

Electronic Supplementary Information of B516141J by W. -K. Lee et al.

4-[5-(cholesteryloxycarbonyl)butyloxy]-4'-octyloxy-2',3'-difluoroazobenzene (2) (F-AOC-4)

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 0.67~2.04 (m, CH, CH_2 , CH_3), 2.29 (q, O-CH- CH_2), 4.03 (t, CH_2 -O), 4.10 (t, CH_2 -O), 5.37 (d, C=CH), 6.84 (d, ArCH), 6.99 (d, ArCH), 7.53 (t, ArCH), 7.90 (d, ArCH). FT-IR (KBr, cm^{-1}): 2941 and 2869 (C-H stretching), 1730 (C=O stretching), 1602 and 1468 (ArC=C stretching), 1248 and 1169 (C-O stretching). Elemental analysis: calcd for $\text{C}_{52}\text{H}_{76}\text{F}_2\text{N}_2\text{O}_4$, C 75.14, H 9.22, N 3.37 %; found C 75.17, H 9.20, N 3.38 %

4-[6-(cholesteryloxycarbonyl)pentyloxy]-4'-octyloxy-2',3'-difluoroazobenzene (2) (F-AOC-5)

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 0.67~2.04 (m, CH, CH_2 , CH_3), 2.29 (q, O-CH- CH_2), 4.03 (t, CH_2 -O), 4.10 (t, CH_2 -O), 5.37 (d, C=CH), 6.84 (d, ArCH), 6.99 (d, ArCH), 7.53 (t, ArCH), 7.90 (d, ArCH). FT-IR (KBr, cm^{-1}): 2941 and 2869 (C-H stretching), 1730 (C=O stretching), 1602 and 1468 (ArC=C stretching), 1248 and 1169 (C-O stretching). Elemental analysis: calcd. for $\text{C}_{53}\text{H}_{78}\text{F}_2\text{N}_2\text{O}_4$, C 75.32, H 9.30, N 3.31 %; found C 75.31, H 9.33, N 3.30 %

4-[7-(cholesteryloxycarbonyl)hexyloxy]-4'-octyloxy-2',3'-difluoroazobenzene (2) (F-AOC-6)

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 0.67~2.04 (m, CH, CH_2 , CH_3), 2.29 (q, O-CH- CH_2), 4.03 (t, CH_2 -O), 4.10 (t, CH_2 -O), 5.37 (d, C=CH), 6.84 (d, ArCH), 6.99 (d, ArCH), 7.53 (t, ArCH), 7.90 (d, ArCH). FT-IR (KBr, cm^{-1}): 2941 and 2869 (C-H stretching), 1730 (C=O stretching), 1602 and 1468 (ArC=C stretching), 1248 and 1169 (C-O stretching). Elemental analysis: calcd for $\text{C}_{54}\text{H}_{80}\text{F}_2\text{N}_2\text{O}_4$, C 75.48, H 9.38, N 3.26 %; found C 75.49, H 9.38, N 3.27 %

4-[9-(cholesteryloxycarbonyl)octyloxy]-4'-octyloxy-2',3'-difluoroazobenzene (2) (F-AOC-8)

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 0.67~2.04 (m, CH, CH_2 , CH_3), 2.29 (q, O-CH- CH_2), 4.03 (t, CH_2 -O), 4.10 (t, CH_2 -O), 5.37 (d, C=CH), 6.84 (d, ArCH), 6.99 (d, ArCH), 7.53 (t, ArCH), 7.90 (d, ArCH). FT-IR (KBr, cm^{-1}): 2941 and 2869 (C-H stretching), 1730 (C=O stretching), 1602 and 1468 (ArC=C stretching), 1248 and 1169 (C-O stretching). Elemental analysis: calcd. for $\text{C}_{56}\text{H}_{84}\text{F}_2\text{N}_2\text{O}_4$, C 75.81, H 9.54, N 3.16 %; found C 75.80, H 9.56, N 3.17 %

4-[10-(cholesteryloxycarbonyl)nonyloxy]-4'-octyloxy-2',3'-difluoroazobenzene (2) (F-AOC-9)

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 0.67~2.04 (m, CH, CH_2 , CH_3), 2.29 (q, O-CH- CH_2), 4.03 (t, CH_2 -O), 4.10 (t, CH_2 -O), 5.37 (d, C=CH), 6.84 (d, ArCH), 6.99 (d, ArCH), 7.53 (t, ArCH), 7.90 (d, ArCH). FT-IR (KBr, cm^{-1}): 2941 and 2869 (C-H stretching), 1730 (C=O stretching), 1602 and 1468 (ArC=C stretching), 1248 and 1169 (C-O stretching). Elemental analysis: calcd. for $\text{C}_{57}\text{H}_{86}\text{F}_2\text{N}_2\text{O}_4$, C 75.96, H 9.62, N 3.11 %; found C 75.94, H 9.62, N 3.12 %

