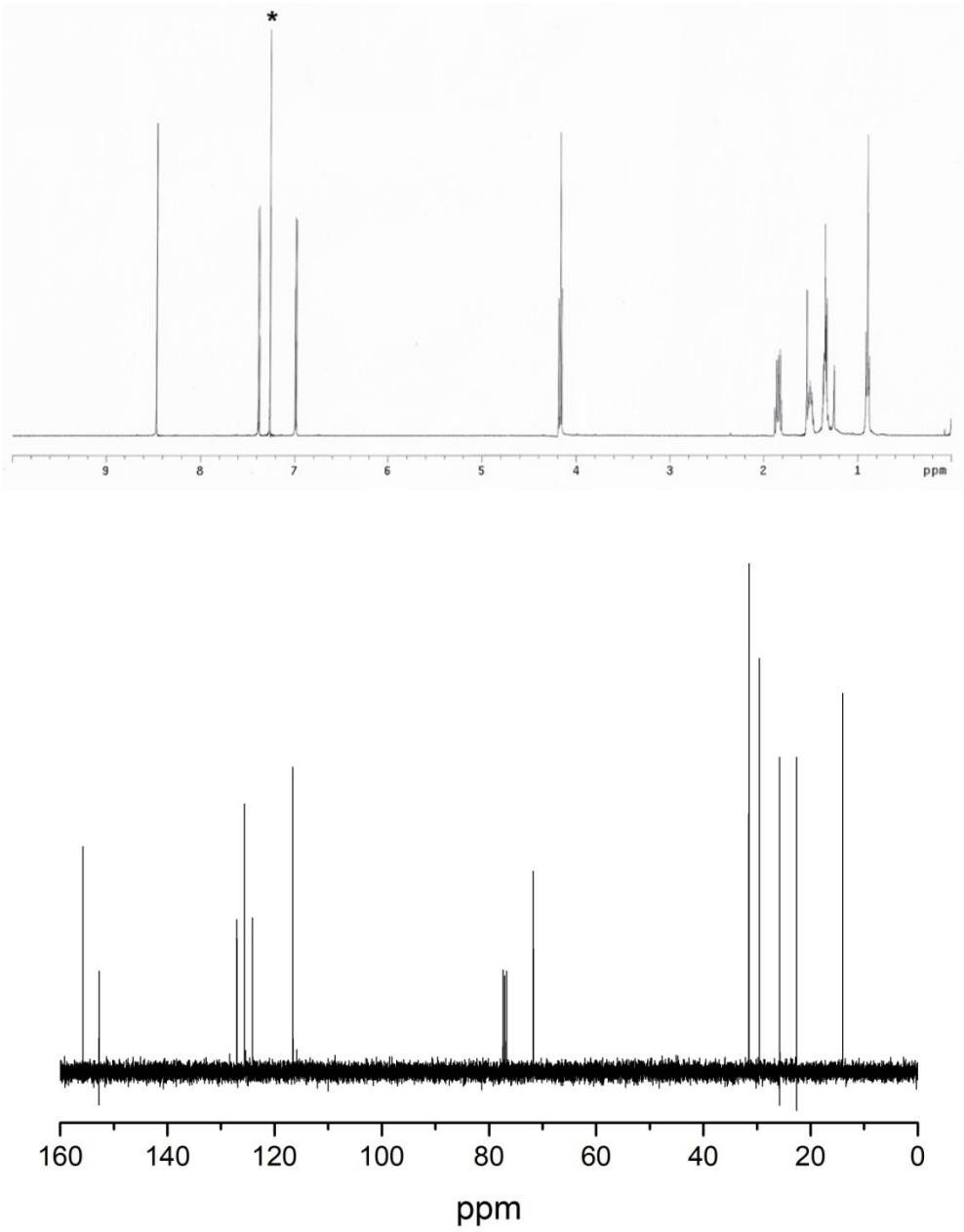


Figure S7. ^{1}H-NMR and ^{13}C-NMR spectra in $CDCl_3$ of **3a**.

