

Supporting Information

***Dynachromes*– Dynamic Electrochromic Polymers Capable of Property Tuning and Patterning via Multiple Constitution Component Exchange**

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| | |
|--|----|
| Experimental | 3 |
| On-substrate polymerization of 3 | 3 |
| Exchange reaction to prepare 5 from 3 | 3 |
| Patterning by dynamic component exchange | 3 |
| Figure S1. On-substrate polymerization of 1 and 2 followed by ATR-IR spectroscopy | 4 |
| Figure S2. On-substrate preparation of 5 from 3 by exchange with 4 followed by ATR-IR spectroscopy. ATR-IR spectrum of 5 obtained by direct on-substrate condensation of 1 and 4 is also shown for comparison. | 4 |
| Figure S3. On-substrate preparation of 5 from 3 via exchange with 4 followed by ATR-FTIR spectroscopy. Derivative spectra of 3 and 5 from 1 and 4 are also shown. | 5 |
| Figure S4. Average film thickness of spray coated films. | 6 |
| Figure S5. Cyclic voltammograms of a film of 5 from 3 on ITO measured in 0.1M TBAPF ₆ /acetonitrile with Ag/Ag ⁺ reference and Pt wire counter electrodes, respectively..... | 7 |
| Figure S6. Cyclic voltammograms of a film of 3 on ITO measured in 0.1M TBAPF ₆ /acetonitrile with Ag/Ag ⁺ reference and Pt wire counter electrodes, respectively..... | 8 |
| Figure S7. CIE <i>L*a*b*</i> color coordinates of a film of 5 from 3 in its original (+), oxidized (+) and neutral (+) states. | 9 |
| Figure S8. Photographs of a film of 5 from 3 (bottom half) on ITO in its original (left), oxidized (middle), and neutral (right) states. The top half of the film is pristine 3 showing its non-electrochromic behavior..... | 10 |
| Figure S9. Photographs of exchanged polymer films obtained from 3 using different molar ratios of 1:4 (ratios are shown below pictures). For comparison, pristine 3 as well as 5 prepared from direct condensation of 1 and 4 are also shown. | 11 |
| Figure S10. Absorbance spectra of the films shown in Figure S9. | 12 |
| Figure S11. CIE <i>L*a*b*</i> color coordinates of the films shown in Figure S9. | 13 |
| Figure S12. ¹ H-NMR of pristine 7 obtained by constitutional component exchange from 1 and 6. | 14 |
| Figure S13. ¹³ C NMR of pristine 7 obtained by constitutional component exchange from 1 and 6. | 15 |
| Figure S14. High resolution mass spectrum of 7 obtained by constitutional component exchange from 1 and 6. | 16 |
| Figure S15. Liquid chromatograph monitored at 254 nm of dichloromethane washings obtained from component exchange of 3 with an excess of 6. The peak at 6.9 min corresponds to unreacted 6. | 17 |
| Figure S16. Liquid chromatograph monitored by total ion count at <i>m/z</i> =573 of dichloromethane washings obtained from component exchange of 3 with an excess of 6..... | 17 |
| Figure S17. ESI mass spectrum of the peaks from Figure S16 corresponding to 7..... | 18 |
| Figure S18. Liquid chromatograph monitored at 254 nm of dichloromethane washings obtained from component exchange of 5 with an excess of 6. The peak at 6.9 min corresponds to unreacted 6. | 18 |
| Figure S19. ESI mass spectra of the peaks at 10.1 (left) and 11.0 (right) min. retention time (top) from the liquid chromatograph monitored as a function of total ion count (bottom)..... | 19 |

Experimental

On-substrate polymerization of **3**

A 1 mL dichloromethane/acetone (9/1 v/v) solution of **1**/**2**/Sc(OTf)₃ in 1:1:0.13 molar ratio was sprayed onto 10 cm² glass or ITO slides using a compressed air spray-gun. The concentration of **1** was 2 mg/mL. The films were placed on a hot plate and covered with a glass crystallization dish. Two vials of trifluoroacetic acid (TFA; 1 mL) each were placed in the crystallization dish to obtain a TFA saturated environment. The substrates were heated at 90° C for 1 hour to ensure the polymerization of **3**. The substrates were then washed with 0.5 vol % triethylamine in dichloromethane to remove any oligomers/monomers and also to neutralize the polymer. The substrates were finally rinsed with neat dichloromethane.

Exchange reaction to prepare **5** from **3**

A dichloromethane solution of **4** was sprayed onto films of **3** using the compressed air spray gun. The mole amount of **4** sprayed on to the films of **3** for dynamic component exchange was equal to the mole amount of **1** used on the same area for the polymerization of **3**. The substrates were heated at 120°C in the TFA saturated environment for 1 hour to complete the exchange. The substrates were subsequently washed as above.

