Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A halogen-bonding foldamer molecular film for selective reagentless anion sensing in water

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S1. Materials and Methods

General. Ultrapure water was obtained from a Milli-Q system (18.2 MΩcm). Dry solvents were drawn from a MBraun MPSP-800 column and used immediately. Electrolyte and analyte solutions were prepared from analytical grade chemicals. All chemicals from commercial suppliers were used as received unless otherwise noted. Mass spectrometry was performed on a Bruker micrOTOF. NMR spectra were recorded on Bruker NMR spectrometers (AVIII HD 500 or AVIII HD 400).

Electrochemical measurements

All experiments were conducted using an Autolab Potentiostat (Metrohm) equipped with a FRA32 module. A three electrode setup was used comprising a gold disk working electrode (BASi; 1.6 mm diameter), a Ag|AgCl leak-free reference electrode (Innovative Instruments or home-made with a Pt-wire frit) and a Pt wire counter electrode. Electrochemical impedance measurements were performed at open circuit potential in the frequency range of 100 kHz to 1 Hz and a 10 mV peak to peak amplitude was used. Impedance-derived capacitance was obtained via $C''(\omega) = Z'/\omega Z^2$ and $C'(\omega) = Z''/\omega Z^2$, where ω is the angular frequency. Electrochemical circuit fitting and data analysis was done with Nova 1.1. All experiments were carried out in pure aqueous solution containing 100 mM electrolyte (100 mM NaCl, titrated with 100 mM sodium salts; constant ionic strength).

Electrode pretreatment and SAM formation

Gold electrodes were polished with an alumina slurry (0.05 µm particle size) and after sonication immersed in piranha acid (3:1 H_2SO_4/H_2O_2) for 10 min. Electrochemical polishing was carried out in 0.5 M KOH between -0.7 and -1.7 V for at least one hour and then in 0.5 M H_2SO_4 between 0 and 1.5 V for at least one hour (both at a scan rate of 0.1 V/s). Immediately afterwards the electrodes were rinsed with water and ethanol and immersed in 0.25 mM **1.XB/HB** solution (1:1 ACN/H_2O) overnight. The electroactive surface area of the electrodes was determined according to standard procedures.[1] Planar gold substrates for surface analysis (XPS, CA and ellipsometry) were prepared by immersion of gold sensor chips (Reichert) into fresh piranha acid (3:1 H_2SO_4/H_2O_2) for at least 30 s followed by extensive rinsing with water and ethanol. SAM formation was carried out as described above.

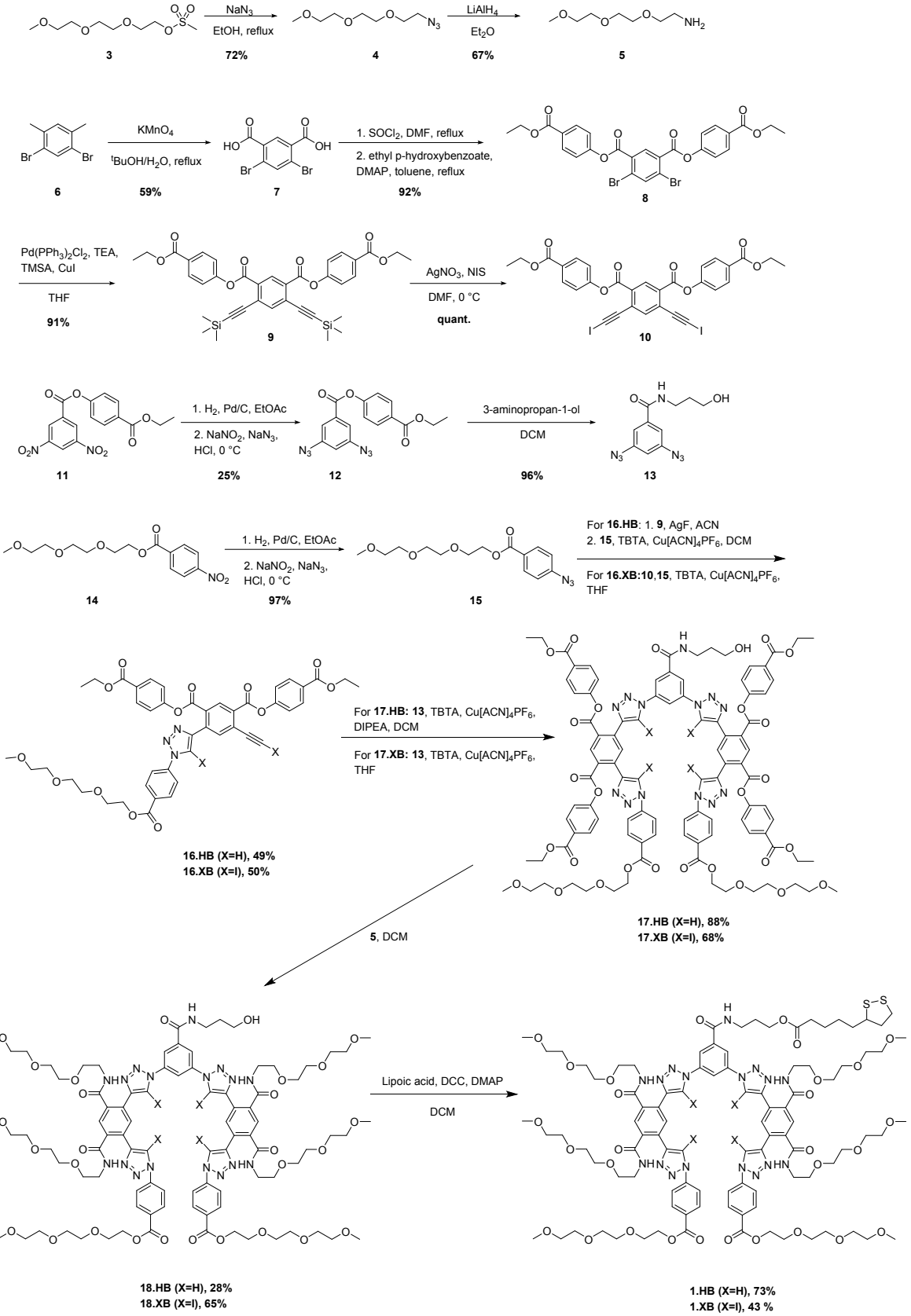
XPS. Samples were analyzed using a Thermo Scientific K-Alpha XPS instrument equipped with a microfocussed monochromated Al X-ray source. The source was operated at 12 keV and a 400 micron spot size was used. The analyzer operates at a constant analyser energy

(CAE) of 200 eV for survey scans and 50 eV for detailed scans. Charge neutralization was applied using a combined low energy electron/ion flood source.

Ellipsometry. Variable angle ellipsometric measurements were conducted on a Beaglehole Instruments Picometer Ellipsometer equipped with a 2 mW Helium-Neon laser (632.8 nm). Five different spots were measured at 51 different angles of incidence (ranging from 80 to 30 degrees). The average dry thickness of SAMs was determined by fitting the data with a one-layer model, taking bare gold as the reference and 1.45 as the refractive index for the SAM layer. IgorPro software programme (WaveMetrics) was used to analyze the data.

Contact Angle. Static water contact-angle measurements were performed in a sessile drop setup using a Goniometer (OCA 20) equipped with a microliter syringe, a telecentric lens system and a CCD camera (320 x 256 pixel, 25 images per second). Deionized water (18.2 MΩcm) was used as the wetting liquid. All the reported values are the average of static contact angles at 5 different spots per sample.

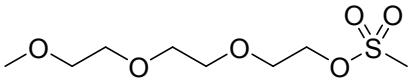
S2. Synthesis of 1.XB/HB



Scheme S1. Synthetic route for the synthesis of 1.XB/HB.

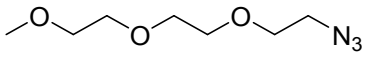
Synthesis and detailed anion binding studies of **2.XB/HB** have been reported separately.[2]

Triethylene glycol mesylate **3**



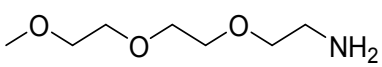
Triethylene glycol monomethyl ether (8 mL, 50 mmol) was added to DCM (125 mL) and combined with Et_3N (7.666 mL, 55 mmol). The mixture was cooled to 0 °C and methylsulfonyl chloride (4.257 mL, 55 mmol) was added. The mixture was stirred at 0 °C for 2 h and allowed to warm to rt. It was then washed with brine and concentrated under vacuum. The residue was partitioned in water and hexanes, the aqueous phase was separated, saturated with NaCl and extracted with DCM. The DCM extracts were dried with anhydrous Na_2SO_4 and concentrated under vacuum to provide 11.798 g (48.69 mmol, 97%) of **3** as a colourless oil. δ_H (400 MHz, $CDCl_3$): 4.39 – 4.33 (m, 2H), 3.77 – 3.72 (m, 2H), 3.68 – 3.58 (m, 6H), 3.54 – 3.49 (m, 2H), 3.35 (s, 3H), 3.05 (s, 3H); δ_C (100 MHz, $CDCl_3$): 71.94, 70.66, 70.58, 69.41, 69.06, 59.08, 37.75; ESI-MS m/z 265.0 $[M+H]^+$.

Triethylene glycol azide **4**



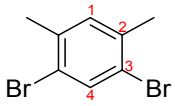
2-(2-(2-methoxyethoxy)ethoxy)ethyl methanesulfonate **3** (1.211 g, 5 mmol) was added to EtOH (10 mL). NaN_3 (390 mg, 6 mmol) was then added and the mixture was heated at reflux overnight. It was then evaporated, the residue redissolved in Et_2O, washed with brine, dried with anhydrous Na_2SO_4 and concentrated under vacuum. Crude material was purified by column chromatography (50% Et_2O/hexanes) to afford 683 mg (3.61 mmol, 72%) of **4** as a colourless oil. δ_H (400 MHz, $CDCl_3$): 3.69 – 3.63 (m, 8H), 3.57 – 3.52 (m, 2H), 3.41 – 3.34 (m, 5H); δ_C (101 MHz, $CDCl_3$): 72.05, 70.83, 70.79, 70.74, 70.15, 59.15, 50.81; ESI-MS m/z 212.1 $[M+Na]^+$.

Triethylene glycol amine **5**



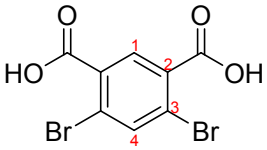
Compound **4** (517 mg, 2.73 mmol) was dissolved in dry Et_2O (6 mL). This solution was then slowly added to 2 M $LiAlH_4$ solution in THF (3 mL) and the mixture was stirred for 1 h at rt. It was then cooled to 0 °C and the excess $LiAlH_4$ was quenched with MeOH. The mixture was then partitioned in Et_2O and water containing Rochelle's salt and the aqueous phase further extracted with DCM. The organic phases were dried with anhydrous Na_2SO_4, filtered and concentrated under vacuum to provide **5** (300 mg, 1.84 mmol, 67%) as a colourless oil. δ_H (400 MHz, $CDCl_3$): 3.69 – 3.58 (m, 6H, CH_2), 3.54 (m, 2H, CH_2), 3.49 (t, J = 5.2 Hz, 2H, CH_2), 3.37 (s, 3H, CH_3), 2.85 (t, J = 5.2 Hz, 2H, NH_2); δ_C (100 MHz, $CDCl_3$): 73.61 (*C*H_2), 72.05 (*C*H_2), 70.72 (*C*H_2), 70.65 (*C*H_2), 70.39 (*C*H_2), 59.15 (*C*H_3), 41.92 (*C*H_2NH_2); ESI-MS m/z 164.1 $[M+H]^+$.

1,5-dibromo-2,4-dimethylbenzene **6**



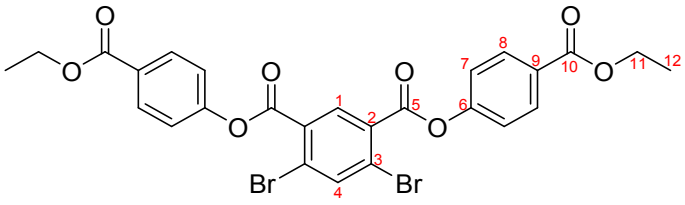
According to a literature procedure,[3] iodine (53 mg, 0.21 mmol) was added to *m*-xylene (3.68 mL, 30 mmol). The flask was covered with aluminium foil and bromine (4.15 mL, 81 mmol) was added dropwise over 2 h. The reaction was stirred at rt in darkness for 36 h and quenched by stirring with 20% KOH solution until the red colour disappeared. The resulting mixture was cooled to 0 °C and the aqueous solution was decanted from the precipitated white solid. The residue was dissolved in DCM, washed with brine, dried with anhydrous Na_2SO_4, filtered and concentrated. The product was purified by short path distillation (132 °C at 16 mbar) to give **6** as a white solid (4.500 g, 17.05 mmol, 57%). δ_H (400 MHz, $CDCl_3$): 7.68 (s, 1H, *H*^{4}), 7.10 (s, 1H, *H*^{1}), 2.31 (s, 6H, C*H*$_3$); δ_C (100 MHz, $CDCl_3$): 137.01 (*C*^{2}), 135.05 (*C*^{4}), 132.73 (*C*^{1}), 122.15 (*C*^{3}), 22.39 (*C*H$_3$), CI-MS 264.9057 $[M+H]^+$.

4,6-dibromoisophtalic acid **7**



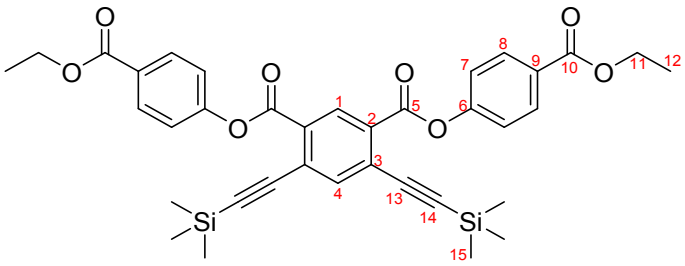
According to a literature procedure,[3] **6** (3.610 g, 13.68 mmol) was added to 1:1 ^{t}BuOH/H_2O (30 mL). $KMnO_4$ (4.755 g, 30.09 mmol) was added and the reaction was heated at reflux for 2 h. It was then brought to rt and another portion of $KMnO_4$ (4.755 g, 30.09 mmol) was added. The mixture was heated to reflux again for 20 h. It was then filtered through Celite and the filter washed with hot water. ^{t}BuOH was evaporated from the resulting clear solution, the resulting aqueous mixture was allowed to cool down to rt, washed with Et_2O and acidified with 1 M HCl. The resulting white precipitate was filtered off and recrystallised in water to afford **7** (2.630 g, 8.12 mmol, 59%) as a white solid. δ_H (400 MHz, $CDCl_3$ + 5% DMSO-d_6): 8.30 (s, 1H, *H*^{4}), 7.88 (s, 1H, *H*^{1}), 7.23 (br s, 2H, COO*H*); δ_C (100 MHz, $CDCl_3$): 166.31 (*C*OOH), 139.32 (*C*^{1}), 134.25 (*C*^{4}), 131.49 (*C*^{2}), 125.11 (*C*^{3}); ESI-MS m/z 322.9 $[M-H]^-$.

