

Supporting Information

Charge separation and recombination in small band gap oligomer – fullerene triads

Bram P. Karsten, Ricardo K. M. Bouwer, Jan.C. Hummelen, René M. Williams and
René A. J. Janssen

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Detailed synthetic procedures

General methods. ^1H -NMR and ^{13}C -NMR spectra were recorded on a 400 MHz NMR (Varian Mercury or Varian 400-MR, 400 MHz for ^1H -NMR and 100 MHz for ^{13}C -NMR) or on a 500 MHz NMR (Varian Unity Plus, 500 MHz for ^1H -NMR and 125 MHz for ^{13}C -NMR). Spectra were recorded in CDCl_3 , or in CS_2 using a D_2O insert for locking and shimming. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). IR spectra were recorded on a Perkin Elmer 1600 FT-IR. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry has been performed on a PerSeptive Biosystems Voyager-DE PRO spectrometer. Recycling GPC was performed on a LC system equipped with JAIGEL 2H and JAIGEL 2.5H. The eluent was chloroform at 3.5 mL/min, the injection volume was 2 mL. Preparative HPLC was performed using a Cosmosil Buckyprep Waters packed column (10x250 mm), using toluene as the eluent at a flow rate of 10 mL/min. Analytical HPLC analysis was performed on a Hewlett Packard HP LC-Chemstation 3D (Agilent/HP1100 Series) using an analytical Cosmosil Buckyprep column (4.6x250 mm).

Materials. Solvents were purchased from Biosolve and used without further purification. THF was distilled over 4 Å molsieves before use. Dichloromethane was distilled over P₂O₅ before use. C₆₀, MP-C₆₀ and PCBM were obtained from Solenne, other chemicals were purchased from Acros or Aldrich and used without purification. N-bromosuccinimide (NBS) was recrystallized from water. Synthesis of compounds **O₁₁** and **O₂₁** has been reported previously.¹ Oxygen and moisture-sensitive reactions were performed under an argon atmosphere.

Compound 1 (n=1): Compound **O₁₁** (1.0 g, 1.35 mmol) was dissolved in THF (50 mL). NBS (0.22 g, 1.24 mmol) was added in small portions at 0°C and the mixture was stirred overnight, while warming to room temperature. Diethyl ether (150 mL) was added and the mixture was washed with water (3 × 50 mL) and saturated NaCl (2 × 50 mL). The organic phase was dried with MgSO₄ and the solvent was evaporated. The compound was purified by flash chromatography on silica, using dichloromethane/heptane as the eluent. Yield: 0.69 g (68 %). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.36 (d, *J* = 5.0 Hz, 1H, Ar-*H*), 7.00 (d, *J* = 5.0 Hz, 1H, Ar-*H*), 6.94 (s, 1H, ArBr-*H*), 2.97-2.87 (m, 4H, Ar-CH₂-), 2.87-2.82 (m, 4H, Ar-CH₂-), 2.26-2.16 (m, 2H, -CH₂CH(C₄H₉)(C₂H₅)), 1.77-1.66 (m, 4H, -CH₂CH₂C₆H₁₃), 1.55-1.20 (m, 36H, -CH₂-), 0.99-0.83 (m, 18H, -CH₃). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 155.81, 155.65, 140.27, 139.79, 137.66, 137.47, 131.62, 130.26, 129.24, 128.15, 126.36, 123.87, 122.61, 113.53, 39.42, 39.37, 37.58, 37.43, 32.82, 32.73, 31.89, 30.58, 30.40, 30.34, 29.99, 29.79, 29.73, 29.55, 29.52, 29.33, 29.29, 28.91, 28.89, 25.91, 23.13, 22.66, 14.20, 14.14, 14.08, 10.91, 10.87. IR (cm⁻¹): 2956, 2923, 2854, 1523, 1494, 1459, 1427, 1378, 1354, 1271, 1250, 1184, 1136, 1122, 817, 724, 696, 660. MALDI-TOF-MS *m/z* (intensity, %): 826.25 (80), 827.25 (45), 828.25 (100), 829.25 (50), 830.26 (25), 831.27 (10).

¹ Karsten, B. P.; Janssen, R. A. J. *Org. Lett.* **2008**, *10*, 3513-3516.

Compound 1 (n=2): Compound **O₂₁** (1.0 g, 0.91 mmol) was dissolved in THF (30 mL). NBS (0.15 g, 0.82 mmol) was added in small portions at 0°C and the mixture was stirred overnight, while warming to room temperature. Diethyl ether (100 mL) was added and the mixture was washed with water (3 × 30 mL) and saturated NaCl (2 × 30 mL). The organic phase was dried with MgSO₄ and the solvent was evaporated. The compound was purified by flash chromatography on silica, using dichloromethane/heptane as the eluent. Yield: 0.52 g (53 %). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.37 (d, *J* = 5.2 Hz, 1H, Ar-*H*), 7.03 (d, *J* = 5.2 Hz, 1H, Ar-*H*), 6.97 (s, 1H, ArBr-*H*), 3.10-3.01 (m, 4H, Ar-CH₂-), 2.93 (d, *J* = 6.9 Hz, 4H, -CH₂CH(C₄H₉)(C₂H₅)), 2.88 (d, *J* = 6.7 Hz, 4H, -CH₂CH(C₄H₉)(C₂H₅)), 2.33-2.19 (m, 4H, -CH₂CH(C₄H₉)(C₂H₅)), 1.80-1.71 (m, 4H, -CH₂CH₂C₆H₁₃), 1.56-1.18 (m, 52H, -CH₂-), 1.00-0.80 (m, 30H, -CH₃). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 155.95, 155.87, 155.36, 155.22, 140.33, 139.92, 138.11, 137.91, 137.76, 131.74, 131.13, 129.34, 129.12, 126.46, 126.30, 124.74, 123.31, 122.84, 133.49, 39.59, 39.52, 37.99, 37.89, 37.81, 37.62, 33.03, 32.87, 32.83, 32.78, 32.74, 31.89, 30.58, 30.40, 30.27, 30.01, 29.72, 29.65, 29.32, 29.29, 28.97, 28.93, 25.96, 25.90, 23.19, 23.15, 22.65, 14.21, 14.17, 14.11, 14.06, 10.93, 10.87. IR (cm⁻¹): 2957, 2924, 2856, 1490, 1458, 1378, 1354, 1182, 1137, 828, 802, 725, 697. MALDI-TOF-MS *m/z* (intensity, %): 1184.6 (70), 1185.64(55), 1186.63 (100), 1187.63 (70), 1188.63 (40), 1189.63 (20), 1190.63 (5).