Patterning by dynamic component exchange

A dichloromethane solution of **6** was spray coated onto films of either **5** or **3** through a mask using the compressed air spray gun. An excess amount of **6** (~ 4 equivalents with respect to **1** used during polymerization on the same area) was necessary to obtain a soluble pattern. Lesser amounts of **6** yielded an insoluble pattern on the substrate. The substrates were then heated at 90°C in the acid saturated environment for 1 hour to complete the exchange. The substrates were then rinsed with the dichloromethane solutions similar to the previous methods.

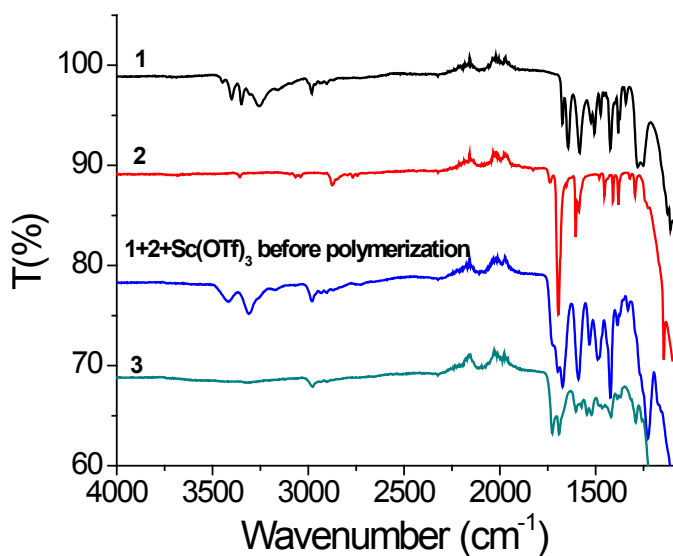


Figure S1. On-substrate polymerization of **1** and **2** followed by ATR-IR spectroscopy

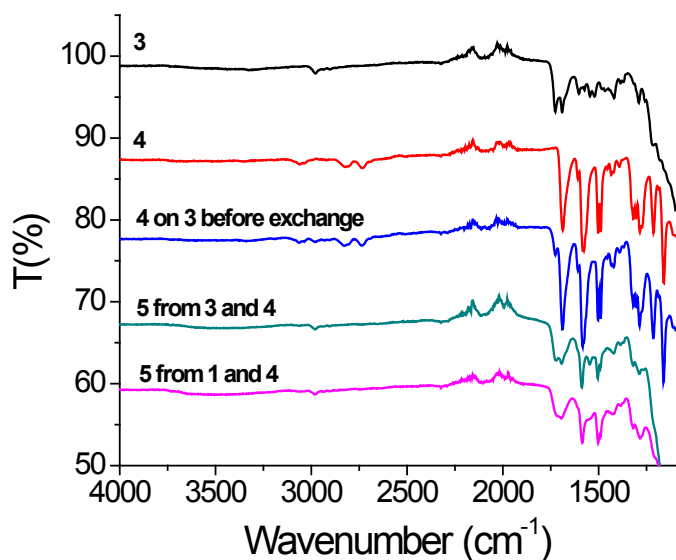


Figure S2. On-substrate preparation of **5** from **3** by exchange with **4** followed by ATR-IR spectroscopy. ATR-IR spectrum of **5** obtained by direct on-substrate condensation of **1** and **4** is also shown for comparison.

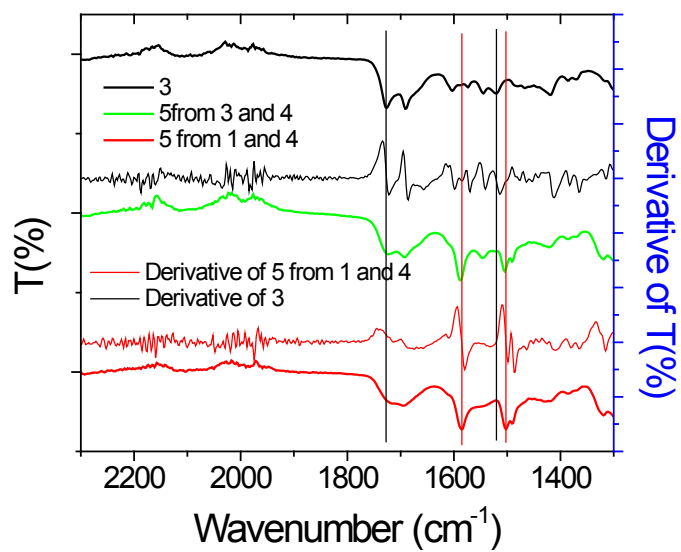


Figure S3. On-substrate preparation of **5** from **3** via exchange with **4** followed by ATR-FTIR spectroscopy. Derivative spectra of **3** and **5** from **1** and **4** are also shown.

