

Click-Chemistry as an Efficient Synthetic Tool for the preparation of Novel Conjugated Polymers

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Electronic Supplementary Information

General: Unless stated otherwise, all reagents were purchased from commercial suppliers (Aldrich and Acros Organics) and used without further purification. All solvents were distilled under nitrogen atmosphere. THF was distilled from sodium/benzophenone and toluene from sodium. CH₂Cl₂ was distilled from CaH₂. DMF and diethylamine were distilled before use. DMF was stored over 4 Å molecular sieves. Tosylazide³ was dried for one week on P₂O₅ prior to use. Unless stated otherwise, reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Column chromatography was performed using silica (0,035-0,070 mm pore diameter ca. 6 nm) obtained from Acros Organics. NMR spectra (¹H and ¹³C) were measured on a Bruker ARX 400 MHz and Varian Unity Inova 500 MHz spectrometer, CDCl₃, CD₃OD and THF-D₈ were used as solvents. High-resolution mass spectra were recorded on a JEOL JMS-SX/SX 102 A tandem mass-spectrometer. UV/VIS spectroscopy experiments were performed on a HP 8453 UV/Visible System. THF and EtOH used for the emission quantum yields measurements was obtained from Merck, UVAsol spectroscopic grade. Emission spectra were recorded on a SPEX 1681 FLUORLOG spectrometer, using anthracene in EtOH as reference for the quantum yield determination. Infrared spectra were performed on a Bruker IFS 28 FT spectrometer. Polystyrene standards used for the determination of the molecular weights were obtained from Aldrich. Size exclusion chromatography was performed on a Shimadzu Size Exclusion Chromatography system equipped with Waters Styragel columns, HR4, HR2 and HR1.

2,7-diazido-9,9-dihexyl-fluorene (1a)

Compound **1a** was prepared using methods as described in references 1 and 2. To a three-necked flask charged with dry and cooled (-78 °C) THF (200 ml) was added under argon atmosphere t-butyllithium (100 ml of a 1,5 M solution in pentane, 150 mmol). To this solution was drop wise added 2,7-dibromo-9,9-dihexyl-fluorene (16 g, 32.5 mmol) dissolved in dry THF (40 ml) followed by stirring for 15 minutes at -78 °C. Then tosylazide³ (30 g, 0.152 mol) dissolved in dry THF (30 ml) was added drop wise finally resulting in a light green solution. During the tosylazide addition the color of the solution turned red. The reaction mixture was stirred for 14 h at -78 °C under argon atmosphere. Subsequently, a saturated solution of aqueous ammonium chloride (15 ml) was added drop wise at -78 °C. and finally the reaction mixture was allowed to warm up to room temperature. THF was removed by rotary evaporation and the residue was extracted with Et₂O (200 ml) and washed with brine (3 × 150 ml) The organic layer was dried over MgSO₄ and concentrated in vacuo. Column chromatography (PE) and recrystallisation (MeOH) afforded **1a** (10.5 g, 25.2 mmol, 76%) as a light yellow solid. ¹H NMR (CDCl₃, 400 MHz) δ 7.6 (d, 2 H, 8.1 Hz), 6.99 (dd, 2 H, 8.1 Hz and 2.1 Hz), 6.94 (d, 2 H, 2.0 Hz), 1.93-1.89 (m, 4 H), 1.12-1.04 (m, 12 H), 0.77 (t, 6 H, 14.2 Hz), 0.57 (s, 4 H); ¹³C NMR (CDCl₃, 400 MHz) δ 152.7, 138.3, 137.7, 120.6, 118.0, 113.7, 55.5, 40.5, 31.6, 29.7, 23.7, 22.7, 14.1; IR (CHCl₃) cm⁻¹: 2930, 2856, 2106, 1464, 1292; HRMS (FAB⁺) calcd. for C₂₅H₃₂N₆ (M⁺) 416.2688 observed; 416.2686.

2,7-diazido-9,9-didodecane-fluorene (1b)

Analogously as described for **1a**, starting from 2,7-dibromo-9,9-didodecane-fluorene.⁴ (13.59 g, 20.5 mmol), **1b** (6.35 g, 10.87 mmol, 53 %) was obtained as a light yellow solid. ¹H NMR (CDCl₃, 400 MHz) δ 7.60 (d, 2 H, 8.1 Hz), 6.99 (dd, 2 H, 2.0 Hz and 8.1 Hz), 6.94 (d, 2 H, 2.0 Hz), 1.93-1.88 (m, 4 H), 1.28-1.05 (m, 36 H), 0.87 (t, 6 H, 13.7 Hz), 0.58 (s, 4 H); ¹³C NMR (CDCl₃, 400 MHz) δ 155.6, 138.7, 137.6, 120.6, 120.5, 117.9, 113.6, 55.4, 40.4, 31.9, 29.9, 29.6, 2* 29.5, 29.3, 29.2, 23.7, 22.7, 14.1; IR (KBr) cm⁻¹: 2925, 2853, 2360, 2102, 1462, 1293; HRMS (FAB⁺) calcd. for C₃₇H₅₆N₂ (M⁺-2 x N₂)(M⁺) 528.4444 observed; 528.4419.

