Electronic Supplementary Information

Glucose selective Surface Plasmon Resonance-based *bis*-boronic acid sensor

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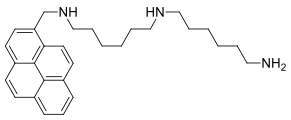
General

Thin layer chromatography was performed using commercially available Macherey-Nagel aluminium backed plates coated with a 0.20 mm layer of silica gel 60 Å with fluorescent indicator UV_{254}. These plates were visualised using either ultraviolet light of 254 nm or 365 nm wavelength, or by staining the plates with vanillin or ninhydrin solution. Silica gel column chromatography was carried out using Fisher or Sigma-Aldrich 60A silica gel (35-70 μm). Nuclear magnetic resonance (NMR) spectra were run in chloroform-D, methanol-D_4, dimethyl-D_6 sulfoxide. Where a Bruker AVANCE 300 was used, ^{1}H spectra were recorded at 300 MHz and ^{13}C at 75 MHz and are proton decoupled. Where a Bruker AVANCE 250 was used, ^{1}H spectra were recorded at 250 MHz and ^{13}C at 62 MHz and are proton decoupled. Chemical shifts (δ) are expressed in parts per million and are reported relative to the residual solvent peak or to tetramethylsilane as an internal standard in 1H and 13C spectra. The multiplicities and general assignments of the spectroscopic data are denoted as: singlet (s), doublet (d), triplet (t), double of doublets (dd), unresolved multiplet (m), broad (br) and aryl (Ar). Infrared spectra were obtained using a Perkin-Elmer 1000 FT-IR spectrometer. Characteristic absorption peaks are reported in wavelength (cm-1). Mass spectrometry was carried out on a Bruker Daltonics MicroTOF Mass spectrometer. All NMR spectra were recorded at room temperature unless otherwise stated, data was processed with Mestrec version 5.2.5-4731 and Topspin 2.0 (Version of: Nov 9th 2006). Chemical shifts (δ) are reported in ppm relative to TMS (δ 0.00) for the ^{1}H NMR and to chloroform (δ 77.0) for the ^{13}C NMR measurements, coupling constant *J* are expressed in Hertz.Capillary melting points were determined using Stuart MDP10. Commercially available solvents and reagents were used without further purification.

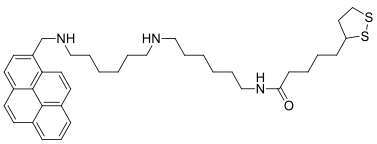
Experimental Procedures

Synthesis of N^1-(6-aminohexyl)-N^6-(pyren-1-ylmethyl)hexane-1,6-diamine:



Bis(hexamethylene)triamine **4** (4.4 g, 20 mmol) and pyrenecarboxyaldehyde (3.76 g, 0.016 mol) were dissolved in DCM / MeOH (1:1, 50 mL) and stirred at room temperature overnight. After crude NMR confirmed the imine formation, $NaBH_4$ (0.605 g, 16 mmol) was added slowly into the reaction and stirred for another 2 hours. After the reaction completed, water was added to quench the reaction. After most of solvents were evaporated, the residue was extracted with DCM and water to give the crude intermediate. This was followed by flash column chromatography using DCM / MeOH / 10 % propylamine as eluent to give the title compound (2.26 g, 33 %) as a light yellow powder; mp 91 ºC; IR (cm^{-1}) 709, 840, 1682, 2927, 2855, 3373; ESI mass [M+H] $C_{29}H_{40}N_3$ calculated 430.3222 found 430.3259; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 1.23-1.50 (m, 16H), 2.46 (t, *J* = 6.0 Hz, 4H), 2.57 (t, *J* = 6.0 Hz, 2H), 2.68 (t, *J* = 6.0 Hz, 2H), 4.38 (s, 2H), 7.88-7.94 (m, 4 H), 8.02-8.10 (m, 4 H), 7.26 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 25.7, 26.2, 26.3, 28.9, 29.0, 32.4, 41.0, 48.87, 48.9, 49.2, 50.8, 122.1, 123.6, 123.86, 123.9, 123.98, 124.0, 124.8, 125.95, 125.98, 126.4, 126.6, 128.0, 129.6, 129.8, 130.3, 133.0 (not all expected ^{13}C resonances observed).