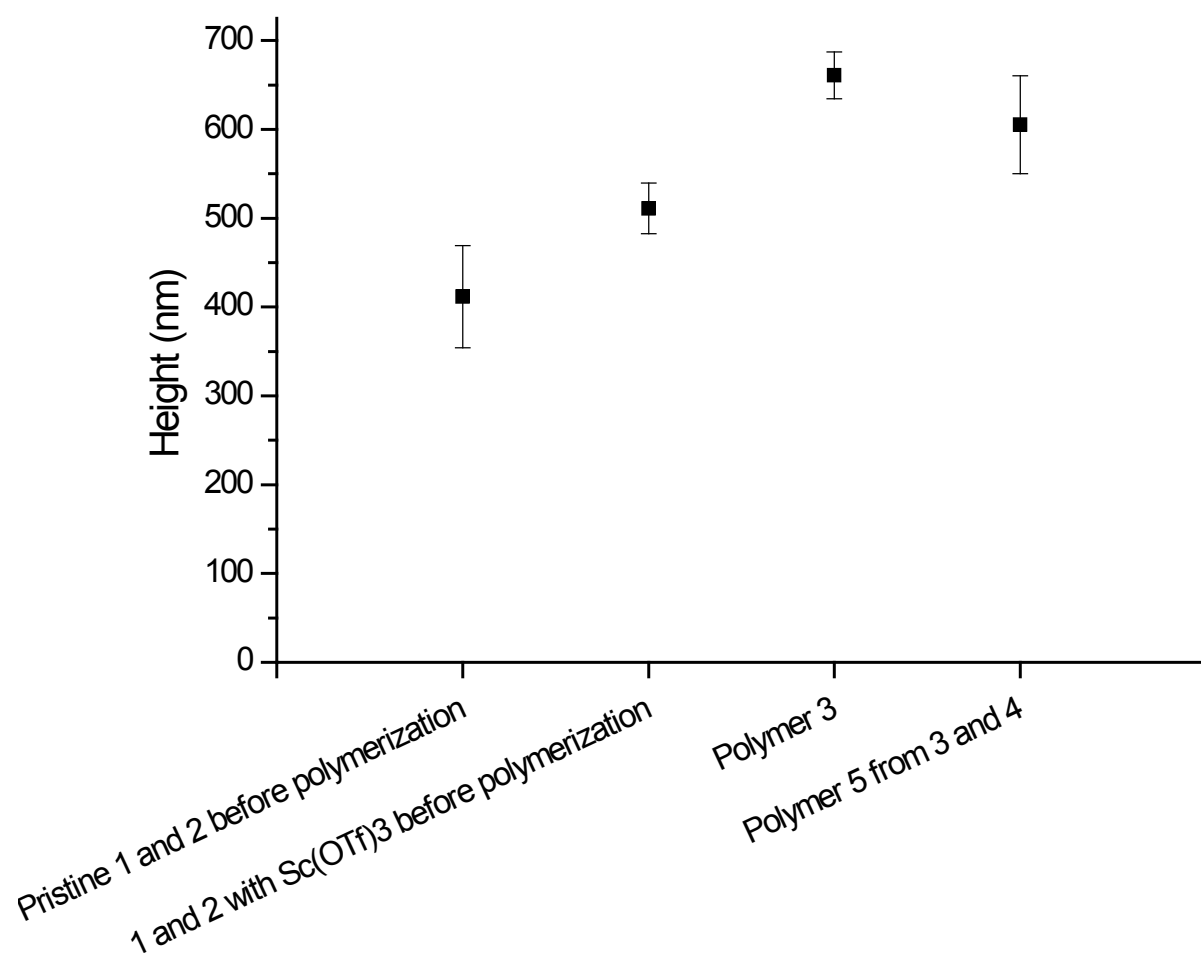


Figure S4. Average film thickness of spray coated films.