Compound O₁₂: A solution of Ni(COD)₂ (0.45 g, 1.64 mmol) and 2,2'-bipyridyl (0.26 g, 1.64 mmol) in toluene (15 mL) was stirred for 30 min, while heating to 80°C. This solution was added to compound **1** (n=1) (0.68 g, 0.82 mmol) and the mixture was stirred at 80°C overnight. The mixture was precipitated in methanol (150 mL), the suspension was filtered over celite and the solids were washed with methanol. The product was recovered from the celite by

redissolution in dichloromethane. The solvent was evaporated and the product was purified by flash chromatography on silica, using dichloromethane/heptane as the eluent. Yield: 0.38 g (62 %). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm): 7.36 (d, $J = 4.6$ Hz, 2H, Ar-*H*), 7.14 (s, 2H, Ar-*H*), 7.01 (d, $J = 4.8$ Hz, 2H, Ar-*H*), 2.97 (t, $J = 7.5$ Hz, 8H, Ar- CH_2 -), 2.89 (d, $J = 7.7$ Hz, 4H, - $\text{CH}_2\text{CH}(\text{C}_4\text{H}_9)(\text{C}_2\text{H}_5)$), 2.86 (d, $J = 7.1$ Hz, 4H, - $\text{CH}_2\text{CH}(\text{C}_4\text{H}_9)(\text{C}_2\text{H}_5)$), 2.34 (m, 2H, - $\text{CH}_2\text{CH}(\text{C}_4\text{H}_9)(\text{C}_2\text{H}_5)$), 2.21 (m, 2H, - $\text{CH}_2\text{CH}(\text{C}_4\text{H}_9)(\text{C}_2\text{H}_5)$), 1.85-1.69 (m, 8H, - $\text{CH}_2\text{CH}_2\text{C}_6\text{H}_{13}$), 1.55-1.20 (m, 72H, - CH_2 -), 1.04-0.84 (m, 36H, - CH_3). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm): 155.81, 155.31, 140.88, 140.24, 137.76, 137.69, 129.33, 128.37, 127.79, 126.26, 125.79, 123.80, 123.49, 39.49, 39.36, 37.70, 37.52, 32.83, 31.93, 31.92, 30.84, 30.41, 30.02, 29.87, 29.82, 29.60, 29.57, 29.34, 29.00, 28.94, 25.93, 25.87, 23.16, 22.68, 14.17, 14.10, 10.93, 10.90. IR (cm^{-1}): 2956, 2922, 2853, 1517, 1487, 1457, 1428, 1377, 1350, 1239, 1182, 1122, 929, 824, 814, 724, 696. MALDI-TOF-MS m/z (intensity, %): 1494.97 (90), 1495.97 (100), 1496.97 (80), 1497.97 (50), 1498.97 (25), 1499.97 (10).

Compound O₂₂: A solution of $\text{Ni}(\text{COD})_2$ (0.24 g, 0.87 mmol) and 2,2'-bipyridyl (0.14 g, 0.87 mmol) in toluene (7.5 mL) was stirred for 30 min, while heating to 80°C. This solution was added to compound **1** ($n=2$) (0.52 g, 0.43 mmol) and the mixture was stirred at 80°C overnight. The mixture was precipitated in methanol (75 mL), the suspension was filtered over celite and the solids were washed with methanol. The product was recovered from the celite by redissolution in dichloromethane. The solvent was evaporated and the product was purified by flash chromatography on silica, using dichloromethane/heptane as the eluent. Yield: 0.35 g (73 %). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm): 7.37 (d, $J = 5.2$ Hz, 2H, Ar-*H*), 7.19 (s, 2H, Ar-*H*), 7.04 (d, $J = 5.2$ Hz, 2H, Ar-*H*), 3.15-3.05 (m, 8H, Ar- CH_2 -), 2.99-2.86 (m, 16H, - $\text{CH}_2\text{CH}(\text{C}_4\text{H}_9)(\text{C}_2\text{H}_5)$), 2.44-2.20 (m, 8H, - $\text{CH}_2\text{CH}(\text{C}_4\text{H}_9)(\text{C}_2\text{H}_5)$), 1.90-1.72 (m, 8H, -

CH₂CH₂C₆H₁₃), 1.80-1.20 (m, 104H, -CH₂-), 1.06-0.81 (m, 60H, -CH₃). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 155.87, 155.45, 155.33, 155.06, 141.02, 140.24, 138.10, 137.96, 137.82, 129.36, 129.21, 128.82, 126.19, 125.98, 125.92, 123.18, 122.84, 39.62, 39.54, 39.37, 38.04, 37.95, 37.84, 37.61, 33.06, 32.88, 31.95, 31.90, 30.95, 30.42, 30.30, 29.97, 29.84, 29.78, 29.73, 29.66, 29.36, 29.34, 28.99, 26.01, 25.96, 25.90, 25.85, 25.80, 23.19, 23.16, 22.66, 14.18, 14.13, 14.06, 10.90. IR (cm⁻¹): 2956, 2923, 2855, 1513, 1485, 1457, 1440, 1378, 1351, 1239, 1180, 1138, 1121, 824, 804, 724, 708. MALDI-TOF-MS m/z (intensity, %): 2211.45 (60), 2212.45 (100), 2213.45 (100), 2214.44 (75), 2215.44 (50), 2216.43 (25), 2217.42 (15).