*2,7-diethynyl-9,9-dihexyl-fluorene (6)*⁸

In a three-necked flask was subsequently added freshly distilled diethylamine (20 ml), THF (10 ml), 2,7-dibromo-9,9-dihexyl-fluorene (5.1 g, 10.36 mmol) and 2-methyl-but-3-yn-2-ol (3.1 g, 35.7 mmol). The solution was degassed with argon for 10 minutes followed by the addition of copper(I)iodide (7 mg, 0.037 mmol) and bis(triphenylphosphine)palladium(II)di-chloride (100 mg, 0.14 mmol). The reaction mixture was stirred for 14 h under argon atmosphere at ambient temperature. The reaction mixture was filtered over Hyflo/silica and concentrated. Column Chromatography (PE/EA 1:2) afforded a light yellow solid (2.3 g, 4.6 mmol, 45%).

Removal of the 2-propanol protective groups: The product above was dissolved in toluene (300 ml) in a roundbottom flask and KOH (2.5 g, 44.6 mmol) was added. The resulting suspension was stirred for 14 h at 100 °C. After cooling to ambient temperature the suspension was filtered over Hyflo. The solvent was removed by rotary evaporation under reduced pressure and the residue was subjected to column chromatography (PE/EA 4:1) to give **6** (1.1 g, 2.88 mmol, 63 %) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 7.63 (d, 2 H, 7.7 Hz), 7.48 (d, 4 H, 8.9 Hz), 3.16 (s, 2 H), 1.96-1.92 (m, 4 H), 1.12-1.01 (m, 12 H), 0.77 (t, 6 H, 14.3 Hz), 0.57 (s, 4 H); ¹³C NMR (CDCl₃, 400 MHz) δ 151.1, 141.1, 131.4, 126.6, 120.9, 120.1, 84.6, 77.5, 55.3, 40.4, 31.6, 29.7, 23.8, 22.7, 14.1; IR (CHCl₃) cm⁻¹: 3303, 2958, 2931, 2858, 1464, 825; HRMS (FAB⁺) calcd. for C₂₉H₃₅ (M⁺) 383.2739 observed; 383.2745.

General polymerisation procedures: P1-P3/P5.

To a schlenk vessel charged with THF (90 ml) and MeCN (10 ml) was added **1b** (1.0 g, 1.71 mmol) and **2**⁵ (to give **P1-P3**) or **3**⁶ (1.71 mmol, to give **P5**). After degassing of the resulting solution with argon for 10 minutes a piece of copper wire (7 mg), a catalytic amount of copper(II)acetate (14 mg) and the ligand tris-benzyltriazoylamine (7 mg) were subsequently added. The reaction vessel was wrapped into aluminum foil to exclude light and the reaction mixture was stirred for one week under an argon atmosphere. For **P1-P3** the initial blue/green solution turned to dark red/black. The polymerisation reaction was terminated at the alkyne terminus by addition of an excess of **5**⁷ (500 mg) followed by additional stirring of the solution for 2 hours. The remaining azides were consumed by the addition of an excess of **4** (1000 mg) and stirring the solution for 2 hours. To the reaction mixture was added a large excess of N,N-diethylcarbamdithioic acid to bind copper ions and the crude polymer **P3** was precipitated by MeOH addition followed by collection via filtration. The obtained polymer was dissolved in THF and again a large excess of N,N-Diethylcarbamdithioic acid was added to the solution followed by polymer precipitation by MeOH addition. The solid polymer material was washed intensively with acetone and water. The polymer was dissolved again in THF and subsequently the polymer was precipitated by the addition of CH₂Cl₂. After standing for ten minutes the precipitate formed was filtered and finally washed with CH₂Cl₂. The polymer was allowed to dry under high vacuum for one day to give polymer **P3**. **P1** and **P2** were obtained by quenching 5 ml aliquots of the reaction mixture described above by subsequent addition of **5** and **4** after 6h and 24h, respectively, followed by work up using the procedure as described above. **P1** was obtained as a black solid. **P2** and **P3** were obtained as a light-brown solid. **P5** was obtained as an off-white solid. The samples were analyzed by SEC to confirm purity. **P5** ¹H NMR (THF-D₈, 500 MHz) δ 8.97 (s), 8.12 (s), 8.04 (s), 2.50-2.46 (m), 2.25 (s), 1.26-1.11 (m), 0.86-0.83 (m), 0.77 (s).

Polymer P4

Starting from **1b** (1.71 mmol) and **2** (1.71 mmol), using the same procedure as described above for **P3** with the exception that the polymerisation was conducted at -10 °C, after which the color of the reaction mixture was turned into blue/green. Finally the polymerization was quenched after 65 h. ¹H NMR (THF-D₈, 500 MHz) δ 9.27 (s), 9.15 (s), 9.09 (s) 8.45-8.37 (m) 8.19-8.06 (m), 2.50-2.46 (m) 2.27 (s), 1.29-1.11 (m), 0.84-0.83 (m), 0.77 (s).

Polymer P6

Starting from **1b** (0.64 g, 1.09 mmol) and **6** (0.418 g, 1.09 mmol), using the same procedure as described above for **P3**, a blue/green reaction mixture was obtained from which polymer **P6** could be isolated as an off-white/yellow solid that was allowed to dry under high vacuum for one day. **P6** ¹H NMR (THF-D₈, 500 MHz) δ 8.95 (s), 8.90 (s), 8.87 (s), 8.12-8.06 (m), 8.03-7.97 (m), 7.94-7.84 (m), 7.61-7.58 (m), 7.48-7.47 (m) 7.18-7.13 (m), 2.49-2.45 (m), 2.27-2.22 (m), 1.31-1.13 (m) 0.90-0.77 (m).

Supplementary Material (ESI) for Chemical Communications
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