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Electronic Supplementary Information

Synthesis, Photophysical and Supramolecular Study of π-Conjugated (diethylene glycol methyl ether) Benzoateethynylene Oligomers and Polymer.

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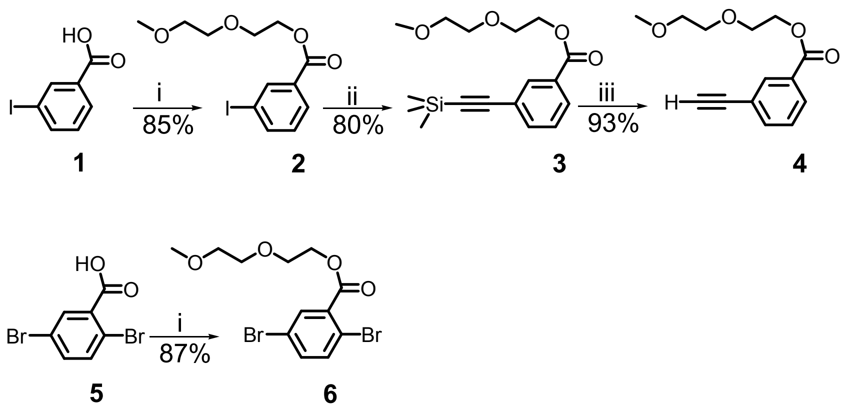
Content:

I. Experimental procedures



Scheme 1S. Reagents and conditions: (i) diethylene glycol methyl ether, DCC/DMAP, CH_2Cl_2, 0 °C, 15h; (ii) TMSA, $[(C_6H_5)_3P]_2PdCl_2$ (5.0 % mol), CuI (1.5 % mol), Et_3N, DMF, 80 °C, 16h; (iii) TBAF, THF, rt, 12 min.

General procedure for the esterification of carboxylic acids. In a two neck round bottomed flask containing the carboxylic acid, the alcohol and the DMAP, anhydrous CH_2Cl_2 is added via cannula. The mixture is cooled to ~0°C and the DCC in DMF is then added in portions. The reaction is stirred for 30 min at 0 ºC and then heated to 40-50 °C and left overnight. After filtering the precipitated urea, the solvent is evaporated in vacuum; the residue is taken up in CH_2Cl_2, washed twice with 0.5 N HCl and once with saturated $NaHCO_3$ solution. The organic layer is separated and dried over $MgSO_4$. The solvent is removed in vacuum and the crude product is ready for the next purification step.

General procedure for the Sonogashira cross-coupling of an acetylene with a bromo- or iodoaryl. To a two neck round bottomed flask containing previously prepared $[(C_6H_5)_3P]_2PdCl_2$, CuI and the halogenaryle, dried (over KOH) and degassed Et_3N is added via cannula. The mixture is heated at 40-50 ºC for 15 min. Then, the acetylene monomer, dissolved in degassed Et_3N, is added via syringe and stirred vigorously overnight at 50-70 °C under a nitrogen atmosphere. The reaction is left to reach room temperature and the ammonium salt is then filtered off, washed with THF and later, the solvent is evaporated. The crude product is ready for the next purification step.

General procedure for the desilylation. To a round bottomed flask charged with the (trimethylsilyl)ethynyl compound, THF and two drops of water, TBAF (0.5 equivalents per silyl group, 1M solution in THF) is added. The mixture is stirred at room temperature for 12 minutes and then the reaction is stopped by passing it thought a plug of dry silica gel and eluting with THF. After the THF evaporation, the product is dried in vacuum and then used without further purification.

Synthesis of (diethylene glycol methyl ether)3-iodobenzoate (2)*. Applying the procedure for the esterification of carboxylic acids.* **1** (4g, 16.12 mmol), diethylene glycol methyl ether (2.13g, 18 mmol), DMAP (39 mg, 0.32 mmol) and 50 mL of CH_2Cl_2 were added to a two neck round bottomed flask and cooled to 0ºC. Then, DCC (3.66g, 18 mmol) was added to the reaction, which was then stirred for 30 min at 0ºC and later heated to 50°C and left overnight. After filtering the precipitated urea and evaporation of the solvent in vacuum, the residue was taken up in CH_2Cl_2, washed twice with 0.5 N HCl and once with saturated $NaHCO_3$ solution. The crude product was purified by chromatography (SiO_2, $CHCl_3$/acetone, 95/5, rf = 0.6) to obtain a colorless, viscous liquid in 81% yielding. UV-Vis (CH_2Cl_2): $\lambda_{máx}$ (288 nm) ε (1.26 x 10_3 $M^{-1}cm^{-1}$). ^{1}H NMR ($CDCl_3$, 300MHz) δ (ppm): 8.37 (t, 1H, Ar), 8.0 (dt, 1H, Ar), 7.87 (dt, 1H, Ar), 7.16 (t, 1H, Ar), 4.49-4.45 (m, 2H, $-COOCH_2-$), 3.84-3.80 (m, 2H, $-CH_2$-β-COO), 3.69-3.66 (m, 2H, $-CH_2-$), 3.57-3.54 (m, 2H, $-CH_2-$), 3.37 (s, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 165.10, 141.86, 138.57, 132.07, 130.10, 128.94, 93.84, 71.98, 70.64, 69.20, 64.49, 59.17.

Synthesis of (diethylene glycol methyl ether) 3-((trimethylsilyl)ethynyl)benzoate (3)*. Applying the procedure for the Sonogashira-Heck cross coupling.* To a two neck flask containing **2** (4.4g, 12.56 mmol), $[(C_6H_5)_3P]_2PdCl_2$ (220 mg, 0.314 mmol) and CuI (18 mg, 0.09 mmol) under nitogen, 50 mL of Et_3N were added. The mixture was heated at 50 ºC for 15 min and then TMSA (25.12 mmol) was added by syringe. The mixture was heated at 60 ºC for 15 h. After filtering the ammonium salt and evaporating the solvent, the crude product was purified by silica gel chromatography ($CHCl_3$/acetone, 95/5, rf = 0.6) to afford a viscous liquid in 91% yield. UV-Vis (CH_2Cl_2): $\lambda_{máx}$ (303 nm) ε (1.13 x 10^3 $M^{-1}cm^{-1}$). ^{1}HNMR ($CDCl_3$, 300MHz) δ (ppm): 8.14 (t, 1H, Ar), 7.98 (dt, 1H, Ar), 7.62 (dt, 1H, Ar), 7.36 (t, 1H, Ar), 4.49-4.46 (m, 2H, $-COOCH_2-$), 3.84-3.81 (m, 2H, $-CH_2$-β-COO), 3.70-3.67 (m, 2H, $-CH_2-$), 3.57-3.54 (m, 2H, $-CH_2-$), 3.38 (s, 3H, $-CH_3$), 0.25 (s, 9H, $-SiCH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 165.86, 136.15, 133.24, 130.36, 129.64, 128.39, 123.63, 103.96, 95.42, 71.99, 70.63, 69.26, 64.32, 59.14, -0.051.