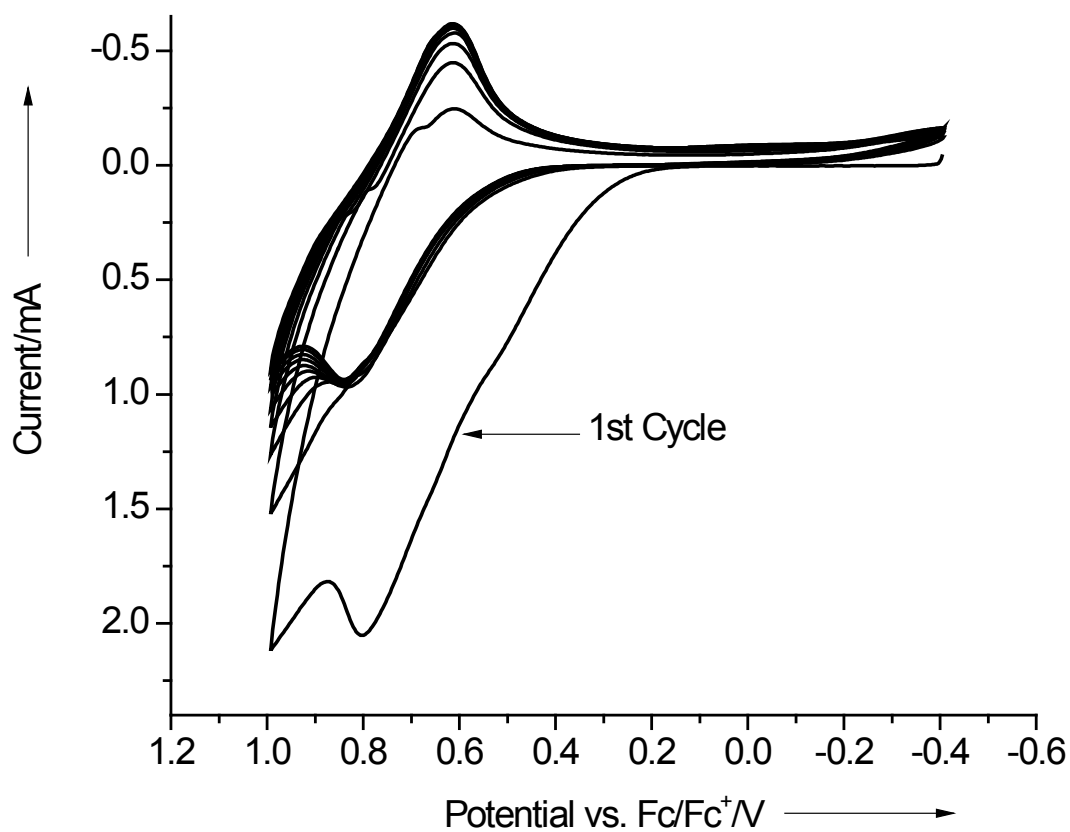


Figure S5. Cyclic voltammograms of a film of **5** from **3** on ITO measured in 0.1M TBAPF₆/acetonitrile with Ag/Ag⁺ reference and Pt wire counter electrodes, respectively.

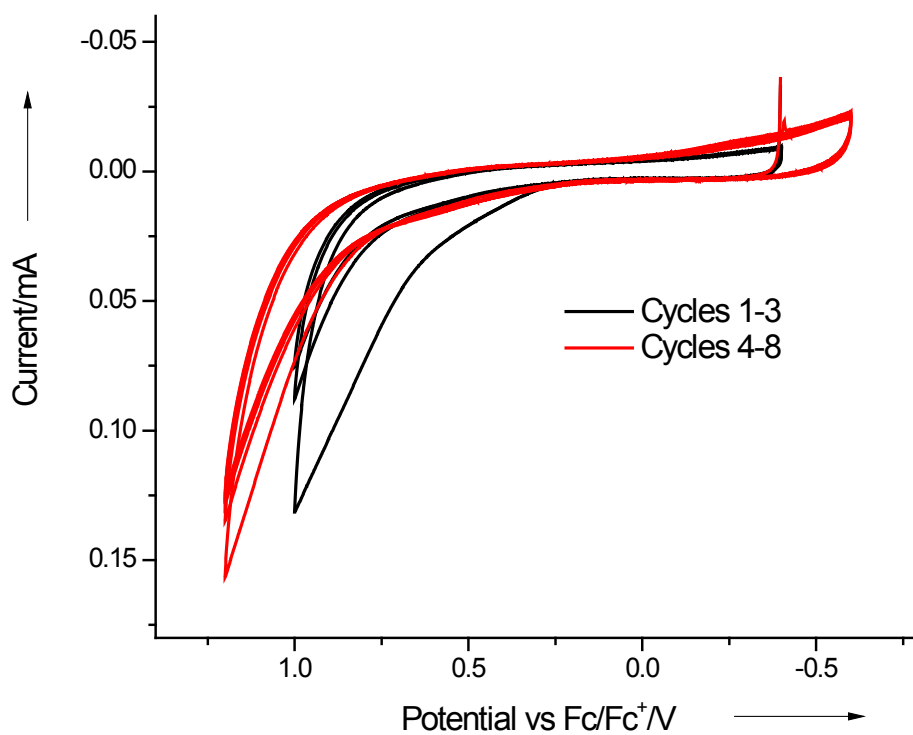


Figure S6. Cyclic voltammograms of a film of **3** on ITO measured in 0.1M TBAPF₆/acetonitrile with Ag/Ag⁺ reference and Pt wire counter electrodes, respectively.

