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Rewritable Chiroptical Switching Supramolecular Nanolayers

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Chemical Reaction Scheme for Producing (*S*)-3-methyl-3-amino-1-(4'cyano-4-azobenzene)pyrrolidine (Compound 3)



Compound 3

General Experimental Methods

Thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} aluminium sheets and developed by UV light and anisaldehyde solution (40 mL H_2SO_4 / 100 mL ethanol / 1.5 mL acetic acid / 12 mL anisaldehdye). Solvents were dried according to literature procedures¹. All solvents were removed by evaporation under reduced pressure.

Flash column chromatography was performed with silica gel (Fluorochem 60A, 40-60 micron, 12 g) packs utilising a Combiflash Rf Teledyne ISCO purification system.

Melting points were recorded on a differential scanning calorimeter (TA Instruments Ltd DSC Q1000 V9.9) running from 30-300 °C at 10 C° / min.

Optical rotation values [α] were determined using a Perkin Elmer Model 241 polarimeter, and are recorded in units of 10⁻¹ deg cm² g⁻¹.

Microanalyses were performed using a Carlo-Erba 1106 elemental analyser.

Infrared spectra were carried out using a Perkin-Elmer Spectrum One spectrometer fitted with a diamond ATR accessory (Graseby Specac Golden Gate) and using a liquid nitrogen cooled MCT detector. All spectra were averaged over 128 scans at a resolution of 4 cm⁻¹.

¹H, ¹³C, and ¹⁹F NMR spectra were recorded in CDCl₃ (unless otherwise stated) on a Varian Inova-500 spectrometer and reported as follows: chemical shift δ (ppm) (number of protons, multiplicity, coupling constant *J* (Hz), assignment). All ¹³C NMR spectra were proton decoupled. The chemical shifts are reported using the residual signal of CHCl₃ as the internal reference ($\delta_{H} = 7.26$ ppm; $\delta_{C} = 77.16$ ppm). All chemical shifts are quoted in parts per million relative to tetramethylsilane ($\delta_{H} = 0.00$ ppm) and coupling constants are given in Hertz. Assignment of spectra was carried out using COSY, HSQC, and HMBC experiments.

Mass Spectra were recorded on a Hiden HPR20 mass spectrometer (fitted with a quadropole analyser scanning across the 5–500 atomic mass unit range utilising chemical ionisation mode) in combination with a Perkin Elmer Pyris 1 Thermogravimetric Analyser (TGA). Solid samples were heated across the 30-300 °C temperature range at a rate of 10 °C min⁻¹ and subsequent volatile components were transported from the TGA to the mass analyser via a

heated quartz inlet capilliary (QIC) tube utilising Helium (CP Grade) as a carrier gas at a rate of 50 ml min⁻¹.

Pulsed plasma deposition of glycidyl methacrylate precursor (+98%, Aldrich, further purified using several freeze-pump-thaw cycles) was carried out in an electrodeless cylindrical glass reactor (5 cm diameter, 520 cm³ volume, base pressure of 1 x 10^{-3} mbar, and with a leak rate² better than 2.1 x 10^{-10} kg s⁻¹⁰ ¹) enclosed in a Faraday cage. The chamber was fitted with a gas inlet, a Pirani pressure gauge, a 30 L min⁻¹ two-stage rotary pump attached to a liquid nitrogen cold trap, and an externally wound copper coil (4 mm diameter, 9 turns, spanning 8-15 cm from the gas inlet). All joints were grease free. An L-C network was used to match the output impedance of a 13.56 MHz radio frequency (RF) power generator to the partially ionised gas load. The RF power supply was triggered by a signal generator and the pulse shape monitored with an oscilloscope. Prior to each experiment, the reactor was cleaned by scrubbing with detergent, rinsing in water and propan-2-ol, followed by oven drying. The system was then reassembled and evacuated. Further cleaning entailed running an air plasma at 0.2 mbar pressure and 50 W power for 30 min. Next a fused silica slide (10 mm diameter, 0.1 mm thickness, UQG Optics Ltd) was inserted into the centre of the reactor, and the chamber pumped back down to base pressure. At this stage, glycidyl methacrylate monomer vapour was introduced at a pressure of 0.2 mbar for 5 min prior to ignition of the electrical discharge. The optimum conditions for high structural retention corresponded to a peak power of 40 W, and a duty cycle on-time of 20 µs and off-time equal to 20 ms. Typical deposition rates and film thicknesses used were 15 nm min⁻¹ and 150 nm respectively.