Synthesis of (diethylene glycol methyl ether) 3-ethynylbenzoate (4). *Applying the procedure for the desilylation.* A round bottom flask charged with **3** (2.60g, 8.11 mmol), 15 mL of THF and three drops of distilled water, 1.60 mL of TBAF (1M solution in THF) were added. The mixture was stirred for 12 min at room temperature and then passed through a plug of silica gel using THF as eluent. After the solvent evaporation, the product was dried in vacuum to afford a dark brown viscous liquid in 93% yielding. UV-Vis (CH_2Cl_2): $\lambda_{máx}$ (299, 309, 331 nm) ε (2.05×10^3, 1.48×10^3, 1.29×10^3 $M^{-1}cm^{-1}$). ^{1}HNMR ($CDCl_3$, 300MHz) δ (ppm): 8.16 (t, 1H, Ar), 8.02 (dt, 1H, Ar), 7.65 (dt, 1H, Ar), 7.39 (t, 1H, Ar), 4.49-4.46 (m, 2H, $-COOCH_2-$), 3.84-3.81 (m, 2H, $-CH_2$-β-COO), 3.70-3.67 (m, 2H, $-CH_2-$), 3.57-3.54 (m, 2H, $-CH_2-$), 3.37 (s, 3H, $-CH_3$), 3.11 (s, 1H, -C≡CH). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 165.74, 136.35, 133.37, 130.50, 129.97, 128.52, 122.61, 82.63, 78.31, 71.98, 70.63, 69.23, 64.40, 59.12.

Synthesis of (diethylene glycol methyl ether) 2,5-dibromobenzoate (6). *Applying the procedure for the esterification of carboxylic acids.* 2,5-dibromobenzoic acid **5** (4g, 14.29 mmol), diethylene glycol methyl ether (1.9g, 16 mmol), DMAP (39 mg, 0.32 mmol) and 50 mL of CH_2Cl_2 were charged in a two neck round bottomed flask and cooled to 0ºC. Then, DCC (3.24g, 16 mmol) was added to the reaction, which was stirred for 30 min at 0ºC and later heated to 50°C and left overnight. After filtering the precipitated urea and evaporating the solvent in vacuum, the residue was taken up in CH_2Cl_2, washed twice with 0.5 N HCl and once with saturated $NaHCO_3$ solution. The organic layer was separated and dried over $MgSO_4$. The crude product was purified by chromatography (SiO_2, CH_2Cl_2, rf = 0.6) to give a transparent viscous liquid in 84 % yielding. UV-Vis (CH_2Cl_2): $\lambda_{máx}$ (294 nm) ε (1.44×10^3 $M^{-1}cm^{-1}$). ^{1}HNMR ($CDCl_3$, 300MHz) δ (ppm): 7.93 (d, 1H, Ar), 7.51 (d, 1H, Ar), 7.42 (dd, 1H, Ar), 4.50-4.47 (m, 2H, $-COOCH_2-$), 3.84-3.80 (m, 2H, $-CH_2$-β-COO), 3.69-3.66 (m, 2H, $-CH_2-$), 3.57-3.54 (m, 2H, $-CH_2-$), 3.38 (s, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 164.79, 135.77, 135.61, 134.33, 133.64, 121.06, 120.59, 71.99, 70.63, 68.97, 64.95, 59.19.

Synthesis of (diethylene glycol methyl ether) 2-iodo-5-(ethynyl)benzoate (12). *Applying the procedure for the desilylation.* A round bottom flask charged with **11** (1.0g, 2.24 mmol), 10 mL of THF and three drops of distilled water were stirred at room temperature. Then, 1.0 mL of TBAF (3.45 mmol, 1M solution in THF) was added, stirred for 12 min and then passed through a plug of silica gel using THF as eluent. After the solvent was evaporated, the product was dried in vacuum to afford a dark red viscous liquid in 90% yield. ^{1}H NMR ($CDCl_3$, 300MHz) δ (ppm): 3.1 (s, 1H, CH≡C), 3.3 (s, 3H, CH_3), 3.5 (t, 2H, CH_2-δ-O-C=O), 3.6 (t, 2H, CH_2-γ-O-C=O), 3.9

(t, 2H, CH_2-β-O-C=O), 4.5 (t, 2H, CH_2-α-O-C=O), 7.2 (dd, 2H, Ar-H-3), 7.89 (dd, 2H, Ar-H-4), 7.91 (s, 2H, Ar-H-6). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 165.79, 136.29, 133.39, 130.30, 129.51, 128.39, 123.53, 104.0, 95.38, 71.98, 70.70, 69.26, 64.40, 59.14.

***Synthesis of polymer I*-nBEgly (13).** *Applying the procedure for the Sonogashira cross coupling.* In a two neck flask containing **12** (300 mg, 0.8 mmol), $[(C_6H_5)_3P]_2PdCl_2$ (28 mg, 0.04 mmol) and CuI (~2 mg, $8X10^{-3}$ mmol) under nitrogen, 33 mL of THF and 50 mL of Et_3N were added. The mixture was heated at 60 ºC for 36 h. After cooling, the entire mixture was precipitated in diethyl ether, centrifuged, re-dissolved in $CHCl_3$ and precipitated twice in diethyl ether. The product was stored in $CHCl_3$ and kept under refrigeration at 5 °C. UV-Vis (CH_2Cl_2): $\lambda_{máx}$ (375 nm) ε (3.75×10^4 $M^{-1}cm^{-1}$). RMN ^1H ($CDCl_3$, 300 MHz) δ (ppm): 8.23-8.16 (m, Ar-H), 8-7.96 (m, Ar-H), 7.70-7.63(m, Ar-H), 7.35-7.26 (m, Ar), 4.54-4.49 (m, -$COOCH_2$), 3.87-3.83 (m, -CH_2-β-COO), 3.71-3.64 (m, -CH_2), 3.58-3.50 (m, -CH_2), 3.38-3.35(m, -CH_3).

Synthesis of 3BEgly-H (14). *Applying the procedure for the Sonogashira-Heck cross-coupling.* To a two neck flask containing **6** (266 mg, 0.70 mmol), $[(C_6H_5)_3P]_2PdCl_2$ (24.58 mg, 0.035 mmol) and CuI (1.33 mg, $7x10^{-3}$ mmol) under nitrogen,50 mL of Et_3N were added. The mixture was heated at 50 ºC for 15 min, 400 mg (1.61 mmol) of **4** in DMF were then added by syringe. The mixture was stirred and heated for 15 h at 50ºC. After filtering off the ammonium salt and evaporating the solvent, the crude product was purified by silica gel chromatography ($CHCl_3$/acetone, 80/20, v/v, rf = 0.6) and then by preparative GPC chromatography (Biorads, Bio-Beds, toluene), to afford a yellow viscous material in 60 % yield. UV-Vis (CH_2Cl_2): $\lambda_{máx}$(335 nm) ε(4.0×10^4 $M^{-1}cm^{-1}$). ^1H NMR ($CDCl_3$, 300MHz) δ (ppm): 8.23 (t, 2H, Ar), 8.17 (s, 1H, Ar), 8.03 (dt, 2H, Ar), 7.74 (tt, 2H Ar), 7.64 (s, 2H, Ar), 7.44 (t, 2H, Ar), 4.56-4.48 (m, 6H, -$COOCH_2$-), 3.86-3.85 (m, 6H, -CH_2-β-COO), 3.71-3.64 (m, 6H, -CH_2-), 3.58-3.50 (m, 6H, -CH_2-), 3.38 (s, 3H, -CH_3), 3.35(2s, 6H, -CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 165.84, 165.23, 136, 134.51, 134.29, 133.91, 133, 130.63, 129.93, 128.65, 123.66, 123.42 123.20, 123.05, 72, 70.66, 69.27, 64.41, 59.15.