Compound **8**



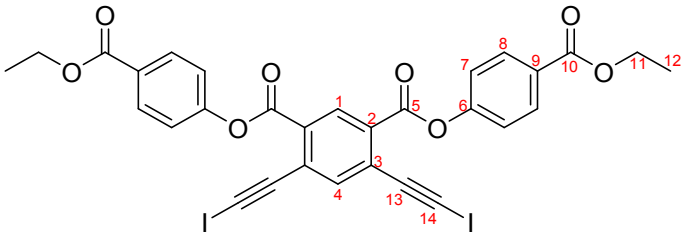
Dibromoisophthalic acid **7** (3.239 g, 10 mmol) was combined with $SOCl_2$ (20 mL) and a few drops of DMF. The mixture was heated at reflux for 5 h, concentrated and dried under vacuum. The resulting acyl chloride was combined with toluene (20 mL), ethyl p-hydroxybenzoate (3.656 g, 22 mmol) and DMAP (61 mg, 0.5 mmol). The reaction was heated under reflux overnight and concentrated under vacuum. The product was purified by column chromatography (0-2% MeOH/DCM) to provide **8** (5.710 g, 9.2 mmol, 92%) as a white solid. δ_H (400 MHz, $CDCl_3$) 8.60 (s, 1H, H^1), 8.06 (s, 1H, H^4), 8.05 – 8.01 (m, 4H, H^8), 7.27 – 7.21 (m, 4H, H^7), 4.29 (q, J = 7.1 Hz, 4H, H^{11}), 1.30 (t, J = 7.1 Hz, 6H, H^{12}); δ_C (101 MHz, $CDCl_3$) 165.59 (C^{10}), 162.19 (C^5), 153.73 (C^6), 140.61 (C^4), 134.92 (C^1), 131.28 (C^8), 129.90, 128.70 (C^9), 127.49, 121.48 (C^7), 61.23 (C^{11}), 14.36 (C^{12}); CI-MS m/z 620.9580 $[M+H]^+$.

Compound **9**



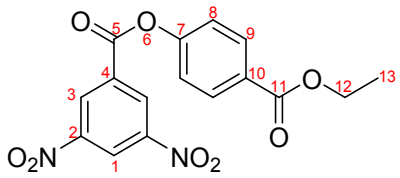
Compound **8** (3.950 g, 6.37 mmol) was added to dry, degassed THF (42 mL) under Ar. $Pd(PPh_3)_2Cl_2$ (223 mg, 0.318 mmol) was then added followed by Et_3N (5.326 mL, 38.21 mmol). The mixture was stirred at rt for 10 min and trimethylsilylacetylene (3.529 ml, 25.47 mmol) and CuI (61 mg, 0.318 mmol) were added. The reaction was stirred at rt for 4 h when it was determined to be complete by TLC. Reaction mixture was partially evaporated under vacuum and partitioned in Et_2O and dilute aqueous solution of citric acid. Organic phase was dried with anhydrous Na_2SO_4, decanted and evaporated. Crude product was dry loaded onto silica and purified by silica chromatography (10-15% Et_2O/hexanes) to provide **9** (3.809 g, 5.82 mmol, 91%) as a white solid. δ_H (400 MHz, $CDCl_3$) 8.81 (s, 1H, H^1), 8.20 – 8.10 (m, 4H, H^8), 7.93 (s, 1H, H^4), 7.40 – 7.30 (m, 4H, H^7), 4.39 (q, J = 7.1 Hz, 4H, H^{11}), 1.41 (t, J = 7.1 Hz, 6H, H^{12}), 0.21 (s, 18H, H^{15}); δ_C (101 MHz, $CDCl_3$) 165.91 (C^{10}), 162.87 (C^5), 154.19 (C^6), 141.13 (C^4), 133.88 (C^1), 131.35 (C^8), 130.26 (C^2), 128.52 (C^9), 128.06 (C^3), 121.69 (C^7), 106.10, 101.27, 61.29 (C^{11}), 14.48 (C^{12}), -0.22 (C^{15}); ESI-MS m/z calcd for $C_{36}H_{39}O_8Si_2$ $[M+H]^+$ 655.21780, found: 655.21777.

Compound **10**



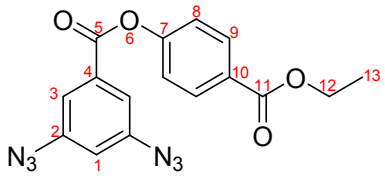
According to a modified literature procedure,[4] compound **9** (131 mg, 0.2 mmol) was dissolved in dry DMF (1.33 mL), combined with $AgNO_3$ (5 mg, 0.03 mmol) and cooled to 0 °C. NIS (94.5 mg, 0.42 mmol) was then added, the reaction was stirred in darkness at 0 °C for 10 min and at rt for 4 h. The reaction mixture was then combined with water (10 mL) and filtered. The collected solid was dissolved in DCM, the solution was washed with water, dried with anhydrous Na_2SO_4, filtered and evaporated, providing **10** (152 mg, 0.2 mmol, quant.) as an off-white solid. δ_H (400 MHz, $CDCl_3$/DMSO-d_6) 8.89 (s, 1H, H^1), 8.19 – 8.09 (m, 4H, H^8), 7.89 (s, 1H, H^4), 7.41 – 7.32 (m, 4H, H^7), 4.40 (q, J = 7.1 Hz, 4H, H^{11}), 1.41 (t, J = 7.1 Hz, 6H, H^{12}); δ_C (101 MHz, $CDCl_3$/DMSO-d_6) 165.41 (C^{10}), 162.21 (C^5), 153.85 (C^6), 141.97 (C^4), 133.48 (C^1), 130.98 (C^8), 130.05 (C^2), 128.41 (C^9), 128.19 (C^3), 121.51 (C^7), 90.06 (C^{13}), 60.95 (C^{11}), 14.17 (C^{12}); ESI-MS m/z calcd for $C_{30}H_{21}I_2O_8$ $[M+H]^+$ 762.93203, found: 762.93197.

Compound **11**



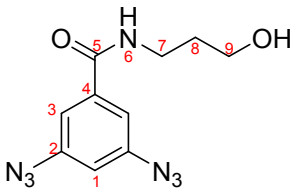
3,5-Dinitrobenzoic acid (1.060 g, 5 mmol) was combined with $SOCl_2$ (5 mL) and a few drops of DMF. The mixture was heated at reflux for 2 h, concentrated and dried under vacuum. The resulting acyl chloride was combined with toluene (8 mL), ethyl p-hydroxybenzoate (914 mg, 5.50 mmol) and DMAP (6 mg, 0.05 mmol). The reaction was heated under reflux overnight and concentrated under vacuum. The product was purified by column chromatography (DCM) to provide **11** (1.761 mg, 4.89 mmol, 98%) as an off-white solid. δ_H (400 MHz, $CDCl_3$) 9.36 – 9.28 (m, 3H, H^1, H^3), 8.22 – 8.12 (m, 2H, H^9), 7.42 – 7.31 (m, 2H, H^8), 4.40 (q, J = 7.1 Hz, 2H, H^{12}), 1.41 (t, J = 7.1 Hz, 3H, H^{13}); δ_C (101 MHz, $CDCl_3$) 165.60 (C^{11}), 160.86 (C^5), 153.51 (C^7), 148.94 (C^2/C^4), 132.98 (C^2/C^4), 131.58 (C^9), 130.05 (C^3), 129.26 (C^{10}), 123.27 (C^1), 121.37 (C^8), 61.46 (C^{12}), 14.45 (C^{13}); ESI-MS m/z calcd for $C_{16}H_{13}O_8N_2$ $[M+H]^+$: 361.06664, found: 361.06653.

Compound **12**



Compound **11** (1.735 g, 4.816 mmol) and 10% Pd/C (170 mg) were added to EtOAc (50 mL). The mixture was stirred in H_2 atmosphere until the reaction was complete. It was then filtered through Celite and concentrated under vacuum. The residue was dissolved in water (50 mL) with conc. HCl (4 mL) and the solution cooled to 0 °C. $NaNO_2$ (731 mg, 10.59 mmol) in small amount of water was then added slowly, followed after 15 min by NaN_3 (751 mg, 11.56 mmol) in small amount of water. The reaction was stirred for 15 min at 0 °C and for 1 h at rt. It was then extracted with EtOAc, the organic phase was washed with brine, dried with anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by silica chromatography (15% Et_2O/hexanes) and the isolated product was recrystallised ($CHCl_3$/hexane) to provide **12** (426 mg, 1.209 mmol, 25%) as a white solid. δ_H (400 MHz, $CDCl_3$) 8.14 (d, J = 8.7 Hz, 2H, *H*^{9}), 7.62 (t, J = 1.6 Hz, 2H, *H*^{3}), 7.29 (d, J = 8.9 Hz, 2H, *H*^{8}), 6.88 (t, J = 2.0 Hz, 1H, *H*^{1}), 4.40 (q, J = 7.1 Hz, 2H, *H*^{13}), 1.41 (t, J = 7.1 Hz, 3H, *H*^{13}); δ_C (101 MHz, $CDCl_3$) 165.84 (*C*^{11}), 163.13 (*C*^{5}), 154.14 (*C*^{7}), 142.74 (*C*^{2}), 132.35 (*C*^{4}), 131.40 (*C*^{9}), 128.65 (*C*^{10}), 121.65 (*C*^{8}), 116.91 (*C*^{3}), 114.70 (*C*^{1}), 61.32 (*C*^{12}), 14.47 (*C*^{13}), ESI-MS m/z 375.0 $[M+Na]^+$.

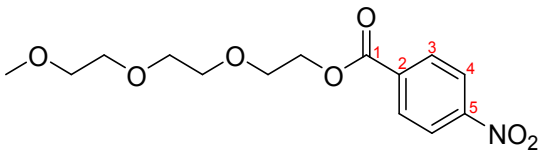
Compound **13**, general procedure for amidation of reactive esters



General procedure for amidation of reactive esters

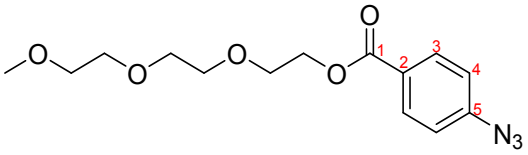
Compound **12** (70 mg, 0.200 mmol) and 3-aminopropan-1-ol (30 µL, 0.400 mmol) were combined in DCM (2 mL) and stirred at rt overnight. The product was purified by silica chromatography (2-3% MeOH/DCM) to provide **13** (50 mg, 0.191 mmol, 96%) as a white solid. δ_H (400 MHz, $CDCl_3$/MeOD) 7.22 – 7.14 (m, 2H, *H*^{3}), 6.70 – 6.62 (m, 1H, *H*^{1}), 3.66 – 3.57 (m, 2H, *H*^{9}), 3.51 – 3.41 (m, 2H, *H*^{7}), 1.83 – 1.65 (m, 2H, *H*^{8}); δ_C (101 MHz, $CDCl_3$/MeOD) 166.59 (*C*^{5}), 142.26 (*C*^{2}), 137.44 (*C*^{4}), 114.11 (*C*^{3}), 112.23 (*C*^{1}), 59.78 (*C*^{9}), 37.43 (*C*^{7}), 31.48 (*C*^{8}); ESI-MS m/z calcd for $C_{10}H_{11}O_2N_7Na$ $[M+Na]^+$ 284.08664, found: 284.08673.

Triethyleneglycol 4-nitrobenzoate **14**



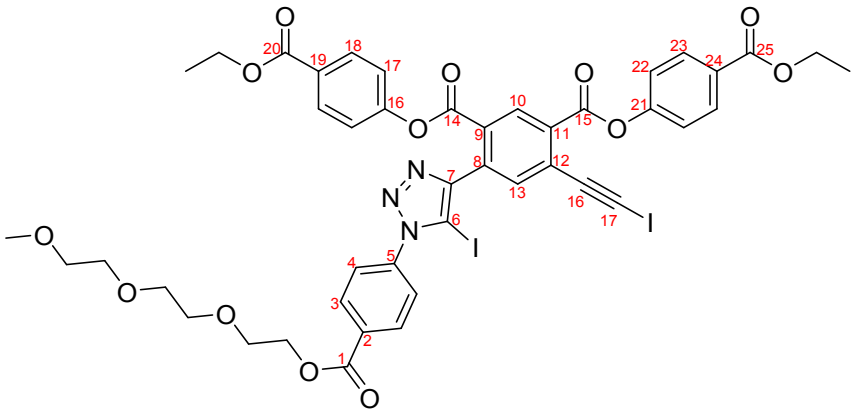
4-nitrobenzoic acid (1.671 g, 10 mmol) was added to $SOCl_2$ (20 mL). A few drops of DMF were then added and the mixture was heated at reflux for 2 h. It was then concentrated and dried under vacuum. The residue was dissolved in dry toluene (20 mL) and combined with tri(ethylene glycol) monomethyl ether (1.600 mL, 11 mmol) and DMAP (61 mg, 0.5 mmol). The reaction was heated at reflux overnight. The resulting mixture was concentrated under vacuum and separated by silica chromatography (0.5-1.5% MeOH/DCM) to provide **14** (2.350 g, 7.50 mmol, 75%) as a brown oil. δ_H (400 MHz, $CDCl_3$) 8.31 – 8.26 (m, 2H, *H*^{4}), 8.25 – 8.20 (m, 2H, *H*^{3}), 4.56 – 4.49 (m, 2H, TEG-C*H*$_2$), 3.88 – 3.83 (m, 2H, TEG-C*H*$_2$), 3.75 – 3.69 (m, 2H, TEG-C*H*$_2$), 3.69 – 3.62 (m, 4H, TEG-C*H*$_2$), 3.56 – 3.51 (m, 2H, TEG-C*H*$_2$), 3.37 (s, 3H, TEG-C*H*$_3$); δ_C (100 MHz, $CDCl_3$) 164.82 (*C*^{1}), 150.68 (*C*^{5}), 135.63 (*C*^{2}), 130.98 (*C*^{3}), 123.65 (*C*^{4}), 72.05, 70.83, 70.79, 70.76, 69.12, 65.10, 59.21; ESI-MS m/z 336.1 $[M+Na]^+$.