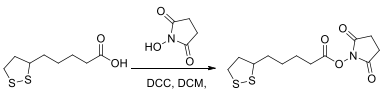
Synthesis of 5-(1,2-dithiolan-3-yl)-N-(6-((6-((pyren-1-ylmethyl)amino)hexyl)amino-hexyl)-pentanamide



N^1-(6-aminohexyl)-N^6-(pyren-1-ylmethyl)hexane-1,6-diamine (0.6 g, 1.4 mmol) was dissolved in DCM (40 mL) and small amount of DMF (2 mL) was added to improve the solubility. Synthetic lipoic acid NHS ester[1,2] (0.466 g, 1.5 mmol) was added to the solution and stirred at room temperature overnight. After the reaction finished, all solvents were evaporated and the residue was purified by flash column chromatography using DCM / MeOH as eluent to give the title compound as a brown powder (0.327 g, 38 %); mp 200 ºC (dec.); IR (cm^{-1}) 953, 1158, 1381, 1598, 2981, 2972, 3331, 3657; ESI mass [M+H] $C_{37}H_{52}N_3OS_2$ calculated 618.3552 found 618.3604; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 0.70-0.84 (m, 2H), 1.20-1.54 (m, 16H), 1.71-1.84 (m, 1H), 2.00-2.05 (m, 2H), 2.27-2.41 (m, 3H), 2.48-2.70 (m, 8H), 2.94-3.13 (m, 4H), 3.34-3.48 (m, 1H), 4.37 (s, 2H), 7.87-7.94 (m, 4H), 8.01-8.09 (m, 4H), 8.24 (d, *J*= 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 25.5, 26.6, 26.8, 27.15, 27.17, 28.1, 28.9, 29.1, 29.4, 29.9, 34.6, 36.5, 38.5, 39.3, 40.2, 49.3, 49.5, 49.8, 51.7, 56.5, 123.1, 124.7, 124.9, 125.0, 125.1, 125.9, 127.1, 127.5, 127.7, 129.0, 130.6, 130.8, 131.3, 133.8, 172.8 (not all expected ^{13}C resonances observed).

Synthesis of Lipoic Acid NHS Ester 2,5-dioxopyrrolidin-1-yl 5-(1,2-dithiolan-3-yl)pentanoate:

The synthetic method was modified from the references.[1,2]



DL-α-lipoic acid (or thioctic acid) (2.163 g, 10 mmol) was dissolved in DCM (50 mL) and cooled to 0 ºC. *N*-hydroxysuccinimide (NHS, 1.38 g, 12 mmol) and *N*, *N'*-dicyclohexyl carbodiimide (DCC, 2.48 g, 12 mmol) were then added to the stirred solution.

