Polymerization of low molecular weight hydrogels to form electrochromic polymers.

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SUPPORTING INFORMATION

1.0 Experimental

Carbazole acetic acid synthesis:

The carbazole acetic acid was prepared following a literature procedure.[1] Carbazole (8.35 g, 0.05 mol) was dissolved in dimethyl sulfoxide (30 mL) and ground NaOH (6 g, 0.15 mol) was added to the solution. The mixture was heated to 85°C for 30 minutes to give a dark-brown solution. Bromoacetic acid (8.34 g, 0.06 mol) was added to the solution in portions for 30 minutes. The resulting solution was stirred overnight, and then poured into 200 mL cold distilled water. The precipitate was filtered under vacuum. HCL (1 M) was added dropwise to the filtrate to reach a pH of between 3 and 4. The resulting white precipitate was collected by filtration under vacuum and washed well with water. The yield was 75%.

^{1}H NMR (DMSO) 8.16 (d, ArH, 2H, J_{HH} = 7.6 Hz), 7.55 (d, ArH, 2H, J_{HH} = 8.2 Hz), 7.44 (dd, ArH, 2H, J_{HH} = 9.3 Hz, J_{HH} = 1.1 Hz), 7.21 (dd, ArH, 2H, J_{HH} = 7.8 Hz, J_{HH} = 1.1 Hz), 5.23 (s, NCH_2, 2H) ppm. ^{13}C NMR (DMSO) 170.5, 140.6, 125.5, 122.1, 120.0, 118.7, 109.3, 44.9 ppm. MS (CI) 226 ($[M+H]^+$). Accurate mass calculated for $C_{14}H_{12}NO_2$: 226.0863. Found: 226.0860.

Standard coupling methodology:

N-Methylmorphine (1.5 eq.) and isobutylchloroformate (1 eq.) were added to carbazole acetic acid (4 g, 0.017 mol) in chloroform (150 mL) at 0 ºC. A solution of alanine methyl ester (1 eq.) and *N*-methylmorphine (1.5 eq.) in chloroform was added. The solution was stirred at

room temperature overnight. The solution was washed with distilled water (2x100 mL), hydrochloric acid (100 mL, 0.1 M), aqueous potassium carbonate (100 mL, 0.1 M), and distilled water again (2x100 mL) and dried with magnesium sulfate, and the solvent was removed in vacuum to give the product in a 53 % yield.

^{1}H NMR ($CDCl_3$) 8.12 (d, ArH, 2H, J_{HH} = 7.8 Hz), 7.05 (m, ArH, 2H), 7.36 (d, ArH, 2H, J_{HH} = 8.2 Hz), 7.31 (m, ArH, 2H), 6.08 (d, NH, 1H, J_{HH} = 7.2 Hz), 4.93 (s, NCH_2, 2H), 4.59 (m, CHNH, 1H), 3.61 (s, OCH_3, 3H), 1.22 (d, CH_3, 3H, J_{HH} = 7.2 Hz) ppm. ^{13}C NMR ($CDCl_3$) 172.4, 167.9, 140.5, 126.5, 123.6, 120.7, 120.4, 108.7, 524, 47.9, 47.2, 17.9 ppm. MS (ES) 333 ([M+Na]$^+$). Accurate mass calculated for $C_{18}H_{18}N_2O_3Na$: 333.1215. Found: 333.1212.

Deprotection of the C-terminus:

A solution of THF:water (30 mL:5 mL) was added to the solution of carbazole alanine-methanoate. Lithium hydroxide (0.3 g) was added. The solution was stirred overnight. After this time, distilled water (100 mL) was added, and then hydrochloric acid (100 mL, 1.0 M) was added drop wise until pH was lowered to pH3. The resulting precipitate was collected by filtration and washed with water to give the product in an 87 % yield