4-[11-(cholesteryloxycarbonyl)decanoyloxy]-4'-octyloxy-2',3'-difluoroazobenzene (2) (F-AOC-10)

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 0.67~2.04 (m, CH, CH_2 , CH_3), 2.29 (q, O-CH- CH_2), 4.03 (t, CH_2 -O), 4.10 (t, CH_2 -O), 5.37 (d, C=CH), 6.84 (d, ArCH), 6.99 (d, ArCH), 7.53 (t, ArCH), 7.90 (d, ArCH). FT-IR (KBr, cm^{-1}): 2941 and 2869 (C-H

stretching), 1730 (C=O stretching), 1602 and 1468 (ArC=C stretching), 1248 and 1169 (C-O stretching). Elemental analysis: calcd. for $\text{C}_{58}\text{H}_{88}\text{F}_2\text{N}_2\text{O}_4$, C 76.11, H 9.69, N 3.06 %; found C 76.12, H 9.70, N 3.06 %

4-[12-(cholesteryloxycarbonyl)undecanoyloxy]-4'-octyloxy-2',3'-difluoroazobenzene (2) (F-AOC-11)

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 0.67~2.04 (m, CH, CH_2 , CH_3), 2.29 (q, O-CH- CH_2), 4.03 (t, CH_2 -O), 4.10 (t, CH_2 -O), 5.37 (d, C=CH), 6.84 (d, ArCH), 6.99 (d, ArCH), 7.53 (t, ArCH), 7.90 (d, ArCH). FT-IR (KBr, cm^{-1}): 2941 and 2869 (C-H stretching), 1730 (C=O stretching), 1602 and 1468 (ArC=C stretching), 1248 and 1169 (C-O stretching). Elemental analysis: calcd. for $\text{C}_{59}\text{H}_{90}\text{F}_2\text{N}_2\text{O}_4$, C 76.25, H 9.76, N 3.01 %; found C 76.25, H 9.75, N 3.02 %

4-[13-(cholesteryloxycarbonyl)dodecanoyloxy]-4'-octyloxy-2',3'-difluoroazobenzene (2) (F-AOC-12)

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 0.67~2.04 (m, CH, CH_2 , CH_3), 2.29 (q, O-CH- CH_2), 4.03 (t, CH_2 -O), 4.10 (t, CH_2 -O), 5.37 (d, C=CH), 6.84 (d, ArCH), 6.99 (d, ArCH), 7.53 (t, ArCH), 7.90 (d, ArCH). FT-IR (KBr, cm^{-1}): 2941 and 2869 (C-H stretching), 1730 (C=O stretching), 1602 and 1468 (ArC=C stretching), 1248 and 1169 (C-O stretching). Elemental analysis: calcd. for $\text{C}_{60}\text{H}_{92}\text{F}_2\text{N}_2\text{O}_4$, C 76.39, H 9.83, N 2.97 %; found C 76.40, H 9.83, N 2.99 %

4-{4-(1H,1H-perfluorooctyloxy)-2,3-difluorophenylazo}phenol (3)

4-(1H,1H-Pentadecafluorooctyloxy)phenylamine (10.3 g; 21 mmol) was dissolved with heating in a mixture of 60 ml of glacial acetic acid, 30.0 mL of concentrated hydrochloric acid and 30.0 mL of water. After cooling to 0~5 °C, diazotization was performed by adding dropwise a solution of NaNO_2 (1.86 g; 27 mmol) in 30.0 mL of water to the acid solution. The prepared diazonium salt solution was slowly added to a stirred solution of 2, 3-difluorophenol (3.64 g; 28 mmol), NaOH (3.00g; 75 mmol), Na_2CO_3 (10.1 g; 95 mmol) and 150 ml of water followed by stirring for 1 h at 0-5 °C. The yellow-orange to yellow-green colored precipitate was filtered off, dried and purified by chromatography using a silica gel column and CH_2Cl_2 as eluent. Dark brown solid product was obtained, 6.50 g (49.0 %), mp 97 °C. δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 4.54 (t, CH_2), 6.78 (t, Ar-H), 7.05 (d, Ar-H), 7.52 (t, Ar-H), 7.93 (d, Ar-H). FT-IR (KBr, cm^{-1}): 3100 (ArC-OH stretching), 2941 and 2869 (C-H stretching), 1602 and 1468 (ArC=C stretching), 1248 and 1169 (C-O stretching). Elemental analysis: calcd. for $\text{C}_{20}\text{H}_9\text{F}_{17}\text{N}_2\text{O}_2$, C 37.99, H 1.43, N 4.43 %; found C 38.00, H 1.44, N 4.45 %