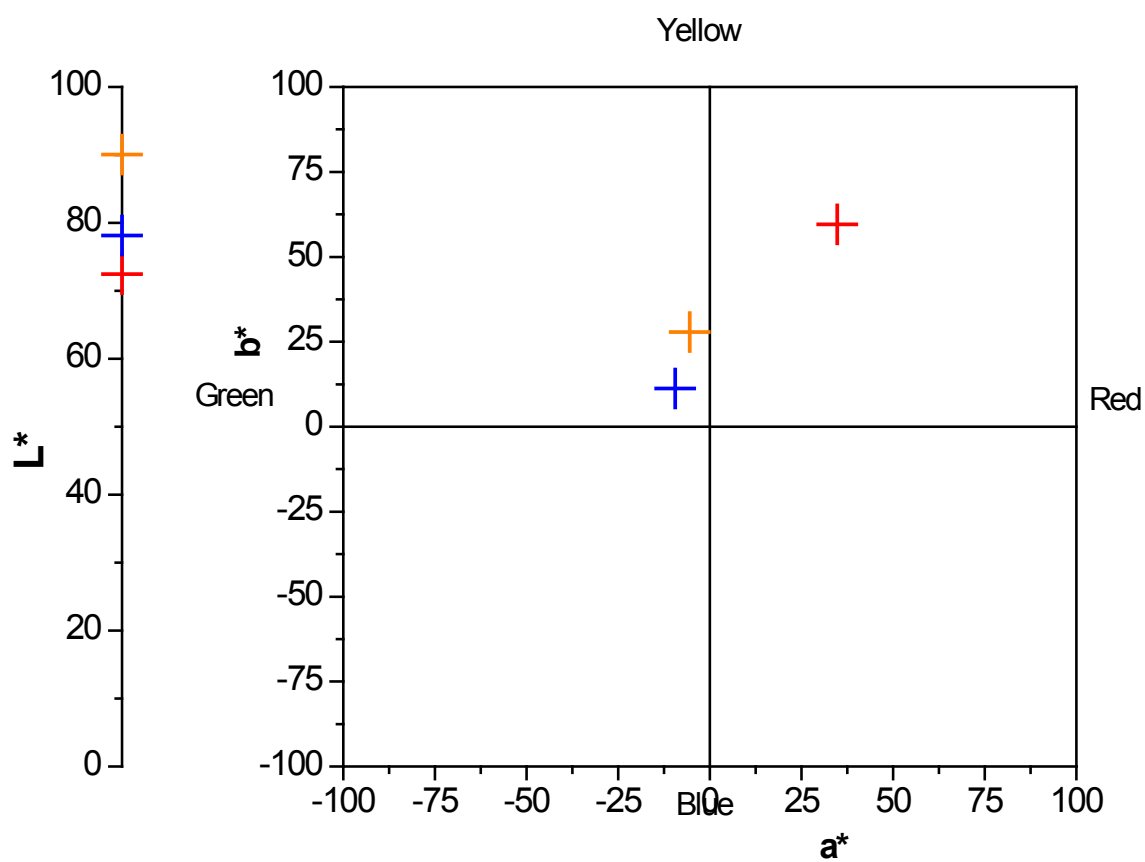


Figure S7. CIE $L^*a^*b^*$ color coordinates of a film of **5** from **3** in its original (+), oxidized (+) and neutral (+) states.