^{1}H NMR (DMSO) 8.75 (d, NH, 1H, J_{HH} = 7.4 Hz), 8.15 (d, ArH, 2H, J_{HH} = 7.7 Hz), 7.54 (d, ArH, 2H, J_{HH} = 8.2 Hz), 7.43 (t, ArH, 2H, J_{HH} = 7.3 Hz), 7.21 (t, ArH, 2H, J_{HH} = 7.3 Hz), 5.13 (d, NCH, 1H, J_{HH} = 16.8 Hz), 5.04 (d, NCH, 1H, J_{HH} = 16.8 Hz), 4.26 (m, CHNH, 1H), 1.34 (d, CH_3, 3H, J_{HH} = 7.3 Hz) ppm. ^{13}C NMR (DMSO) 173.9, 167.3, 140.6, 125.6, 122.2, 120.1, 118.9, 109.4, 47.6, 15.2, 17.3 ppm. MS (ES) 319 ([M+Na]$^+$). Accurate mass calculated for $C_{17}H_{16}N_2O_3Na$: 319.1059. Found: 319.1055.

Hydrogelation:

GdL method: 10 mg of the protected amino acid was suspended in deionized water (2 mL) and an equimolar amount of NaOH (0.1 M) was added to dissolve the protected amino acid. The mixture was stirred for about 30 minutes to provide a clear solution and the pH of the solutions was measured (about 10). Measured quantities of GdL were added to the solutions to control the pH to form gels. The samples were left to stand overnight.

Electropolymerisation: Electropolymerisation was performed using either an AUTOLAB PGSTAT 12 and GPES control software or a Dropsens μSTAT 400 BIPOTENTIOSTAT and Dropview control software. AFM was carried out on a Nanosurf FlexAFM; FTIR was done

on a PerkinElmer Spectrum 100 spectrophotometer and UV-Vis using a Varian Cary 50 probe spectrophotometer

Electropolymerisation from acetonitrile:

In initial studies, a solution of 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) in acetonitrile was prepared, into which was dissolved 2 mg mL^{-1} of Carb-Ala. This solution was put into a beaker and covered with a custom made lid to prevent evaporation. TEC-15 FTO glass (Sigma) was used as a working electrode, with conductive copper tape wrapped around the upper section to ensure good electrical contact with the wires, the surface area was ~ 0.5 cm^2. Polymerisation was carried out by repeated cycling between 0 V and 1.2 V versus Pt at a scan rate of 200 mVs^{-1}.

Larger area samples were also prepared for SEM. Carb-Ala was dissolved 0.1 mol dm^{-3} TBATFB in acetonitrile at a concentration of 5 mg/ml. The working area was FTO glass (average area 5.8 cm^2, or which ~80% was dipped into solution). A copper wire was glued to the FTO slide with silver paint used to ensure a good contact; this contact was then sealed with epoxy resin. Platinum mesh was used as the counter electrode, and platinum wire as the pseudo-reference electrode. Polymerization was carried out by repeated cyclic voltammograms (10 scans) between 0 – 1.1 V vs Ag/AgCl at a scan rate of 40 mV/s.

Electropolymerisation of drop coated films:

A 6 mM solution of the monomer in THF was prepared and 8 μL was used to drop-coat 10 μg of the monomer onto TEC-15 FTO glass electrode. This primer layer was then electropolymerised by cyclic voltammetry from 0 – 1.1 V at 200 mV s^{-1} for 100 scans. Further monomer was deposited onto the primer layer, 10 μg at a time, with each drop being allowed to evaporate before the next drop was added. 200 μg were deposited in this step. This second layer was then polymerised by the same method as the first. The primer layer ensured that the polymer properly adhered to the surface during polymerisation. For carbazole-based polymers, a 1 M solution of perchloric acid was used as the electrolyte. The coated glass electrode was used as the working electrode, platinum foil as the counter electrode and a silver/silver chloride reference electrode (3 mol dm^{-3} KCl) as the reference electrode.