Triethyleneglycol 4-azidobenzoate **15**



Compound **14** (2.350 g, 7.50 mmol) and 10% Pd/C (200 mg) were added to EtOAc (75 mL). The mixture was vigorously stirred under H_2 atmosphere for 24 h. It was then filtered through Celite and the filtrate concentrated under vacuum. The residue was dissolved in 1 M HCl and the solution was cooled to 0 °C. $NaNO_2$ (543 mg, 7.88 mmol) in small amount of water was then added slowly. The resulting yellow solution was stirred for 10 min at 0 °C and NaN_3 (536 mg, 8.25 mmol) in small amount of water was added slowly. The mixture was stirred for 10 min at 0 °C and for 30 min at rt. It was then neutralised with sat. aq. $NaHCO_3$ and extracted with Et_2O. Combined organic phases were dried with anhydrous Na_2SO_4, filtered and concentrated under vacuum. The product was purified by silica chromatography (30-40% EtOAc/hexanes) to afford **15** (2.247 g, 7.26 mmol, 97%) as a yellow oil. δ_H (400 MHz, $CDCl_3$): 8.11 – 7.98 (m, 2H, *H*^{2}), 7.12 – 6.99 (m, 2H, *H*^{3}), 4.53 – 4.36 (m, 2H, TEG-C*H*$_2$), 3.90 – 3.78 (m, 2H, TEG-C*H*$_2$), 3.78 – 3.61 (m, 6H, TEG-C*H*$_2$), 3.59 – 3.47 (m, 2H, TEG-C*H*$_2$), 3.37 (s, 3H, TEG-C*H*$_3$); δ_C (100 MHz, $CDCl_3$): 165.86 (*C*^{1}), 144.93 (*C*^{2}), 131.67 (*C*^{3}), 126.80 (*C*^{5}), 118.93 (*C*^{4}), 72.07 (TEG-*C*H$_2$), 70.84 (TEG-*C*H$_2$), 70.79 (TEG-*C*H$_2$), 70.74 (TEG-*C*H$_2$), 69.36 (TEG-*C*H$_2$), 64.34 (TEG-*C*H$_2$), 59.18; ESI-MS m/z calcd for $C_{14}H_{19}O_5N_3Na$ $[M+Na]^+$: 332.12169, found: 332.12151.

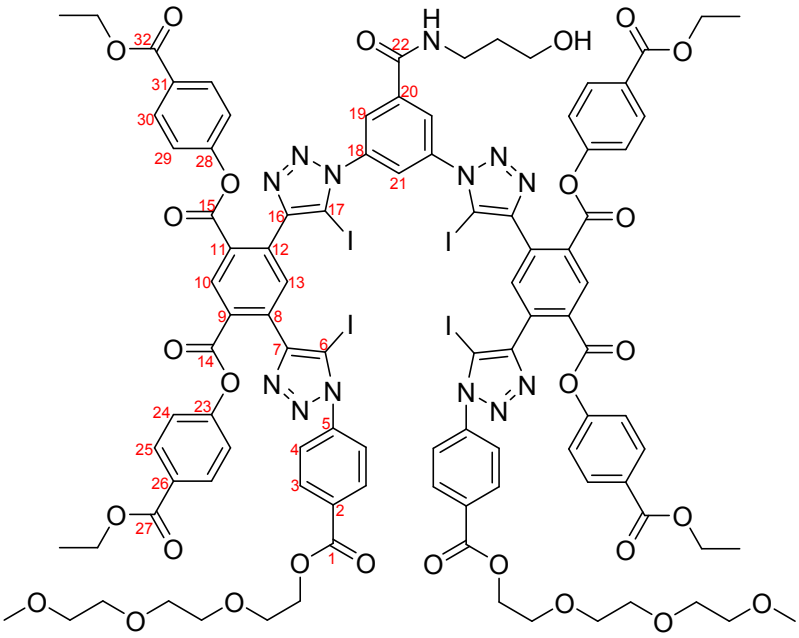
Compound **16.XB**, general procedure for azide-iodoalkyne cycloaddtion



General procedure for azide-iodoalkyne cycloaddition

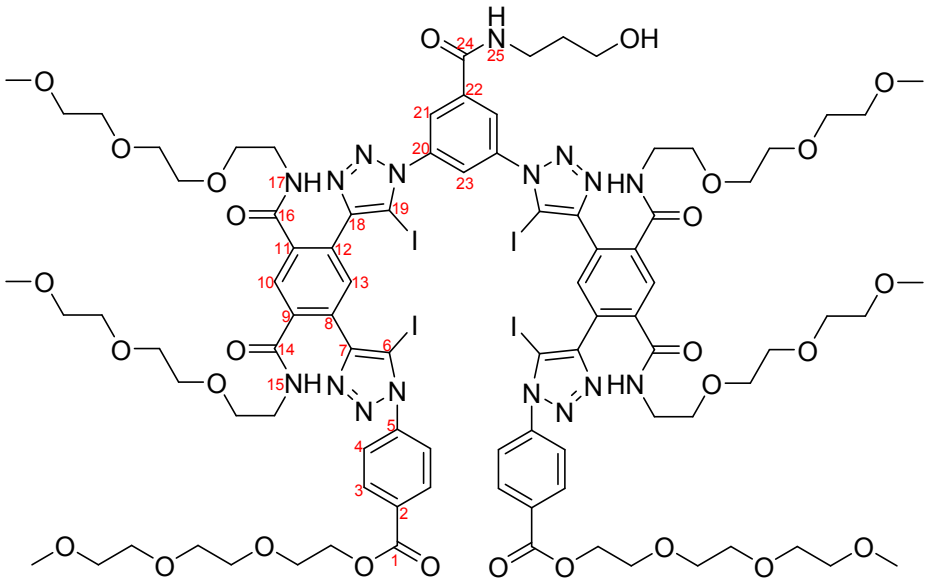
Compounds **15** (155 mg, 0.5 mmol) and **10** (457 mg, 0.6 mmol) were added to dry THF (5 mL) $Cu[MeCN]_4PF_6$ (19 mg, 0.05 mmol) and TBTA (27 mg, 0.05 mmol) were then added simultaneously. The reaction was then stirred overnight at rt under Ar atmosphere in darkness. The mixture was then partitioned between aqueous solution of Na_2EDTA and DCM. Organic fraction was dried with anhydrous Na_2SO_4, decanted and concentrated under vacuum. The residue was purified by silica chromatography (1-1.5% MeOH/DCM) to provide **16.XB** (270 mg, 0.252 mmol, 50%) as a yellow solid. δ_H (400 MHz, $CDCl_3$) 8.93 (s, 1H, H^{10}), 8.28 – 8.21 (m, 2H, H^3), 8.17 – 8.09 (m, 2H, H^{18}/H^{23}), 8.09 – 8.03 (m, 2H, H^{18}/H^{23}), 7.92 (s, 1H, H^{13}), 7.68 – 7.60 (m, 2H, H^4), 7.40 – 7.34 (m, 2H, H^{17}/H^{22}), 7.25 – 7.19 (m, 2H, H^{17}/H^{22}), 4.54 – 4.47 (m, 2H, TEG-CH_2), 4.42 – 4.29 (m, 4H, OCH_2CH$_3$), 3.88 – 3.81 (m, 2H, TEG-CH_2), 3.73 – 3.68 (m, 2H, TEG-CH_2), 3.68 – 3.59 (m, 4H, TEG-CH_2), 3.55 – 3.47 (m, 2H, TEG-CH_2), 3.33 (s, 3H, TEG-CH_3), 1.41 – 1.32 (m, 6H, OCH$_2$CH_3); δ_C (101 MHz, $CDCl_3$) 165.70 (C^{20}/C^{25}), 165.62 (C^{20}/C^{25}), 165.17 (C^1), 163.40 (C^{14}/C^{15}), 162.48 (C^{14}/C^{15}), 154.07 (C^{16}/C^{21}), 153.92 (C^{16}/C^{21}), 149.93 (C^7), 139.93 (C^5), 138.69 (C^{13}), 134.94 (C^8), 133.71 (C^{10}), 131.99 (C^9/C^{11}), 131.86 (C^2), 131.30 (C^{18}/C^{23}), 131.22 (C^{18}/C^{23}), 130.96 (C^3), 129.80 (C^9/C^{11}), 128.52 (C^{19}/C^{24}), 128.50 (C^{19}/C^{24}), 128.41 (C^{12}), 125.96 (C^4), 121.63 (C^{17}/C^{22}), 121.38 (C^{17}/C^{22}), 91.31 (C^{16}), 80.40 (C^6), 71.92, 70.69, 70.65, 70.60, 69.08, 64.71, 61.19 (OCH_2CH$_3$), 61.16 (OCH_2CH$_3$), 59.05, 20.69 (C^{17}), 14.37 (OCH$_2$$CH_3$), 14.34 (OCH$_2$$CH_3$); ESI-MS m/z calcd for $C_{44}H_{40}O_{13}N_3I_2$ $[M+H]^+$ 1072.06450, found: 1072.06392.

Compound **17.XB**



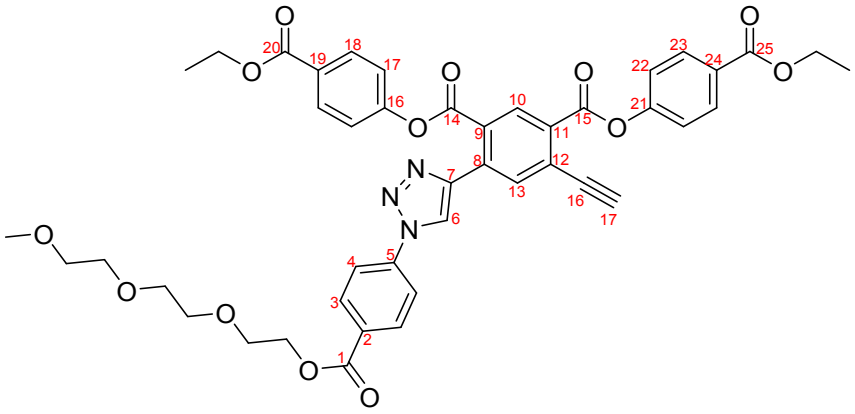
General procedure for azide-iodoalkyne cycloaddition was used to couple compound **16.XB** (84 mg, 0.102 mmol) and **13** (17.5 mg, 0.0500 mmol). The product was purified by silica chromatography (20-25% acetone/DCM) to provide **17.XB** (68 mg, 0.0342 mmol, 68%) as a white solid. δ_H (500 MHz, $CDCl_3$) 8.94 – 8.78 (m, 2H, H^{10}), 8.73 (s, 2H), 8.61 (s, 2H), 8.43 (s, 4H), 8.07 (t, J = 8.0 Hz, 8H, H^3, H^{25}/H^{30}), 7.99 (d, J = 7.9 Hz, 4H, H^{25}/H^{30}), 7.81 (d, J = 8.2 Hz, 4H, H^4), 7.37 – 7.27 (m, 8H, H^{24}, H^{29}), 4.50 (d, J = 39.8 Hz, 6H, TEG-CH_2), 4.37 (q, J = 7.1 Hz, 4H, OCH_2CH$_3$), 4.30 (q, J = 7.1 Hz, 4H, OCH_2CH$_3$), 3.91 – 3.75 (m, 6H, TEG-CH_2), 3.65 (ddt, J = 36.5, 19.9, 4.5 Hz, 18H, TEG-CH_2), 3.56 – 3.43 (m, 6H, TEG-CH_2), 3.34 (s, 6H, TEG-CH_3), 3.27 (s, 3H, TEG-CH_3), 1.39 (t, J = 7.1 Hz, 6H, OCH$_2$CH_3), 1.33 (t, J = 7.1 Hz, 6H, OCH$_2$CH_3); δ_C (126 MHz, $CDCl_3$) 165.74 (C^{27}/C^{32}), 165.64 (C^{27}/C^{32}), 165.32, 164.99, 164.84 (C^{24}), 154.22 (C^{23}/C^{28}), 154.15 (C^{23}/C^{28}), 145.38 (C^7/C^{18}), 145.00 (C^7/C^{18}), 139.71, 137.79, 133.95, 133.70, 133.12, 131.85, 131.42, 131.26 (C^{25}/C^{30}), 131.20 (C^{25}/C^{30}), 130.31, 128.59, 128.53, 128.45, 122.05, 121.72 (C^{24}/C^{29}), 121.64 (C^{24}/C^{29}), 120.59, 119.83 (C^4), 71.99, 71.92, 70.74, 70.67, 70.63, 70.53, 69.23, 65.22, 64.57, 61.21 (OCH$_2$CH$_3$), 61.17 (OCH$_2$CH$_3$), 59.13, 59.05, 14.41 (OCH$_2$$CH_3$), 14.36 (OCH$_2$$CH_3$); ESI-MS m/z calcd for $C_{102}H_{100}O_{31}N_{12}Na$ $[M+H]^+$ 2011.65096, found: 2011.65445.