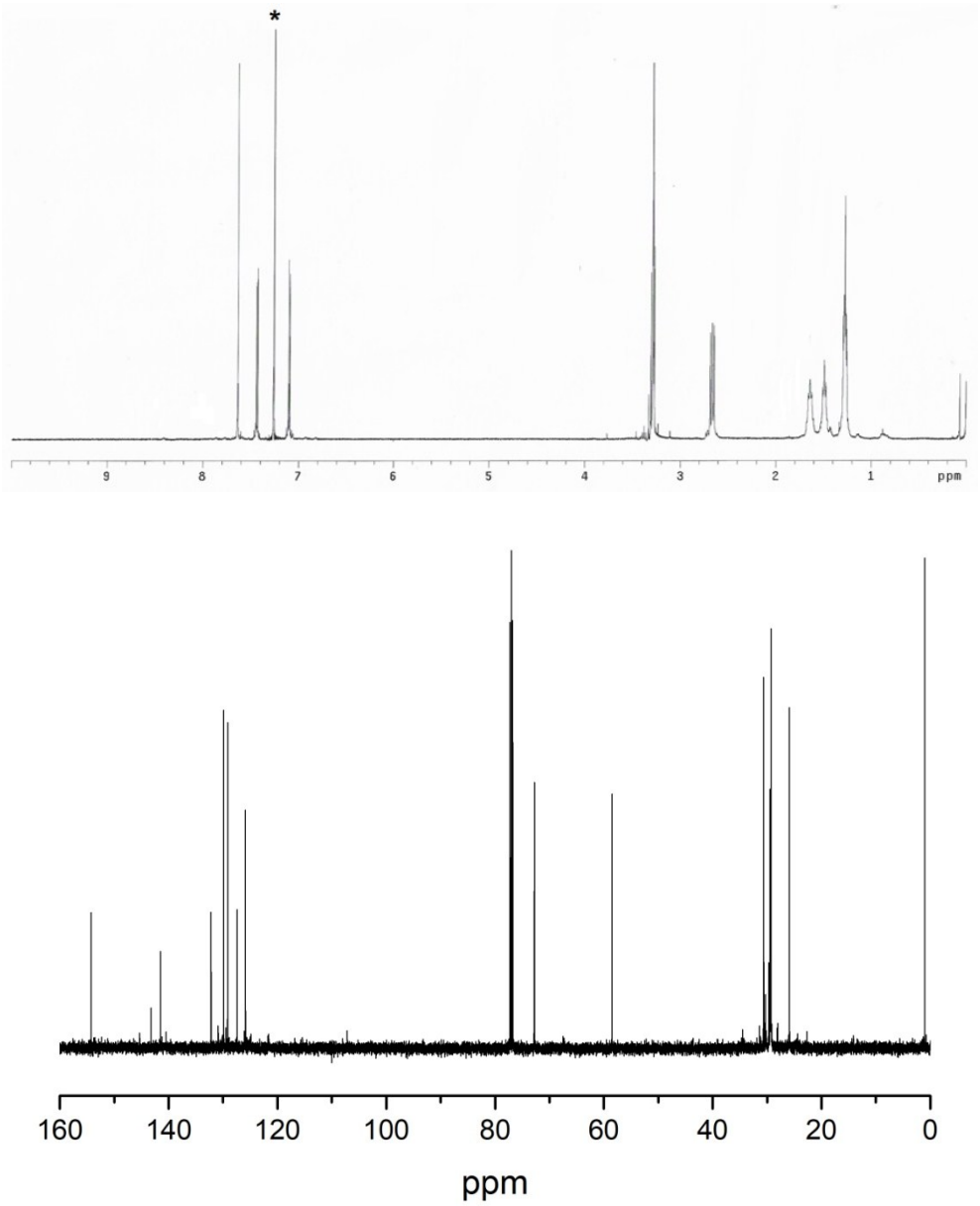


Figure S8. ^{1}H-NMR and ^{13}C-NMR spectra in $CDCl_3$ of **3b**.