Electrochemical growth of gel layers: Gel layers were grown on either an FTO glass working electrode or a 1.6 mm diameter gold disc electrode. Platinum foil was used as the counter electrode, and a silver/silver chloride reference electrode was used. The method has

been described in detail elsewhere, briefly 100 μL of a 100 mg mL^{-1} solution of the monomer was added to 5 mL of a 0.1 mol dm^{-3} NaCl solution. The pH of the solution was adjusted to between 7 and 8 and then 36.5 mg hydroquinone was added. Oxidation of hydroquinone releases protons which cause a surface localised pH drop, inducing gel formation on the electrode surface. A potential of 0.7 V was applied for 500 s. The gel grown on disc electrodes is hemi-spherical reflecting the diffusion of protons away from the surface.

In the case of the larger samples grown for SEM studies, gel layers were grown by cyclic voltammetry measurements which were run continuously for 30 scans between a potential range of 0 - 1.0 V vs Ag/AgCl at a scan rate of 40 mV/s. Carb-Ala gelator solution concentration was 5 mg/ml in 0.1 moldm^{-3} NaCl with 1 equivalent of 0.1 M NaOH. Hydroquinone was added to a 10 ml aliquot adjusted to pH 8 at a concentration of 7.2 mg/ml.

Electropolymerisation of gels: poly(Carb-Ala) was grown by placing a preformed gel into 1 mol dm^{-3} perchloric acid. Electropolymerisation was initiated by cycling to above the first oxidation potential for the monomer, with each subsequent scan redox peaks appeared that were connected to the oxidation and re-reduction of oligomer or polymer on the surface.

Large area films were prepared on FTO slides by running continuous cyclic voltammetry measurements (100 scans) between 0 V and 1.1 V vs Ag/AgCl at a scan rate of 40 mV/s. The electrolyte was 1 M $HClO_4$. The polymer layer grown became darker/browner after drying overnight the brown colour is most likely due to the decomposition of hydroquinone.

2.0 Results and Discussion.

Electropolymerisation of drop coated Carb-Ala film in 1 mol dm^{-3} perchloric acid.

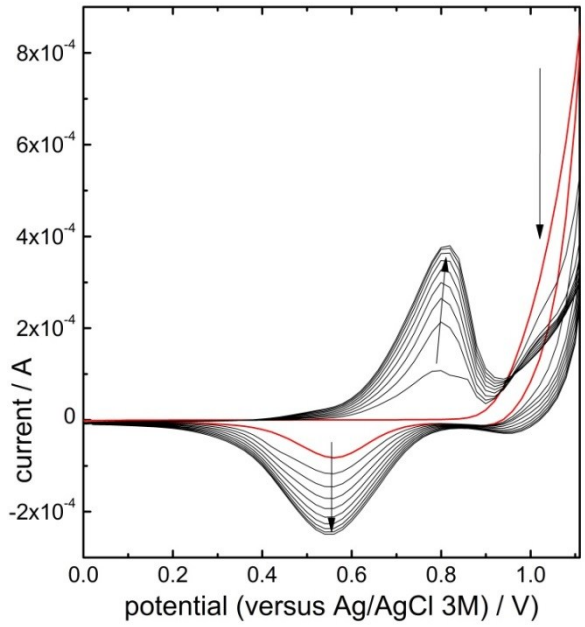

Figure S1. First ten CVs taken during the electropolymerisation of a drop-coated film of carb-ala-OH in an aqueous solution of 1 mol dm^{-3} perchloric acid. Monomer oxidation is occurring above ~0.95 V and the redox wave below 0.9 V is due to oxidation and re-reduction of the polymer.