Compound **18.XB**



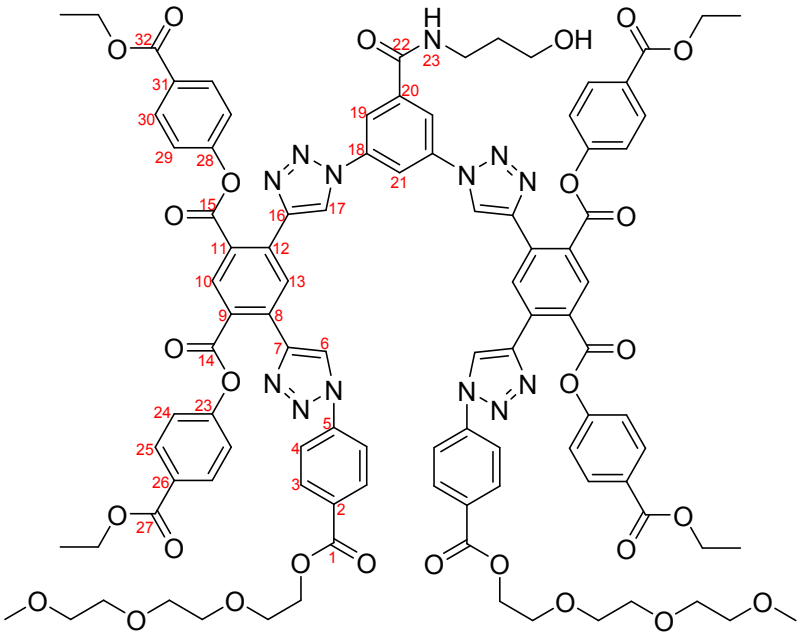
General procedure for amidation of active esters was used to react **17.XB** (68 mg, 0.0342 mmol) and **5** (56 mg, 0.342 mmol). The product was purified by silica chromatography (3-6% MeOH/DCM) to provide **18.XB** (44 mg, 0.0222 mmol, 65%) as an off-white solid. δ_H (500 MHz, $CDCl_3$) 8.29 (s, 3H, H^{21}, H^{25}), 8.22 (d, J = 8.2 Hz, 4H, H^{3}), 8.01 – 7.94 (m, 3H, H^{10}, H^{23}), 7.74 (s, 2H, H^{13}), 7.71 (d, J = 8.1 Hz, 4H, H^{4}), 7.41 (s, 2H, H^{15}/H^{17}), 7.28 (s, 2H, H^{15}/H^{17}), 4.52 – 4.48 (m, 4H, TEG-CH_2), 3.84 (t, J = 4.8 Hz, 4H, TEG-CH_2), 3.75 – 3.37 (m, 70H, TEG-CH_2), 3.34 (s, 6H, TEG-CH_3), 3.23 (s, 6H, TEG-CH_3), 3.18 (s, 6H, TEG-CH_3); δ_C (126 MHz, $CDCl_3$) 167.84 (C^{14}/C^{16}), 167.75 (C^{14}/C^{16}), 165.38 (C^{1}), 165.06 (C^{24}), 150.34 (C^{7}, C^{18}), 140.35 (C^{5}), 137.58 (C^{8}/C^{12}), 137.42 (C^{20}), 137.22 (C^{8}/C^{12}), 133.94 (C^{13}), 131.62 (C^{2}), 130.90 (C^{3}), 130.08 (C^{9}/C^{11}), 129.78 (C^{9}/C^{11}), 129.13 (C^{10}), 126.65 (C^{21}), 126.22 (C^{4}), 125.92 (C^{23}), 82.46 (C^{6}/C^{19}), 81.53 (C^{6}/C^{19}), 71.97, 71.86, 71.76, 70.74, 70.71, 70.66, 70.56, 70.42, 70.36, 70.15, 70.09, 69.46, 69.40, 69.16, 64.70, 60.11, 59.12, 58.96, 58.89, 39.99; ESI-MS m/z calcd for $C_{90}H_{119}O_{28}N_{17}I_4$ $[M+2H]^{2+}$ 1197.23260, found: 1197.23133.

Compound **16.HB**



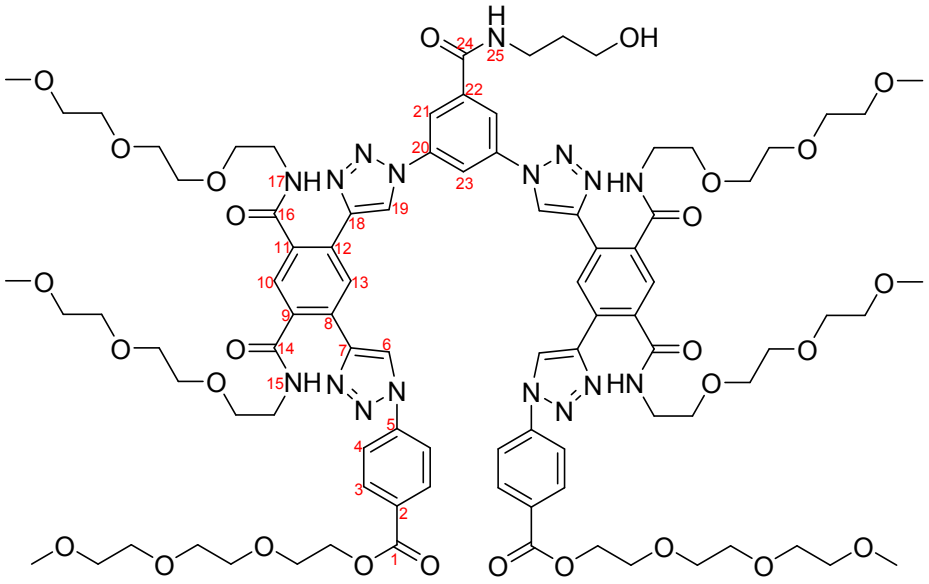
Compound **9** (236 mg, 0.36 mmol) and AgF (109 mg, 0.86 mmol) were added to dry MeCN. Reaction was stirred for 8 h at rt, added to 1M HCl and stirred for 5 min. The aqueous suspension was then extracted with Et_2O, organic fractions washed with water (2x), dried with anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was passed through a short silica column (DCM). This afforded deprotected alkyne (127 mg, 0.25 mmol) which was combined with **15** (64 mg, 0.21 mmol) in dry DCM. TBTA (11 mg, 0.021 mmol) and $Cu[MeCN]_4PF_6$ (7.7 mg, 0.021 mmol) were then added. The mixture was stirred at rt under Ar for 20 h and loaded directly onto a silica column (5-9% acetone/DCM) to provide **16.HB** (84 mg, 0.102 mmol, 49%) as a white solid. δ_H (400 MHz, $CDCl_3$) 8.81 (s, 1H, H^{10}), 8.62 (s, 1H, H^{6}), 8.28 (s, 1H, H^{13}), 8.19 (d, J = 8.4 Hz, 2H, H^{3}), 8.10 (dd, J = 8.6, 6.9 Hz, 4H, H^{18}, H^{23}), 7.85 (d, J = 8.5 Hz, 2H, H^{4}), 7.33 (dd, J = 14.5, 8.5 Hz, 4H, H^{17}, H^{22}), 4.49 (t, J = 4.7 Hz, 2H, TEG-CH_2), 4.42 – 4.29 (m, 4H, OCH_2CH$_3$), 3.84 (t, J = 4.8 Hz, 2H, TEG-CH_2), 3.75 – 3.58 (m, 7H, TEG-CH_2, H^{17}), 3.52 (dd, J = 5.8, 3.5 Hz, 2H, TEG-CH_2), 3.33 (s, 3H, TEG-CH_3), 1.37 (q, J = 7.1 Hz, 6H, OCH$_2$CH_3); δ_C (101 MHz, $CDCl_3$) 165.75 (C^{20}/C^{25}), 165.67 (C^{20}/C^{25}), 165.27 (C^{14}/C^{15}), 164.65 (C^{14}/C^{15}), 162.53, 154.03 (C^{16}/C^{21}), 154.02 (C^{16}/C^{21}), 144.40 (C^{7}), 139.71 (C^{5}), 136.94 (C^{13}), 134.44 (C^{8}), 133.41 (C^{10}), 131.53 (C^{3}), 131.31 (C^{18}/C^{23}), 131.25 (C^{18}/C^{23}), 130.56, 128.63, 128.49, 127.31, 122.14 (C^{6}), 121.64 (C^{17}/C^{22}), 121.61 (C^{17}/C^{22}), 120.02 (C^{4}), 86.95 (C^{16}), 80.62 (C^{17}), 71.94, 70.71, 70.68, 70.63, 69.14, 64.62, 61.22 (OCH$_2$CH$_3$), 59.08, 14.37 (OCH$_2$CH$_3$); ESI-MS m/z calcd for $C_{44}H_{41}O_{13}N_3Na$ $[M+Na]^+$ 842.25316, found: 842.25292.

Compound **17.HB**



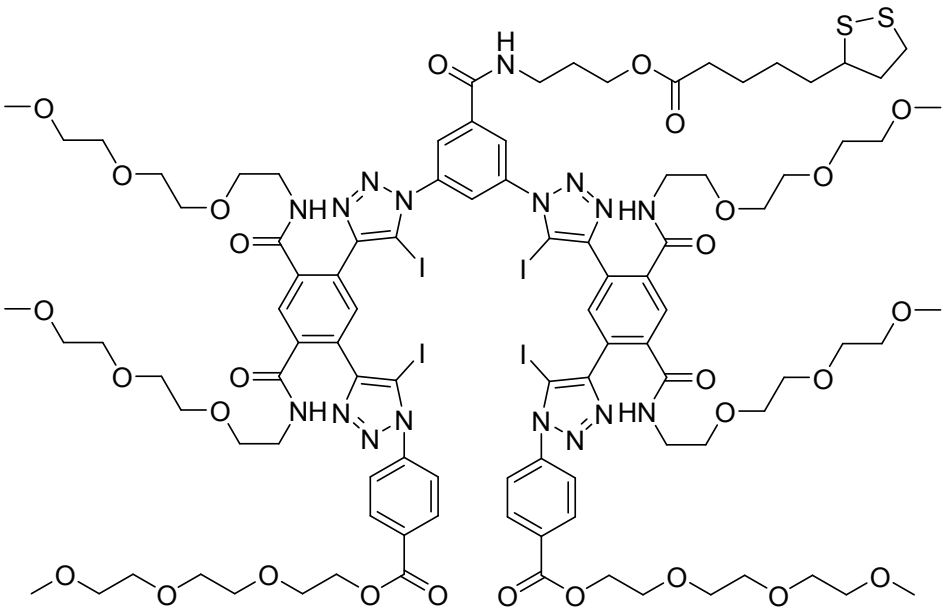
Compound **16.HB** (172 mg, 0.210 mmol) and **13** (26 mg, 0.100 mmol) were added to dry DCM. $Cu(MeCN)_4PF_6$ (7.5 mg, 0.02 mmol), TBTA (10.6 mg, 0.02 mmol) and DIPEA (7 µL, 0.04 mmol). The reaction was stirred under Ar atmosphere for 1 d. It was then diluted with DCM, washed with aqueous Na_2EDTA solution, dried with anhydrous Na_2SO_4, decanted and concentrated under vacuum. The product was purified by silica chromatography (3–4.5% MeOH/DCM) to provide **17.HB** (168 mg, 0.0884 mmol, 88%) as an off-white solid. δ_H (500 MHz, $CDCl_3$) 8.88 – 8.67 (m, 4H), 8.53 (s, 2H), 8.36 (s, 2H), 8.23 (s, 1H, H^{21}), 8.11 (s, 2H), 8.04 (d, J = 8.1 Hz, 8H, H^3, H^{25}/H^{30}), 7.94 (d, J = 8.1 Hz, 4H, H^{25}/H^{30}), 7.84 (s, 1H, H^{23}), 7.74 (d, J = 8.2 Hz, 4H, H^4), 7.29 (d, J = 8.2 Hz, 4H, H^{24}/H^{29}), 7.26 – 7.18 (m, 4H, H^{24}/H^{29}), 4.45 (t, J = 4.7 Hz, 4H, TEG-CH_2), 4.37 (q, J = 7.1 Hz, 4H, OCH_2CH$_3$), 4.28 (q, J = 7.1 Hz, 4H, OCH_2CH$_3$), 3.82 (t, J = 4.8 Hz, 4H, TEG-CH_2), 3.79 – 3.54 (m, 18H, TEG-CH_2), 3.51 (dd, J = 5.8, 3.6 Hz, 4H, TEG-CH_2), 3.32 (s, 6H, TEG-CH_3), 1.39 (t, J = 7.1 Hz, 6H, OCH$_2$CH_3), 1.31 (t, J = 7.1 Hz, 6H, OCH$_2$CH_3); δ_C (126 MHz, $CDCl_3$) 165.75 (C^{14}/C^{16}), 165.65 (C^{14}/C^{16}), 165.26, 164.89 164.86, 154.15 (C^{23}/C^{28}), 154.04 (C^{23}/C^{28}), 145.24 (C^7/C^{16}), 144.73 (C^7/C^{16}), 139.58 (C^5), 138.17, 137.45, 133.97, 133.51, 133.25, 131.44, 131.31, 131.23, 130.40, 128.64, 128.55, 128.26, 127.97, 122.46, 122.22, 121.72, 121.62, 119.76, 118.04, 72.01, 70.78, 70.75, 70.69, 69.20, 64.64, 61.29, 60.72, 59.13, 31.57, 14.45 (OCH$_2$CH$_3$), 14.39 (OCH$_2$CH$_3$). ESI-MS m/z calcd for $C_{98}H_{94}N_{13}NaO_{28}$ $[M+H+Na]^{2+}$ 961.81145, found: 961.81183.

Compound **18.HB**



General procedure for amidation of reactive esters was used to react **17.HB** (161 mg, 0.0848 mmol) and **5** (111 mg, 0.678 mmol). The product was purified by silica chromatography (5-8% MeOH/DCM) followed by preparative TLC (7% MeOH/$CHCl_3$) to provide **18.HB** (44 mg, 0.0238 mmol, 28%) as a white solid. δ_H (500 MHz, $CDCl_3$) 8.81 – 8.38 (m, 4H), 8.38 – 7.63 (m, 17H), 7.62 – 7.30 (m, 3H), 4.49 (s, 4H), 4.01 – 2.90 (m, 87H), 2.72 (s, 3H), 1.35 – 1.11 (m, 2H); δ_C (126 MHz, $CDCl_3$) 169.47, 169.18, 165.46, 145.14, 139.90, 137.73, 137.30, 134.62, 134.25, 133.17, 131.38, 130.11, 128.49, 128.27, 121.21, 120.62, 119.71, 117.44, 72.02, 71.88, 71.72, 70.77, 70.69, 70.57, 70.45, 70.29, 70.07, 69.89, 69.32, 69.22, 64.59, 59.84, 59.14, 58.97, 58.78, 39.80, 37.65, 32.00, 29.78; ESI-MS m/z calcd for $C_{90}H_{123}N_{17}O_{28}$ $[M+2H]^{2+}$ 944.93562, found: 944.93554.