Compound 2 (n=1, m=1): O₁₁ (315 mg, 0.42 mmol), DMF (130 μL, 1.7 mmol) and POCl₃ (160 μL, 1.7 mmol) were dissolved in dry dichloromethane (2 mL). The mixture was stirred at 40°C for 48h. 1M NaOH (5 mL) was added, the mixture was stirred vigorously and the phases were separated. The aqueous phase was extracted with dichloromethane. The combined organic phases were dried with MgSO₄ and the solvent was evaporated. The crude product was purified by flash chromatography on silica, using dichloromethane/heptane as the eluent. Yield: 227 mg (67 %). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 9.92 (s, 2H, -COH), 7.66 (s, 2H, Ar-H), 3.02 (t, *J* = 7.9 Hz, 4H, Ar-CH₂-), 2.92 (d, *J* = 6.8 Hz, 4H, -CH₂CH(C₄H₉)(C₂H₅)), 2.24 (m, 2H, -CH₂CH(C₄H₉)(C₂H₅)), 1.80 (m, 4H, -CH₂CH₂C₆H₁₃), 1.53-1.24 (m, 36H, -CH₂-), 0.96 (t, *J* = 7.4 Hz, 6H, -CH₃), 0.91-0.85 (m, 12H, -CH₃). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 182.75, 157.32, 142.58, 141.12, 139.06, 138.08, 137.76, 124.76, 39.56, 37.61, 32.79, 31.85, 30.86, 29.77, 29.74, 29.49, 29.26, 28.84, 25.90, 23.09, 22.63, 14.08, 14.05, 10.87. IR (cm⁻¹): 2958, 2924, 2854, 1652, 1528, 1463, 1417, 1243, 1155, 744, 669. MALDI-TOF-MS m/z (intensity, %): 804.34 (100), 805.34 (60), 806.34 (30), 807.35 (10).

Compound 2 (n=1, m=2): **O**₁₂ (300 mg, 0.20 mmol), DMF (70 μ L, 0.9 mmol) and POCl₃ (80 μ L, 0.9 mmol) were dissolved in dry dichloromethane (1.5 mL). The mixture was stirred at 40°C for 48h. 1M NaOH (5 mL) was added, the mixture was stirred vigorously and the phases were separated. The organic phase was dried with MgSO₄ and the solvent was evaporated. The crude product was purified by flash chromatography on silica, using dichloromethane/heptane as the eluent. Yield: 280 mg (90 %). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 9.90 (s, 2H, -COH), 7.65 (s, 2H, Ar-H), 7.18 (s, 2H, Ar-H), 3.07-2.96 (m, 8H, Ar-CH₂-), 2.95-2.89 (m, 8H, -CH₂CH(C₄H₉)(C₂H₅)), 2.40-2.32 (m, 2H, -CH₂CH(C₄H₉)(C₂H₅)), 2.29-2.21 (m, 2H, -CH₂CH(C₄H₉)(C₂H₅)), 1.86-1.76 (m, 8H, -CH₂CH₂C₆H₁₃), 1.55-1.23 (m, 72H, -CH₂-), 1.04-0.80 (m, 36H, -CH₃). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 182.69, 156.97, 155.79, 141.98, 141.62, 141.09, 139.18, 139.07, 138.60, 138.05, 137.75, 127.77, 127.04, 126.11, 121.47, 39.63, 39.27, 37.67, 37.50, 32.80, 31.93, 31.89, 31.11, 30.85, 29.91, 29.85, 29.80, 29.61, 29.55, 29.34, 29.32, 28.98, 28.88, 25.90, 25.80, 23.14, 22.67, 14.15, 14.13, 14.08, 10.93. IR (cm⁻¹): 2957, 2923, 2854, 1655, 1528, 1440, 1421, 1391, 1337, 1243, 1157, 862, 825, 743, 723, 670. MALDI-TOF-MS m/z (intensity, %): 1550.97 (85), 1551.97 (100), 1552.97 (80), 1553.97 (45), 1554.96 (25), 1555.96 (10).

Compound 2 (n=2, m=1): **O**₂₁ (280 mg, 0.25 mmol), DMF (80 μ L, 1.0 mmol) and POCl₃ (100 μ L, 1.1 mmol) were dissolved in dry dichloromethane (2 mL). The mixture was stirred at 40°C for 48h. 1M NaOH (5 mL) was added, the mixture was stirred vigorously and the phases were separated. The aqueous phase was extracted with dichloromethane. The combined organic phases were dried with MgSO₄ and the solvent was evaporated. The crude product was purified by flash chromatography on silica, using dichloromethane/heptane as the eluent. The product was further purified by recycling GPC. Yield: 202 mg (68 %). ¹H-NMR (400

MHz, CDCl₃) δ (ppm): 9.92 (s, 2H, -COH), 7.68 (s, 2H, Ar-*H*), 3.14 (t, *J* = 7.1 Hz, 4H, Ar-CH₂-), 2.99 (d, *J* = 6.5 Hz, 4H, -CH₂CH(C₄H₉)(C₂H₅)), 2.95 (d, *J* = 6.3 Hz, 4H, -CH₂CH(C₄H₉)(C₂H₅)), 2.28 (m, 4H, -CH₂CH(C₄H₉)(C₂H₅)), 1.84 (qu, *J* = 7.2 Hz, 4H, -CH₂CH₂C₆H₁₃), 1.58-1.20 (m, 52H, -CH₂-), 1.02-0.93 (m, 12H, -CH₃), 0.92-0.82 (m, 18H, -CH₃). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 182.67, 157.15, 156.16, 141.93, 140.63, 139.52, 139.38, 138.64, 137.88, 125.56, 125.32, 39.65, 38.11, 37.76, 33.02, 32.82, 32.78, 31.85, 30.81, 29.73, 29.68, 29.64, 29.27, 28.95, 28.88, 28.86, 25.98, 25.91, 25.87, 23.16, 23.12, 22.63, 14.12, 14.09, 14.04, 10.90, 10.88. IR (cm⁻¹): 2957, 2921, 2854, 1651, 1525, 1458, 1439, 1427, 1402, 1387, 1352, 1336, 1246, 1162, 887, 747, 726, 677, 662. MALDI-TOF-MS *m/z* (intensity, %): 1162.71 (100), 1163.71 (80), 1164.71 (50), 1165.71 (25), 1166.72 (10).