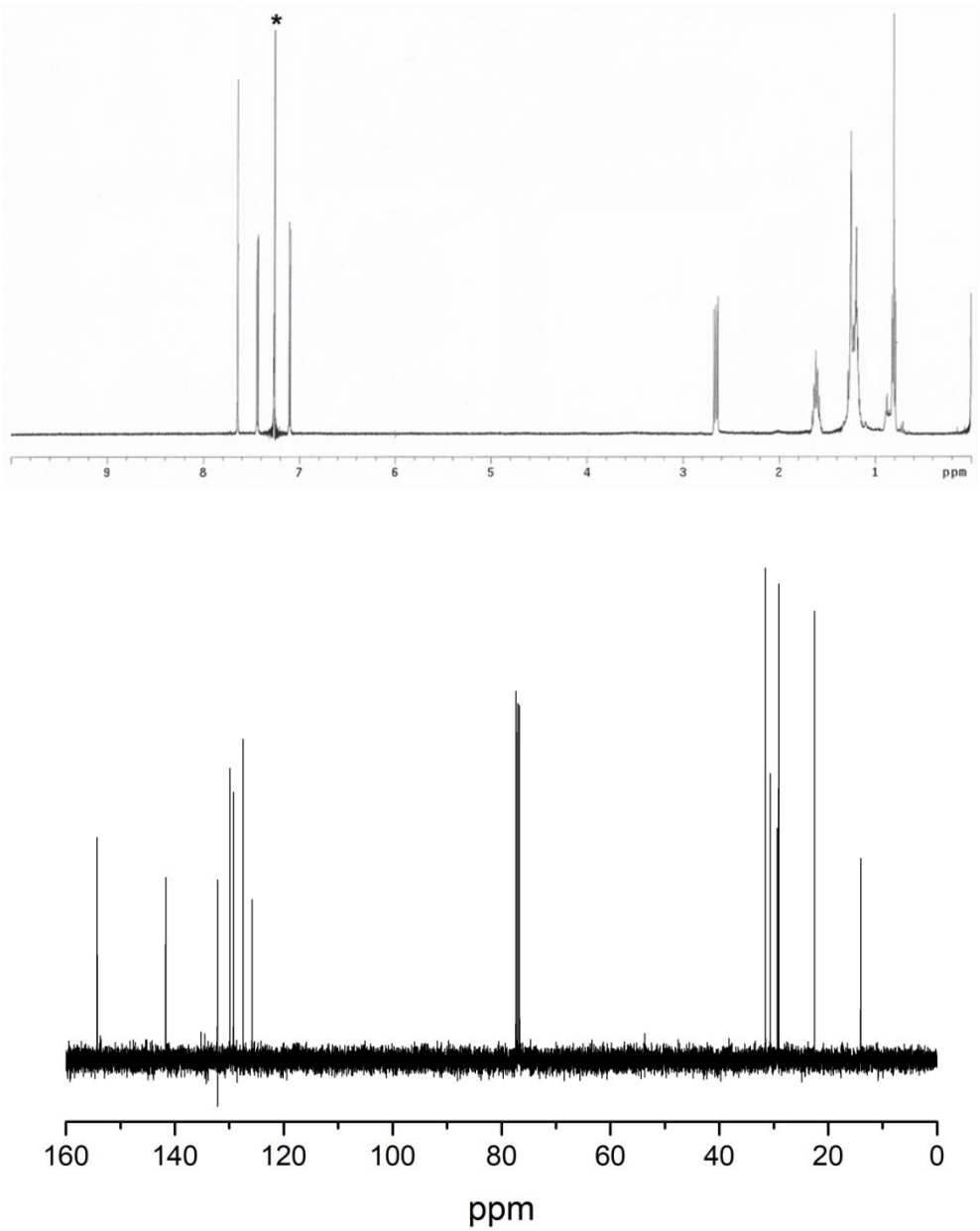


Figure S9. ^{1}H-NMR and ^{13}C-NMR spectra in $CDCl_3$ of **3c**.