Title compound **1.XB**



Compound **18.XB** (30 mg, 0.0125 mmol), lipoic acid (7.8 mg, 0.0375 mmol), N,N'-dicyclohexylcarbodiimide (7.8 mg, 0.0375 mmol) and a catalytic amount of 4-dimethylaminopyridine were dissolved in 8 mL dry DCM. After stirring under N_2 in the dark for 18 h the product was isolated by preparative TLC (DCM/MeOH/acetone 8:1:1) as an off-white solid (14 mg, 43%). δ_H (500 MHz, $CDCl_3$) 8.40 (d, *J* = 2.0 Hz, 2H), 8.26 (d, *J* = 8.3 Hz, 4H), 8.09 (m, 3H), 7.82 (s, 2H), 7.74 (d, *J* = 8.3 Hz, 4H), 7.16 (m, 2H), 7.10 (m, 2H), 4.53 (t, *J* = 4.8 Hz, 4H), 4.21 (t, *J* = 6.1 Hz, 2H), 3.87 (t, *J* = 4.8 Hz, 4H), 3.76 – 3.71 (m, 4H), 3.70 – 3.67 (m, 4H), 3.67 – 3.51 (m, 52H), 3.47 (m, 20H), 3.37 (s, 6H), 3.26 (s, 6H), 3.22 (s, 6H), 3.20 – 3.04 (m, 2H), 2.44 (m, 1H), 2.33 (t, *J* = 7.4 Hz, 2H), 1.99 (q, *J* = 6.5 Hz, 1H), 1.94 – 1.85 (m, 1H), 1.74 – 1.55 (m, 4H), 1.46 (m, 2H). δ_C (126 MHz, $CDCl_3$) 173.71, 167.52, 165.32, 164.51, 150.56, 150.37, 140.26, 137.66, 137.62, 137.27, 134.14, 131.65, 130.88, 130.10, 129.75, 129.23, 126.71, 126.13, 71.93, 71.82, 71.71, 70.70, 70.67, 70.62, 70.54, 70.50, 70.38, 70.36, 70.11, 70.01, 69.44, 69.13, 64.66, 61.89, 59.08, 58.92, 58.84, 56.43, 56.37, 50.86, 40.27, 40.24, 39.95, 39.82, 38.54, 37.32, 34.58, 34.05, 33.50, 28.77, 28.73, 28.62, 24.68, 24.54; ESI-MS m/z calcd for $C_{98}H_{131}O_{29}N_{17}I_4S_2$ $[M+2H]^{2+}$ 1290.74539, found: 1290.74512.

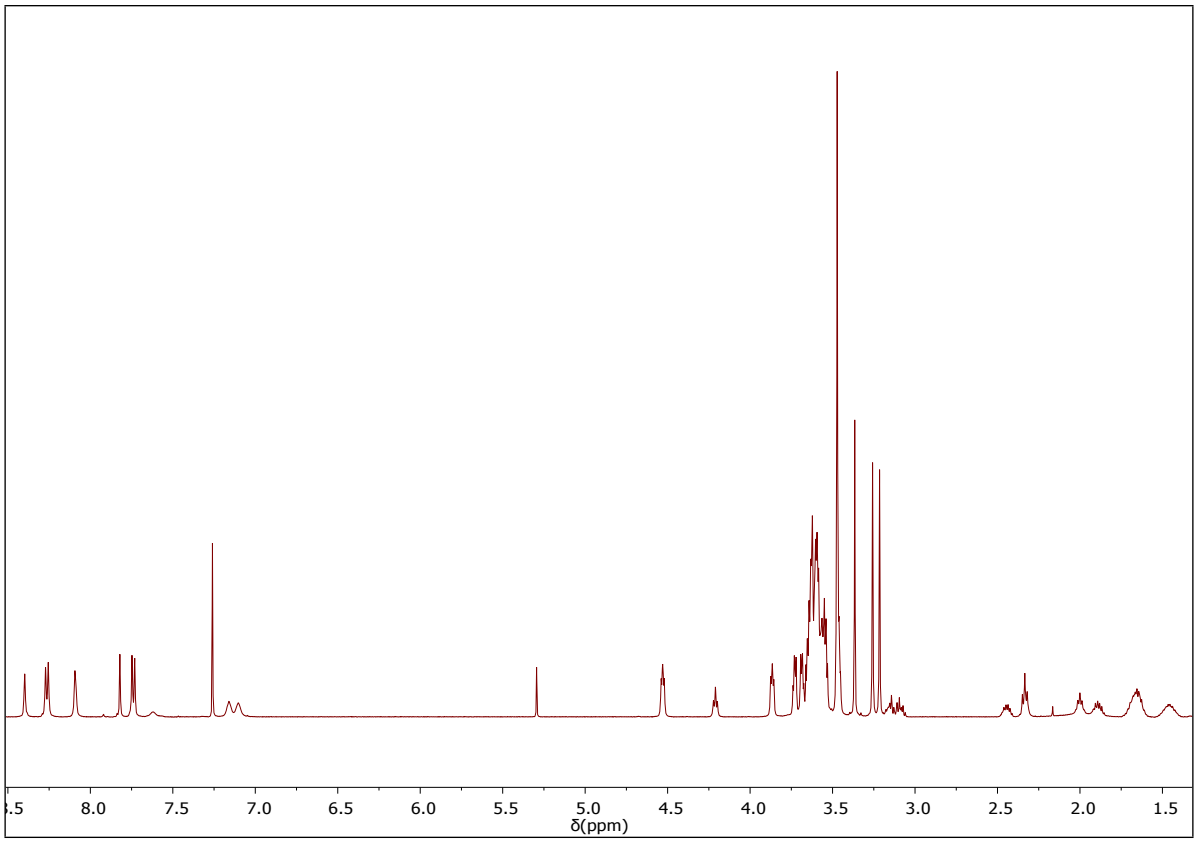


Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) of 1.XB.

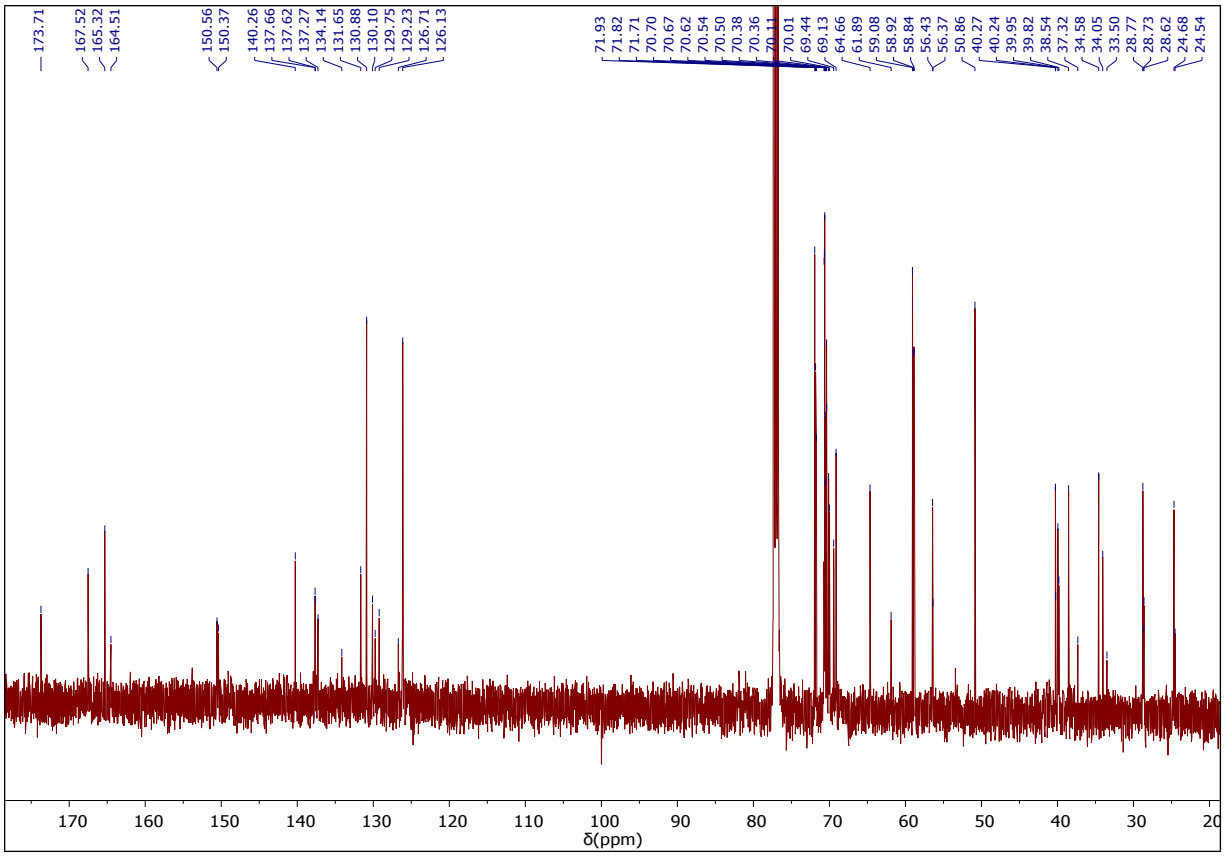
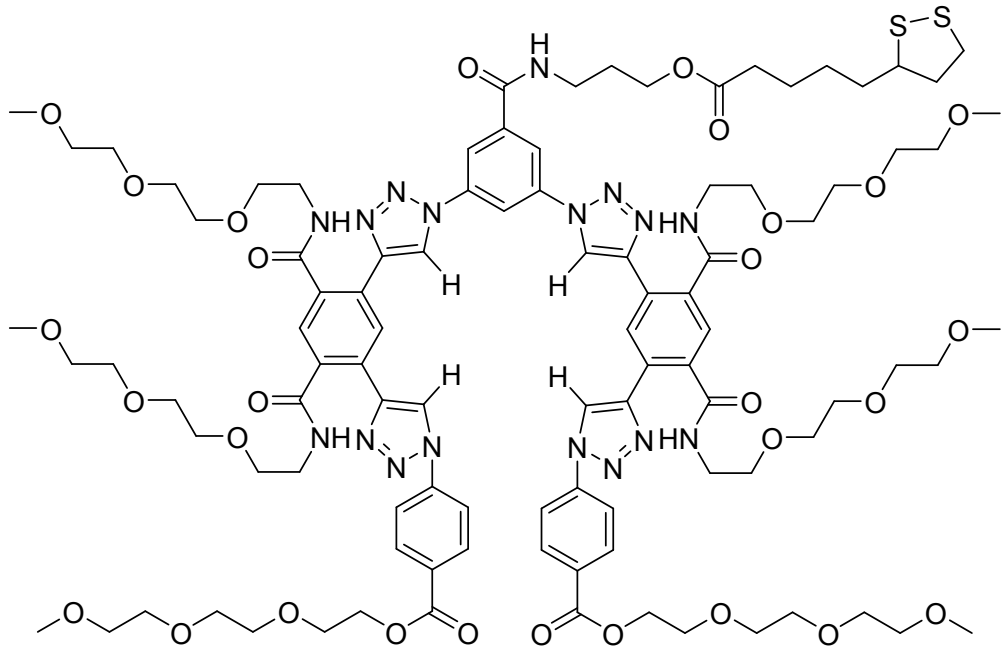


Figure S2. ^{13}C NMR (126 MHz, $CDCl_3$) of 1.XB.

Title compound **1.HB**



Compound **18.HB** (20 mg, 0.0106 mmol), lipoic acid (6.6 mg, 0.0318 mmol), N,N'-dicyclohexylcarbodiimide (6.6 mg, 0.0318 mmol) and a catalytic amount of 4-dimethylaminopyridine were dissolved in 7 mL dry DCM. After stirring under N_2 in the dark for 18 h the product was isolated by preparative TLC (DCM/MeOH/acetone 11:1:1) as a white solid (16 mg, 73 %). δ_H (500 MHz, $CDCl_3$) 8.67 (d, *J* = 15.8 Hz, 4H), 8.42 (s, 3H), 8.30 – 8.13 (m, 6H), 8.04 (s,1H), 7.94 (d, *J* = 8.2 Hz, 4H), 7.82 (s,1H), 7.57 (s,4H), 4.52 (t, *J* = 4.7 Hz, 4H), 4.27 (t, *J* = 6.4 Hz, 2H) 3.88 (t, *J* = 4.8 Hz, 4H), 3.82 (s, 4H), 3.77 – 3.49 (m, 60H), 3.48 – 3.40 (m, 10H), 3.38 (s, 6H), 3.32 (m, 4H), 3.23 (s, 6H), 3.18 – 3.04 (m, 10H), 2.49 – 2.3 (m, 4H), 2.09 (m, 2H), 1.88 (m, 10H), 1.67 (m, 4H), 1.48 (m, 2H). δ_C (101 MHz, $CDCl_3$) 173.64, 169.21, 168.99, 165.40, 145.15, 144.95, 139.91, 137.57, 134.70, 134.46, 131.39, 130.14, 128.68, 128.37, 121.26, 120.92, 119.82, 117.88, 71.94, 71.79, 71.63, 70.70, 70.68, 70.62, 70.53, 70.47, 70.34, 70.23, 70.03, 69.79, 69.30, 69.20, 69.15, 64.53, 62.21, 59.06, 58.86, 58.68, 56.36, 40.25, 40.22, 39.78, 39.69, 38.49, 37.48, 34.61, 34.07, 33.20, 28.79, 28.73, 28.71, 24.70, 24.51; ESI-MS m/z calcd for $C_{98}H_{131}O_{29}N_{17}I_4S_2$ $[M+2H]^{2+}$ 1038.95210, found: 1038.94983.

