**SUPPLEMENTARY INFORMATION**

**Structure-property relationships in azobenzene-based twist-bend nematogens**

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**Section 1: Materials/ General methods/ Instrumentation**

*Materials*

All reagents and solvents were available commercially and purchased from Sigma Aldrich, TCI Chemicals or Alfa Aesar and were used as received unless otherwise stated.

*General methods*

Solvents were evaporated at approximately 20 mm Hg using a water aspirator pump connected to a Buchi rotary evaporator and trace solvents in a Thermo Scientific vacuum oven at 1.0 mm Hg and 50 °C.

Reactions were monitored using thin layer chromatography (TLC) carried out on aluminium-backed plates with a coating of Merck Kieselgel 60 F254 silica and an appropriate solvent system. Silica gel coated aluminium plates were purchased from Merck KGaA. Spots were visualised using UV light (254 nm) or by oxidation with either an aqueous permanganate dip or iodine.

*Instrumentation*

Infrared spectra were recorded on a Thermo Scientific Nicolet IR100 FT-IR spectrometer with an ATR diamond cell. Proton (1H) and carbon (13C) NMR spectra were recorded on a Varian Unity INOVA 400 MHz NMR spectrometer with pulsed field gradients and waveform generator or a 300 MHz Bruker Ultrashield NMR. The chemical shifts (δ) are quoted in parts per million (ppm) (SiMe4, δ = 0), using residual non-deuterated solvent signals as reference. Coupling constants (*J* values) are quoted in Hertz (Hz) and are vicinal 3*J*, unless otherwise indicated. The splitting patterns are reported using the following abbreviations: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), m (multiplet), and combinations thereof. 13C NMR spectra are proton decoupled unless otherwise stated. Ar refers to an aromatic ring.

The purity of final products were verified using C,H,N elemental analysis performed by the Micro Analytical Laboratory in the School of Chemistry at the University of Manchester or the Centre for Chemical Instrumental Analysis and Services at the University of Sheffield.

**Section 2: Synthetic procedures**

*6-bromo-1-[4-(4-methoxyphenyl)phenyl]hexan-1-one (MeOBK5Br).*



Scheme 2.1: Synthesis of MeOBK5Br.

A method adapted from Percec *et al.* [[1](#_ENREF_1)] was used for the synthesis of 6-bromo-1-[4-(4-methoxyphenyl)phenyl]hexan-1-one (MeOBK5Br), as shown in Scheme 2.1. To 4-methoxybiphenyl (18.53 g, 1.01 x 10−1 mol), dichloromethane (200 ml) was added with stirring under a nitrogen protective atmosphere. After cooling to 0˚C, anhydrous aluminium chloride (16.02 g, 1.2 x 10−1 mol) was added to give a pale green solution. 6-Bromohexanoyl chloride (17 ml, 5.7 x 10−2 mol) was dissolved in dichloromethane (100 ml) and added dropwise over a period of 2 h. The reaction mixture was left to stir rapidly at 0°C for 1 h and then at 40˚C for 24 h. The cooled solution was poured over a mixture of crushed ice (100 g), distilled water (100 ml) and 20 % hydrochloric acid (100 ml) to destroy the aluminium chloride complex. The aqueous layer was discarded and the organic layer was washed twice with distilled water (2 x 100 ml), and dried over anhydrous magnesium sulfate. The dichloromethane was removed *in vacuo* to yield a cream solid. The product was recrystallized from hot ethyl acetate (100 ml) with hexane (20 ml) as a co-solvent. The white crystals were collected by vacuum filtration, recrystallised from ethanol (100 ml x 2) and dried in a vacuum oven at 50°C overnight.

Yield: 18.297 g, 88.8 %. Melting point: 99.5 – 100.2 °C. Infrared 𝜈̅ cm-1: 2938, 2864, 2835 (sp3 C-H); 1677 (C=O); 1597, 1494 (Ar C=C); 1253 (Ar C-O); 805 (p. disubs. benzene C-H). 1H NMR: (300 MHz, Chloroform-d) δ ppm: 1.50 – 1.66 (m, 2 H, -C(O)-CH2-CH2-CH2-CH2-CH2-Br), 1.82 (tt, J=7.5, 7.3 Hz, 2 H, -C(O)-CH2-CH2-CH2-), 1.95 (tt, J=7.4, 6.8 Hz, 2 H, -CH2-CH2-CH2-Br), 3.03 (t, J=7.3 Hz, 2 H, -C(O)-CH2-CH2-), 3.46 (t , J=6.8 Hz, 2 H, -CH2-CH2-Br), 3.88 (s, 3 H, CH3-O-Ar), 7.02 (d, J=8.9 Hz, 2 H, Ar), 7.60 (d, J=8.9 Hz, 2 H, Ar), 7.66 (d, J=8.5 Hz, 2 H, Ar), 8.03 (d, J=8.5 Hz, 2 H, Ar). 13C NMR: (75 MHz, Chloroform-d) δ ppm: 23.45, 27.93, 33.70, 38.29, 55.41, 114.42, 126.65, 128.37, 128.67, 132.25, 135.07, 145.27, 159.92, 199.56.