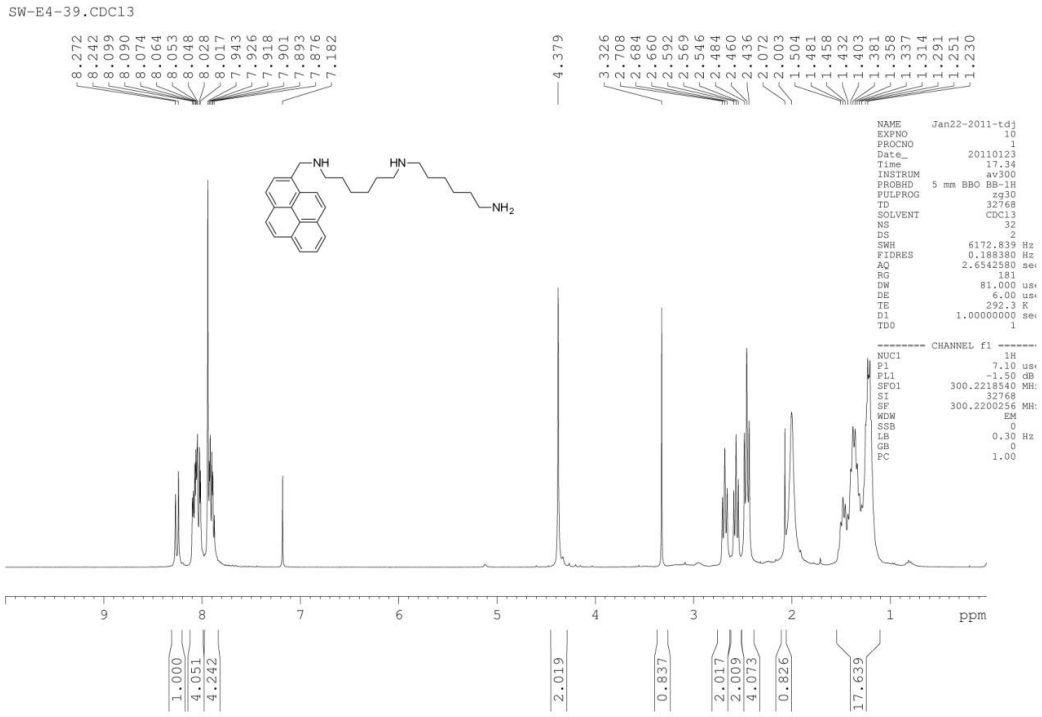
The reaction was continuously stirred and warmed to room temperature overnight. After the reaction finished, the reaction mixture was filtered through celite and the solvent was removed. The residue was then purified by flash column chromatography using DCM / MeOH as eluent to give lipoic acid NHS ester (2.8 g, 92 %); ESI mass [M+Na] $C_{12}H_{17}NNaO_4S_2$ calculated 326.0497 found 326.0486; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 1.45-1.55 (m, 2H), 1.61-1.77 (m, 4H), 1.81-1.92 (m, 1H), 2.35-2.46 (m, 1H), 2.56 (t, *J* = 7.5 Hz, 2H), 2.78 (m, 4H), 3.01-3.16 (m, 2H), 3.47-3.56 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 24.4, 25.6, 28.3, 30.8, 34.4, 38.5, 40.2, 56.1, 168.5, 169.2.

References

1. Stokes, R. J.; Macaskill, A.; Dougan, J. A.; Hargreaves, P. G.; Stanford, H. M.; Smith, W. E.; Faulds, K.; Graham, D. *Chem. Commun.* **2007**, 2811.
2. Chen, G.; Ning, X.; Park, B.; Boons, G.-J.; Xu, B. *Langmuir* **2009**, *25*, 2860.