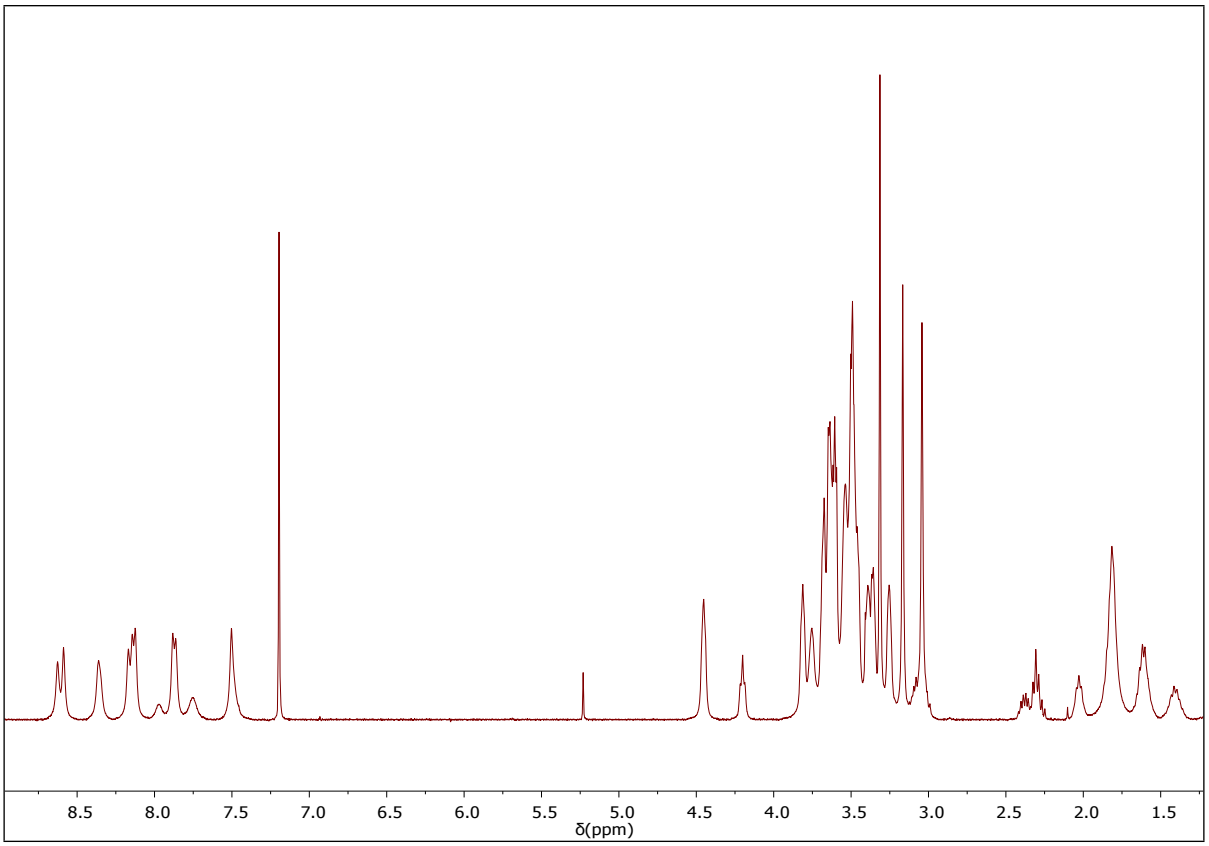


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) of 1.HB.

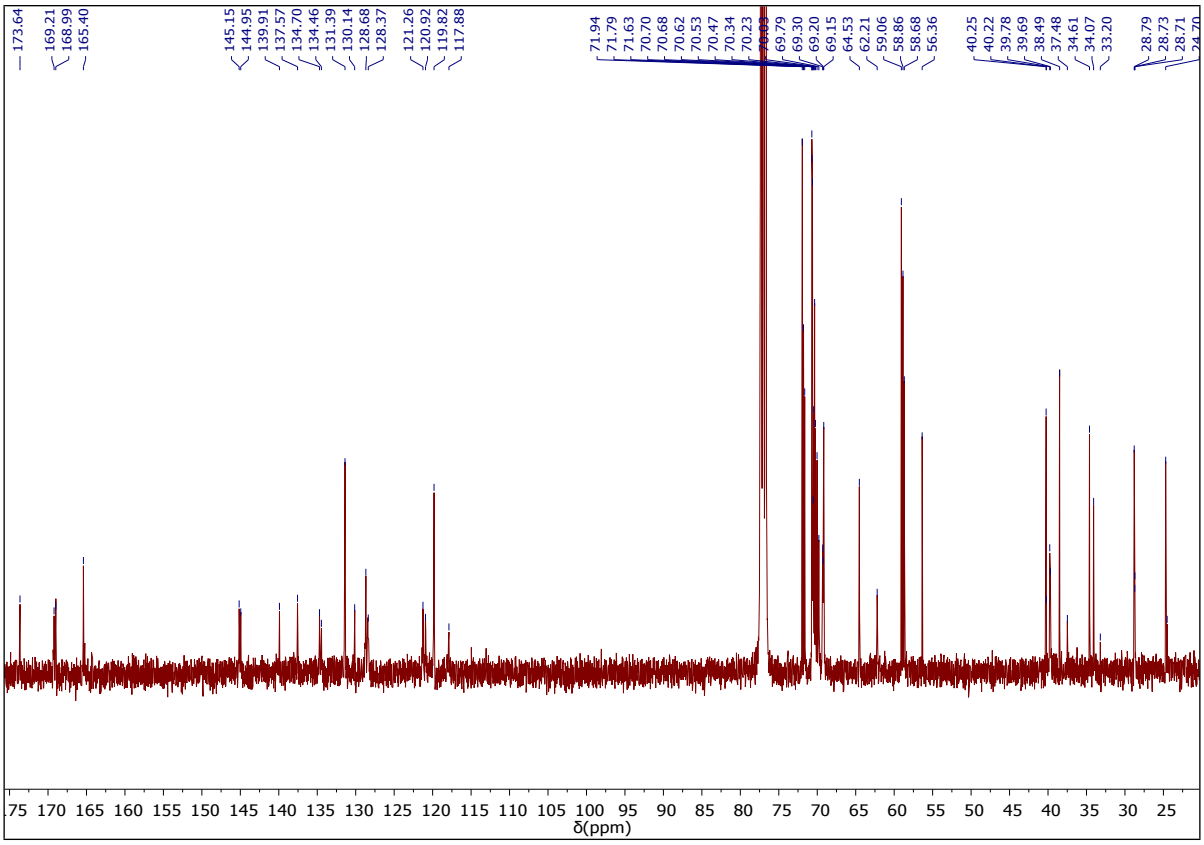


Figure S4. ^{13}C NMR (101 MHz, $CDCl_3$) of 1.HB.

S3. Surface Characterization of Foldamer SAMs

S3.1 XPS

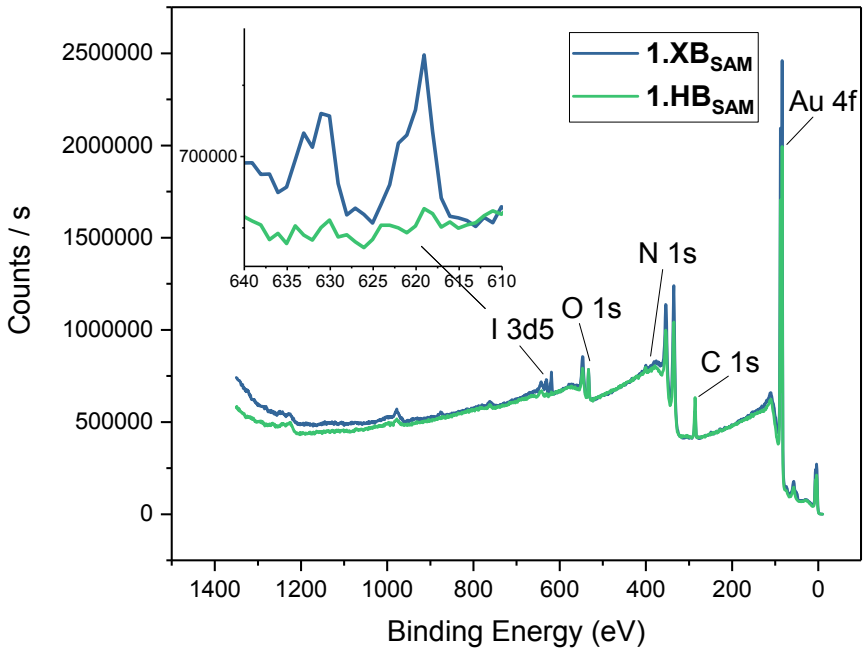


Figure S5. Low resolution survey XPS spectra of 1.XB/HB$_{SAM}$ indicating identical composition of both films apart from presence of iodine for 1.XB$_{SAM}$. Inset: Magnification of I 3d region.

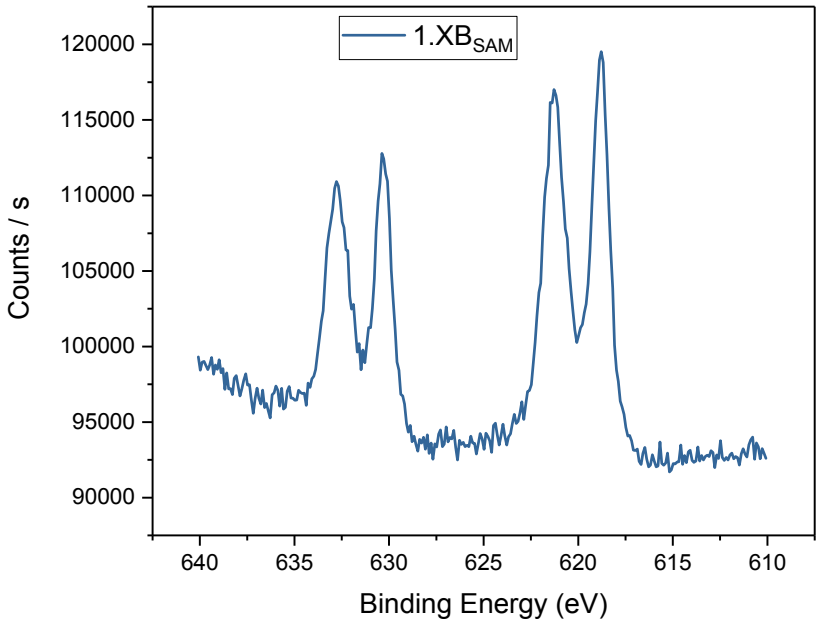


Figure S6. High resolution I 3d XPS spectrum of 1.XB$_{SAM}$.

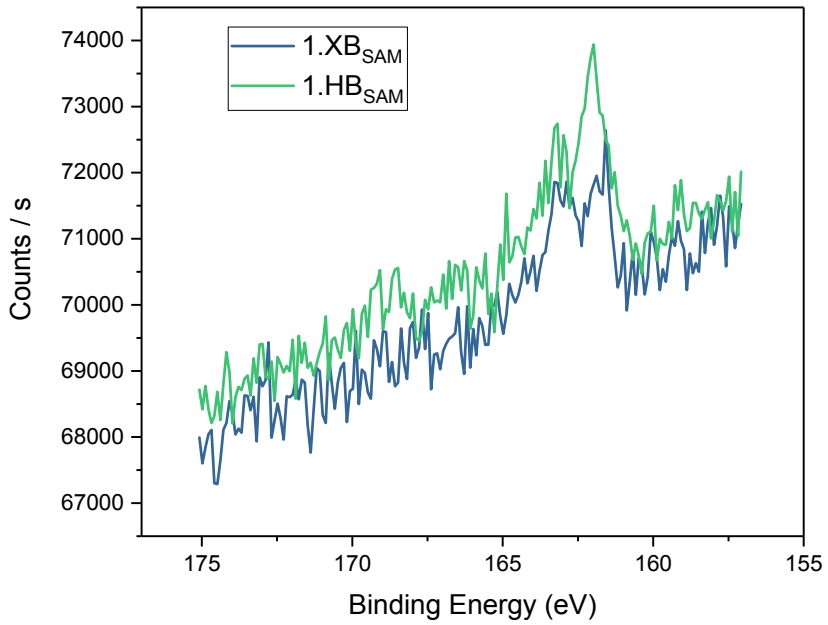


Figure S7. High resolution S 2p XPS spectra of 1.XB/HB$_{SAM}$.

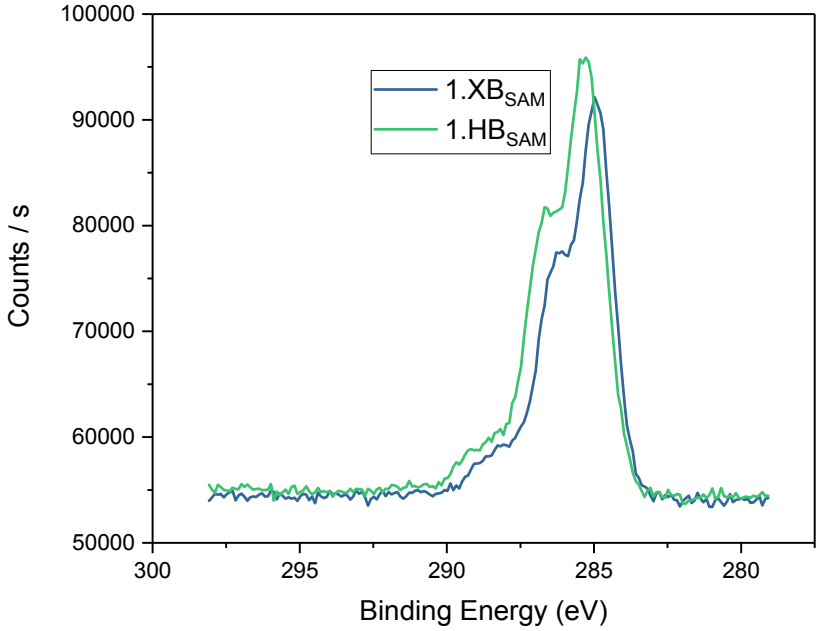


Figure S8. High resolution C 1s XPS spectra of 1.XB/HB$_{SAM}$.

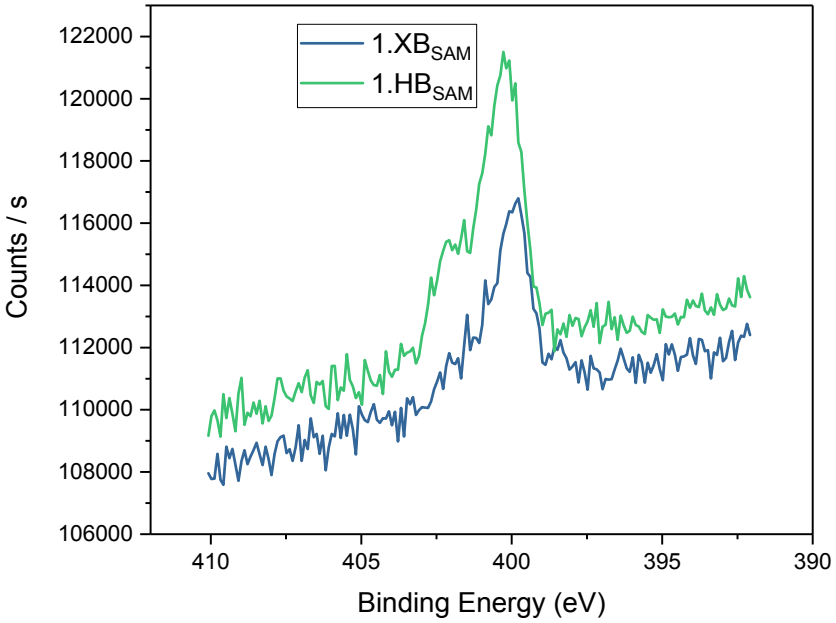


Figure S9. High resolution N 1s XPS spectra of 1.XB/HB$_{SAM}$.