Compound 2 (n=2, m=2): O₂₂ (304 mg, 0.14 mmol), DMF (50 μ L, 0.6 mmol) and POCl₃ (60 μ L, 0.7 mmol) were dissolved in dry dichloromethane (1 mL). The mixture was stirred at 40°C for 48h. 1M NaOH (3 mL) was added, the mixture was stirred vigorously and the phases were separated. The organic phase was dried with MgSO₄ and the solvent was evaporated. The crude product was purified by flash chromatography on silica, using dichloromethane/heptane as the eluent. Yield: 257 mg (82 %). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 9.91 (s, 2H, -COH), 7.68 (s, 2H, Ar-*H*), 7.21 (s, 2H, Ar-*H*), 3.18-3.10 (m, 8H, Ar-CH₂-), 3.02-2.92 (m, 16H, -CH₂CH(C₄H₉)(C₂H₅)), 2.45-2.37 (m, 2H, -CH₂CH(C₄H₉)(C₂H₅)), 2.33-2.24 (m, 6H, -CH₂CH(C₄H₉)(C₂H₅)), 1.91-1.80 (m, 8H, -CH₂CH₂C₆H₁₃), 1.60-1.20 (m, 104H, -CH₂-), 1.07-0.82 (m, 60H, -CH₃). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 182.61, 157.00, 155.95, 155.60, 155.47, 141.70, 141.35, 140.10, 140.05, 139.48, 138.84, 138.34, 138.13, 138.03, 128.89, 128.25, 126.39, 126.09, 123.59, 121.99, 39.68, 39.60, 39.35, 38.13, 37.80, 37.61, 33.06, 32.85, 31.94, 31.87, 31.09, 30.80, 29.87, 29.78, 29.71, 29.67, 29.35, 29.30,

28.98, 28.88, 26.01, 25.93, 25.88, 25.83, 25.77, 23.19, 23.14, 22.66, 14.17, 14.14, 14.11, 14.06, 10.96, 10.89. IR (cm^{-1}): 2956, 2923, 2855, 1655, 1527, 1457, 1414, 1391, 1378, 1332, 1244, 1154, 825, 803, 745, 725, 672. MALDI-TOF-MS m/z (intensity, %): 2267.47 (60), 2268.47 (95), 2269.46 (100), 2270.45 (75), 2271.44 (50), 2272.44 (25), 2273.44 (15).

T₁₁: Compound **2** ($n=1$, $m=1$) (226 mg, 0.28 mmol), C₆₀ (2.0 g, 2.8 mmol), and N-methylglycine (0.26 g, 3.0 mmol) were dissolved in ODCB (250 mL) and stirred at 120°C for 5h. The solvent was evaporated. The excess of C₆₀ was removed by column chromatography on silica, using CS₂ as the eluent. The product was subsequently eluted with toluene and the solvent was evaporated. The product was redissolved in ODCB, precipitated in methanol and dried in a vacuum oven. Yield: 453 mg (67 %). About 7 mg of the product was further purified by preparative HPLC. ¹H-NMR (500 MHz, CS₂) δ (ppm): 7.19 (s, 2H, Ar-*H*), 5.16 (s, 2H, MP-*H*), 4.93 (d, $J = 9.4$ Hz, 2H, MP-*H*), 4.23 (d, $J = 9.4$ Hz, 2H, MP-*H*), 2.93 (s, 6H, N-CH₃), 2.89 (t, $J = 7.2$ Hz, 4H, Ar-CH₂-), 2.77 (d, $J = 6.8$ Hz, 4H, -CH₂CH(C₄H₉)(C₂H₅)), 2.30-2.19 (m, 2H, -CH₂CH(C₄H₉)(C₂H₅)), 1.65 (m, 4H, -CH₂CH₂C₆H₁₃), 1.50-1.14 (m, 36H, -CH₂-), 0.97-0.80 (m, 18H, -CH₃). ¹³C-NMR (125 MHz, CS₂) δ (ppm): 155.71, 155.67, 154.90, 153.55, 153.07, 152.98, 147.06, 147.04, 146.73, 146.72, 146.16, 146.11, 146.02, 146.00, 145.95, 145.89, 145.84, 145.71, 145.51, 145.42, 145.25, 145.20, 145.12, 145.10, 145.02, 145.00, 144.92, 144.48, 144.45, 144.14, 142.93, 142.90, 142.80, 142.49, 142.40, 142.01, 141.95, 141.89, 141.84, 141.78, 141.71, 141.68, 141.66, 141.45, 141.39, 140.54, 140.03, 139.95, 139.72, 139.54, 138.75, 137.37, 136.77, 136.69, 136.60, 136.54, 135.62, 135.47, 130.35, 129.82, 129.79, 127.37, 123.75, 79.23, 79.15, 77.04, 77.02, 69.91, 69.89, 68.46, 40.24, 40.22, 39.34, 39.21, 37.19, 36.91, 33.31, 33.29, 33.25, 33.23, 32.24, 30.83, 30.81, 30.21, 30.19, 29.95, 29.85, 29.70, 29.37, 29.27, 26.46, 26.42, 26.30, 26.27, 23.77, 23.74, 23.24, 14.74,

14.57, 11.37, 11.36, 11.23, 11.21. IR (cm⁻¹): 2953, 2920, 2850, 2777, 1461, 1260, 1088, 1016, 796, 768. MALDI-TOF-MS m/z (intensity, %): 2298.30 (50), 2299.30 (100), 2300.30 (95), 2301.31 (70), 2302.28 (50). HPLC: 1 peak at 5.3 min.