*1-[4-(6-Bromohexyl)phenyl]-4-methoxybenzene (MeOB6Br).*



Scheme 2.2: Synthesis of MeOB6Br.

The synthesis of 1-[4-(6-bromohexyl)phenyl]-4-methoxybenzene (MeOB6Br)was carried out according to Scheme 2,2, as adapted from previously reported literature [[2](#_ENREF_2)]. Under an atmosphere of nitrogen, a dry solution of 6-bromo-1-[4-(4-methoxyphenyl)phenyl] hexan-1-one (MeOBK5Br)(5.031 g, 1.40 x 10-2 mol) in trifluoroacetic acid (11 ml, 1.44 x 10‑1 mol) was cooled to 0°C. To this solution, triethylsilane (5.0 ml, 3.13 x 10-2 mol) was added dropwise over a period of 10 min with rapid stirring. As a cream precipitate formed, dry dichloromethane (10 ml) was added to the solution. The mixture was left to stir for 1 h under ice, and then overnight at room temperature. Dichloromethane (50 ml) and distilled water (150 ml) were added, and the organic layer collected. The aqueous layer was washed twice with dichloromethane (50 ml x 2). All organic extracts were combined, dried over magnesium sulfate, and the solvent removed *in vacuo*. The pale yellow crystals were recrystallised twice from ethanol, and dried in a vacuum oven overnight at 50 °C to give a white powder.

Yield: 2.326 g, 48.2 %. Melting point: 40.4 – 41.3 °C. Infrared 𝜈̅ cm-1: 2964, 2932, 2853 (sp3 C-H); 1605, 1581, 1497 (Ar C=C); 1464 (CH2 C-H); 1248 (Ar C-O); 814, 805 (p. disubs. benzene C-H). 1H NMR: (300 MHz, Chloroform-d) δ ppm: 1.27 – 1.49 (m, 4 H, Ar-CH2-CH2-CH2-CH2-CH2-CH2-Br), 1.62 (tt, J=7.5, 7.3 Hz, 2 H, Ar-CH2-CH2-CH2-), 1.82 (tt, J=7.3, 6.9 Hz, 2 H, -CH2-CH2-CH2-Br), 2.60 (t, J=7.5 Hz, 2 H, Ar-CH2-CH2-), 3.36 (t, J=6.9 Hz, 2 H, -CH2-CH2-Br), 3.80 (s, 3 H, CH3-O-Ar), 6.92 (d, J=8.9 Hz, 2H, Ar), 7.18 (d, J=8.3 Hz, 2 H, Ar), 7.43 (d, J=8.3 Hz, 2 H, Ar), 7.47 (d, J=8.9 Hz, 2 H, Ar). 13C NMR: (75 MHz, Chloroform-d) δ ppm: 28.07, 28.44, 31.28, 32.77, 34.00, 35.42, 55.36, 114.17, 126.63, 127.99, 128.80, 133.71, 138.29, 141.07, 158.96.

*4-Hydroxy-4’-ethylazobenzene (EtABOH)*



Scheme 2.3: Synthesis of 4-hydroxy-4’-ethylazobenzene (EtABOH).

4-Hydroxy-4’-ethylazobenzene (EtABOH) wasprepared according to Scheme 2.3, adapted from a method described elsewhere [[3-7](#_ENREF_3)]. Thus, to an ice-cold stirred solution of the 4-ethylaniline (25.35 g, 2.09 x 10-1 mol, 1.0 mol eq.), in 3 M hydrochloric acid (500 ml), a cooled solution of sodium nitrite (16.39 g, 2.36 x 10­-1 mol, 1.1 mol. eq.) in distilled water (100 ml) was added slowly. The diazonium salt formed was slowly added to a stirred solution of phenol (19.93 g, 2.12 x 10­-1 mol, 1.0 mol. eq.) in a 2.5 M solution of sodium hydroxide (300 ml) to give a coloured precipitate that was left to stir for 30 min. The precipitate was collected by vacuum filtration, twice recrystallised from a 50 % v/v solution of methanol in distilled water (400 ml), and dried in a vacuum oven overnight at 50 °C to give a dark red powder.