Electropolymerisation of Carb-Ala dissolved in acetonitrile

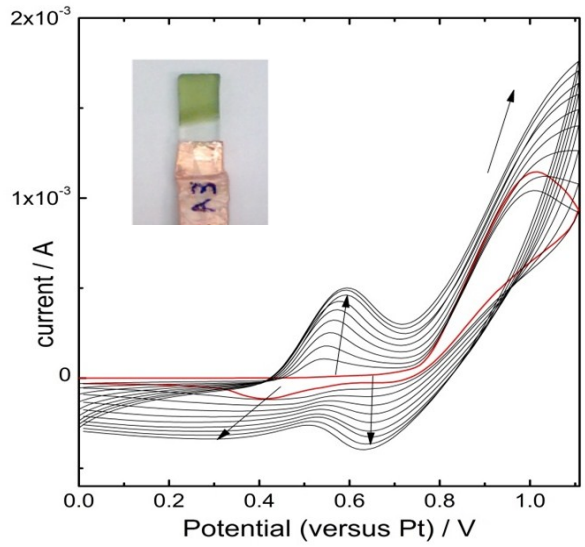

Figure S2. Cyclic voltammograms measured during the electropolymerisation of Carb-Ala from acetonitrile. The first scan is shown in red and change in peaks in subsequent scans is shown by the direction of the arrows. The scan rate was 50 mV s^{-1}. The inset shows a photograph of the green poly(Carb-Ala) film deposited on the electrode surface.

Electropolymerisation of carbazole dissolved in acetonitrile.

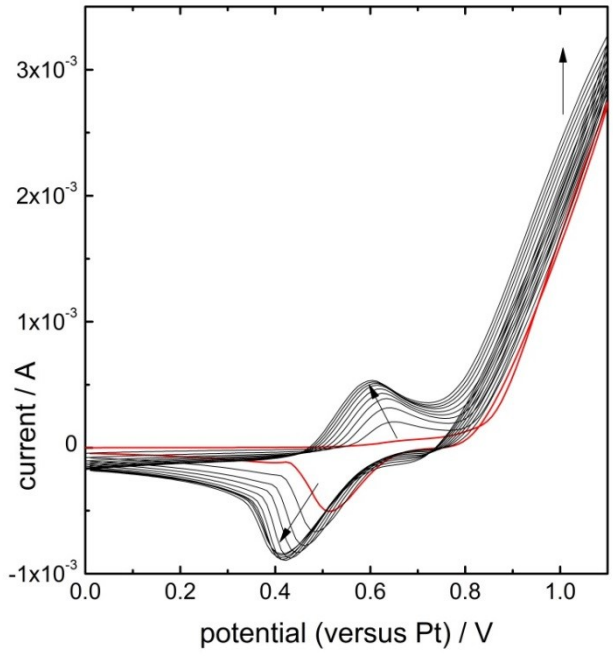

Figure S3. First ten CVs taken during the electropolymerisation of 2 mg/mL carbazole from a 0.1 mol dm^{-3} solution of TBATFB. Monomer oxidation is occurring above 0.8 V and the redox wave centred on 0.56 V is due to the oxidation and re-reduction of the surface supported polymer.

FTIR comparing poly(carbazole) with poly(Carb-Ala) grown from acetonitrile solution and poly(Carb-Ala) grown from a gel.