T₁₂: Compound **2** (n=1, m=2) (281 mg, 0.18 mmol), C₆₀ (1.3 g, 1.8 mmol), and N-methylglycine (0.18 g, 2.0 mmol) were dissolved in ODCB (225 mL) and stirred at 120°C for 5h. The solvent was evaporated. The excess of C₆₀ was removed by column chromatography on silica, using CS₂ as the eluent. The product was subsequently eluted with toluene and the solvent was evaporated. The product was redissolved in ODCB, precipitated in methanol and dried in a vacuum oven. Yield: 161 mg (29 %). About 15 mg of the product was further purified by preparative HPLC. ¹H-NMR (400 MHz, CS₂) δ (ppm): 7.19 (s, 2H, Ar-*H*), 6.92 (s, 2H, Ar-*H*), 5.15 (s, 2H, MP-*H*), 4.91 (d, *J* = 9.4 Hz, 2H, MP-*H*), 4.22 (d, *J* = 9.4 Hz, 2H, MP-*H*), 2.92 (s, 6H, N-CH₃), 2.92-2.70 (m, 16H, Ar-CH₂-), 2.31-2.20 (m, 4H, -CH₂CH(C₄H₉)(C₂H₅)), 1.76-1.61 (m, 8H, -CH₂CH₂C₆H₁₃), 1.52-1.10 (m, 72H, -CH₂-), 0.99-0.77 (m, 36H, -CH₃). ¹³C-NMR (100 MHz, CS₂) δ (ppm): 155.74, 155.69, 154.90, 154.57, 153.58, 153.11, 153.02, 147.07, 147.05, 146.76, 146.75, 146.19, 146.13, 146.03, 146.01, 145.96, 145.91, 145.85, 145.72, 145.52, 145.43, 145.42, 145.26, 145.21, 145.13, 145.04, 145.01, 144.93, 144.49, 144.47, 144.16, 142.94, 142.91, 142.81, 142.50, 142.41, 142.03, 142.01, 141.96, 141.91, 141.85, 141.79, 141.73, 141.70, 141.68, 141.46, 141.41, 140.44, 140.04, 139.96, 139.73, 139.56, 138.62, 137.83, 137.50, 137.37, 136.78, 136.70, 136.62, 136.56, 135.62, 135.48, 129.97, 129.85, 129.83, 128.00, 125.59, 124.00, 123.36, 79.25, 79.19, 77.07, 69.92, 68.48, 40.25, 40.23, 39.36, 39.24, 39.14, 37.26, 37.21, 36.98, 36.93, 33.31, 33.26, 33.06, 33.03, 32.26, 31.03, 30.86, 30.21, 30.16, 30.10, 29.97, 29.86, 29.72, 29.39, 29.29, 29.20, 26.46, 26.44, 26.29, 26.25, 23.79, 23.76, 23.62, 23.25, 23.23, 14.73, 14.56, 11.38, 11.30, 11.28,

11.24. IR (cm^{-1}): 2952, 2960, 2851, 2780, 1494, 1462, 1376, 1332, 1241, 1216, 1179, 1121, 1107, 1030, 825, 768, 725. MALDI-TOF-MS m/z (intensity, %): 3045.55 (30), 3046.53 (75), 3047.53 (100), 3048.53 (100), 3049.53 (80), 3050.53 (55), 3051.52 (30), 3052.55 (15). HPLC: 1 peak at 4.6 min.

T₂₁: Compound **2** ($n=2$, $m=1$) (135 mg, 0.12 mmol), C₆₀ (0.86 g, 1.2 mmol), and N-methylglycine (0.12 g, 1.4 mmol) were dissolved in ODCB (150 mL) and stirred at 120°C for 5h. The solvent was evaporated. The excess of C₆₀ was removed by column chromatography on silica, using CS₂ as the eluent. The product was subsequently eluted with toluene and the solvent was evaporated. The product was redissolved in ODCB, precipitated in methanol and dried in a vacuum oven. Yield: 238 mg (77 %). About 50 mg of the product was further purified by preparative HPLC. ¹H-NMR (400 MHz, CS₂) δ (ppm): 7.19 (s, 2H, Ar-*H*), 5.15 (s, 2H, MP-*H*), 4.91 (d, $J = 9.4$ Hz, 2H, MP-*H*), 4.22 (d, $J = 9.4$ Hz, 2H, MP-*H*), 2.98 (t, $J = 7.0$ Hz, 4H, Ar-CH₂-), 2.92 (s, 6H, N-CH₃), 2.84 (d, $J = 6.8$ Hz, 4H, -CH₂CH(C₄H₉)(C₂H₅)), 2.79 (d, $J = 6.6$ Hz, 4H, -CH₂CH(C₄H₉)(C₂H₅)), 2.31-2.18 (m, 4H, -CH₂CH(C₄H₉)(C₂H₅)), 1.67 (qu, $J = 7.0$ Hz, 4H, -CH₂CH₂C₆H₁₃), 1.50-1.10 (m, 52H, -CH₂-), 0.97-0.75 (m, 30H, -CH₃). ¹³C-NMR (100 MHz, CS₂) δ (ppm): 155.75, 155.71, 154.95, 154.43, 153.57, 153.59, 153.15, 153.05, 147.06, 147.03, 146.79, 146.22, 146.11, 146.00, 145.95, 145.90, 145.84, 145.71, 145.51, 145.42, 145.40, 145.26, 145.18, 145.13, 145.11, 145.13, 145.02, 144.99, 144.92, 144.46, 144.14, 142.92, 142.89, 142.80, 142.48, 142.39, 142.02, 142.01, 141.95, 141.89, 141.83, 141.79, 141.73, 141.69, 141.67, 141.45, 141.39, 140.45, 140.03, 139.94, 139.71, 139.57, 138.72, 137.73, 137.69, 136.74, 136.67, 136.63, 136.57, 135.60, 135.49, 130.69, 129.88, 126.13, 123.14, 79.18, 77.46, 77.07, 69.90, 68.47, 40.21, 40.18, 39.36, 39.25, 37.70, 37.34, 37.09, 33.24, 33.20, 32.21, 30.74, 30.07, 30.02, 29.64, 29.61, 29.36, 29.28, 29.14, 26.35,

26.31, 23.75, 23.71, 23.68, 23.19, 14.68, 14.53, 14.50, 11.33, 11.22, 11.19, 11.17, 11.14. IR (cm⁻¹): 2952, 2921, 2852, 2779, 1541, 1495, 1462, 1429, 1376, 1331, 1242, 1179, 1122, 1030, 900, 768, 726. MALDI-TOF-MS *m/z* (intensity, %): 2656.52 (40), 2657.51 (85), 2658.51 (100), 2659.51 (85), 2660.50 (60), 2661.51 (40), 2662.46 (20). HPLC: 1 peak at 4.7 min.