Synthesis of 3BEgly-N3 (15). *Applying the procedure for the Sonogashira-Heck cross-coupling.* To a two neck flask containing **6** (307 mg, 0.80 mmol), $[(C_6H_5)_3P]_2PdCl_2$ (28.36 mg, 0.040 mmol) and CuI (1.53 mg, $8x10^{-3}$ mmol) under nitrogen, 60 mL of Et_3N/DMF (50/10 mL) were added . The mixture was heated at 50 ºC for 15 min and then **5** 900 mg (2.62 mmol) in 10 mL of DMF were added by syringe. The mixture was stirred and heated for 15 h at 50ºC. After filtering off the ammonium salt and evaporating the solvent, the crude product was purified by chromatography (SiO_2, $CHCl_3$/acetone, 90/10 v/v, rf = 0.3) to give an orange pasty liquid in 70% yield. UV-Vis (CH_2Cl_2): $\lambda_{máx}$(384 nm) ε(3.26 x 10^4 $M^{-1}cm^{-1}$). ^1H NMR ($CDCl_3$, 300MHz) δ (ppm): 8.13 (d, 1H, Ar), 7.81 (m, 2H, Ar), 7.60-7.52 (m, 4H, Ar), 7.43 (d, 2H, Ar), 4.55-4.42 (dt, 6H, -$COOCH_2$), 3.87-3.70 (m, 14H, -NCH_2, -CH_2-β-COO), 3.68-3.65 (m, 6H, -CH_2), 3.56-3.51 (m, 6H, -CH_2-), 3.37 (2s, 6H, -CH_3), 3.35 (s, 3H, -CH_3), 1.30-1.24 (m, 12, CH_3-β-N). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 167.76, 167.65, 165.43, 150.07, 150.02, 134.72, 134.51, 134.26, 134.10, 133.69, 132.96, 132.23, 132.09, 131.82, 128.65, 128.49, 126.65, 123.44, 123.05, 119.13, 119.04, 118.54, 96.09, 91.84, 88.73, 71.99, 70.64, 69.22, 64.50, 64.20, 64.01, 59.14, 49.32, 42.18, 14.52, 11.34.

Synthesis of 3BEgly-I (16). A heavy walled glass flask equipped with a Teflon screw valve was charged with **15** (500 mg, 0.54 mmol) and iodomethane (10 mL). The solution was placed under vacuum and the flask was sealed; the solution was heated under vigorous stirring at 110 ºC for 15 h. After cooling, the remaining iodomethane was vacuum removed. THF was then added and the precipitate was filtered off. After THF evaporation, the crude product was purified by chromatography (SiO_2, $CHCl_3$/acetone, 80/20 v/v, rf = 0.7) to afford a yellow viscous liquid in 80 % yield. UV-Vis (CH_2Cl_2): $\lambda_{máx}$(343 nm) ε(8.41 x 10^4 $M^{-1}cm^{-1}$). ^1H NMR ($CDCl_3$, 300MHz) δ (ppm): 8.16 (s, 1H, Ar), 8-7.96 (m, 4H, Ar), 7.63(s, 2H, Ar), 7.35-7.26 (m, 2H, Ar), 4.54-4.49 (m, 6H, , -$COOCH_2$), 3.87-3.83 (m, 6H, -CH_2-β-COO), 3.71-3.64 (m, 6H, -CH_2), 3.58-3.50 (m, 6H, -CH_2), 3.38(2s, 6H, -CH_3), 3.35 (s, 3H, -CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 165.86, 165.76, 165.05, 141.64, 141.55, 135.38, 135.33, 135.07, 134.91, 134.48, 134.25, 134.02, 133.97, 133.93, 132.11, 123.36, 122.94, 122.90, 94.65, 94.56, 94.52, 90.41, 90.29, 90.23, 71.96, 70.60, 69.18, 69.02, 64.90, 64.57, 59.18.

Synthesis of 5BEgly-H (17)*. Applying the procedure for the Sonogashira-Heck cross-coupling.* To a two neck flask containing **16** (200 mg, 0.70 mmol), $[(C_6H_5)_3P]_2PdCl_2$ (8 mg, 0.01 mmol) and CuI (1.0 mg, 2.27×10^{-3} mmol) under nitrogen, 60 mL of Et_3N/toluene (54/6 mL) were added. The mixture was heated at 50 ºC for 15 min and then **4** (400 mg, 1.61 mmol), in 2 mL of toluene, was added by syringe. The mixture was stirred and heated for 15 h at 50ºC. After filtering off the ammonium salt and evaporating the solvent, the crude product was first purified by silica gel chromatography (SiO_2, $CHCl_3$/acetone, 80/20 v/v, rf = 0.6) and then by preparative GPC chromatography (Biorads, Bio-Beds, toluene) to afford a yellow viscous pasty material in 50 %

yield, UV-Vis (CH_2Cl_2): $\lambda_{máx}$(367 nm) ε(11.62 x 10^4 $M^{-1}cm^{-1}$). ^{1}H NMR ($CDCl_3$, 300MHz) δ (ppm) 8.24 (t, 2H, Ar), 8.18 (s, 3H, Ar), 8.03 (dt, 2H, Ar), 7.77 (dt, 2H, Ar), 7.69 (s, 6H, Ar), 7.44 (t, 2H, Ar), 4.57-4.48 (m, 10H, , -$COOCH_2$), 3.88-3.83 (m, 10H, -CH_2-β-COO), 3.71-3.64 (m, 10H, -CH_2), 3.58-3.50 (m, 10H, -CH_2), 3.4-3.3 (5s, 15H CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): 165.79, 165,03, 165.12, 165.03, 136.10, 134.70, 134.49, 133.92, 133.80, 132.91, 130.55, 129.86, 128.61, 123.59, 123.49, 123.33, 123.21, 122.94, 122.70, 95.45, 95.35, 95.11, 91.01, 90.82, 89.02, 88.92, 71.96, 70.63, 69.23, 64.55, 59.11

Synthesis of 5BEgly-N3 (18). *Applying the procedure for the Sonogashira-Heck cross-coupling.* To a two neck flask containing **16** (305 mg, 0.31 mmol), $[(C_6H_5)_3P]_2PdCl_2$ (11 mg, 0.01 mmol) and CuI (0.06 mg, $3x10^{-3}$ mmol) under nitrogen, 60 mL of Et_3N/DMF (50/10 mL) were added. The mixture was heated at 50 ºC for 15 min and then **10** (328 mg, 0.1 mmol) in 3 mL of DMF was added by syringe. The mixture was stirred and heated by 15 h at 50ºC. After filtering off the ammonium salt and the solvent evaporated, the crude product was purified by silica gel chromatography (CH_2Cl_2/acetone, 80/20 v/v, rf = 0.6) to afford a yellow viscous pasty in 71% yield. UV-Vis (CH_2Cl_2): $\lambda_{máx}$(344 nm) ε(4.55 x 10^5 $M^{-1}cm^{-1}$). ^{1}H NMR ($CDCl_3$, 300MHz) δ (ppm): 8.18(dd, 2H, Ar), 7.83 (s, 3H, Ar), 7.70-7.58 (m, 7H, Ar), 7.44 (d, 1H, Ar), 7.22 (m, 1H, Ar), 4.60-4.43 (dt, 10, -$COOCH_2$), 3.88-3.76 (m, 18, -NCH_2, -CH_2-β-COO), 3.68-3.65 (m, 10, -CH_2), 3.56-3.53 (m, 10, -CH_2), 3.37-3.35 (s, 15, -CH_3), 1.31-1.24 (m, 12, CH_3-β-N). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 167.76, 165.43, 165.34, 165.15, 150.11, 134.75, 134.66, 134.50, 134.41, 134.30, 134.18, 134.13, 133.91, 133.01, 132.10, 131.93, 126.71, 124.13, 124.04, 123.40, 123.01, 122.78, 122.28, 119.07, 118.95, 96.54, 96.44, 95.26, 91.14, 90.67, 88.71, 88.61, 72.00, 71.98, 70.66, 69.21, 64.56, 64.21, 59.15, 49.35, 41.93, 14.56, 11.31.