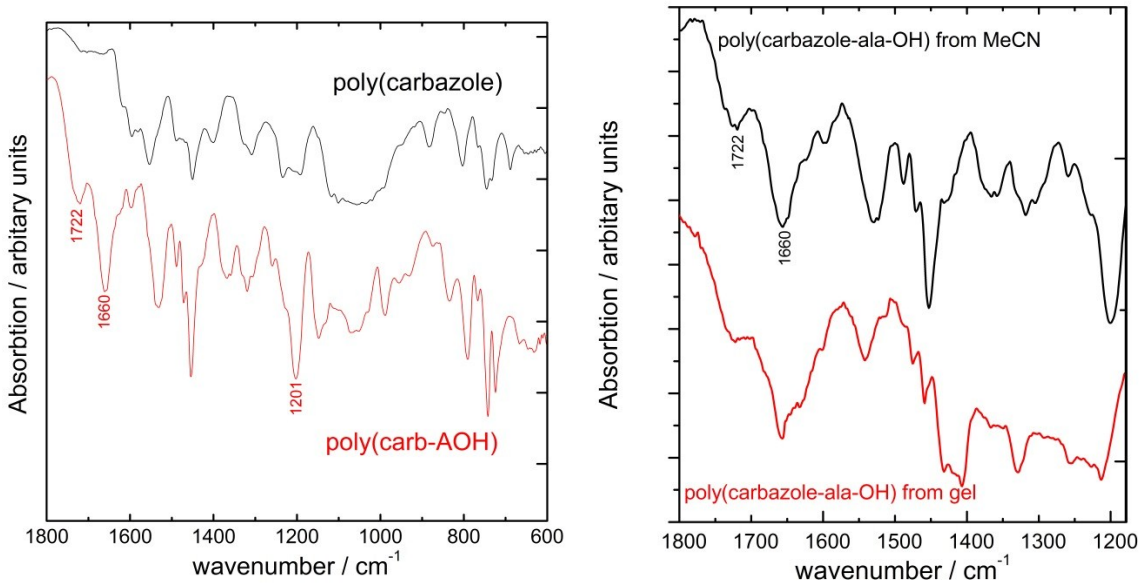

Figure S4. (a) FTIR spectra of poly(carbazole) and poly(Carb-Ala) . The films were grown by the electropolymerisation of monomer dissolved in acetonitrile in the presence of 0.1 mol dm^{-3} tetrabutylammonium tetrafluoroborate background electrolyte. (b) FTIR of poly(Carb-Ala) grown from a solution in MeCN (reproduced from Figure S4 (a)) and poly(Carb-Ala) grown from a pre-formed gel (prepared and polymerized in in D_2O).

NMR spectra comparing Carb-Ala with poly(Carb-Ala) grown from acetonitrile solution and poly(Carb-Ala) grown from a gel.