T₂₂: Compound **2** (n=2, m=2) (243 mg, 0.11 mmol), C₆₀ (0.98 g, 1.4 mmol), and N-methylglycine (0.12 g, 1.4 mmol) were dissolved in ODCB (225 mL) and stirred at 120°C for 5h. The solvent was evaporated. The excess of C₆₀ was removed by column chromatography on silica, using CS₂ as the eluent. The product was subsequently eluted with toluene and the solvent was evaporated. The product was redissolved in ODCB, precipitated in methanol and dried in a vacuum oven. Yield: 260 mg (64 %). About 50 mg of the product was further purified by preparative HPLC. ¹H-NMR (400 MHz, CS₂) δ (ppm): 7.21 (s, 2H, Ar-*H*), 6.97 (s, 2H, Ar-*H*), 5.16 (s, 2H, MP-*H*), 4.92 (d, *J* = 9.5 Hz, 2H, MP-*H*), 4.22 (d, *J* = 9.4 Hz, 2H, MP-*H*), 3.04-2.95 (m, 8H, Ar-CH₂-), 2.93 (s, 6H, N-CH₃), 2.90-2.79 (m, 16H, -CH₂CH(C₄H₉)(C₂H₅)), 2.35-2.18 (m, 8H, -CH₂CH(C₄H₉)(C₂H₅)), 1.81-1.65 (m, 8H, -CH₂CH₂C₆H₁₃), 1.56-1.10 (m, 104H, -CH₂-), 1.02-0.75 (m, 60H, -CH₃). ¹³C-NMR (100 MHz, CS₂) δ (ppm): 155.77, 155.73, 154.95, 154.56, 154.48, 154.35, 153.60, 153.18, 153.08, 147.08, 147.05, 146.82, 146.80, 146.24, 146.13, 146.03, 146.01, 145.97, 145.91, 145.85, 145.72, 145.54, 145.44, 145.42, 145.27, 145.21, 145.15, 145.05, 145.02, 145.01, 144.93, 144.49, 144.17, 144.15, 142.93, 142.91, 142.81, 142.50, 142.40, 142.04, 142.02, 141.96, 141.91, 141.85, 141.80, 141.74, 141.71, 141.46, 141.41, 140.59, 140.38, 140.35, 140.04, 139.95, 139.73, 139.60, 138.64, 137.98, 137.81, 137.77, 136.77, 136.69, 136.65, 136.60, 135.61, 135.50, 130.77, 129.89, 129.03, 126.61, 125.86, 125.70, 123.34, 122.73, 79.26, 77.12, 77.10, 69.93, 68.50, 40.25, 40.22, 39.48, 39.40, 39.28, 37.87, 37.75, 37.40, 37.12, 33.32, 33.27, 33.24, 33.20, 33.10,

33.07, 32.26, 31.05, 30.80, 30.11, 30.08, 29.70, 29.66, 29.41, 29.32, 29.25, 29.23, 29.19, 26.36, 26.32, 26.28, 26.23, 23.80, 23.77, 23.74, 23.72, 23.64, 23.24, 23.21, 14.74, 14.58, 14.55, 14.52, 11.38, 11.31, 11.28, 11.26, 11.21, 11.19, 11.18, 11.15. IR (cm⁻¹): 2953, 2921, 2852, 2780, 1541, 1490, 1456, 1376, 1332, 1242, 1179, 1121, 1030, 900, 829, 769, 726. MALDI-TOF-MS m/z (intensity, %): 3762.9 (50), 3063.9 (70), 3764.9 (90), 3765.87 (100), 3766.90 (70), 3767.82 (50). HPLC: 1 peak at 4.3 min.

Femtosecond PIA

If only first-order decay into the charge-separated state (CSS) is assumed for these triads, and the CSS of the triads also recombines in a first order fashion, this leads to the following set of differential equations describing the population of the singlet excited state and the charge separated state:

$$\begin{aligned}\frac{d[S_1]}{dt} &= -k_{CS}[S_1] \\ \frac{d[CSS]}{dt} &= k_{CS}[S_1] - k_{CR}[CSS]\end{aligned}\tag{1}$$

Solving these equations for $[S_1]$ and $[CSS]$, leads to single exponential decay for the singlet excited state of the oligomer and a biexponential function for the population of the CSS:

$$\begin{aligned}[S_1] &= [S_1]_0 \exp(-k_{CS}t) \\ [CSS] &= \frac{k_{CS}}{k_{CS} - k_{CR}} [S_1]_0 (\exp(-k_{CR}t) - \exp(-k_{CS}t))\end{aligned}\tag{2}$$

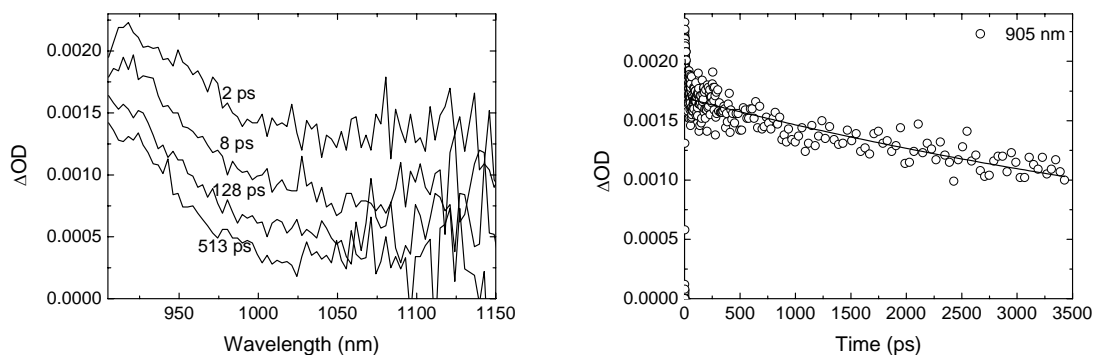
As both excited states absorb light in the wavelength region probed, the total absorption can be fitted with the sum of both populations, both multiplied with their absorption coefficient. This means that the transient can be fitted at all wavelengths by a simple biexponential function:

$$\Delta OD = A_0 + A_1 \exp\left(\frac{t-t_0}{\tau_{CS}}\right) + A_2 \exp\left(\frac{t-t_0}{\tau_{CR}}\right)\tag{3}$$