Derivatization of the epoxide-group-containing nanofilms with the chiroptical molecule (*S*)-3-methyl-3-amino-1-(4'-cyano-4-azobenzene)pyrrolidine (Compound 3) entailed immersion of the coated substrate into 5–40 μ M dilutions in a saline sodium citrate solution (3 M sodium chloride, 0.3 M sodium citrate at pH = 4.5) for 72 h. Afterwards, the samples were thoroughly rinsed in saline sodium citrate solution, high purity water, methanol, and propan-2-ol in order to remove any unreacted (*S*)-3–methyl-3-amino-1-(4'-cyano-4-azobenzene)pyrrolidine molecules.

Film thickness measurements were carried out using а spectrophotometer (nkd-6000, Aquila Instruments Ltd). The acquired transmittance-reflectance curves (350-1000 nm wavelength range) were fitted to a Cauchy model for dielectric materials using a modified Levenberg-Marguardt method ³.

X-ray photoelectron spectroscopy (XPS) analysis was undertaken on a VG ESCALAB MKII spectrometer. The instrument was equipped with an unmonochromated Mg K $\alpha_{1,2}$ X-ray source (1253.6 eV) and a hemispherical analyser operating in the constant analyser energy mode (CAE, pass energy = 20 eV). XPS core level spectra were fitted to Gaussian component peaks^{4,5} with equal full-width-at-half-maximum (fwhm) using Marquardt minimization software assuming a linear background. Elemental concentrations were calculated using experimentally derived instrument sensitivity (multiplication) factors where, C(1s) : O(1s) : N(1s) = 1.00 : 0.45 : 0.95. The absence of any Si(2p) signal from the underlying silica substrate was taken as being indicative of pin-hole free film coverage with a thickness exceeding the XPS sampling depth (2 - 5 nm)⁶.

UV-Vis absorption spectra of the (*S*)-3-methyl-3-amino-1-(4'-cyano-4azobenzene)pyrrolidine (Compound 3) derivatized pulsed plasma deposited poly(glycidyl methacrylate) nanofilms were measured using a UV-Vis-NIR spectrometer (Varian Carey 5) across the 200 – 700 nm wavelength range.

Linear birefringence of the (S)-3-methyl-3-amino-1-(40-cyano-4azobenzene) pyrrolidine (Compound 3) derivatized pulsed plasma poly(gylcidyl methacrylate) films was investigated by using a small 2 mm diameter laser (2 mW power output, Laserglow Technologies) to supply 488 nm linear s-polarized pump radiation, Figure S11. Light from a halogen lamp (Type 7023, FCR a1/215, Phillips Lighting), which was polarized at 45° with respect to the polarized direction of the writing light, was used as a probe light. Its wavelength was chosen to be 633 nm with a monochromator (nkd-6000 spectrophotometer, Aquila Instruments Ltd). The induced alignment in the sample film was monitored by the measurement of the power of the light after an analyzer with a photodetector (Aquila Instruments Ltd), and the data were collected with a computer. The birefringence (δn) induced by the change in the alignment of the azobenzene moiety was calculated with the following equation:

 $I / I_0 = \sin^2 d \pi \delta n / (\lambda)$

Where I is the transmitted light after the analyzer, I_0 is the intensity of the light passing through the polarizers, d is the film thickness, and λ represents the wavelength of the probe light.



Figure S1. Schematic diagram of the experimental laser setup for linear birefringence measurements using polarizers (P), mirror (M), detector (D), shutter (S), and analyser (A).

Supramolecular chiral structure in the (*S*)-3-methyl-3-amino-1-(4'-cyano-4-azobenzene)pyrrolidine derivatized nanofilms was induced by exposure to circular polarized light (CPL) generated by passing 488 nm radiation (2 mm diameter laser with 2 mW power output, Laserglow Technologies) through a multiple order $\lambda/4$ quartz waveplate.

Circular dichroism spectroscopy (CD) of the (S)-3-methyl-3-amino-1-(4'cyano-4-azobenzene)pyrrolidine derivatized pulsed plasma deposited poly(glycidyl methacrylate) nanofilms following exposure to circularly polarized light (CPL) irradiation was recorded across the 250 – 650 nm wavelength range with a spectropolarimeter (Jasco J-810) transmitting a sequence of equal amounts of alternating pulses of left and right circularly polarized light at a switching rate of 50 kHz at each wavelength. The obtained spectra show the change in the molar extinction coefficient ($\Delta \epsilon$) for right and left-circularly polarized light as a measure of the difference in sample absorbance of the right and left-circularly polarized light as a function of wavelength after passing through the sample (due to the predominant reduction of the electric field vector (E) of one type of polarized light form over the other form). Circular dichroism spectra were recorded in degrees of ellipticity where $\Delta \theta~$ = 3298.2 $\Delta \epsilon,$ and tan θ