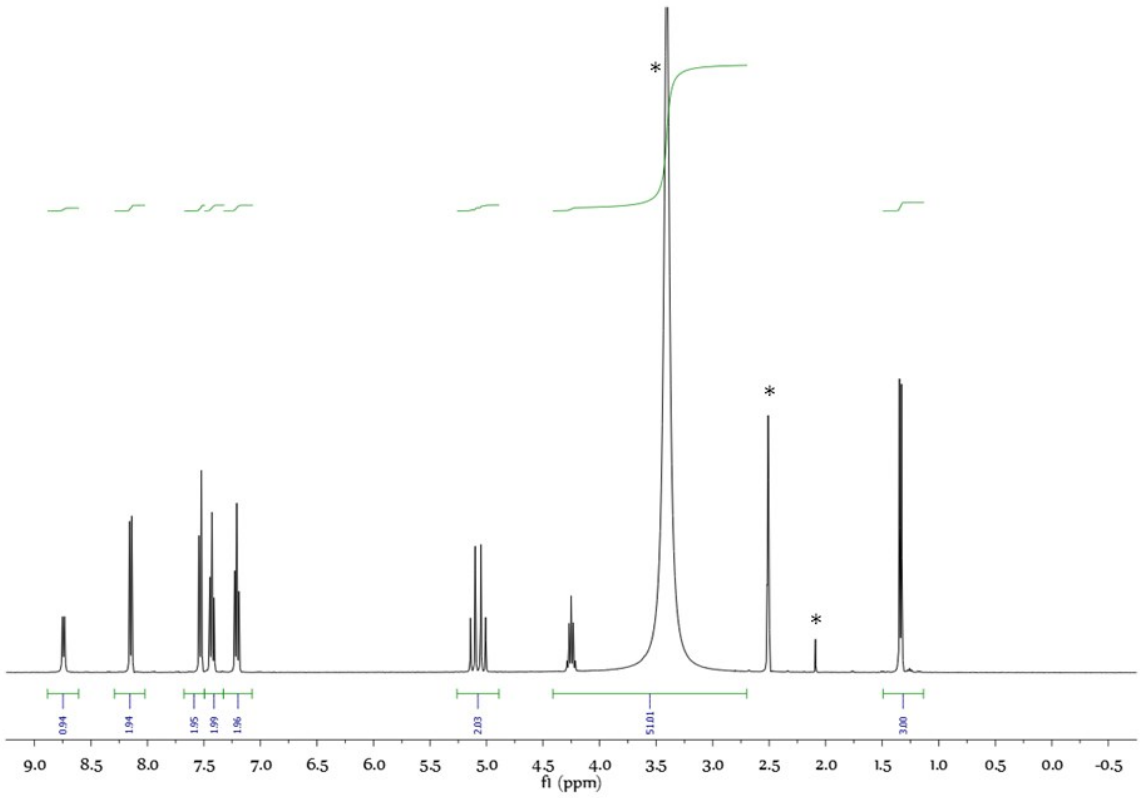

Figure S5. ^{1}H NMR spectrum of Carb-Ala collected in d_6-DMSO. Solvent peaks due to solvents are marked with a *.

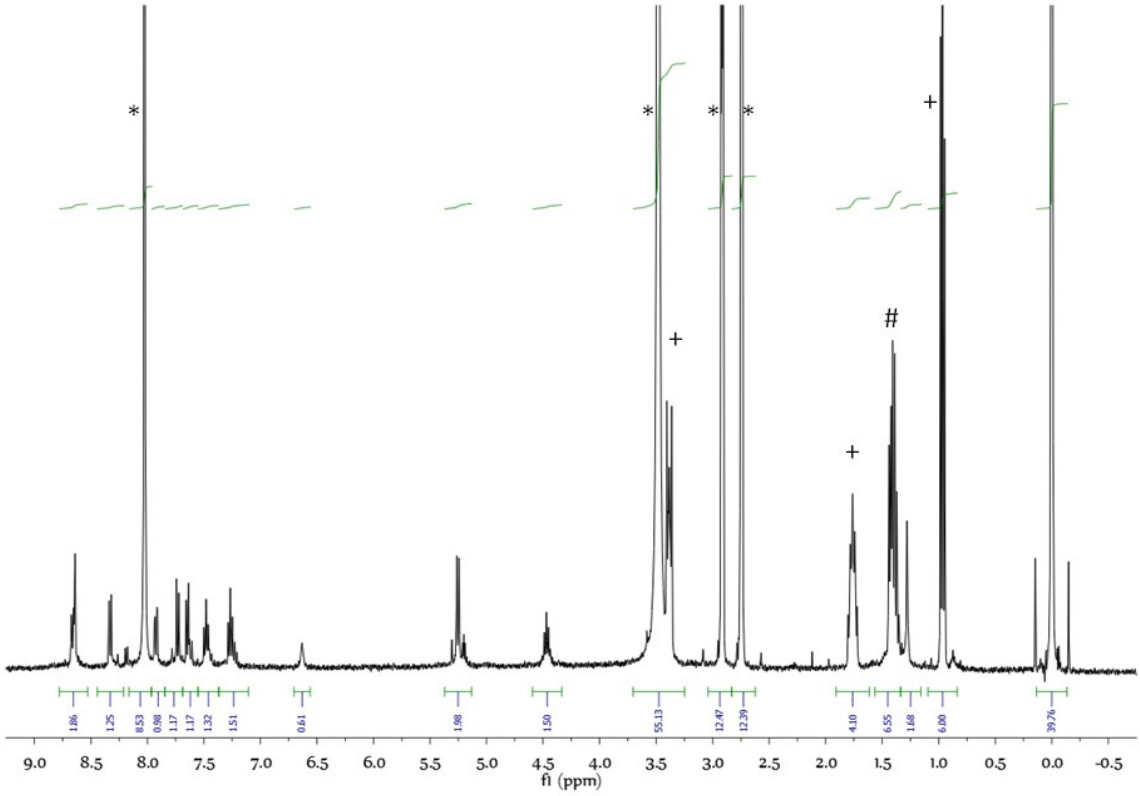

Figure S6. ^{1}H NMR spectrum of poly(Carb-Ala) grown from a solution in MeCN collected in d_7-DMF. Peaks due to solvents are marked with a *. The peaks due to the tetrabutylammonium tetrafluoroborate buffer are marked with a +. The peak parked with a # is due to both one of the CH_2 in the tetrabutylammonium group as well as the CH_3 from the alanine. The peak at 0 ppm is from TMS, added as a calibrant. . As can be seen by comparison with Fig. S7, there is residual monomer left, since no attempt was made to fractionate the sample.