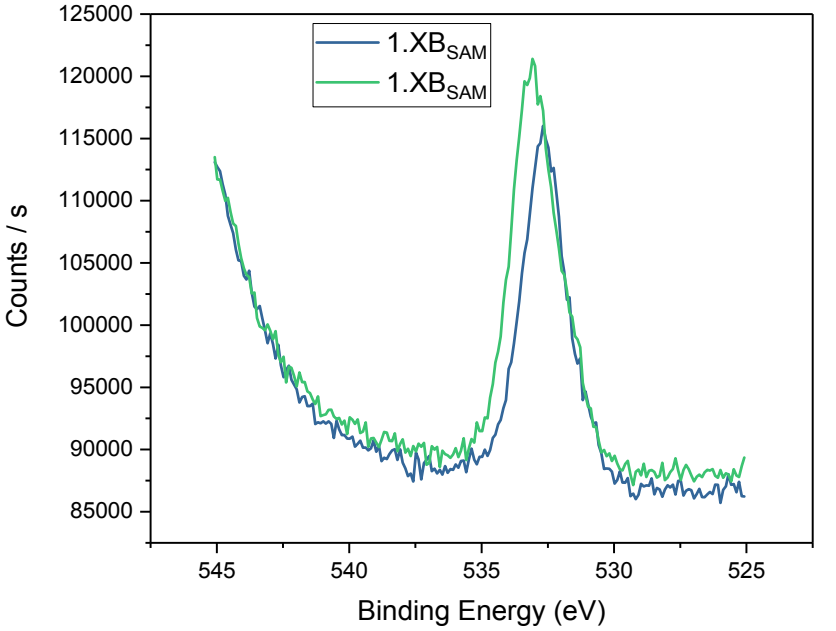


Figure S10. High resolution O 1s XPS spectra of 1.XB/HB$_{SAM}$.

Table S1. High resolution XPS peak data and atomic composition of 1.XB_{SAM}. Errors represent one standard deviation of triplicate measurements. BE = binding energy. The remaining atomic % arise from the underlying gold substrate.

Peak	Start BE (eV)	Peak BE (eV)	End BE (eV)	Atomic %
C 1s	293.41 ± 0.76	285.66 ± 0.26	278.91 ± 0.29	49.31 ± 4.56
N 1s	407.42 ± 2.52	400.31 ± 0.15	393.75 ± 0.29	8.74 ± 1.79
O 1s	537.08 ± 0.50	532.77 ± 0.13	526.41 ± 2.08	13.38 ± 1.31
S 2p	166.55 ± 1.16	163.44 ± 0.13	159.84 ± 1.10	1.05 ± 0.24
I 3d	625.41 ± 0.58	620.28 ± 0.77	614.75 ± 1.523	1.86 ± 0.13

Table S2. High resolution XPS peak data and atomic composition of 1.HB_{SAM}. Errors represent one standard deviation of triplicate measurements. BE = binding energy. The remaining atomic % arise from the underlying gold substrate.

Peak	Start BE (eV)	Peak BE (eV)	End BE (eV)	Atomic %
C 1s	296.08 ± 1.73	286.08 ± 0.20	278.08 ± 1.73	53.22 ± 2.70
N 1s	408.08 ± 0.50	400.91 ± 0.31	393.25 ± 3.55	8.71 ± 0.66
O 1s	537.08 ± 0.50	532.94 ± 0.11	524.75 ± 1.53	14.80 ± 0.66
S 2p	168.31 ± 2.39	163.13 ± 0.25	159.00 ± 0.00	1.19 ± 0.21

The peak binding energy of sulfur of around 163 eV is consistent with Au-S interactions[5] futher confirming formation of a well-defined SAM through the disulfide anchor group.

Table S3. Experimental and theoretical elemental composition of 1.XB/HB_{SAM} determined by XPS. Values were normalized to S = 2. Errors represent one standard deviation of triplicate measurements.

	1.XB_{SAM}		1.HB_{SAM}	
	Experimental	**Theoretical**	**Experimental**	**Theoretical**
C	93.92 ± 8.69	98	101.86 ± 5.17	98
N	16.65 ± 3.42	17	16.68 ± 1.25	17
O	25.47 ± 2.48	29	28.33 ± 1.02	29
S	2 ± 0.46	2	2 ± 0.39	2
I	3.54 ± 0.24	4	-	-

S3.2 Water Contact Angle

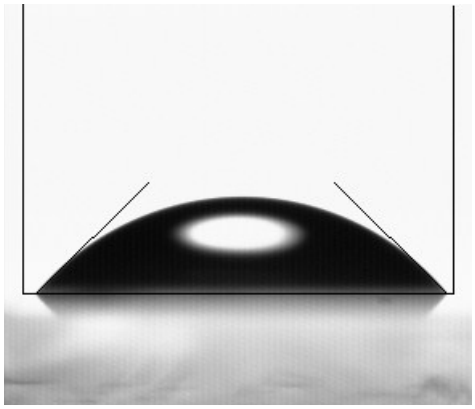


Figure S11. Water contact angle measurement of $1.HB_{SAM}$.

S4. Electrochemical Characterization of Foldamer SAMs and Sensor Performance

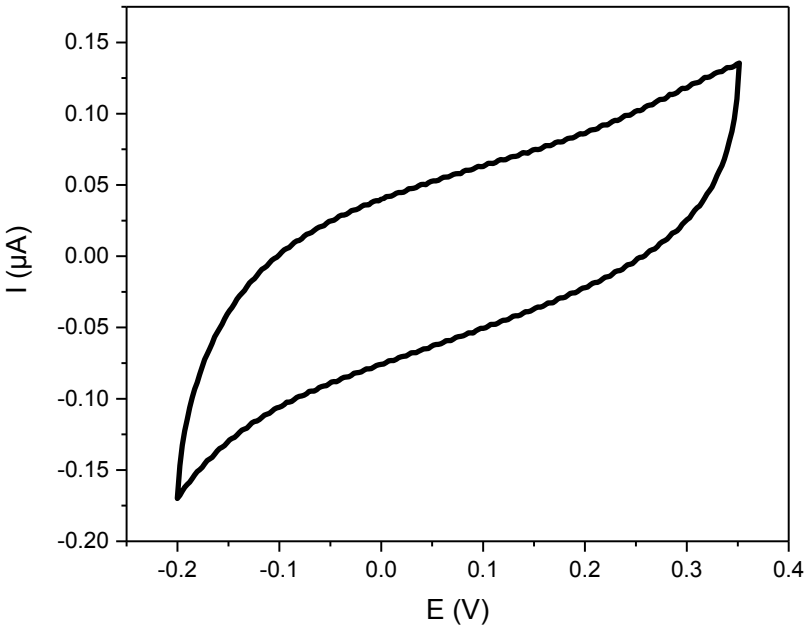


Figure S12. CV of 1.XB$_{SAM}$ in 100 mM NaCl at a scan rate of 0.1 V/s.

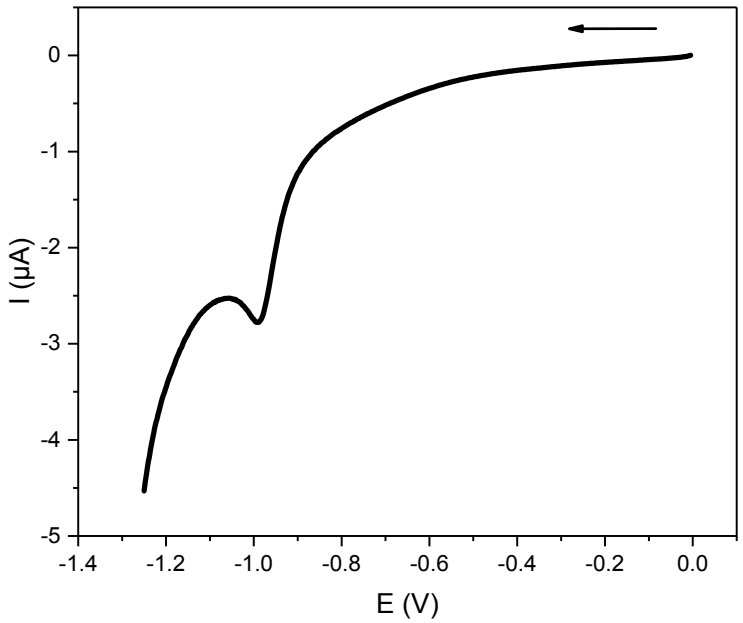


Figure S13. CV of reductive desorption of 1.XB$_{SAM}$ in 500 mM KOH (degassed) at a scan rate of 0.1 V/s. Arrow indicates direction of scan.

The molecular surface coverage (Γ) was calculated according to $\Gamma = \frac{Q}{2 * F * A_e}$, where Q is the charge associated with the reductive desorption and A_e the electroactive surface area of the gold electrode.

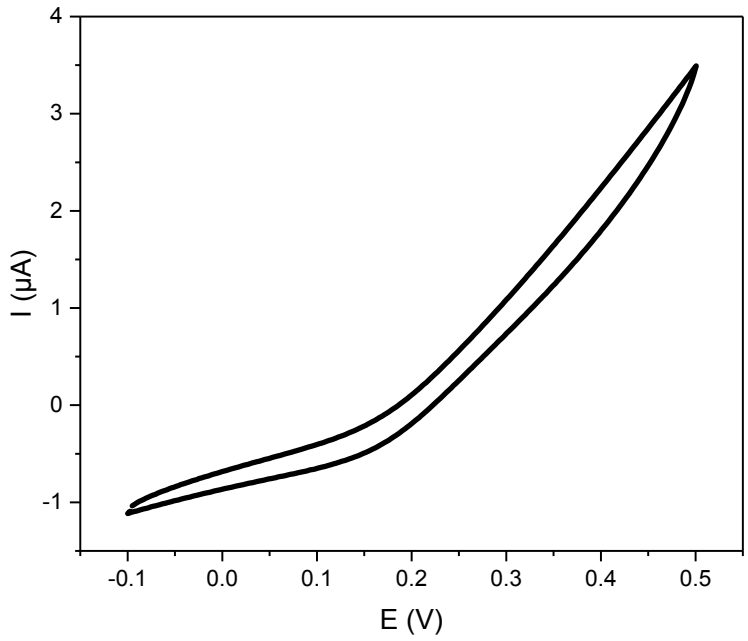


Figure S14. CV of 1.XB$_{SAM}$ in 10 mM $Fe(CN)_6^{3-/4-}$ and 100 mM NaCl at a scan rate of 0.1 V/s.

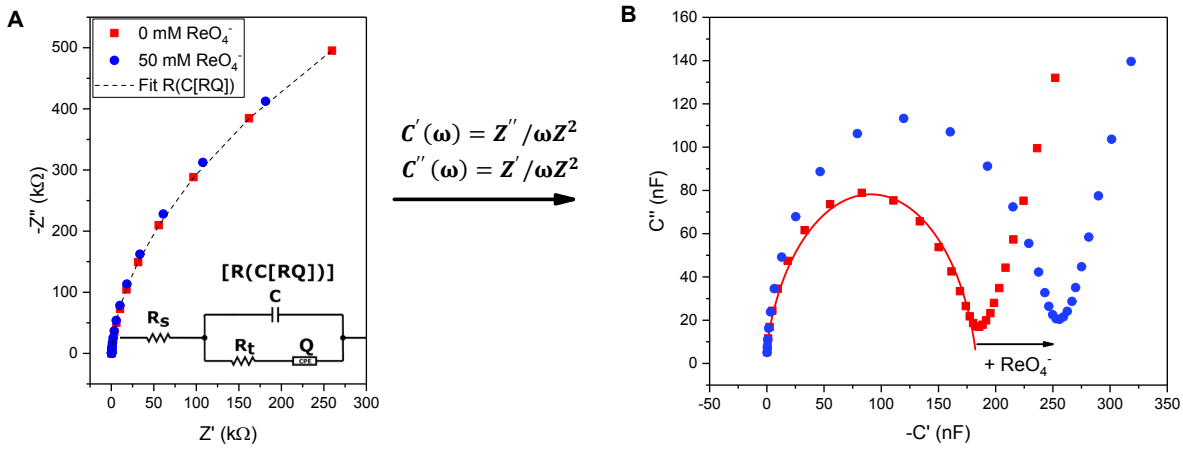


Figure S15. EIS/ECS response of 1.XB$_{SAM}$ on gold disk electrode in 100 mM NaCl at open-circuit potential (≈ 0 V) in presence (blue circles) and absence (red squares) of 50 mM perrhenate. A) Impedimetric Nyquist plot and fitting to the equivalent circuit $R_S(C[R_TQ])$. Transformation of impedimetric data via $C''(\omega) = Z'/\omega Z^2$ and $C'(\omega) = Z''/\omega Z^2$ to obtain capacitive data. B) Capacitive Nyquist plot and fitting to semicircle to obtain C as the x-intersect.

The capacitance obtained from fitting to the equivalent circuit is in excellent agreement with the capacitance obtained from a graphical semicircle fit. Neither R_T nor Q are analytically useful/sensitive functions.

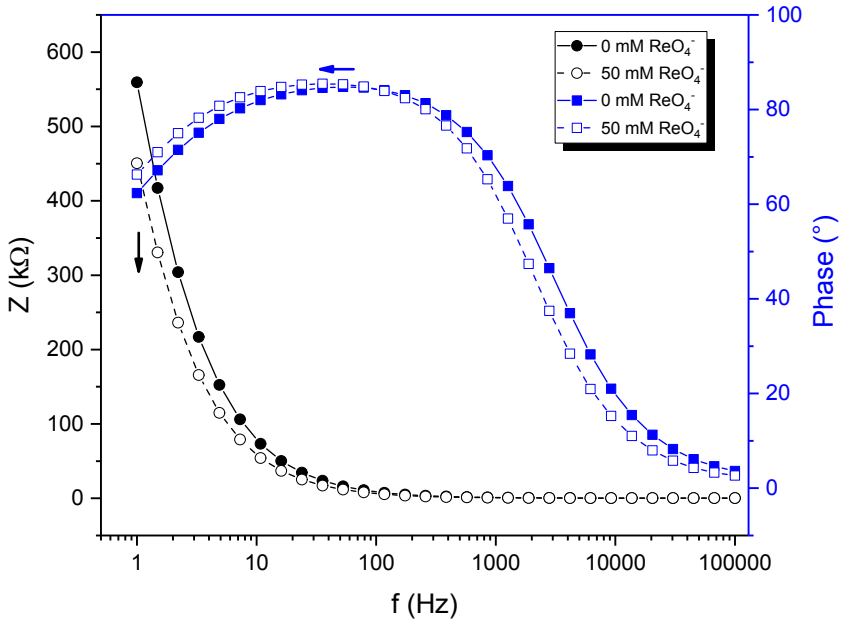


Figure S16. Bode plots of impedance (black, circles) and phase (blue, squares) vs. frequency of 1.XB_{SAM} in the presence (empty symbols) and absence (filled symbols) of 50 mM ReO_4^-.