 $= (E_{I} - E_{r}) / (E_{I} + E_{r}).$

4-cyano-4'-hydroxy-azobenzene (1)^{7,8,4}



4-Aminobenzonitrile (1.18 g, 0.01 mol, Aldrich) was dissolved in 50 ml of conc. sulphuric acid and 50 ml of H₂O and the mixture cooled to 0°C. A solution of sodium nitrite (0.69 g, 0.01 mol, Aldrich) in H₂O (50ml), was slowly added whilst maintaining the reaction temperature below 5 °C. To the cooled solution, sodium hydroxide (0.46 g, 0.02 mol) and phenol (0.94 g, 0.01 mol, BDH Chemicals Ltd), dissolved in 10 ml of H₂O, were added leading to the precipitation of azobenzene dye (Compound 1). The reaction mixture subsequently stirred for a further 1 h at room temperature and the precipitated azobenzene dye isolated by filtration and washed with H₂O. The residue was then dissolved in chloroform (150 ml) and concentrated in vacuo to yield the title compound (1) as a bright orange powder (2.0 g, 90 %); mp = 203-204 °C (Lit. $mp^9 = 202-204$ °C). Calculated for C₁₃H₉N₃O: C, 69.96; H, 4.04; N, 18.83%; found: C, 68.92; H, 4.04; N, 18.56. v_{max} (ATR) 3232 (OH), 3064, 2236 (CN), 1601, 1583, 855 cm⁻¹; $\delta_{\rm H}$ (500MHz, CDCl₃) 7.93 (2H, d J = 8.5, 3-H), 7.91 (2H, d J = 8.7, 2'-H, 7.78 (2H, d J = 8.5, 2-H), 6.98 ppm (2H, d J = 8.7, 3'-H); 5.31 ppm (1H, bs, OH). δ_C (125MHz, CDCl₃) 162.1, 155.0, 146.1, 133.0, 125.2, 122.6 , 118.0, 115.6, 112.6; *m*/*z* (CI) 222.07 (M-H⁻).

4-cyano-4'-trifluoromethanesulfonyloxyazobenzene (2)¹⁰.



To a solution of 4-cyano-4'-hydroxyazobenzene (**Compound 1**, 0.10 g, 0.50 mmol) in anhydrous pyridine (10 mL, Aldrich), cooled to 0 °C, was dropped trifluoromethanesulfonic anhydride (0.16 g, 0.56 mmol, Aldrich) over a 5 min period. The mixture was stirred for 5 min at this temperature, allowed to warm to room temperature and stirred for further 18 h. The solution was poured over ice (100 g) and 5 % aqueous HCl (150 ml) was added. The resultant organic precipitate was filtered to yield a terracotta orange powder (1.59 g, 89.1 %) without further purification: mp = 73-74 °C. Calculated for C₁₄H₈O₃N₃SF₃: C, 47.32, H, 2.25, N, 11.83%; found C, 47.39, H, 2.22; N, 11.61 %. v_{max} (ATR) 3094, 3063, 2236 (CN); 1251 cm⁻¹, 1215 (SO₃), 1133 (SO₃) , 855 cm⁻¹. $\delta_{\rm H}$ (500MHz, CDCl₃) 8.06 (2H, d *J* = 8.9, ArH), 8.01 (2H, d *J* = 8.6, ArH), 7.84 (2H, d *J* = 8.6, ArH), 7.42 (2H, d *J* = 8.9, ArH); $\delta_{\rm C}$ (125MHz, CDCl₃) 154.1, 151.4, 151.3, 133.3, 125.0, 123.5, 122.3, 118.3, 114.7, 119.8 (q, ¹*J*_{C,F} = 320.9 Hz, CF₃); $\delta_{\rm F}$ (188 MHz, CDCl₃) -72.71 ppm (CF₃). *m/z* (CI⁻) 354.02 (M-H⁻).