Yield: 21.433 g, 45.3 %. Melting point: 115.75 °C. Infrared cm-1: 3166 (br. O-H); 2966, 2931 (sp3 C-H); 1603, 1586, 1505 (Ar C=C); 1191 (Ar O-H); 835, 821 (p. disubs. benzene C-H). 1H NMR: (300 MHz, Chloroform‑d) δ ppm: 1.31 (t, *J*=7.7 Hz, 3 H, Ar-CH2-CH3), 2.75 (q, J=7.7 Hz, 2 H, Ar-CH2-CH3), 6.93 (d, J=8.5 Hz, 2 H, Ar), 7.35 (d, J=8.5 Hz, 2 H, Ar), 7.71 - 7.97 (m, 4 H, Ar). 13C NMR: (75 MHz, Chloroform-d) δ ppm: 15.41, 28.81, 115.92, 122.65, 124.84, 128.58, 147.08, 147.32, 150.90, 158.30.

*MeOB6OABX and MeOBO5OABX dimers*



Scheme 2.4: Synthesis of MeOB6OABX and MeOBO5OABX dimers, .

The synthesis of the MeOB6OABX and MeOBO5OABX dimers involved a Williamson’s ether synthesis, catalysed via an in-situ Finkelstein substitution, see Scheme 2.4. Thus, to a solution of either MeOBO5Br or MeOB6Br (1 mol eq.) in N,N-dimethylformamide (6–8 ml), the appropriate substituted 4-hydroxyazobenzene (XABOH) (1 mol eq.), potassium carbonate (10 mol eq.), and a catalytic quantity of sodium iodide (0.3 mol eq.) were added. The mixture was stirred at 90˚C for 24 - 72 h, and then allowed to cool to room temperature. The cooled mixture was poured into distilled water (10 ml per ml of N,N-dimethylformamide), and the resulting precipitate was collected *via* vacuum filtration, washed with ice-cold ethanol, and dried by vacuum suction. After recrystallising from toluene (25 - 40 ml) three times, the golden yellow products were dried in a vacuum oven at 50˚C for 12 h to give the reported yields. The actual quantities used in the syntheses and yields obtained for the MeOB6OABX and MeOBO5OABX dimers are given in Tables 1 and 2, respectively.

**Table 1.** Quantities of reagents used and yields obtained in the syntheses of the MeOB6OABX dimers.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Dimer | MeOB6Br / mg | XABOH / mg | K2CO3 / g | NaI / mg | Yield / mg |
| MeOB6OABMe | 302 | MeABOH  195 | 1.282 | 33 | 221 (53 %) |
| MeOB6OABEt | 300 | EtABOH  196 | 1.380 | 13 | 243 (57 %) |
| MeOB6OABBu | 302 | BuABOH  221 | 1.353 | 46 | 321 (71 %) |
| MeOB6OABOMe | 302 | MeOABOH  198 | 1.272 | 23 | 217 (51 %) |
| MeOB6OABOBu | 303 | BuOABOH  255 | 1.340 | 57 | 306 (66 %) |
| MeOB6OABCN | 300 | CNABOH  195 | 1.263 | 30 | 327 (77 %) |

**Table 2.** Quantities of reagents used and yields obtained in the syntheses of the MeOBO5OABX dimers.

| Dimer | MeOBO5Br / mg | XABOH / mg | K2CO3 / g | NaI / mg | Yield / mg |
| --- | --- | --- | --- | --- | --- |
| MeBO5OABMe | 306 | MeABOH  186 | 1.189 | 30 | 269 (62 %) |
| MeOBO5OABEt | 300 | EtABOH  223 | 1.413 | 13 | 187 (44 %) |
| MeOBO5OABBu | 300 | BuABOH  218. | 1.558 | 30 | 284 (63 %) |
| MeOBO5OABOMe | 302 | MeOABOH  198 | 1.272 | 23 | 217 (51 %) |
| MeOBO5OABOBu | 303 | BuOABOH  253 | 1.252 | 35 | 338 (73 %) |
| MeOBO5OABCN | 308 | CNABOH  192 | 1.207 | 30 | 272 (64 %) |