4-{8-(cholesteryloxycarbonyl)heptyloxy}-4'-perfluorooctyloxy-2',3'-difluoroazobenzene (4) (F-AOCF-7)

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 0.60~1.91 (m, CH, CH_2 , CH_3), 2.27 (m, -C=C- CH_2 -, -O-CO- CH_2 -), 4.54 (m, - $\text{CF}_2\text{CH}_2\text{Ar}$ -, -OCH-), 5.36 (m, -C=CH-), 6.78 (t, Ar-H), 7.05 (d, Ar-H), 7.52 (t, Ar-H), 7.93 (d, Ar-H). FT-IR (KBr, cm^{-1}): 2941 and 2868 (aliphatic C-H stretching), 1737 (C=O stretching), 1587 (aromatic C=C stretching), 1246 and 1145 (C-O stretching). Elemental analysis: calcd. for $\text{C}_{55}\text{H}_{67}\text{F}_{17}\text{N}_2\text{O}_4$, C 57.79, H 5.91, N 2.45 %; found C 57.78, H 5.91, N 2.46 %

4-{5-(cholesteryloxycarbonyl)butyloxy}-4'-perfluorooctyloxy-2',3'-difluoroazobenzene (4) (F-AOCF-4)

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 0.60~1.91 (m, CH, CH_2 , CH_3), 2.27 (m, -C=C- CH_2 -, -O-CO- CH_2 -), 4.54 (m, - $\text{CF}_2\text{CH}_2\text{Ar}$ -,

OCH-), 5.36 (m, -C=CH-), 6.78 (t, Ar-H), 7.05 (d, Ar-H), 7.52 (t, Ar-H), 7.93 (d, Ar-H). FT-IR (KBr, cm^{-1}): 2941 and 2868 (aliphatic C-H stretching), 1737 (C=O stretching), 1587 (aromatic C=C stretching), 1246 and 1145 (C-O stretching). Elemental analysis: calcd. for $\text{C}_{52}\text{H}_{61}\text{F}_{17}\text{N}_2\text{O}_4$ C 56.73, H 5.58, N 2.54 %; found C 56.73, H 5.58, N 2.56 %

4-{6-(cholesteryloxy)pentyl}-4'-perfluorooctyloxy-2',3'-difluoroazobenzene (4) (F-AOCF-5)

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 0.60~1.91 (m, CH, CH_2 , CH_3), 2.27 (m, -C=C- CH_2 -, -O-CO- CH_2 -), 4.54 (m, - $\text{CF}_2\text{CH}_2\text{Ar}$, -OCH-), 5.36 (m, -C=CH-), 6.78 (t, Ar-H), 7.05 (d, Ar-H), 7.52 (t, Ar-H), 7.93 (d, Ar-H). FT-IR (KBr, cm^{-1}): 2941 and 2868 (aliphatic C-H stretching), 1737 (C=O stretching), 1587 (aromatic C=C stretching), 1246 and 1145 (C-O stretching). Elemental analysis: calcd. for $\text{C}_{53}\text{H}_{63}\text{F}_{17}\text{N}_2\text{O}_4$, C 57.09, H 5.69, N 2.51 %; found C 57.10, H 5.70, N 2.52 %

4-{7-(cholesteryloxy)hexyl}-4'-perfluorooctyloxy-2',3'-difluoroazobenzene (4) (F-AOCF-6)

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 0.60~1.91 (m, CH, CH_2 , CH_3), 2.27 (m, -C=C- CH_2 -, -O-CO- CH_2 -), 4.54 (m, - $\text{CF}_2\text{CH}_2\text{Ar}$, -OCH-), 5.36 (m, -C=CH-), 6.78 (t, Ar-H), 7.05 (d, Ar-H), 7.52 (t, Ar-H), 7.93 (d, Ar-H). FT-IR (KBr, cm^{-1}): 2941 and 2868 (aliphatic C-H stretching), 1737 (C=O stretching), 1587 (aromatic C=C stretching), 1246 and 1145 (C-O stretching). Elemental analysis: calcd. for $\text{C}_{54}\text{H}_{65}\text{F}_{17}\text{N}_2\text{O}_4$ C 57.44, H 5.80, N 2.48 %; found C 57.44, H 5.80, N 2.48 %

4-{9-(cholesteryloxy)octyl}-4'-perfluorooctyloxy-2',3'-difluoroazobenzene (4) (F-AOCF-8)