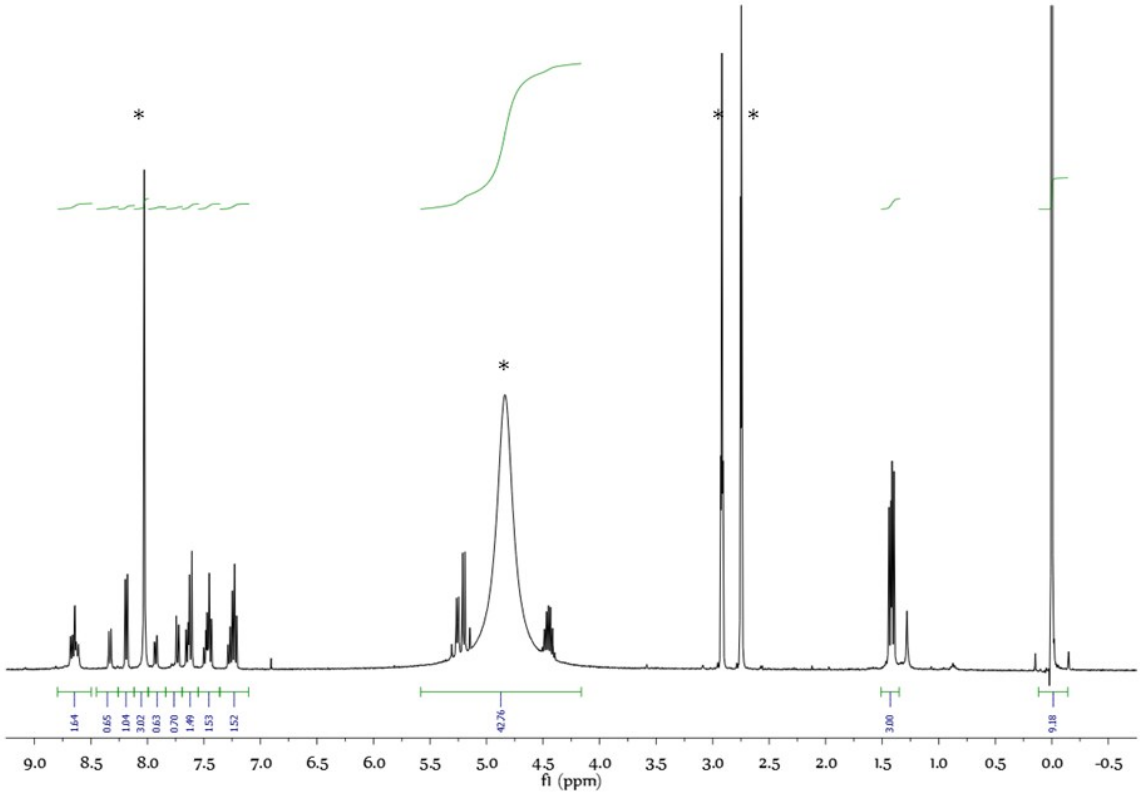

Figure S7. ^{1}H NMR spectrum of poly(Carb-Ala) grown from a pre-formed gel collected in d_7-DMF. Peaks due to solvents are marked with a *. The peak at 0 ppm is from TMS, added as a calibrant. For this sample, a gel was grown on an electrode, then polymerized. The polymer was removed from the film, freeze-dried and dissolved in DMF for NMR. As can be seen by comparison with Fig. S7, there is residual monomer left, since no attempt was made to fractionate the sample. Comparing Fig. S8 and Fig. S9, there is more residual monomer present in the sample prepared from the pre-formed gel. We attribute this to the differences in polymerisation protocol. When directly polymerized from solution, the polymer is less likely to trap monomer. However, ensuring that complete polymerisaton of the gel has occurred is difficult before analysis.