***MeOB6OABMe***

Infrared cm-1: 3074 (Ar C-H); 2960, 2923, 2852, 2842 (sp3 C-H); 1606, 1581, 1498 (Ar C=C); 1469 (CH2 C-H); 1393 (CH3 C-H); 1245 (Ar C-O); 824, 809 (p. disubs. benzene C-H). 1H NMR: (300 MHz, Chloroform-d) δ ppm: 1.44 - 1.60 (m, 4 H, -Ar-CH2-CH2-**CH2**-**CH2**-CH2-CH2-O-), 1.66 - 1.79 (m, 2 H, -Ar-CH2-**CH2**-CH2-), 1.81 - 1.92 (m, 2 H, -CH2-**CH2­**-CH2-O-), 2.46 (s, 3 H, -Ar-**CH3**), 2.69 (t, *J*=7.63 Hz, 2 H, -Ar-**CH2**-CH2-), 3.87 (s, 3 H, **CH3**-O-Ar-), 4.06 (t, *J*=6.50 Hz, 2 H, -CH2-**CH2**-O-), 6.96 - 7.05 (m, 4 H, Ar), 7.23 - 7.28 (m, 2 H, Ar), 7.33 (d, *J*=8.10 Hz, 2 H, Ar), 7.48 - 7.57 (m, 4 H, Ar), 7.82 (d, *J*=8.29 Hz, 2 H, Ar), 7.89 - 7.96 (m, 2 H, Ar). 13C NMR: (75 MHz, Chloroform-d) δ ppm: 21.46, 25.90, 28.98, 29.13, 31.37, 35.44, 55.33, 68.24, 114.17, 114.69, 122.54, 124.58, 126.61, 127.97, 128.80, 129.69, 133.71, 138.25, 140.74, 141.15, 146.93, 150.89, 158.95, 161.45. Elemental analysis: Calculated for C32H34N2O2: C, 80.30 %, H, 7.16 %, N, 5.85 %. Found: C, 80.40 %, H, 7.28 %, N, 5.85 %.

***MeOB6OABEt***

Infrared cm-1: 2989, 2970, 2913, 2901 (sp3 C-H); 1603, 1581, 1498 (Ar C=C); 1247 (Ar C-O); 847, 830, 820 (p. disubs. benzene C-H). 1H NMR: (300 MHz, Chloroform‑d) δ ppm: 1.31 (t, *J*=7.5 Hz, 3 H, ‑Ar‑CH2‑CH3), 1.42 – 1.63 (m, 4 H, ‑CH2‑CH2‑CH2‑CH2‑CH2‑CH2‑O‑), 1.86 (tt, J=7.2, 6.5 Hz, 2 H, ‑CH2‑CH2‑CH2‑O‑), 2.69 (q, J=7.5 Hz, 2 H, Ar‑CH2‑CH3), 3.86 (s, 3 H, CH3‑O‑Ar), 4.06 (t, J=6.5 Hz, 2 H, ‑CH2‑CH2‑O‑), 6.95 – 7.06 (m, 4 H, Ar), 7.25 (d, J=8.3 Hz, 2 H, Ar), 7.34 (d, J=8.5 Hz, 2 H, Ar), 7.45 – 7.57 (m, 4 H, Ar), 7.83 (d, J=8.5 Hz, 2 H, Ar), 7.91 (d, J=9.0 Hz, 2 H, Ar). 13C NMR: (75 MHz, Chloroform‑d) δ ppm: 15.43, 25.89, 28.80, 28.95, 29.12, 31.34, 35.43, 55.33, 68.24, 114.16, 114.68, 122.60, 124.56, 126.59, 127.96, 128.47, 128.78, 133.72, 138.25, 141.13, 147.01, 151.08, 151.53, 158.95, 161.44. Elemental analysis: Calculated for C33H36N2O2: C, 80.45 %, H, 7.37 %, N, 5.69 %. Found: C, 80.01 %, H, 7.43 %, N, 5.63 %.

***MeOB6OABBu***

Infrared cm-1: 2960, 2915, 2849 (sp3 C-H); 1603, 1582, 1498 (Ar C=C); 1474 (CH2 C-H); 1246 (Ar C-O); 845, 830, 820 (p. disubs. benzene C-H). 1H NMR: (300 MHz, Chloroform-d) δ ppm: 1H NMR: (300 MHz, Chloroform‑d) δ ppm: 0.97 (t, *J*=7.3 Hz, 3 H, ‑CH2‑CH3), 1.37 – 1.88 (m, 12 H, Ar‑CH2‑CH2‑CH2‑CH2‑CH2‑CH2‑O‑, -Ar-CH2-CH2-CH2-CH3), 2.63 – 2.76 (m, 4 H, Ar‑CH2‑CH2‑CH2‑CH2‑CH2‑CH2‑O‑, -Ar-CH2-CH2-CH2-CH3), 3.87 (s, 3 H, CH3‑O‑Ar), 4.06 (t, J=6.4 Hz, 4 H, ‑CH2‑CH2‑O‑), 6.95 – 7.06 (m, 4 H, Ar), 7.26 (d, J=8.3 Hz, 2 H, Ar), 7.33 (d, J=8.5 Hz, 2 H, Ar), 7.45 – 7.59 (m, 4 H, Ar), 7.83 (d, J=8.3 Hz, 2 H, Ar), 7.92 (d, J=9.0 Hz, 2 H, Ar). 13C NMR: (75 MHz, Chloroform-d) δ ppm: 13.98, 22.37, 25.91, 28.98, 29.13, 31.39, 33.51, 35.44, 35.57, 55.33, 68.22, 114.15, 114.67, 120.10, 122.53, 123.50, 124.58, 126.61, 127.98, 128.81, 129.06, 133.70, 138.24, 141.16, 145.77, 146.95, 151.05, 158.93, 161.43. Elemental analysis: Calculated for C35H40N2O2: C, 80.73 %, H, 7.74 %, N, 5.38 %. Found: C, 80.71 %, H, 7.92 %, N, 5.36 %.