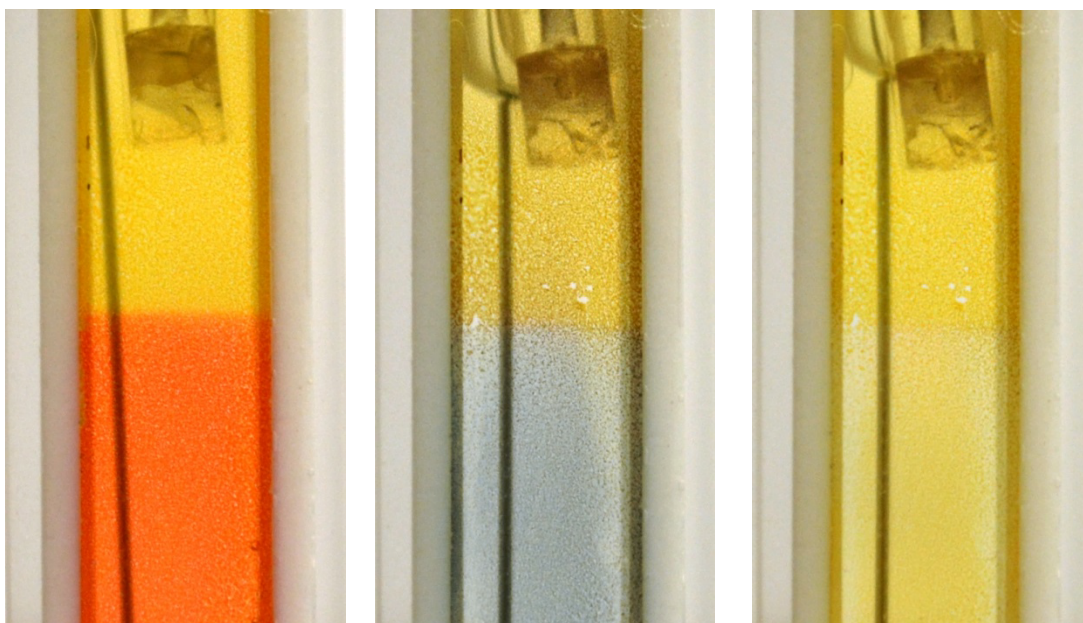


Figure S8. Photographs of a film of **5** from **3** (bottom half) on ITO in its original (left), oxidized (middle), and neutral (right) states. The top half of the film is pristine **3** showing its non-electrochromic behavior.

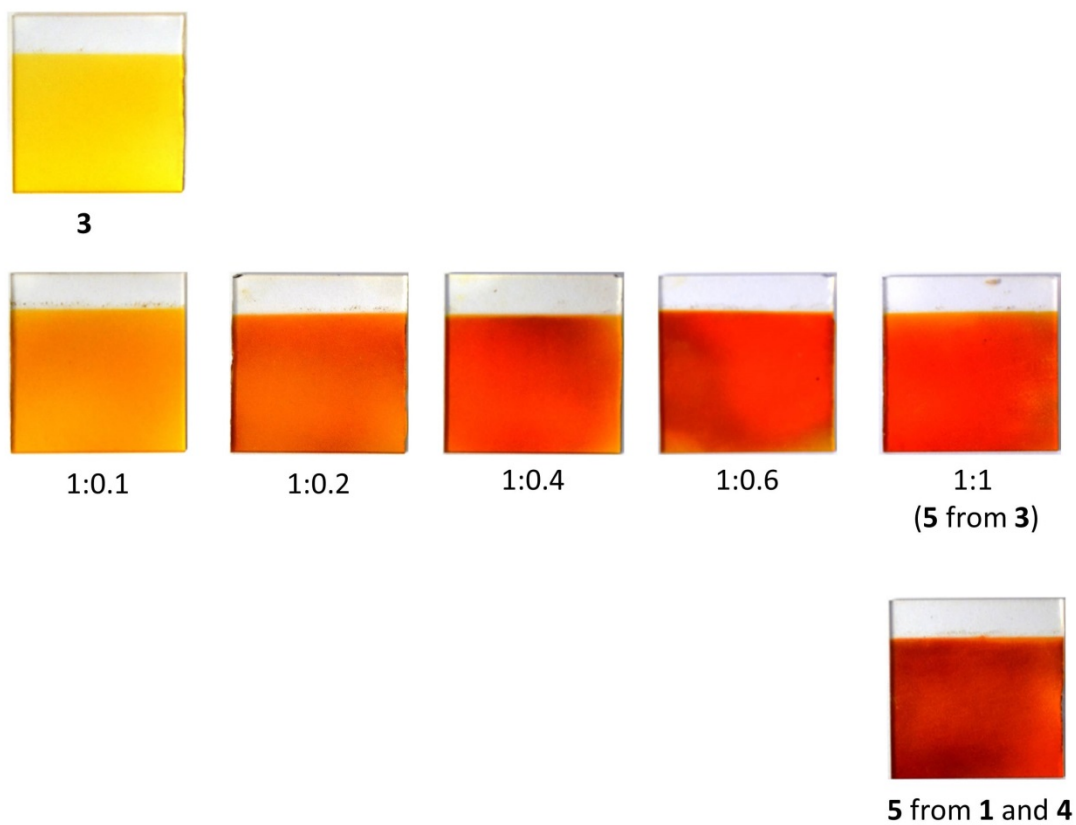


Figure S9. Photographs of exchanged polymer films obtained from **3** using different molar ratios of **1:4** (ratios are shown below pictures). For comparison, pristine **3** as well as **5** prepared from direct condensation of **1** and **4** are also shown.