NMR Spectrums

Proton NMR of N¹-(6-aminohexyl)-N⁶-(pyren-1-ylmethyl)hexane-1,6-diamine



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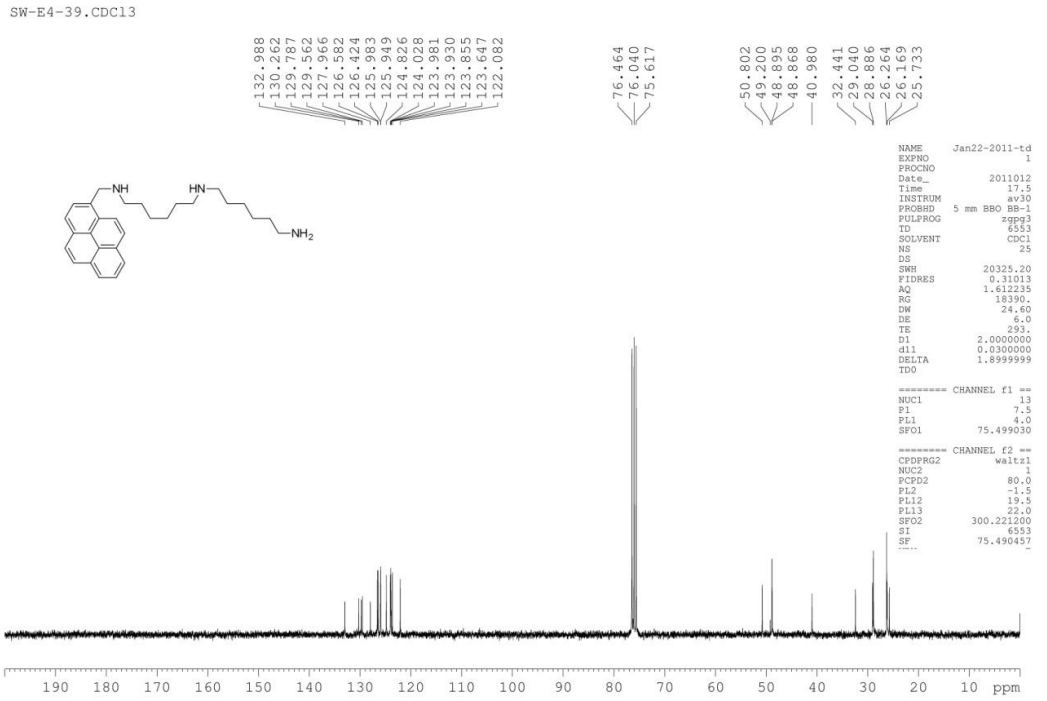
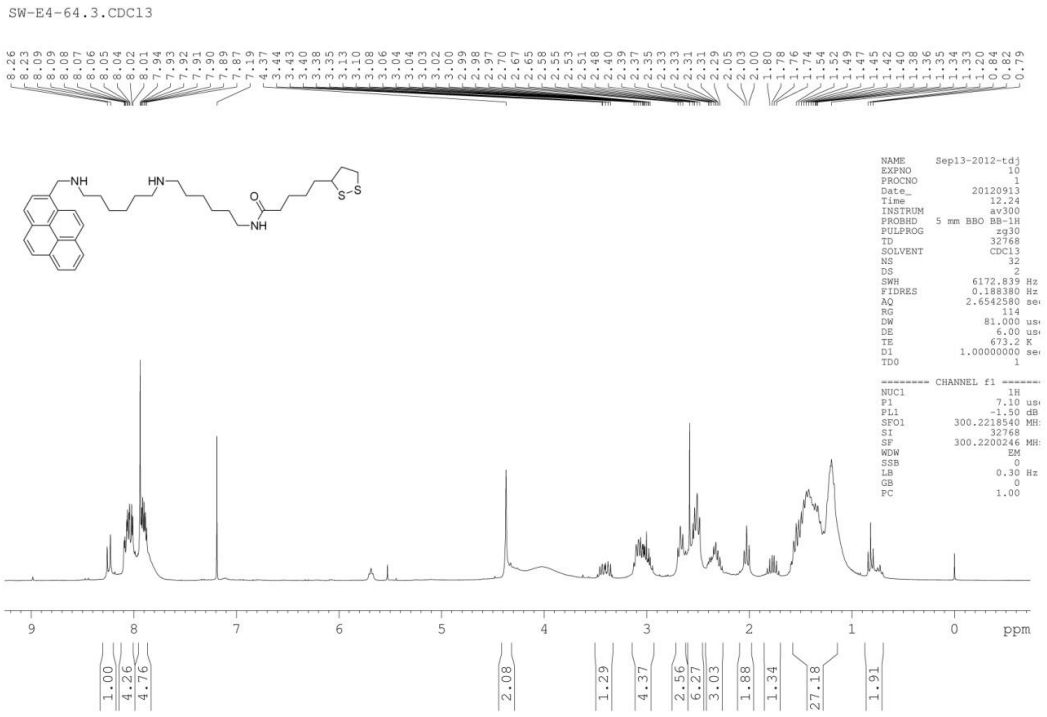
Carbon NMR of N¹-(6-aminohexyl)-N⁶-(pyren-1-ylmethyl)hexane-1,6-diamine



Proton NMR of 5-(1,2-dithiolan-3-yl)-N-(6-((6-((pyren-1-ylmethyl)amino)hexyl)amino-hexyl)-pentanamide



Carbon NMR of 5-(1,2-dithiolan-3-yl)-N-(6-((6-((pyren-1-ylmethyl)amino)hexyl)amino-hexyl)-pentanamide