microwave palladium А pressure tube was charged with (II)dibenzylideneacetone $(Pd_2(dba)_3)$ (15.1)0.027 mmol), mg, bis(diphenylphosphino)ferrocene (dppf), (30.6 mg, 0.054 mmol) and NaO^tBu (78.2 mg, 0.82 mmol). The solid materials were then suspended in 8 mL of toluene and the reaction vessel was degassed by bubbling argon gas through a needle for 10 min. 4-Cyanoazobenzenetriflate (Compound 2) (150 mg, 0.54 mmol) was dissolved in 1 mL of toluene was then added and the tube sealed with a teflon-lined septum cap. (S)-3-methyl-3-aminopyrrolidine (81.62 mg, 0.815 mmol, Accel Pharmtech LLC) dissolved in 1 mL of toluene was then added to the tube by syringe. The reaction mixture was heated at 100 °C for 5 h when TLC analysis of the reaction mixture indicated complete consumption of the 4-cyanoazobenzenetriflate (Compound 2). The reaction mixture was cooled to room temperature and 2 g of silica gel added and the solvent removed in vacuo. The resultant impregnated silica was dry loaded on to a silica gel column and purified by flash-column chromatography eluting wiht 20 - 40 % ethyl acetate / petroleum. Following recrystallization from chloroform the title amine (Compound 3) was obtained as a ruby red solid (86.4 mg, 52 %). Mp: 210-211 °C; $[\alpha]_{D}^{25}$ = -16.3 (c 0.55, MeOH). Calculated for C₁₈H₁₉N₅: C, 70.82, H, 6.23, N, 22.95%; found C, 70.88, H, 6.03; N, 23.09 %. v_{max} (ATR) 3477 cm⁻¹ (v_{NH2} antisymmetric primary amine); 3371 (v_{NH2} symmetric primary amine); 3094 cm⁻¹ (v_{CH} aromatic); 3063 cm⁻¹ (v_{CH} aromatic) 2945 cm⁻¹ (v_{CH} aliphatic); 2850 cm⁻¹ (v_{CH} aliphatic); 2236 cm⁻¹ (v_{CN} nitrile); 1602 cm⁻¹ ($v_{C=C}$ aromatic); 1587 cm⁻¹ ($v_{C=C}$ aromatic); 1550 cm⁻¹ (δ_{NH2} primary amine scissors); 1440 cm⁻¹ (v_{CH2} aliphatic); 854 cm⁻¹ (δ_{CH} 1,4-disubstituted benzene) 828 cm⁻¹ (δ_{NH2} primary amine wag). δ_{H} (500MHz, CD₃OD) 7.88 (2H, d, J 8.9, 3-H); 7.82 (2H, d, J 8.9, 2-H) 7.80 (2H, d, J 8.9, 2'-H), 6.86 (2H, d, J 8.9, 3'-H), 3.29 ppm (1H, quint J 6.5, 5"-HH), 3.14 ppm (1H, quint J 6.5, 5"-HH), 2.92 (1H, d J 11.6, 2"-HH); 2.85 (1H, d J 11.6, 2"-HH),1.84 (2H, t J 7.8, 4"-H₂), 1.33 (3H, s, CH₃). δ_C (125MHz, CD₃OD) 164.2,

155.4, 145.4, 133.0, 125.6, 122.7, 118.4, 116.0, 112.4, 57.7, 46.3, 44.9, 38.9, 24.7. *m*/*z* (CI) 304.39 [M-H]⁻.



Figure S2. FTIR spectrum of Compound 1.



Figure S3. ¹H NMR spectrum of Compound 1.



Figure S4. ¹³C NMR spectrum of Compound 1.



Figure S5. FTIR spectrum of Compound 2.



Figure S6. ¹H NMR spectrum of Compound 2.



Figure S7. ¹³C NMR spectrum of Compound 2.



Figure S8. ¹⁹F NMR spectrum of Compound 2.



Figure S9. FTIR spectrum of Compound 3.



Figure S10. ¹H NMR spectrum of Compound 3.



Figure S11. ¹³C NMR spectrum of Compound 3.

Analysis of (S)-3-methyl-3-amino-1-(4'-cyano-4-azobenzene)pyrrolidine (Compound 3) Derivatized Pulsed Plasma Deposited Poly(glycidyl methacrylate) Nanofilms

Table S1. XPS atomic percentages for (S)-3-methyl-3-amino-1-(4'-cyano-4-azobenzene)pyrrolidine (Compound 3) derivatized pulsed plasma deposited poly(glycidyl methacrylate) nanofilms.