***MeOB6OABOMe***

Infrared cm-1: 2960, 2914, 2849 (sp3 C-H); 1601, 1579, 1495 (Ar C=C); 1240 (Ar C-O); 843, 820 (p. disubs. benzene C-H). 1H NMR: (300 MHz, Chloroform-d) δ ppm: 1.43 - 1.58 (m, 4 H, -Ar-CH2-CH2-**CH2**-**CH2**-CH2-CH2-O-), 1.65 – 1.78 (m, 2 H, -Ar-CH2-**CH2**-CH2), 1.79 - 1.91 (m, 2 H, -CH2-**CH2**-CH2-O-), 2.68 (t, J=7.63 Hz, 2 H, Ar-**CH2**-CH2-), 3.86 (s, 3 H, **CH3**-O-Biphenyl), 3.91 (s, 3 H, **CH3**-O-Azobenzene), 4.05 (t, *J*=6.40 Hz, 2 H, -CH2-**CH2**-O-), 6.95 - 7.06 (m, 6 H, Ar), 7.26 (d, *J*=8.10 Hz, 2 H, Ar), 7.46 - 7.57 (m, 4 H, Ar), 7.86 - 7.94 (m, 4 H, Ar). 13C NMR: (75 MHz, Chloroform-d) δ ppm: 25.90, 28.98, 29.14, 31.38, 35.44, 55.33, 55.57, 68.21, 113.85, 114.16, 114.33, 114.67, 122.68, 122.79, 124.32, 124.35, 126.60, 127.98, 128.81, 133.70, 138.23, 141.16, 146.92, 147.10, 158.92, 161.18, 161.51. Elemental analysis: Calculated for C32H34N2O3: C, 77.70 %, H, 6.93 %, N, 5.66 %. Found: C, 77.73 %, H, 7.02 %, N, 5.66 %.

***MeOB6OABOBu***

Infrared cm-1: 3071 (Ar C-H); 2957, 2873, 2850 (sp3 C-H); 1602, 1579, 1496 (Ar C=C); 1473 (CH2 C-H); 1382 (CH3 C-H); 1243 (Ar C-O); 845, 820 (p. disubs. benzene C-H). 1H NMR: (300 MHz, Chloroform-d) δ ppm: 1.03 (t, J=7.35 Hz, 3 H, -CH2-**CH3**), 1.42 – 1.63 (m, 6 H, -Ar-CH2-CH2-**CH2-CH­2**-CH2-CH2-O-, CH2-**CH2**-CH3), 1.66 – 1.92 (m, 6 H, Ar-CH2-**CH2**-CH2-CH­2-**CH2**-CH2-O-, -CH2-**CH2**-CH2-CH3), 2.69 (t, J=7.63 Hz, 2 H, -Ar-**CH2­**-CH2-), 3.87 (s, 3 H, **CH3**-O-Ar), 4.06 (td, J=6.45, 3.86 Hz, 4 H, -CH2-CH­2-CH2-**CH2**-O-, -O-**CH2**-CH2-CH2-CH3), 6.96 – 7.05 (m, 6 H, Ar), 7.26 (d, J=8.10 Hz, 2 H, Ar), 7.46 – 7.58 (m, 4 H, Ar), 7.90 (d, J=8.29 Hz, 4 H, Ar). 13C NMR: (75 MHz, Chloroform‑d) δ ppm: 13.86, 19.24, 25.89, 28.97, 29.14, 31.27, 31.35, 35.43, 55.33, 68.02, 68.21, 114.17, 114.67 (br.), 124.30 (br.), 126.60, 127.97, 128.79, 133.73, 138.25, 141.15, 146.97, 146.98, 158.95, 161.13, 161.19. Elemental analysis: Calculated for C35H40N2O3: C, 78.33 %, H, 7.51 %, N, 5.22 %. Found: C, 77.99 %, H, 7.57 %, N, 5.18 %.