Synthesis of 5BEgly-I (19). A heavy walled glass flask equipped with a Teflon screw valve was charged with **18** (250 mg, 0.17 mmol) and iodomethane (10 mL). The solution was placed under vacuum and the flask was sealed; the solution was then heated to 110 ºC for 15 h with vigorous stirring. After cooling, the remaining iodomethane was vacuum removed. Then, THF was added and the precipitate was filtered off. After THF evaporation, the crude product was first purified by chromatography (CH_2Cl_2/acetone, 80/20 v/v, rf = 0.6) and then by preparative GPC chromatography (Biorads, Bio-Beds, toluene) to afford a yellow viscous liquid in 73 % yield. UV-Vis (CH_2Cl_2): $\lambda_{máx}$(368 nm) ε(1.24 x 10^5 $M^{-1}cm^{-1}$). ^{1}HNMR ($CDCl_3$, 300MHz) δ (ppm): 8.20-8.18 (m, 3H, Ar), 7.99-7.97 (m, 4H, Ar), 7.73-7.61 (m, 6H, Ar), 7.36-7.33 (dd, 2H, Ar), 4.57-4.50 (m, 10H, -COOCH$_2$), 3.88-3.83 (m, 10H, -CH$_2$-β-COO), 3.71-3.64 (m, 10H, -CH$_2$), 3.58-3.51 (m, 10H, -CH$_2$), 3.38-3.33 (s, 15H, CH$_3$).

Synthesis of 7BEgly-H (20). *Applying the procedure for the Sonogashira-Heck cross-coupling.* To a two neck falsk containing **19** (200 mg, 0.13 mmol), $[(C_6H_5)_3P]_2PdCl_2$ (5 mg, 6. 84 x10^{-3} mmol) and CuI (1.0 mg, 2.27x10^{-3} mmol) under nitrogen, 50 mL of Et$_3$N/toluene (47/3 mL) were added. The mixture was heated at 50 ºC for 15 min and then **4** (102 mg, 0.41 mmol) in 2 mL of toluene was added by syringe. The mixture was stirred and heated by 15 h at 50ºC. After filtering off the ammonium salt and the solvent evaporate, the crude product was first purified by silica gel chromatography (SiO$_2$, CH$_2$Cl$_2$/acetone, 80/20 v/v, rf = 0.3) and then by preparative GPC chromatography to afford a yellow pasty solid in 43% yield. UV-Vis (CH$_2$Cl$_2$): $\lambda_{\text{máx}}$(372 nm) ε(12.96 x 10^4 M^{-1}cm^{-1}). ^{1}HNMR (CDCl$_3$, 300MHz) δ (ppm): 8.24-8.19 (m, 7H, Ar), 8.04-8.02 (dt, 2H, Ar), 7.78-7.63 (m, 12H, Ar), 7.47-7.41 (t, 2H, Ar), 4.56-4.48 (m, 14H, -COOCH$_2$), 3.86-3.83 (m, 14H, -CH$_2$-β-COO), 3.71-3.63 (m, 14H, -CH$_2$), 3.58-3.50 (m, 14H, CH$_2$), 3.38-3.34 (m, 21H, -CH$_3$). ^{13}C NMR (CDCl$_3$, 75 MHz): 165.90, 165.21, 136.15, 134.75-133.90, 132.97, 132.14, 130.58, 129.90, 128.63, 123.45, 95.20, 90.95, 89.02, 71.98, 70.65, 69.25, 64.50.

II. Selected NMR spectra

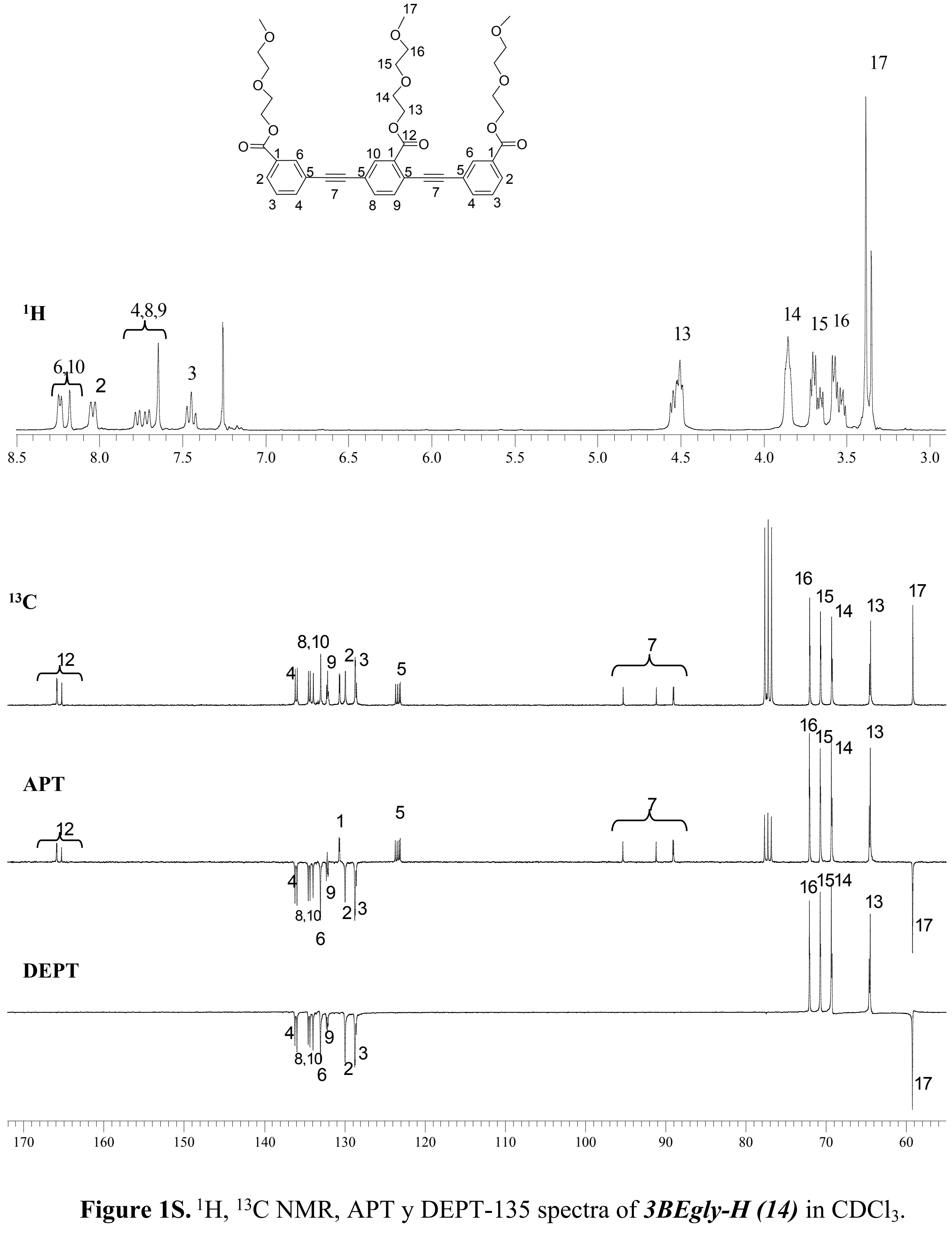


Figure 1S. ¹H, ¹³C NMR, APT y DEPT-135 spectra of ***3BEgly-H (14)*** in $CDCl_3$.