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 0.60~1.91 (m, CH, CH_2 , CH_3), 2.27 (m, -C=C- CH_2 -, -O-CO- CH_2 -), 4.54 (m, - $\text{CF}_2\text{CH}_2\text{Ar}$, -OCH-), 5.36 (m, -C=CH-), 6.78 (t, Ar-H), 7.05 (d, Ar-H), 7.52 (t, Ar-H), 7.93 (d, Ar-H). FT-IR (KBr, cm^{-1}): 2941 and 2868 (aliphatic C-H stretching), 1737 (C=O stretching), 1587 (aromatic C=C stretching), 1246 and 1145 (C-O stretching). Elemental analysis: calcd. for $\text{C}_{56}\text{H}_{69}\text{F}_{17}\text{N}_2\text{O}_4$, C 58.13, H 6.01, N 2.42 %; found C 58.11, H 6.00, N 2.43 %

4-{10-(cholesteryloxy)nonyl}-4'-perfluorooctyloxy-2',3'-difluoroazobenzene (4) (F-AOCF-9)

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 0.60~1.91 (m, CH, CH_2 , CH_3), 2.27 (m, -C=C- CH_2 -, -O-CO- CH_2 -), 4.54 (m, - $\text{CF}_2\text{CH}_2\text{Ar}$, -OCH-), 5.36 (m, -C=CH-), 6.78 (t, Ar-H), 7.05 (d, Ar-H), 7.52 (t, Ar-H), 7.93 (d, Ar-H). FT-IR (KBr, cm^{-1}): 2941 and 2868 (aliphatic C-H stretching), 1737 (C=O stretching), 1587 (aromatic C=C stretching), 1246 and 1145 (C-O stretching). Elemental analysis: calcd. for $\text{C}_{57}\text{H}_{73}\text{F}_{17}\text{N}_2\text{O}_4$, C 58.46, H 6.11, N 2.39 %; found C 58.46, H 6.10, N 2.39 %

4-{11-(cholesteryloxy)decyl}-4'-perfluorooctyloxy-2',3'-difluoroazobenzene (4) (F-AOCF-10)

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 0.60~1.91 (m, CH, CH_2 , CH_3), 2.27 (m, -C=C- CH_2 -, -O-CO- CH_2 -), 4.54 (m, - $\text{CF}_2\text{CH}_2\text{Ar}$, -OCH-), 5.36 (m, -C=CH-), 6.78 (t, Ar-H), 7.05 (d, Ar-H), 7.52 (t, Ar-H), 7.93 (d, Ar-H). FT-IR (KBr, cm^{-1}): 2941 and 2868 (aliphatic C-H stretching), 1737 (C=O stretching), 1587 (aromatic C=C stretching), 1246 and 1145 (C-O stretching). Elemental analysis: calcd. for $\text{C}_{58}\text{H}_{73}\text{F}_{17}\text{N}_2\text{O}_4$ C 58.78, H 6.21, N 2.36 %; found C 58.78, H 6.21, N 2.36 %

4-{12-(cholesteryloxy)undecyl}-4'-perfluorooctyloxy-2',3'-difluoroazobenzene (4) (F-AOCF-11)

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 0.60~1.91 (m, CH, CH_2 , CH_3), 2.27 (m, -C=C- CH_2 -, -O-CO- CH_2 -), 4.54 (m, - $\text{CF}_2\text{CH}_2\text{Ar}$, -

OCH-), 5.36 (m, -C=CH-), 6.78 (t, Ar-H), 7.05 (d, Ar-H), 7.52 (t, Ar-H), 7.93 (d, Ar-H). FT-IR (KBr, cm^{-1}): 2941 and 2868 (aliphatic C-H stretching), 1737 (C=O stretching), 1587 (aromatic C=C stretching), 1246 and 1145 (C-O stretching). Elemental analysis: calcd. for $\text{C}_{59}\text{H}_{75}\text{F}_{17}\text{N}_2\text{O}_4$, C 59.09, H 6.30, N 2.34 %; found C 59.10, H 6.33, N 2.34 %

4-{13-(cholesteryloxy)dodecyl}-4'-perfluorooctyloxy-2',3'-difluoroazobenzene (4) (F-AOCF-12)

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 0.60~1.91 (m, CH, CH_2 , CH_3), 2.27 (m, -C=C- CH_2 -, -O-CO- CH_2 -), 4.54 (m, - $\text{CF}_2\text{CH}_2\text{Ar}$, -OCH-), 5.36 (m, -C=CH-), 6.78 (t, Ar-H), 7.05 (d, Ar-H), 7.52 (t, Ar-H), 7.93 (d, Ar-H). FT-IR (KBr, cm^{-1}): 2941 and 2868 (aliphatic C-H stretching), 1737 (C=O stretching), 1587 (aromatic C=C stretching), 1246 and 1145 (C-O stretching). Elemental analysis: calcd. for $\text{C}_{60}\text{H}_{77}\text{F}_{17}\text{N}_2\text{O}_4$, C 59.40, H 6.40, N 2.31 %; found C 59.39, H 6.38, N 2.33 %