***MeOB6OABCN***

Infrared cm-1: 2922, 2869, 2852, (sp3 C-H); 2221 (C≡N); 1606, 1582, 1498 (Ar C=C); 1468 (CH2 C-H); 1393 (CH3 C-H); 1246 (Ar C-O); 841, 824 (p. disubs. benzene C-H). 1H NMR: (300 MHz, Chloroform-d) δ ppm: 1.40 – 1.63 (m, 4 H, Ar-CH2-CH2-**CH2-CH2**-CH2-CH2-O-), 1.66 – 1.79 (m, 2 H, Ar-CH2-**CH2**-CH2-), 1.81 – 1.93 (m, 2 H, -CH2-**CH2**-CH2-O-), 2.69 (t, J=7.63 Hz, 2 H, Ar-**CH2**-CH2-), 3.87 (s, 3 H, **CH3**-O-Ar), 4.08 (t, J=6.40 Hz, 2 H, -CH2-**CH2**-O-), 6.96 – 7.07 (m, 4 H, Ar), 7.23 – 7.28 (m, 2 H, Ar), 7.46 – 7.57 (m, 4 H, Ar), 7.78 – 7.84 (m, 2 H, Ar), 7.93 – 8.00 (m, 4 H, Ar). 13C NMR: (75 MHz, Chloroform-d) δ ppm: 25.89, 28.96, 29.06, 31.37, 35.44, 55.34, 68.40, 113.13, 114.17, 114.89, 118.70, 123.09, 125.50, 126.61, 127.97, 128.81, 133.18, 133.67, 138.27, 141.10, 146.71, 154.81, 158.95, 162.73. Elemental analysis: Calculated for C33H32N2O2: C, 78.50 %, H, 6.38 %, N, 8.58 %. Found: C, 78.46 %, H, 6.36 %, N, 8.62 %.

***MeOBO5OABMe***

Yield: 269 mg, 62 %. Infrared cm-1: 2932, 2876, 2859 (sp3 C-H); 1599, 1581, 1493 (Ar C=C); 1468 (CH2 C-H); 1237 (Ar C-O); 842, 824 (p. disubs. benzene C-H). 1H NMR: (300 MHz, Chloroform-d) δ ppm: 1.66 – 1.79 (m, 2 H, -O-CH2-CH2-**CH2**-CH2-CH2-O-), 1.87 – 2.00 (m, 4 H, -O-CH2-**CH2**-CH2-**CH2**-CH2-O-), 2.45 (s, 3 H, -Ar-**CH3**), 3.86 (s, 3 H, **CH3**-O-Ar), 4.03 – 4.14 (m, 4 H, -O-**CH2**-CH2-CH2-CH2-**CH2**-O-), 6.93 – 7.05 (m, 6 H, Ar), 7.32 (d, J=8.29 Hz, 2 H, Ar), 7.46 – 7.53 (m, 4 H, Ar), 7.81 (d, J=8.29 Hz, 2 H, Ar), 7.88 – 7.95 (m, 2 H, Ar). 13C NMR: (75 MHz, Chloroform-d) δ ppm: 21.45, 22.75, 28.98, 29.06, 55.34, 67.81, 68.09, 114.16, 114.69, 114.77, 122.53, 124.57, 127.71, 129.68, 133.41, 133.52, 140.76, 146.98, 150.88, 158.15, 158.68, 161.36. Elemental analysis: Calculated for C31H32N2O3: C, 77.47 %, H, 6.71 %, N, 5.83 %. Found: C, 77.10 %, H, 6.94 %, N, 5.80 %.

***MeOBO5OABEt***

Infrared cm-1:, 2967, 2930, 2901 (sp3 C-H); 1602, 1583, 1497 (Ar C=C); 1240 (Ar C-O); 843, 824 (p. disubs. benzene C-H). 1H NMR: (300 MHz, Chloroform-d) δ ppm: 1.31 (t, *J*=7.5 Hz, 3 H, -Ar-CH2-CH3), 1.66 – 1.80 (m, 2 H, -O-CH2-CH2-CH2-CH2-CH2-O-), 1.93 (tt, J=7.7, 6.4 Hz, 4 H, -O-CH2-CH2-CH2-CH2-CH2-O-), 2.75 (q, J=7.5 Hz, 2 H, Ar-CH2-CH3), 3.86 (s, 3 H, CH3-O-Ar), 4.02 – 4.14 (two overlapping t, J=6.4 Hz, 4 H, -O-CH2-CH2-CH2-CH2-CH2-O-), 6.94 – 7.07 (m, 6 H, Ar), 7.35 (d, J=8.5 Hz, 2 H, Ar), 7.45 – 7.54 (m, 4 H, Ar), 7.84 (d, J=8.5 Hz, 2 H, Ar), 7.92 (d, J=8.9 Hz, 2 H, Ar). 13C NMR: (75 MHz, Chloroform-d) δ ppm: 15.43, 22.75, 28.80, 28.98, 29.06, 55.34, 67.82, 68.10, 114.17, 114.69, 114.78, 122.62, 124.58, 127.71 (br.), 128.48, 133.42, 133.53, 147.02, 147.04, 151.08, 158.17, 158.69, 161.37. Elemental analysis: Calculated for C32H34N2O3: C, 77.70 %, H, 6.93 %, N, 5.66 %. Found: C, 77.47 %, H, 7.19 %, N, 5.56 %.