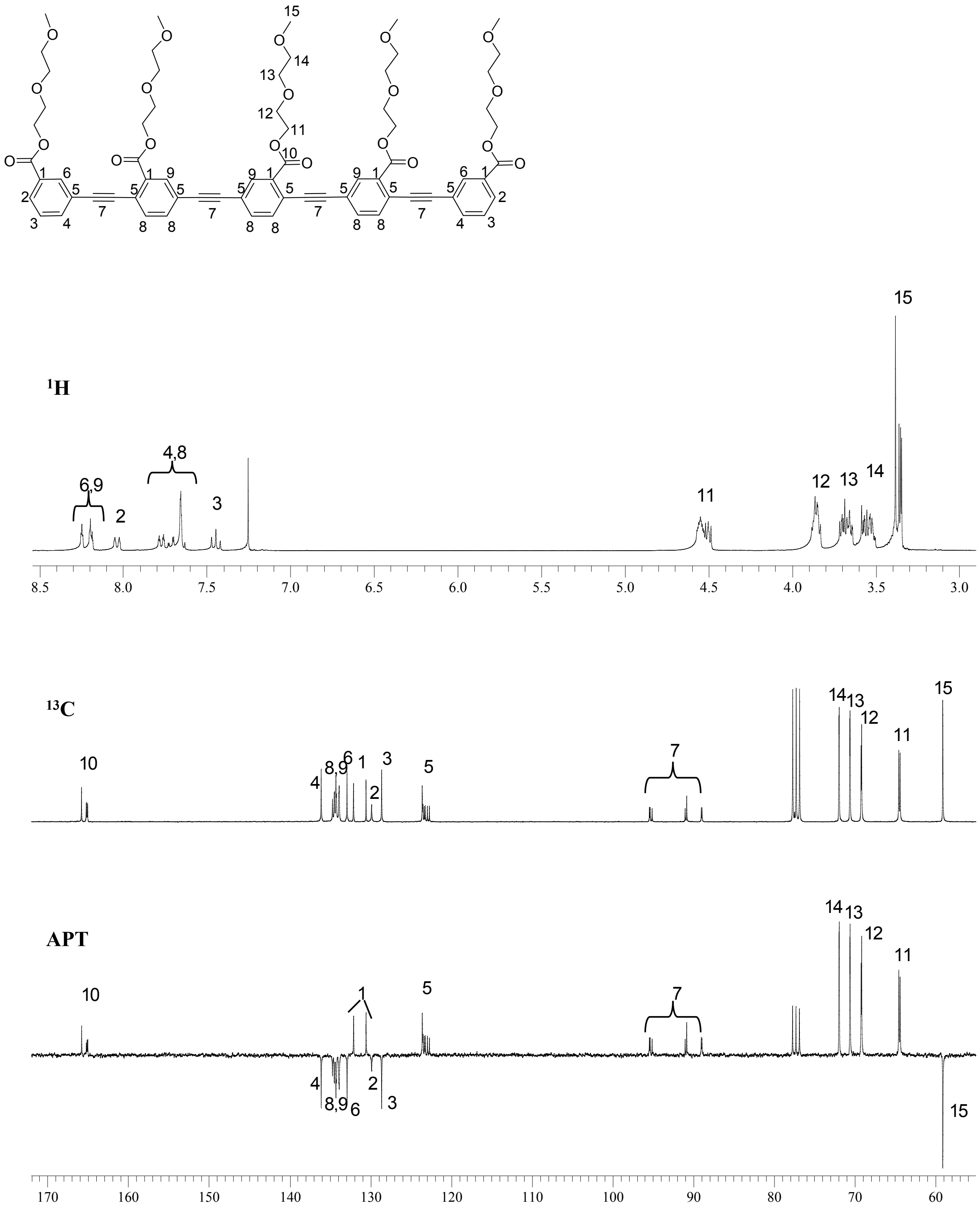


Figure 2S. ^{1}H , ^{13}C NMR, APT y DEPT-135 spectra of ***5BEgly-H (17)***in CDCl$_3$.

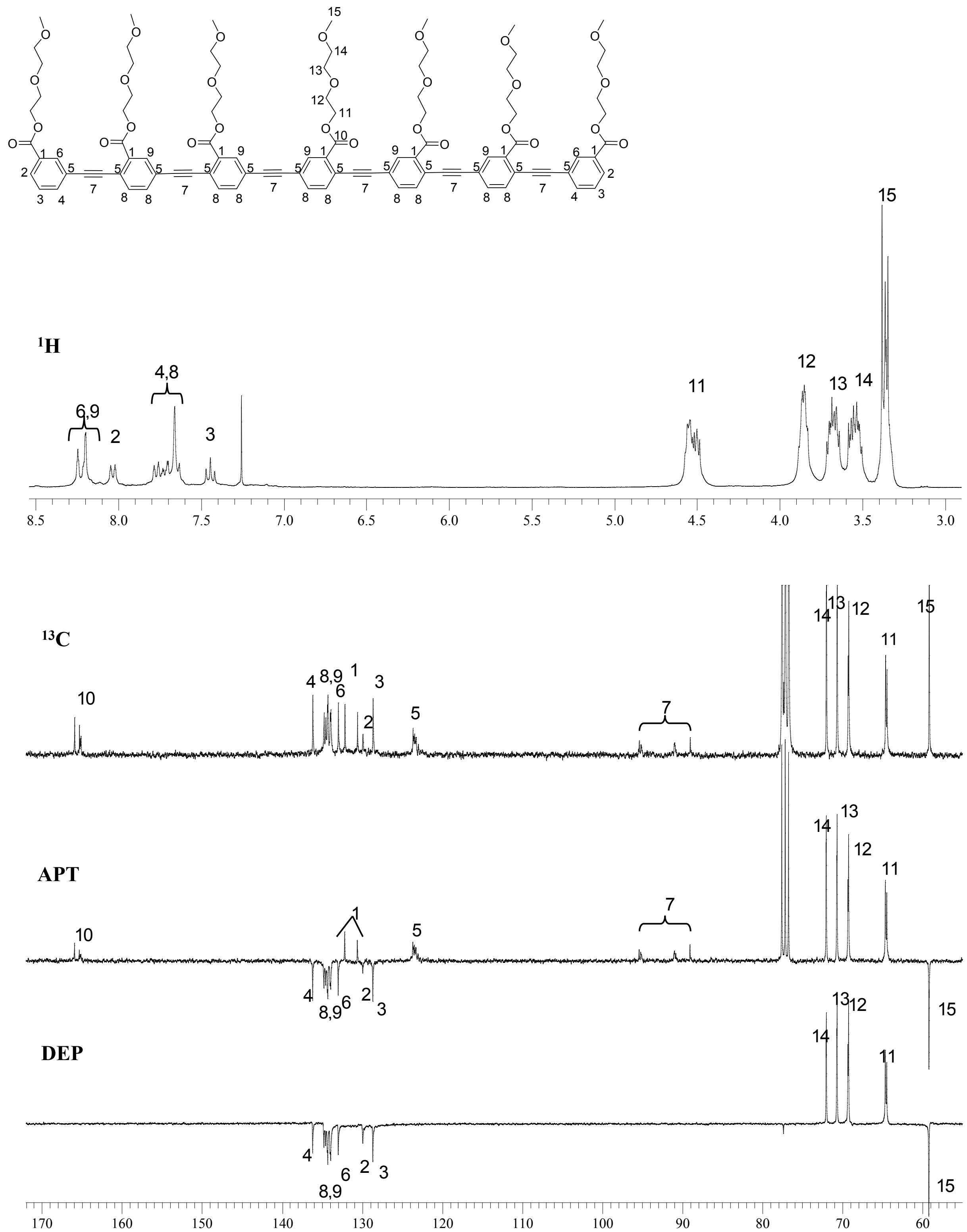


Figure 3S. ^{1}H , ^{13}C NMR, APT y DEPT-135 spectra of ***7BEgly-H (20)*** in CDCl$_3$.