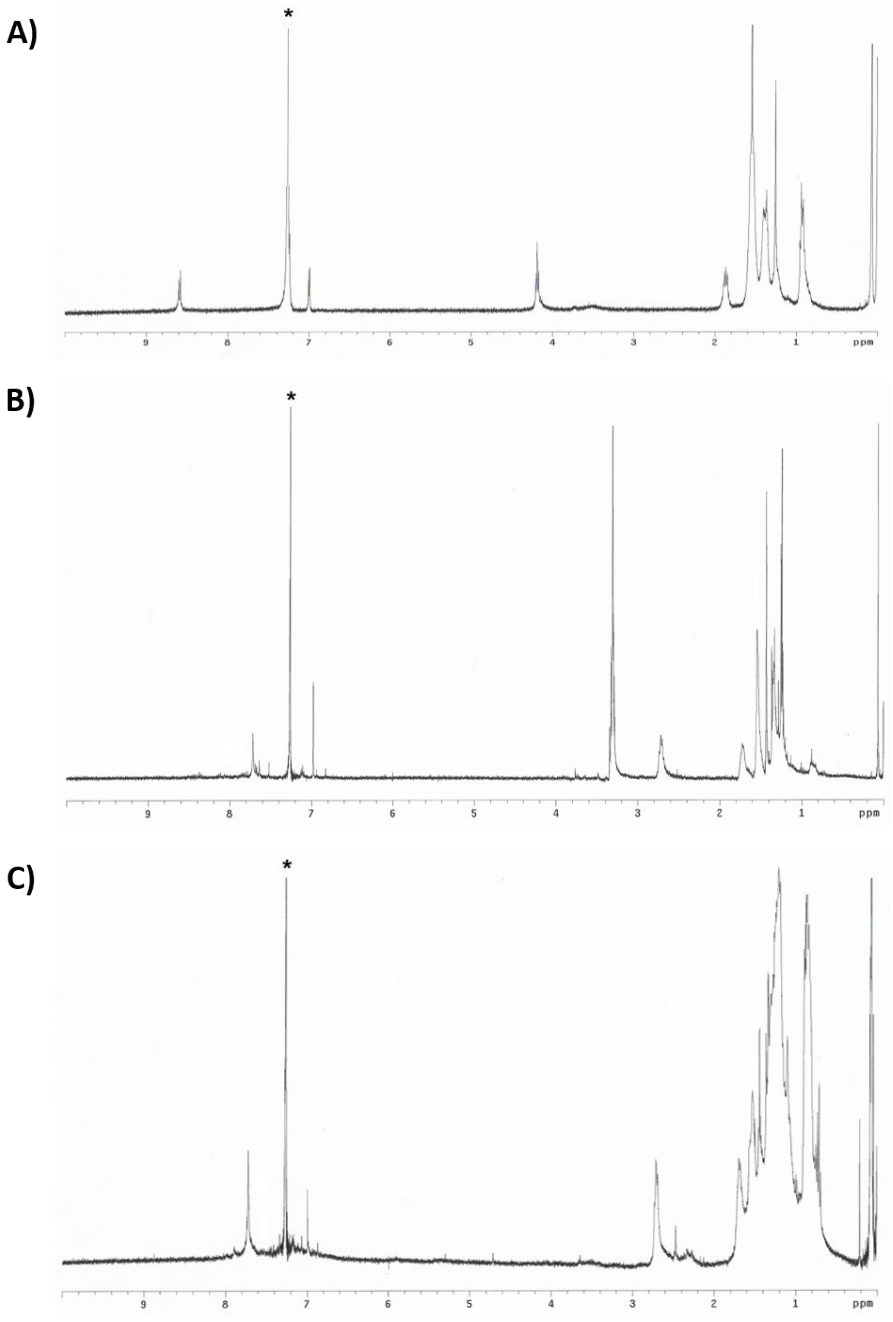


Figure S10. ^{1}H-NMR spectra in $CDCl_3$ of **P3a** (A), **P3b** (B) and **P3c** (C).