***MeOBO5OABBu***

Infrared cm-1: 2958, 2928, 2874, 2857 (sp3 C-H); 1602, 1582, 1497 (Ar C=C); 1469 (CH2 C-H); 1393 (CH3 C-H); 1239 (Ar C-O); 842, 824, 809 (p. disubs. benzene C-H). 1H NMR: (300 MHz, Chloroform-d) δ ppm: 0.97 (t, J=7.25 Hz, 3 H, -CH2-**CH3**), 1.33 – 1.48 (m, 2 H, -CH2-**CH2**-CH3­), 1.60 – 1.79 (m, 4 H, -CH2-**CH2**-CH2-CH3, -O-CH2-CH2-**CH2**-CH2-CH2-O-­), 1.86 – 2.00 (m, 4 H, -O-CH2-**CH2**-CH2-**CH2**-CH2-O-), 2.71 (t, J=7.72 Hz, 2H, Ar-**CH2**-CH2-), 3.87 (s, 3 H, **CH3**-O-Ar), 4.03 – 4.14 (m, 4 H, -O-**CH2**-CH2-CH2-CH2-**CH2**-O-), 6.93 – 7.06 (m, 6 H, Ar), 7.33 (d, J=8.29 Hz, 2 H, Ar), 7.46 – 7.54 (m, 4 H, Ar), 7.81 – 7.86 (m, 2 H, Ar), 7.89 – 7.96 (m, 2 H, Ar). Elemental analysis: Calculated for C34H38N2O3: C, 78.13 %, H, 7.33 %, N, 5.36 %. Found: C, 78.11 %, H, 7.43 %, N, 5.21 %.

***MeOBO5OABOMe***

Infrared cm-1: 2955, 2931, 2874, 2839 (sp3 C-H); 1601, 1579, 1494 (Ar C=C); 1468 (CH2 C-H); 1393 (CH3 C-H); 1237 (Ar C-O); 842, 824, 809(p. disubs. benzene C-H). 1H NMR: (300 MHz, Chloroform-d) δ ppm: 1.66 - 1.78 (m, 2 H, -O-CH2-CH2-**CH2**-CH2-CH2-O-), 1.85 - 1.99 (m, 4 H, -O-CH2-**CH2**-CH2-**CH2**-CH2-O-), 3.85 (s, 3 H, **CH3**-O-B), 3.90 (s, 3 H, **CH3**-O-A), 4.01 - 4.13 (m, 4 H, -O-**CH2**-CH2-CH2-CH2-**CH2**-O-), 6.91 - 7.04 (m, 8 H, Ar), 7.44 - 7.52 (m, 4 H, Ar), 7.85 - 7.93 (m, 4 H, Ar). 13C NMR: (75 MHz, Chloroform-d) δ ppm: 22.75, 28.98, 29.06, 55.34, 55.56, 67.81, 68.08, 114.15, 114.17, 114.70, 114.77, 124.37, 124.40, 127.71, 138.36, 144.95, 158.15, 161.15, 161.59. Elemental analysis: Calculated for C31H32N2O4: C, 74.98 %, H, 6.50 %, N, 5.64 %. Found: C, 74.78 %, H, 6.60 %, N, 5.61 %.

***MeOBO5OABOBu***

Infrared 𝜈̅ cm-1: 3071 (Ar C-H); 2956, 2932, 2873 (sp3 C-H); 1601, 1580, 1495 (Ar C=C); 1469 (CH2 C-H); 1239 (Ar C-O); 843, 824 (p. disubs. benzene C-H). 1H NMR: (300 MHz, Chloroform-d) δ ppm: 1.02 (t, J=7.4 Hz, 3 H, -CH2-CH3), 1.49 - 1.59 (m, 2 H, -CH2-CH2-CH3), 1.66 – 2.01 (m, 8 H, -O-CH2-CH2-CH2-CH2-CH2-O-, -O-CH2-CH2-CH2-CH3), 3.86 (s, 3 H, CH3-O-Ar), 4.02 - 4.14 (m, 6 H, -O-CH2-CH2-CH2-CH2-CH2-O-, -O-CH2-CH2-CH2-CH3), 6.94 – 7.04 (m, 8 H, Ar), 7.44 – 7.55 (m, 4 H, Ar), 7.88 (d, J=8.9 Hz, 4 H, Ar). 13C NMR: (75 MHz, Chloroform‑d) δ ppm: 15.43, 22.75, 28.80, 28.98, 29.06, 55.34, 67.82, 68.10, 114.17, 114.69, 114.78, 122.62, 124.58, 127.71 (br.), 128.48, 133.42, 133.53, 147.02, 147.04, 151.08, 158.17, 158.69, 161.37. Elemental analysis: Calculated for C34H37N3O2: C, 75.81 %, H, 7.11 %, N, 5.20 %. Found: C, 75.36 %, H, 7.26 %, N, 5.17 %.