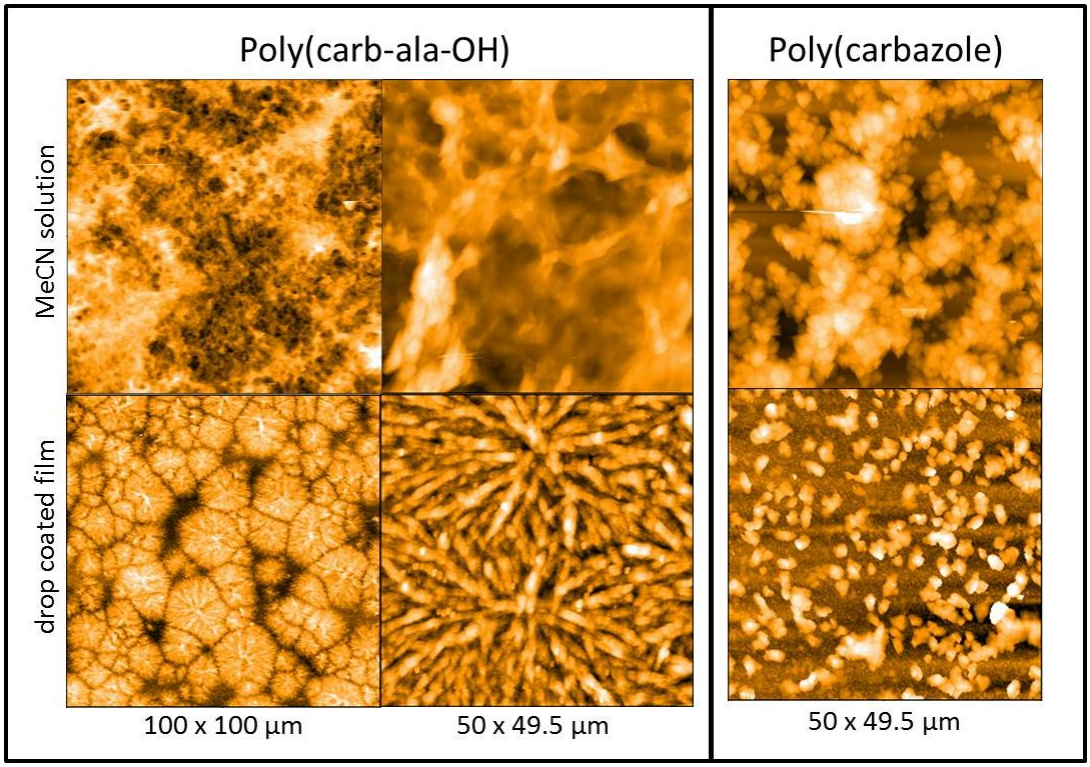

Figure S8. AFM images showing poly(Carb-Ala) and poly(carbazole) deposited from solution (above) and formed by electropolymerizing a drop coated film in aqueous solution (below). The samples were all formed on FTO glass slides.

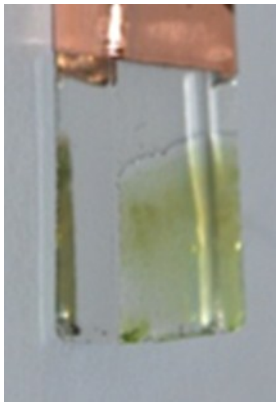

Figure S9. Photograph of polymer formed from a Carb-Ala gel, the film was hard to image as the polymer remained soft and 'gel-like'.

References

1. Y.-P. Tian, X.-J. Zhang, J.-Y. Wu, H.-K. Fun, M.-H. Jiang, Z.-Q. Xu, A. Usman, S. Chantrapromma and L. K. Thompson, *New Journal of Chemistry*, 2002, **26**, 1468-1473.