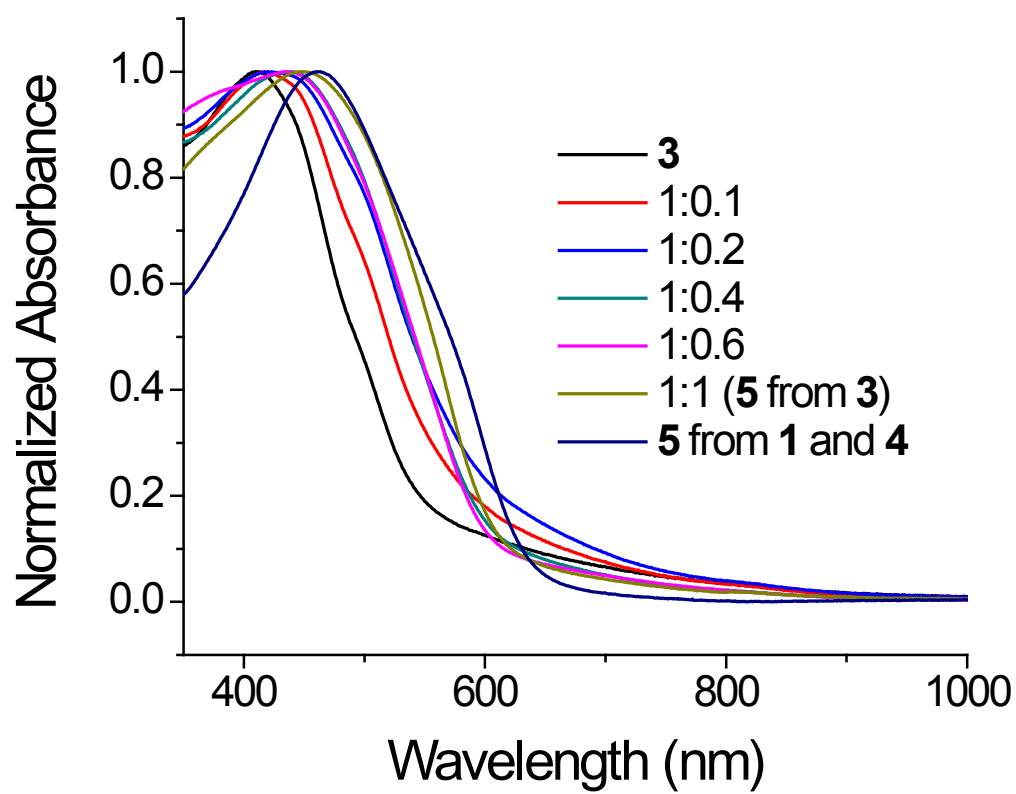


Figure S10. Absorbance spectra of the films shown in Figure S9.