III. Optical spectra in solution

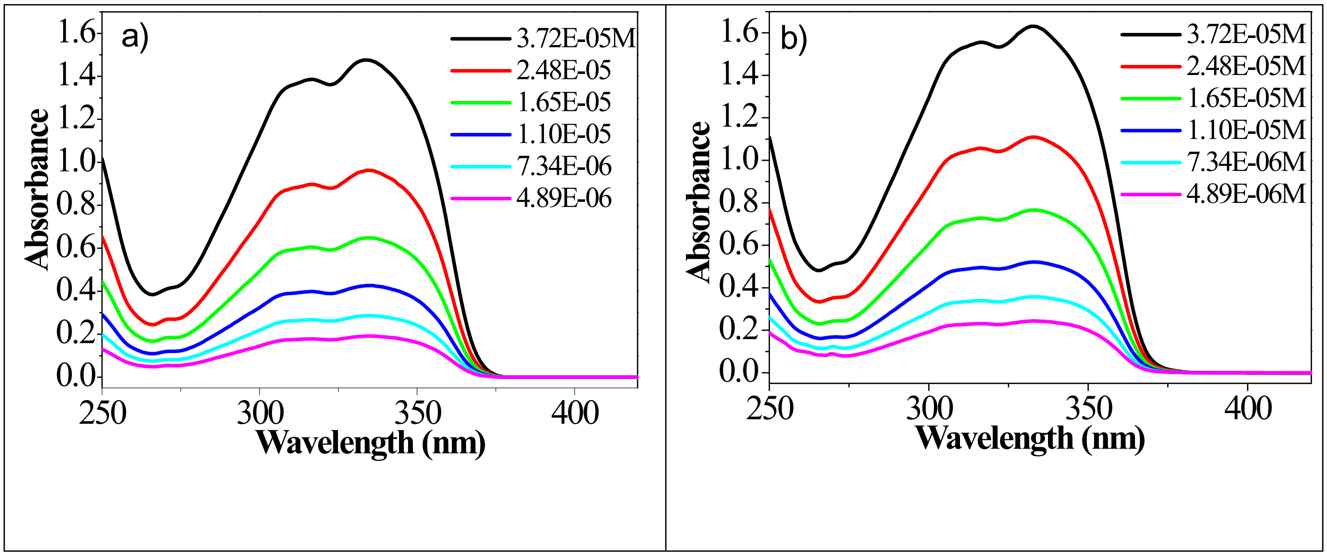


Figure 4S. Normalized UV-Vis spectra of trimer **3BEgly-H (14)** in a) CH_2Cl_2 and b) THF at different concentrations.

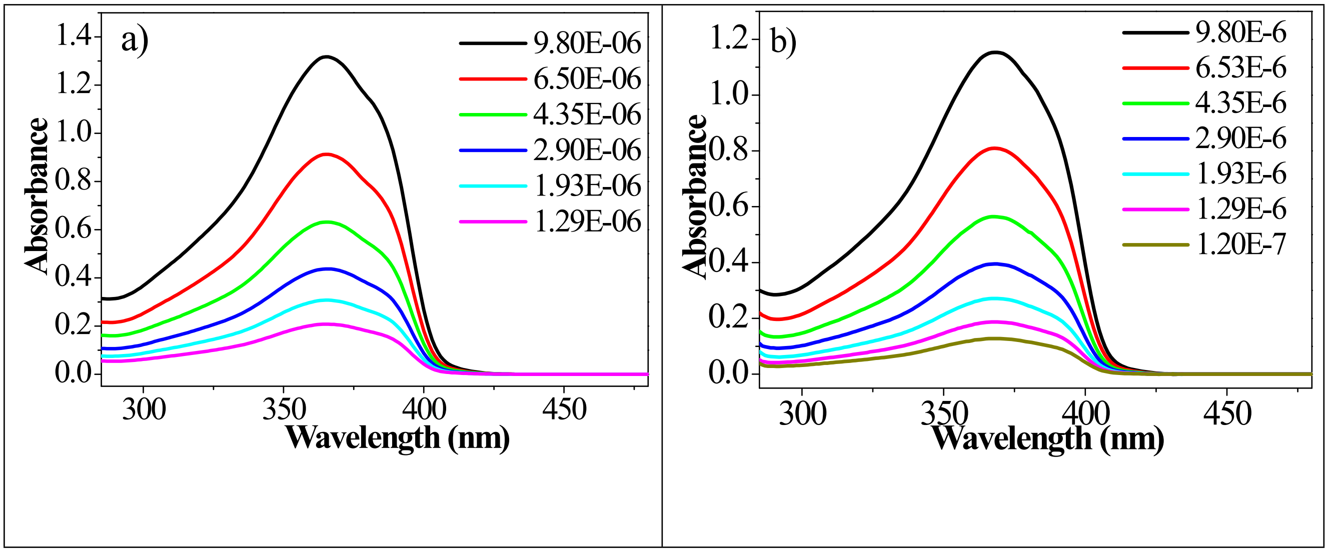


Figure 5S. Normalized UV-Vis spectra of pentamer **5BEgly-H (17)** in a)THF and b) toluene at different concentrations.