IV. Thermal properties

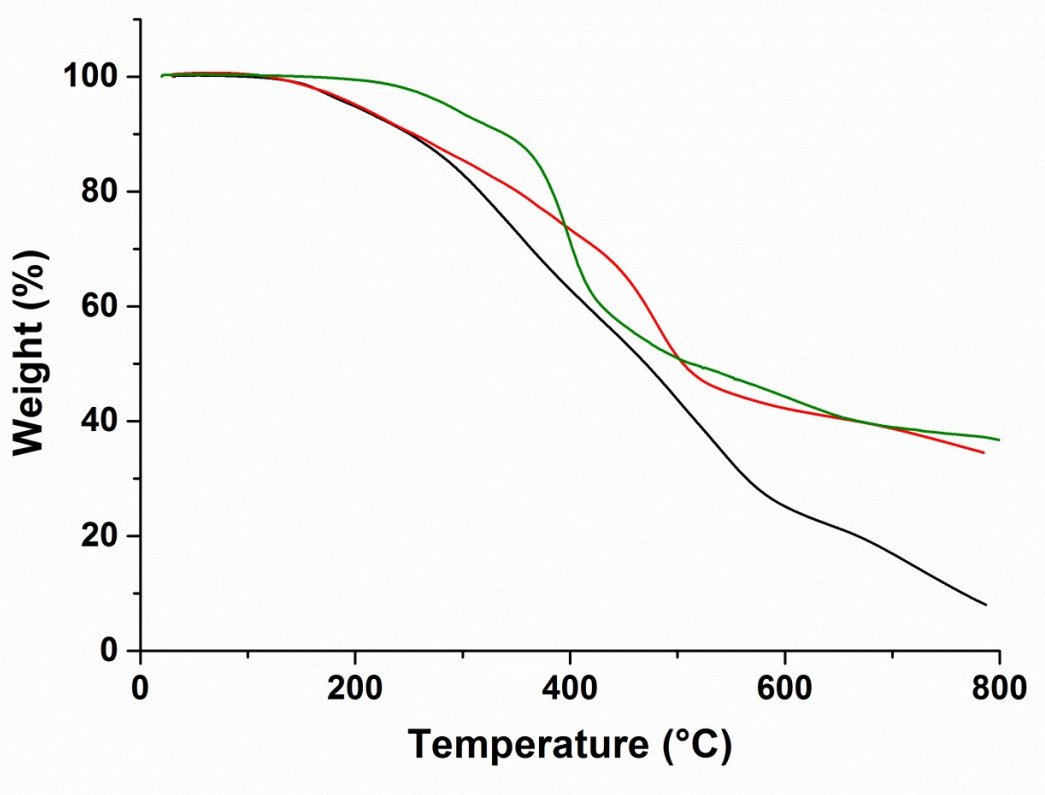


Figure S11. TGA of **P3a** (green line), **P3b** (red line) and **P3c** (black line).

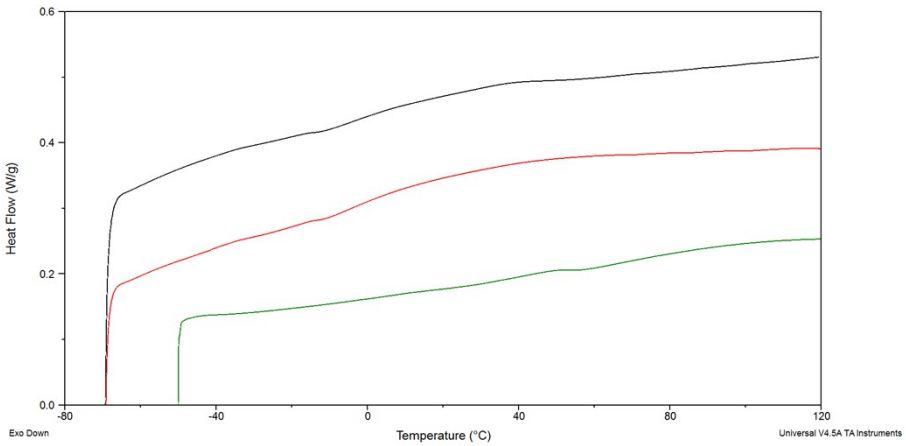


Figure S12. DSC of **P3a** (green line), **P3b** (red line) and **P3c** (black line)

V. Optical properties

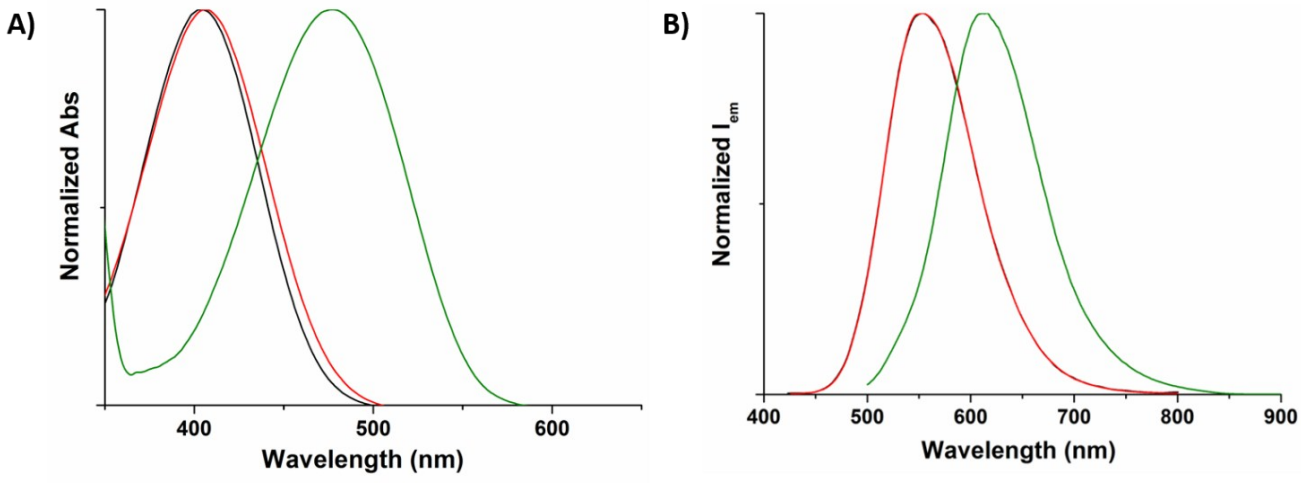


Figure S13. Normalized absorption (A) and photoluminescence (B) spectra in $CHCl_3$ of monomers **3a-c** (green full line: 3a; red full line: 3b; black full line: 3c).