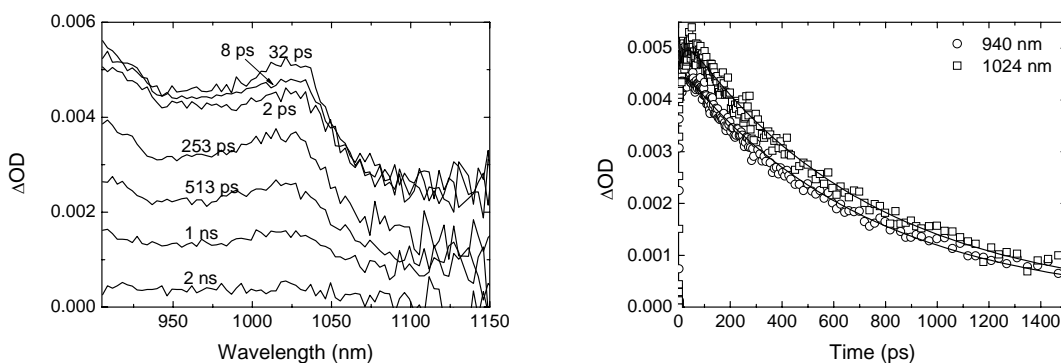
Where ΔOD is the recorded signal, A_0 is a correction for the zero-level of the signal, which is determined by measuring some points before the excitation pulse, t_0 is the time of the excitation pulse, $\tau_{CS} = k_{CS}^{-1}$, the time constant for charge separation, and $\tau_{CR} = k_{CR}^{-1}$, the time constant for charge recombination. Both A_0 and t_0 are experimentally determined and are fixed during the fitting procedure.

In the following graphs, the fs-PIA data for the oligomers and triads not depicted in the main text are shown. In each case, the spectral evolution is depicted in the left graph, the PIA signal at selected wavelengths is shown in the right graph. The solid line represents a biexponential fit.

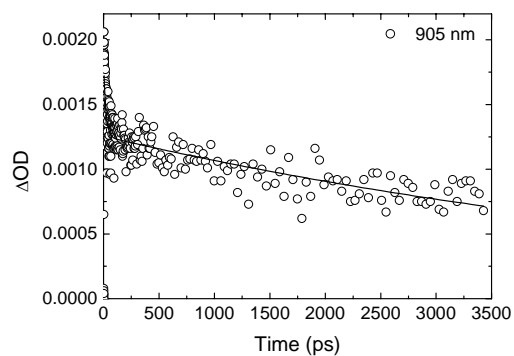
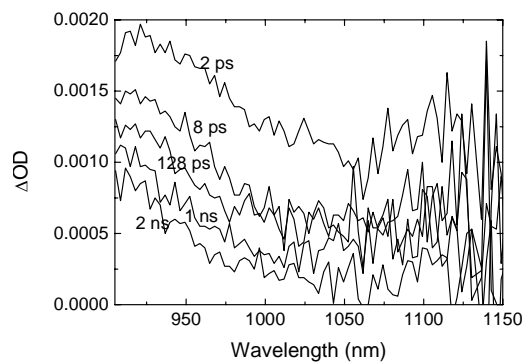
O₁₁ in toluene



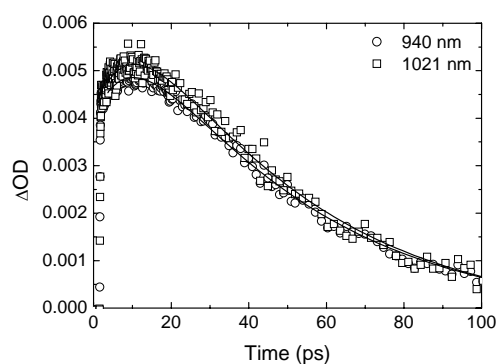
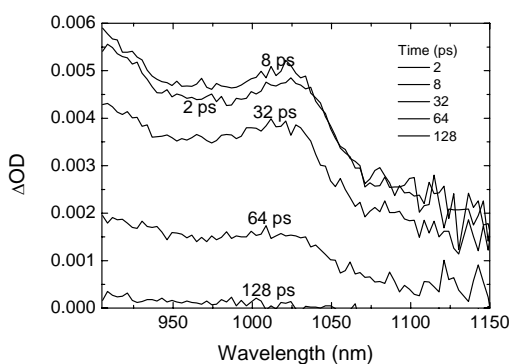
T₁₁ in toluene



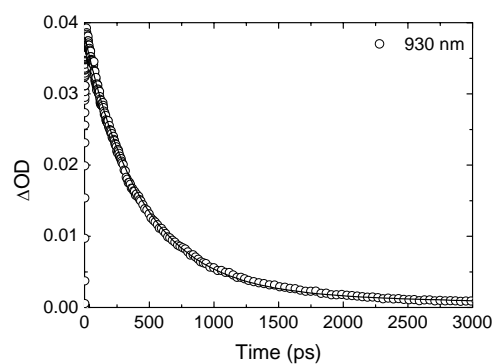
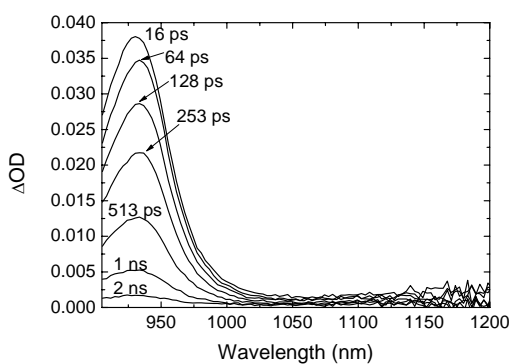
O₁₁ in ODCB



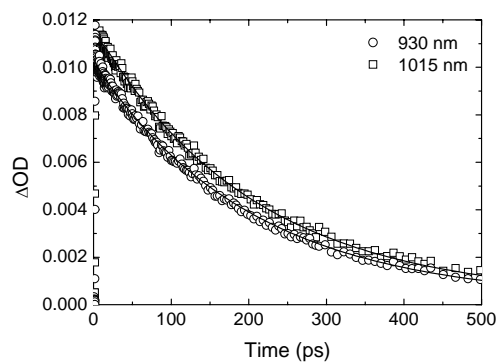
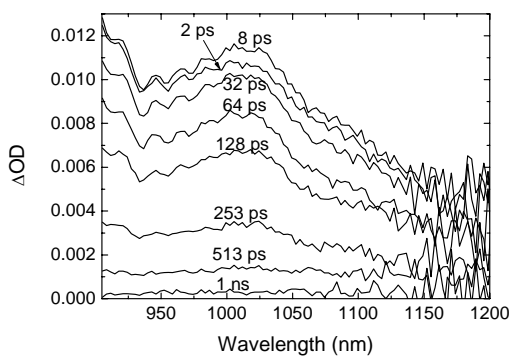
T₁₁ in ODCB