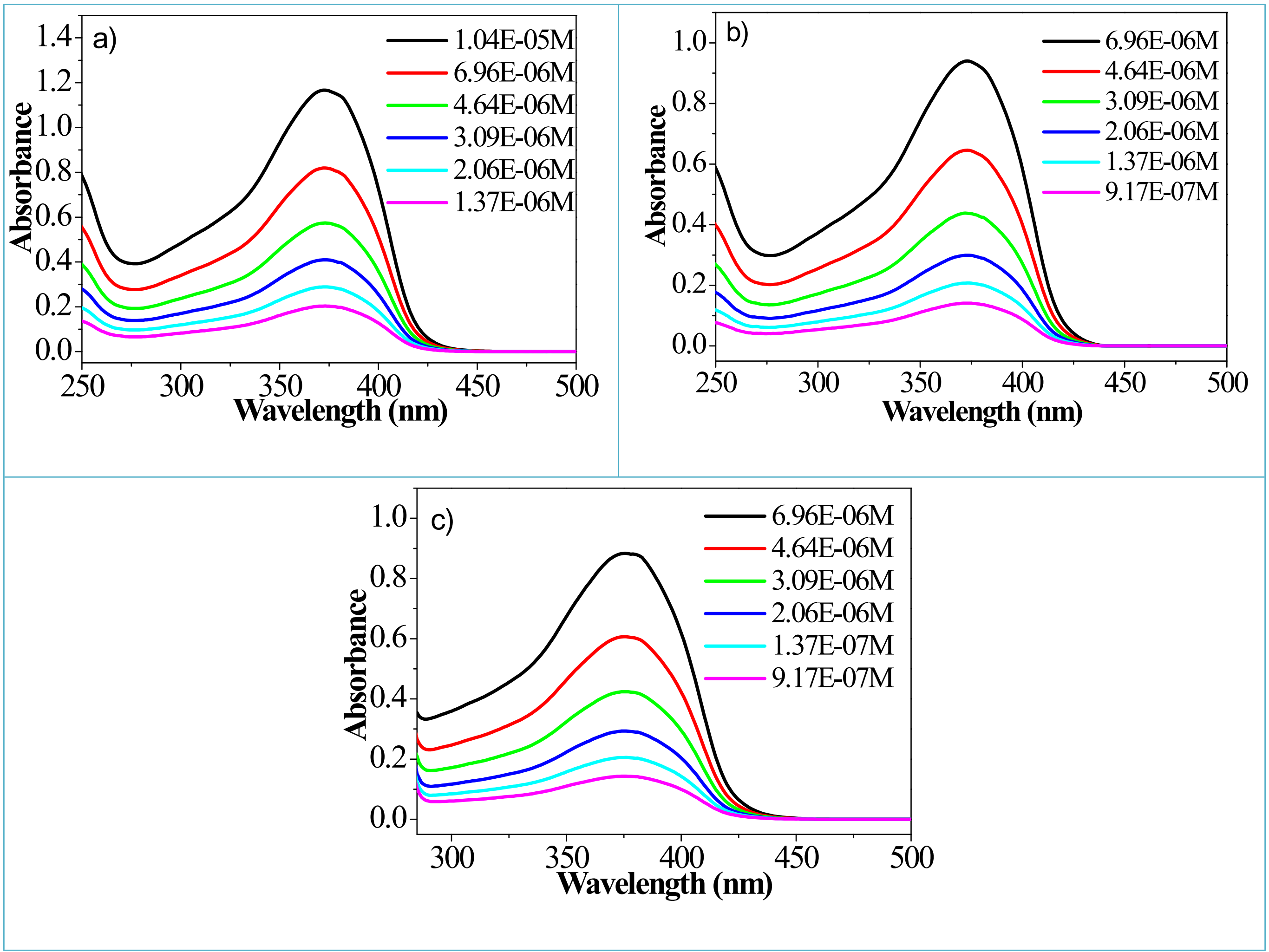


Figure 6S. Normalized UV-Vis spectra of heptamer **7BEgly-H (20)** in a) CH_2Cl_2, b) THF and c) toluene at different concentrations

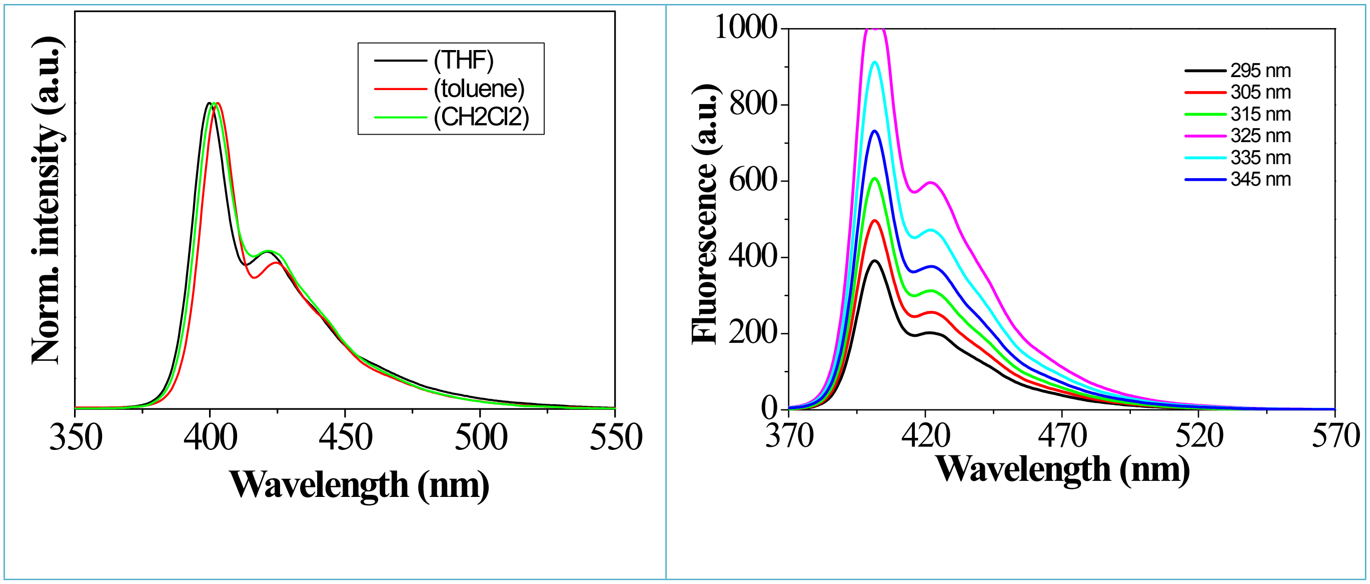


Figure 7S. Left, fluorescence spectra of **5BEgly-H (14)** in different solvents. Right, fluorescence spectra of **5BEgly-H (14)** at different excitation wavelengths in CH_2Cl_2

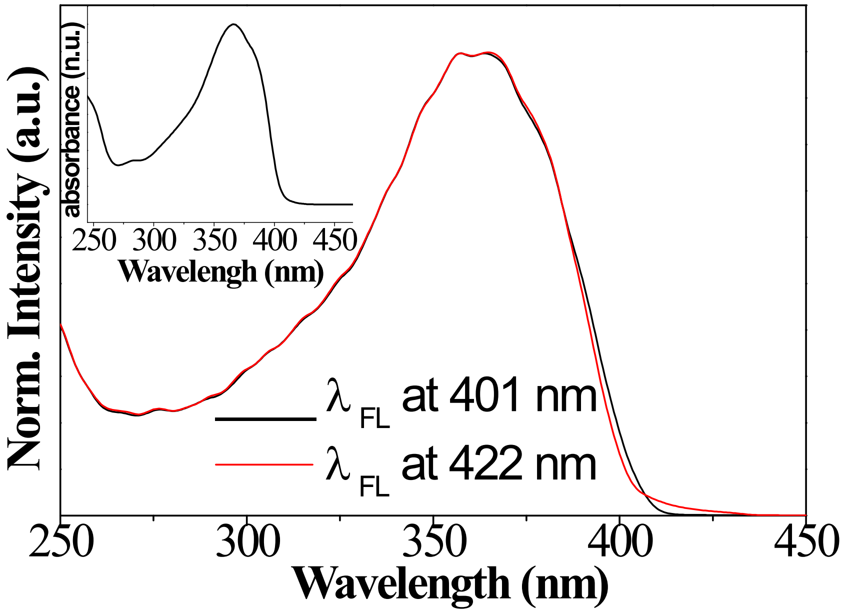


Figure 8S. Excitation spectra at the main emission peak (401 nm) and at the shoulder (422 nm) for **5BEgly-H (14)** in CH_2Cl_2. Insert: corresponding UV-Vis spectrum.