VI. X-Ray diffraction and reflectivity

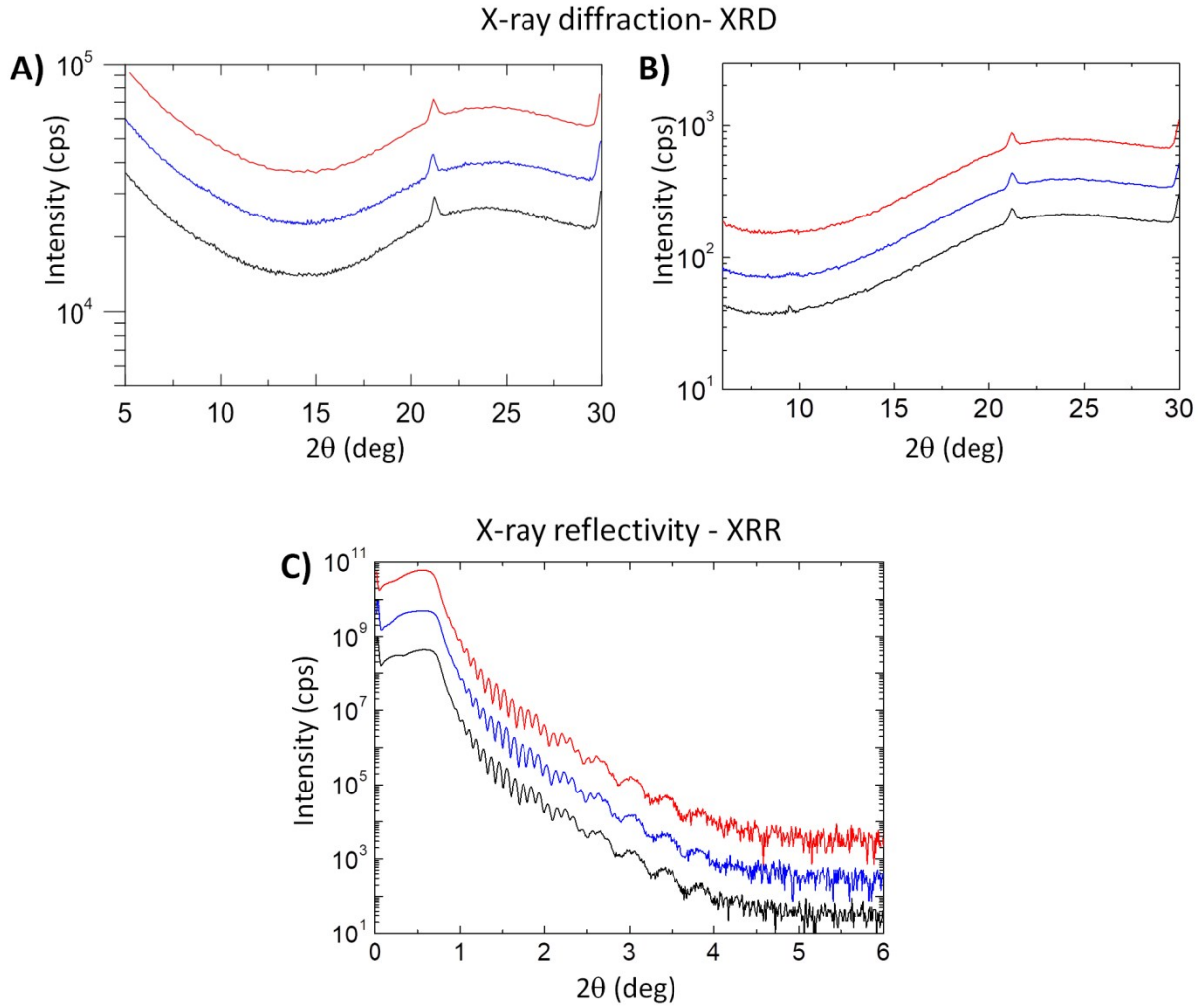


Figure S14. X-ray diffraction of thin films of **P3a** (red full line), **P3b** (blue full line) and **P3c** (black full line) deposited on ITO by doctor blade (A) and spray coating (B) from chlorobenzene. X-ray reflectivity of thin films of **P3a** (red full line), **P3b** (blue full line) and **P3c** (black full line) deposited on ITO by spray coating from chlorobenzene (C).