Sample	Elemental Composition		
	% C	% O	% N
Theoretical glycidyl methacrylate (GMA)	70.0	30.0	-
Pulsed plasma poly(glycidyl methacrylate)	70.6	29.4	-
Theoretical glycidyl methacrylate + Compound 3	78.8	9.1	12.1
Pulsed plasma poly(glycidyl methacrylate) +	72.1	25.1	2.8
Compound 3 (5 μM)			
Pulsed plasma poly(glycidyl methacrylate) +	74.5	20.3	5.2
Compound 3 (10 μM)			
Pulsed plasma poly(glycidyl methacrylate) +	76.6	15.2	8.2
Compound 3 (15 μM)			
Pulsed plasma poly(glycidyl methacrylate) +	78.7	9.4	11.9
Compound 3 (20 μM)			
Pulsed plasma poly(glycidyl methacrylate) +	79.1	9.2	11.7
Compound 3 (25 μM)			
Pulsed plasma poly(glycidyl methacrylate) +	78.8	9.3	11.9
Compound 3 (30 μM)			
Pulsed plasma poly(glycidyl methacrylate) +	79.0	9.0	12.0
Compound 3 (35 μM)			
Pulsed plasma poly(glycidyl methacrylate) +	78.9	9.1	12.0
Compound 3 (40 µM)			



Figure S12. XPS nitrogen concentration following (*S*)-3-methyl-3-amino-1-(4'-cyano-4-azobenzene)pyrrolidine (Compound 3) functionalization of pulsed plasma deposited poly(glycidyl methacrylate) nanofilm for 72 h as a function of dilution.



Figure S13. UV-Vis absorption spectrum of 20 μ M (*S*)-3-methyl-3-amino-1-(4'-cyano-4-azobenzene)pyrrolidine (Compound 3) derivatized pulsed plasma deposited poly(glycidyl methacrylate) nanofilm.

Table S2. Linear birefringence measurements of a 20 μM (*S*)-3-methyl-3-amino-1-(4'cyano-4-azobenzene)pyrrolidine (Compound 3) derivatized pulsed plasma poly(gylcidyl methacrylate) nanofilm monitored using cross-polarised 633 nm probe radiation and polarized 488 nm pump radiation (using Figure S1).

Sample	Birefringence / δn
20 μM (S)-3-methyl-3-amino-1-(4'-cyano-4- azobenzene)pyrrolidine (Compound 3) derivatized pulsed plasma deposited poly(glycidyl methacrylate) nanofilm (i.e. pump radiation off)	0.001
20 μM (<i>S</i>)-3-methyl-3-amino-1-(4'-cyano-4- azobenzene)pyrrolidine (Compound 3) derivatized pulsed plasma deposited poly(glycidyl methacrylate) nanofilm + 250 s exposure to linear polarized 488 nm pump radiation (i.e. pump radiation on).	0.088
20 μ M (<i>S</i>)-3-methyl-3-amino-1-(4'-cyano-4- azobenzene)pyrrolidine (Compound 3) derivatized pulsed plasma deposited poly(glycidyl methacrylate) nanofilm + 250 s exposure to linear polarized 488 nm pump radiation + 150 s no pump radiation (i.e. pump radiation off)	0.071
20 μ M (<i>S</i>)-3-methyl-3-amino-1-(4'-cyano-4- azobenzene)pyrrolidine (Compound 3) derivatized pulsed plasma deposited poly(glycidyl methacrylate) nanofilm + 250 s exposure to linear polarized 488 nm probe radiation + 250 s exposure to circular polarized 488 nm probe radiation	0.002



Figure S14. Circular dichroism (CD) spectra of (*S*)-3-methyl-3-amino-1-(40-cyano-4azobenzene)pyrrolidine (Compound 3) derivatized pulsed plasma deposited poly(glycidyl methacrylate) film following a cycle of ordering using 488 nm radiation (2 mm laser diameter and laser intensity = 2 mW cm⁻²) (a) 3.5 h exposure of right circularly polarized light (black squares); (b) exposure (a) followed by 3.5 h exposure of left circularly polarized light (white squares); (c) exposure (b) followed by 3.5 h exposure to right circularly polarized light (black circles); (d) exposure (c) followed by 3.5 h exposure of left circularly polarized light (white circles); (e) exposure (d) followed by 3.5 h exposure to right circularly polarized light (black triangles); (f) exposure (e) followed by 3.5 h exposure of left circularly polarized light (white triangles); and (g) exposure (f) followed by 3.5 h exposure to right circularly polarized light circularly polarized light (black diamonds).



Figure S15. Relative intensity of the background subtracted circular dichroism (CD) spectra at 500 nm wavelength for a (S)-3-methyl-3-amino-1-(40-cyano-4-azobenzene) pyrrolidine (Compound 3) derivatized pulsed plasma deposited poly(glycidyl methacrylate) film (laser intensity 1.9 mW cm⁻²). Measurements correspond to the azobenzene derivatized plasmachemical film following each 3.5 h exposure to right circularly polarized light (black squares) and then 3.5 h exposure to left circularly polarized light (white squares) using 488 nm radiation, as a function of the cumulative exposure (photon fluence).

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