IV. Theoretical calculations

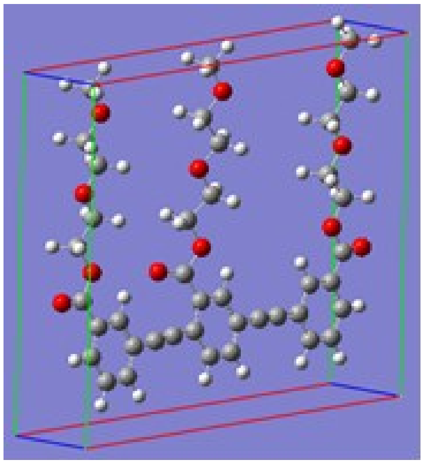
Molecular geometry was explored in the framework of the molecular mechanics in order to identify the main conformations. Successively, the geometry was refined at the AM1 level.

AM1 results with the dihedral constraint of 180° for the backbone of trimer ***3BEgly-H (14)***

front view side view

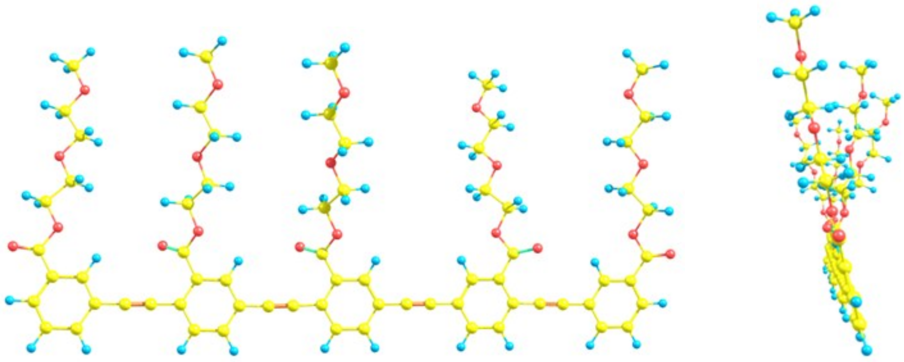
Energy -0.552149341Eh

Frequency 18 negative ones in the range of -90.0-4.0 cm^{-1}. Source: 3PEGLYH_AM1_arguslab.



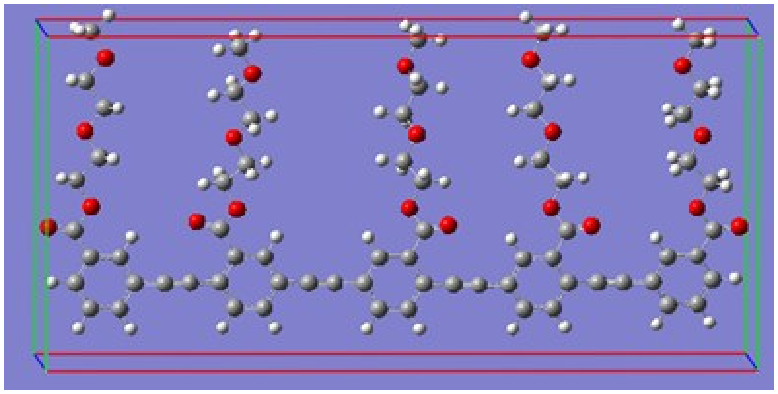
On the left the envelope of the molecule in an elementary triclinic cell: **a**(red axes): 2.03 nm; **b** (green axes): 1.60 nm (but the maximum distance H-H along this axes is 1.47 nm); **c** (blue axes): 0.41 nm.

AM1 results with the dihedral constraint of 180° for the backbone of ***5BEgly-H (17)***



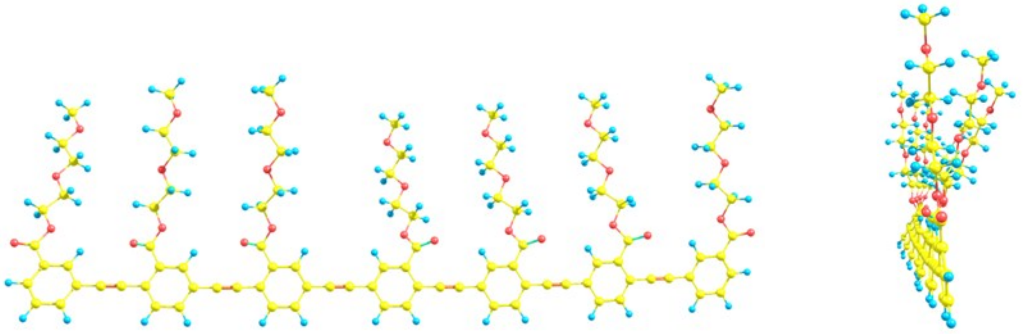
front view side view

Energy -0.855259995Eh, Frequency all positive, Source: 5AM1_gfrozen.



On the left the envelope of the molecule in an elementary triclinic cell; **a** (red axes): 3.36 nm, **b** (green axes): 1.58 nm (but the maximum distance H-H along this axes is 1.48 nm): **c** (blue axes) 0.91nm.

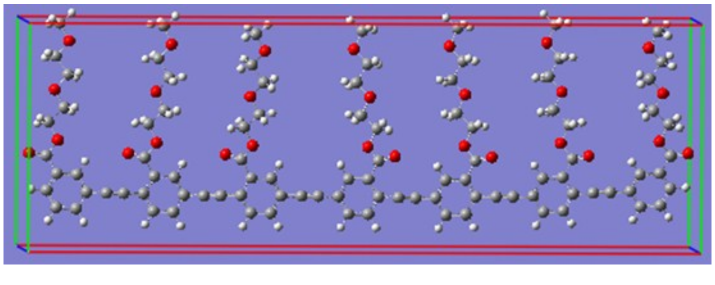
AM1 results with the dihedral constraint (180°) for the backbone of ***5BEgly-H (20)***



front view

side view

Energy -1.158201994Eh, Frequency all positive, Source: 7AM1_gfrozen.



On the left the envelope of the molecule in an elementary triclinic cell; **a** (red axes): 4.70 nm, **b** (green axes): 1.59 nm (but the maximum distance H-H along this axes is 1.47 nm), **c** (blue axes): 0.91 nm.

Table 1s. TD-B3LYP/6-311G** singlet and triplet excitation energies (nm) and corresponding oscillator strengths for **3BEgly-H** with different dihedral angles between the benzoates

[90°,90°]		**[90°,45°]**		**[45°,45°]**	
Singlet	Triplet	Singlet	Triple	*Singlet*	*Triplet*
347.89 (0.00)	459.69	358.29 (1.40)	509.90	345.82 (0.68)	490.97
327.39 (0.50)	396.98	334.44 (0.13)	412.79	333.40 (0.20)	396.67
321.48 (0.00)	389.94	328.39 (0.10)	385.70	321.18 (0.02)	389.02
313.22 (0.00)	361.10	348.08 (0.04)	362.79	316.86 (0.00)	343.77

Table 2s. TD-B3LYP/6-311G** singlet and triplet excitation energies (nm) and corresponding oscillator strengths for **5BEgly-H** with different dihedral angles between the benzoates

[45°, 45°, 0°, 10°]		**[60°, 45°, 45°, 60°]**		**[60°, 60°, 90°, 60°]**	
Singlet	Triplet	Singlet	Triple	*Singlet*	*Triplet*
425.59 (2.67)	591.19	400.03 (2.19)	544.34	399.21 (0.00)	496.53
392.20 (0.08)	518.59	398.78 (0.10)	491.96	381.72 (1.42)	486.01
381.84 (0.03)	458.51	363.75 (0.01)	445.44	373.51 (0.48)	456.00
379.89 (0.00)	404.68	363.14 (0.04)	405.04	360.37 (0.15)	401.60

V. Temperature dependent X-ray scattering patterns of *5BEgly-H*