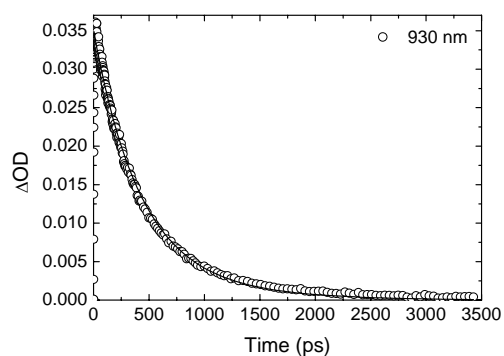
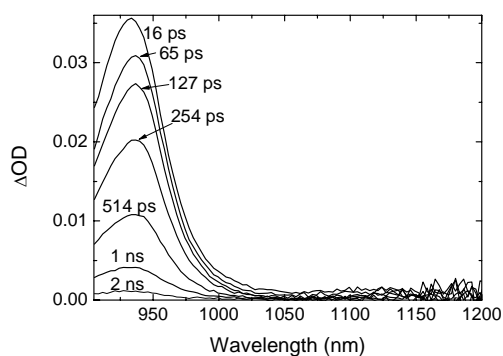
O₂₁ in toluene



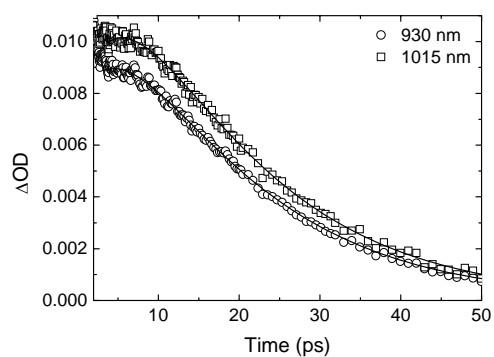
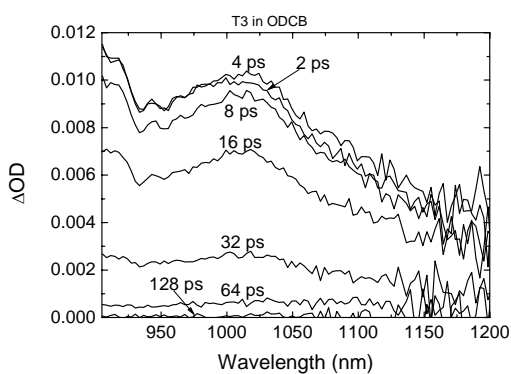
T₂₁ in toluene



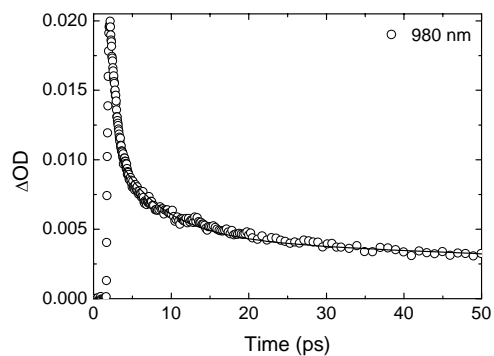
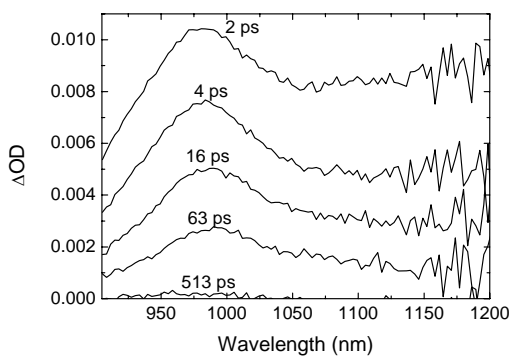
O₂₁ in ODCB



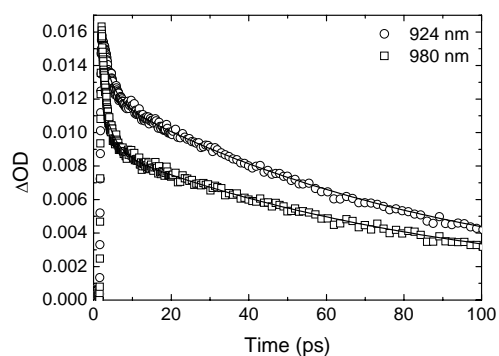
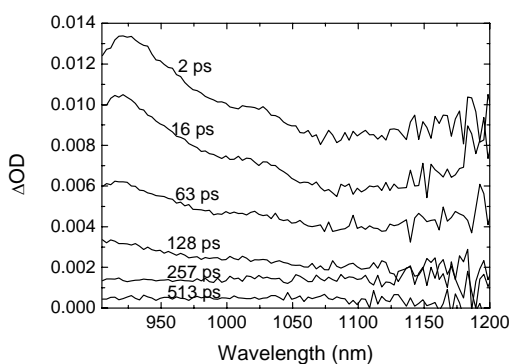
T₂₁ in ODCB



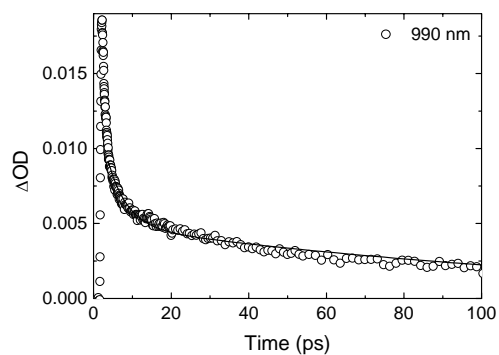
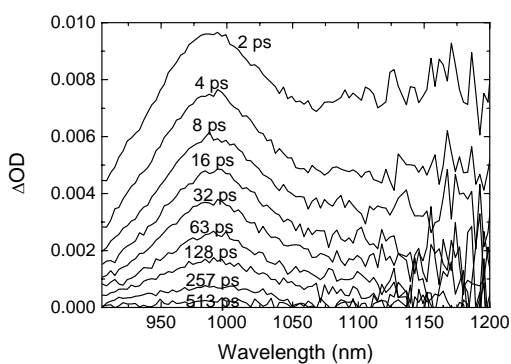
O₂₂ in toluene



T₂₂ in toluene



O₂₂ in ODCB



T_{22} in ODCB