The high phase angle of ≈ 85° is further evidence for formation of a densely packed SAM.

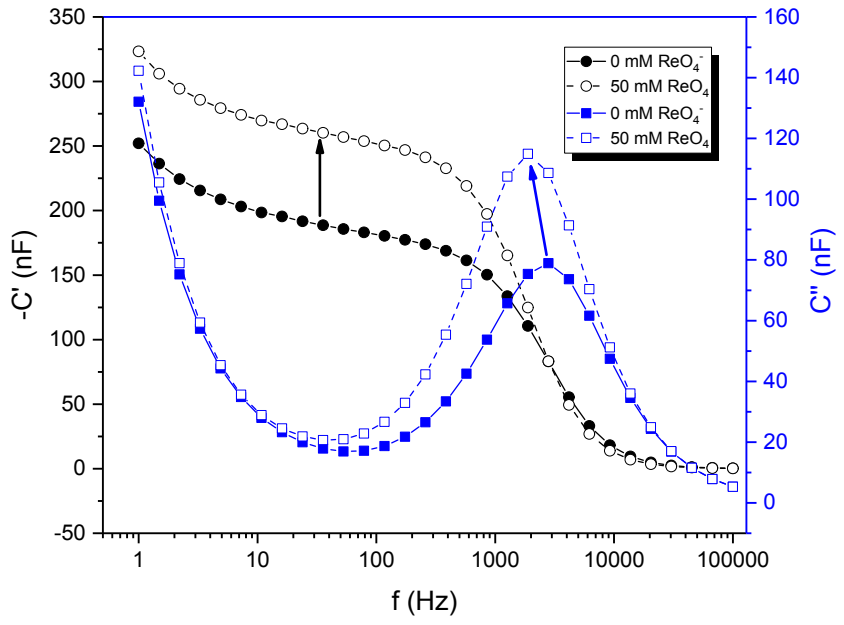


Figure S17. Bode plots of real (black, circles) and imaginary (blue, squares) capacitance vs. frequency of 1.XB_{SAM} in the presence (empty symbols) and absence (filled symbols) of 50 mM ReO_4^-.

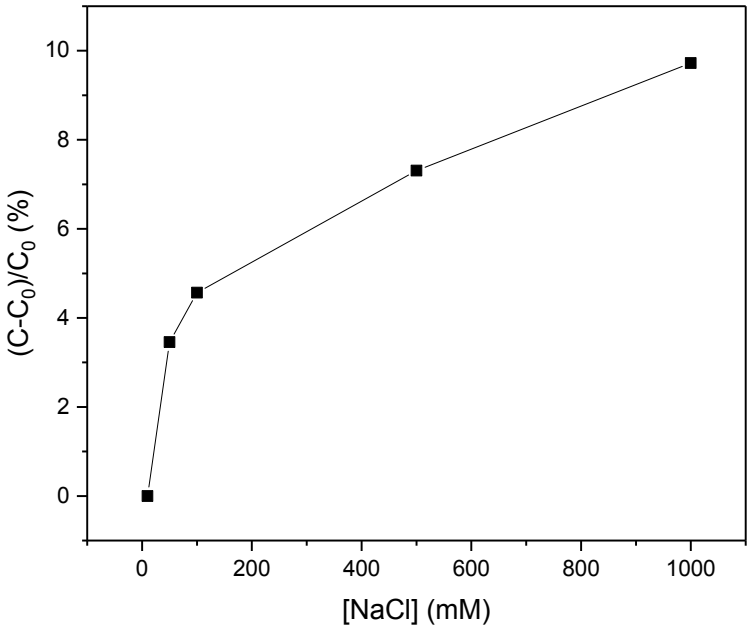


Figure S18. Normalized capacitance increase of 1.XB$_{SAM}$ in the presence of various concentrations of NaCl as electrolyte.

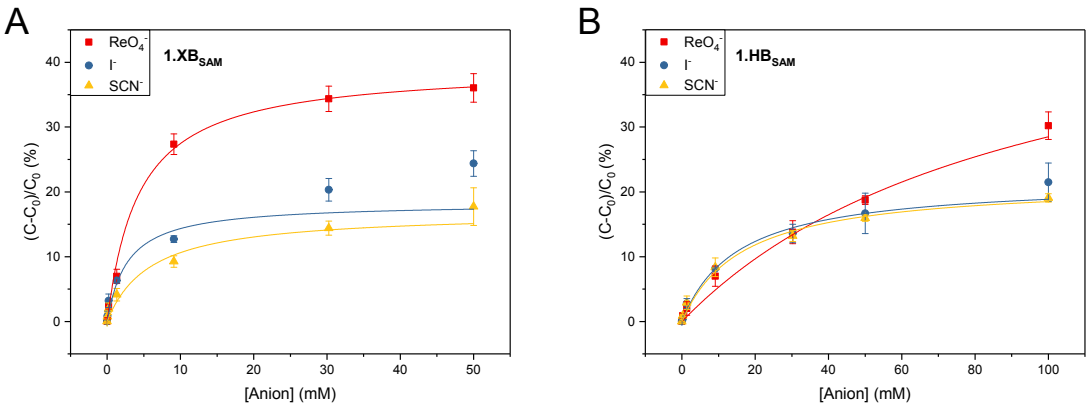


Figure S19. Normalized capacitance increase of 1.XB$_{SAM}$ (A) and 1.HB$_{SAM}$ (B) at OCP in the presence of increasing amounts of perrhenate (red squares), iodide (blue circles) and thiocyanate (yellow triangles). Fits were obtained according to a Langmuir adsorption model (eq. 2). Error bars represent one standard deviation across three separate electrodes. Note the different concentration ranges for both graphs.

The different magnitudes of the capacitance increase for different anions (e.g. up to 35% for perrhenate vs. 15% for thiocyanate) might arise from the different hydration of these anions.

The limit of detection (LOD) of the sensory interface was determined according to $LOD = \frac{3 * \sigma_{C_0}}{s}$ where σ_{C_0} is the standard deviation of the blank (interface in absence of target anion; baseline) and s the slope of the linear region of the sensor. It should be noted that due to the Langmuir adsorption behaviour no

true linear range exists, however at low concentrations (below 9 mM) the response is almost linear and a LOD can be calculated. When restricting the linear region to lower concentrations the LODs for all anions are even lower, in particular if only the slope at 0 equiv. anion is considered. The LOD for perrhenate, a surrogate for pertechnetate, is hereby low enough that pertechnetate sensing in nuclear waste water samples, whose pertechnetate levels have been reported in the 10-100 µM range, could be conducted.[6]

Importantly, it should also be noted that there is a difference in selectivity of **1.XB$_{SAM}$** and **1.HB$_{SAM}$** for the tested anions. This shows that anion binding is indeed dependent on the specifically engineered tetra-proto/iodo triazole binding site and not purely dominated by the desolvation (hydrophobicity) of the anions (i.e. Hofmeister bias). Thus, sensing of any desired anion should be achievable via the novel methodology, if the appropriately designed receptor is utilised.

Table S4. Binding constants, R^2 and y_{max} for various anions for 1.XB/HB$_{SAM}$ according to Langmuir adsorption isotherm (eq. 2). y_{max} - maximum capacitance increase at [Anion] = ∞.

	1.XB$_{SAM}$			**1.HB$_{SAM}$**		
Anion	**K (M^{-1})**	**R^2**	**y_{max} (%)**	**K (M^{-1})**	**R^2**	**y_{max}**
ReO_4^-	231	0.9899	39.3	11	0.9910	55.6
I^-	362	0.9740	18.3	66	0.9993	21.7
SCN^-	170	0.9796	16.9	61	0.9955	21.5

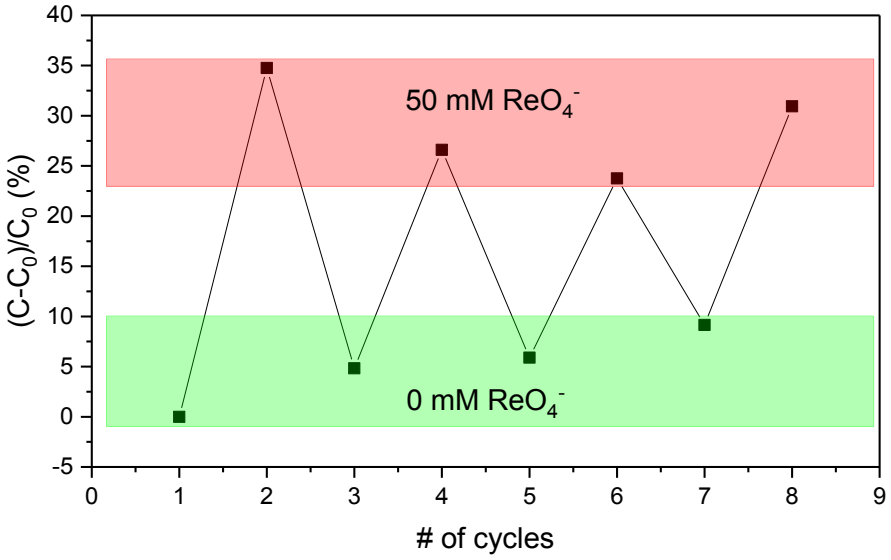


Figure S20. Normalized capacitance change of 1.XB$_{SAM}$ in alternating presence and absence of ReO_4^-.

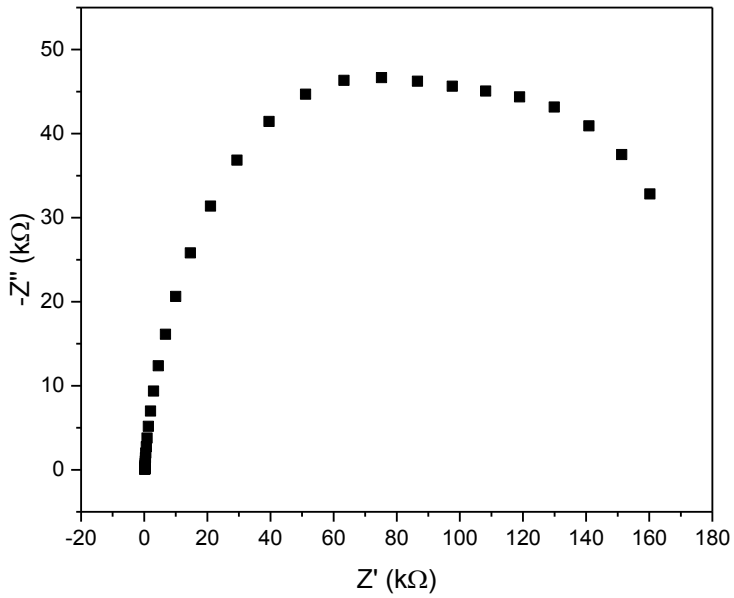


Figure S21. Impedimetric Nyquist plot of 1.XB$_{SAM}$ in 10 mM Fe(CN)$_6^{3-/4-}$ and 100 mM NaCl at 0.21 V in the AC frequency range of 100 kHz – 0.1 Hz.

As can be seen in Fig. S19, the charge-transfer resistance (R_{ct}) of **1.XB$_{SAM}$** in the presence of Fe(CN)$_6^{3-/4-}$ is very large (> 200 kΩ) and addition of target anions does not lead to significant perturbations. Potentially the high Faradaic impedance might not report on additional interfacial changes (binding). This is also relevant for many other thick/blocking films (e.g. films prepared by polymerisation or diazonium chemistry) whereby R_{ct} might not be a sensitive transducer for (an)ion binding while the capacitance could be. Furthermore, and in contrast to the non-Faradaic capacitive measurements, the impedimetric baseline stability of **1.XB$_{SAM}$** in the presence of Fe(CN)$_6^{3-/4-}$ is very poor.

S5. Solution-phase Binding Studies by ITC

Experimental details and detailed discussion about anion binding of **2.XB/HB** in solution have been reported separately.[2]

Table S5. Binding constants of various anions to 2.XB in water as determined by ITC, errors in parentheses. $\beta_2 = K_1 * K_2$.

Guest	β_2 [M]$^{-2}$	K_1 [M^{-1}]	K_2 [M^{-1}]
NaI	1.45 (0.04) × 10^{10}	3.16 (0.05) × 10^{4}	4.59 (0.14) × 10^{5}
$NaReO_4$	6.66 (0.55) × 10^{8}	4.91 (0.18) × 10^{4}	1.35 (0.07) × 10^{4}
NaSCN	3.40 (0.16) × 10^{7}	5.38 (0.20) × 10^{3}	6.33 (0.51) × 10^{3}
NaBr	3.43 (0.47) × 10^{6}	1.03 (0.11) × 10^{3}	3.34 (0.42) × 10^{3}
$NaClO_4$	1.21 (0.13) × 10^{5}	5.55 (0.63) × 10^{1}	2.19 (0.08) × 10^{3}

Table S6. Binding constants of various anions to 2.HB in water as determined by ITC, errors in parentheses.

Guest	K [M^{-1}]
NaI	3876 (21)
NaSCN	346 (14)
$NaClO_4$	2000 (14)

S6. References

1. J. Tkac and J. J. Davis, *J. Electroanal. Chem.*, 2008, **621**, 117-120.
2. A. Borissov, I. Marques, J. Y. C. Lim, V. Félix, M. D. Smith and P. D. Beer, *J. Am. Chem. Soc.*, 2019, **141**, 4119-4129.
3. Y. Shi, T. Suguri, C. Dohi, H. Yamada, S. Kojima and Y. Yamamoto, *Chem. Eur. J.*, 2013, **19**, 10672-10689.
4. M. J. Langton, Y. Xiong and P. D. Beer, *Chem. Eur. J.*, 2015, **21**, 18910-18914.
5. C. D. Bain, H. A. Biebuyck and G. M. Whitesides, *Langmuir*, 1989, **5**, 723-727.
6. B. Wakoff and K. L. Nagy, *Environ. Sci. Technol*, 2004, **38**, 1765-1771.