***MeOBO5OABCN***

Infrared cm-1: 2944, 2930, 2875, 2838 (sp3 C-H); 2230 (C≡N); 1600, 1580, 1495, 1456 (Ar C=C); 1469 (CH2 C-H); 1391 (CH3 C-H); 1241 (Ar C-O); 826, 807 (p. disubs. benzene C-H). 1H NMR: (300 MHz, Chloroform-d) δ ppm: 1.65 - 1.78 (m, 2 H, -O-CH2-CH2-**CH2**-CH2-CH2-O-), 1.86 - 1.99 (m, 4 H, -O-CH2-**CH2**-CH2-**CH2**-CH2-O-), 3.87 (s, 3 H, **CH3**-O-Ar), 4.02 - 4.11 (m, 4 H, -O-**CH2**-CH2-CH2-CH2-**CH2**-O-), 6.94 - 7.05 (m, 6 H, Ar), 7.45 - 7.58 (m, 6 H, Ar), 7.63 - 7.73 (m, 4 H, Ar). 13C NMR: (75 MHz, Chloroform-d) δ ppm: 22.76, 28.98, 29.05, 55.36, 67.78, 67.92, 110.03, 114.16, 114.75, 115.09, 119.16, 127.09, 127.71, 128.35, 131.34, 132.58, 133.38, 133.45, 145.25, 158.14, 158.68, 159.70. Elemental analysis: Calculated for C31H29N3O3: C, 75.74 %, H, 5.95 %, N, 8.55 %. Found: C, 75.70 %, H, 6.09 %, N, 8.54 %.

*1,5-bis(4-Ethylazobenzene-4’-yloxy)pentane, EtABO5OABEt*



Scheme 2.5: Synthesis of EtABO5OABEt.

The synthesis of EtABO5OABEt was carried out as shown in Scheme 2.5. To a stirred solution of 1,5-dibromopentane (0.40 ml, 2.95 x 10-3 mol, 1.0 mol eq.) in N,N-dimethylformamide (20 ml), 4’-hydroxy-4’-ethylazobenzene (2.089 g, 9.23 x 10-3 mol, 3.1 mol eq.), potassium carbonate (4.146 g, 3.00 x 10-2 mol, 10.2 mol eq.), and a catalytic quantity of sodium iodide (101 mg, 6.78 x 10-4 mol, 0.2 mol eq.) were added. The mixture was stirred at 90˚C for 36 h, and then left to cool to room temperature. The cooled mixture was poured into distilled water (250 ml), and the resulting precipitate was collected *via* vacuum filtration, washed with ice-cold ethanol, and dried by vacuum suction. The golden yellow powder was recrystallised from ethanol (50 ml) three times, and dried in a vacuum oven at 50˚C for 12 h.

Yield: 1.044 g, 68 %. Infrared cm-1: 2966, 2944, 2869 (sp3 C-H); 1599, 1579, 1497 (Ar C=C); 1245 (Ar C-O); 835 (p. disubs. benzene C-H). 1H NMR: (300 MHz, Chloroform-d) δ ppm: 1.32 (t, *J*=7.7 Hz, 6 H, -Ar-CH2-CH3 x 2), 1.73 (quin, J=7.2 Hz, 2 H, -O-CH2-CH2-CH2-CH2-CH2-O-), 1.95 (tt, J=7.2, 6.4 Hz, 4 H, -O-CH2-CH2-CH2-CH2-CH2-O-), 2.76 (q, J=7.7 Hz, 4 H, Ar-CH2-CH3 x 2), 4.10 (t, J=6.3 Hz, 4 H, -O-CH2-CH2-CH2-CH2-CH2-O-), 7.03 (d, J=9.0 Hz, 4 H, Ar), 7.35 (d, J=8.3 Hz, 4 H, Ar), 7.85 (d, J=8.3 Hz, 4 H, Ar), 7.94 (d, J=9.0 Hz, 4 H, Ar). 13C NMR: (75 MHz, Chloroform-d) δ ppm: 15.44, 22.74, 28.82, 28.98, 68.06, 114.70, 122.63, 124.59, 128.49, 147.05, 151.08 (br.), 161.35. Elemental analysis: Calculated for C33H36N4O2: C, 76.12 %, H, 6.97 %, N, 10.76 %. Found: C, 76.08 %, H, 6.92 %, N, 10.64 %.

**Section 3: References**

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