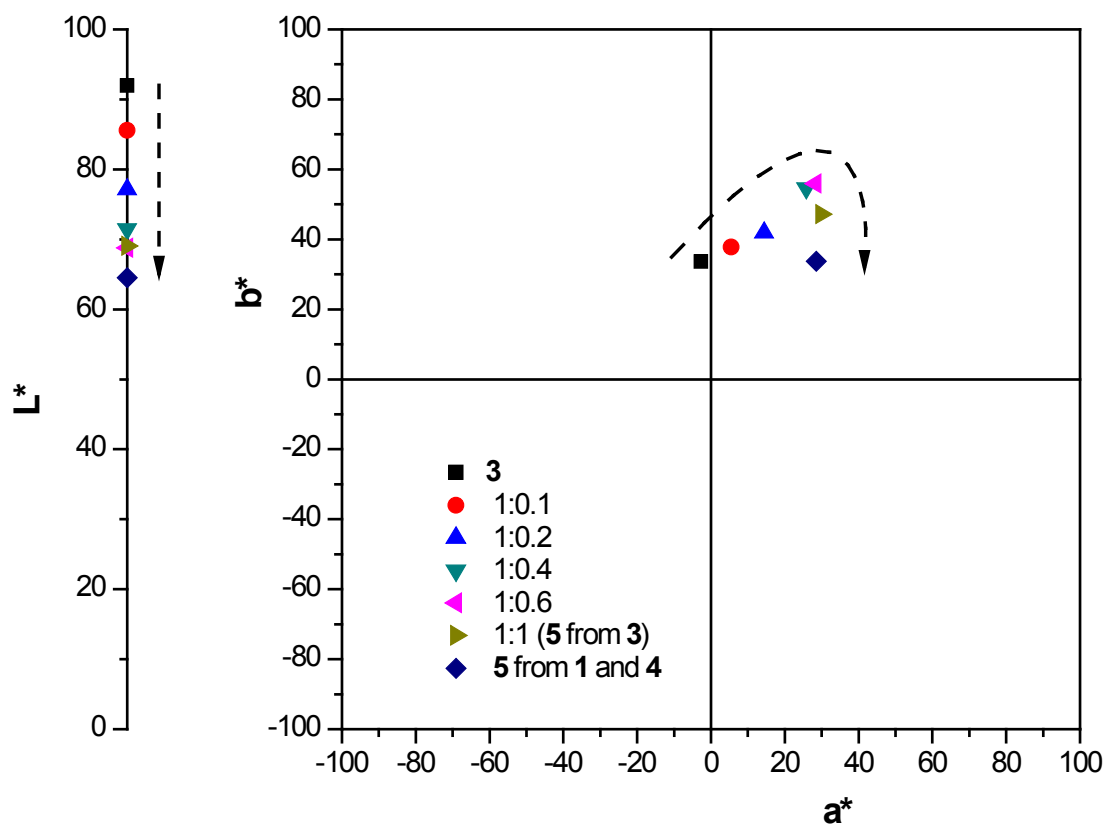


Figure S11. CIE $L^*a^*b^*$ color coordinates of the films shown in Figure S9.

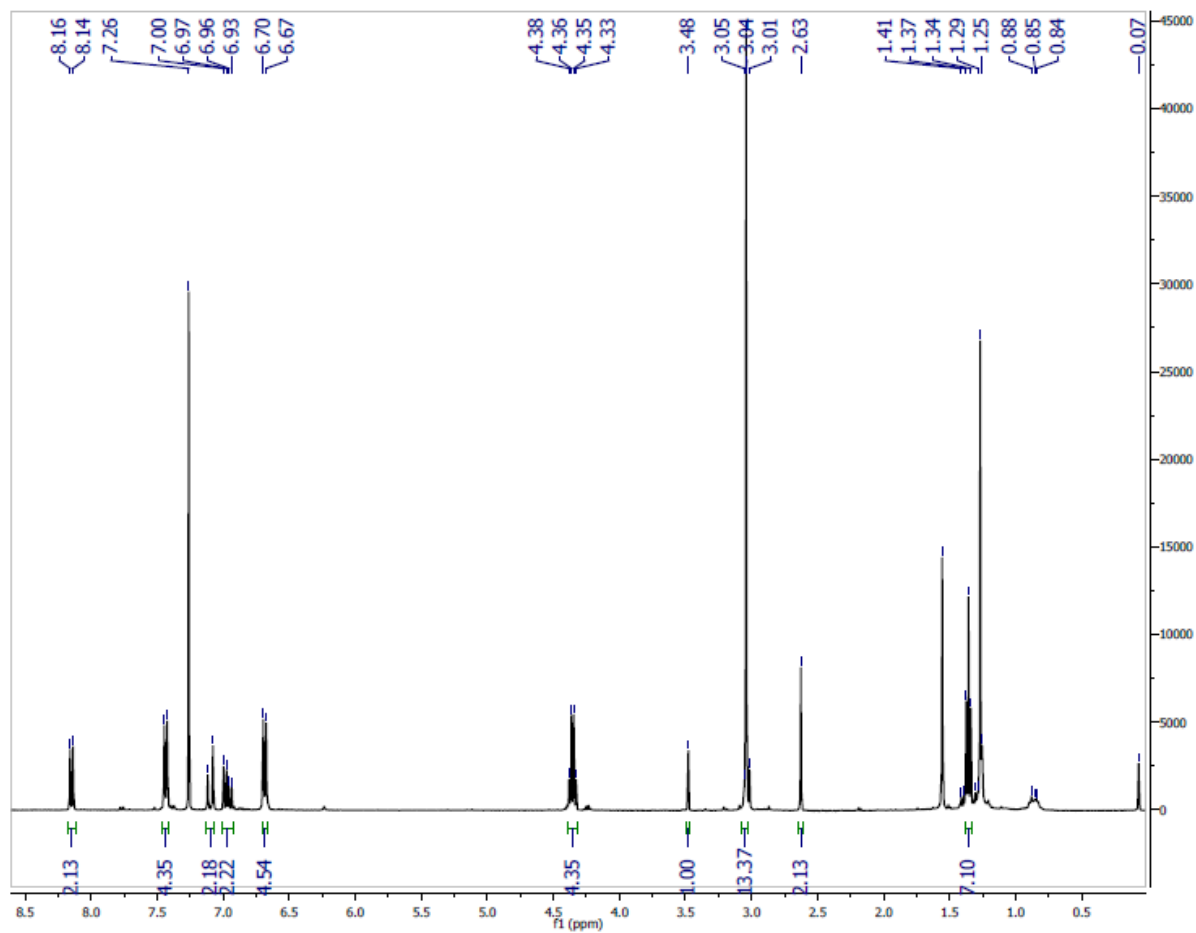


Figure S12. ¹H-NMR of pristine 7 obtained by constitutional component exchange from 1 and 6.

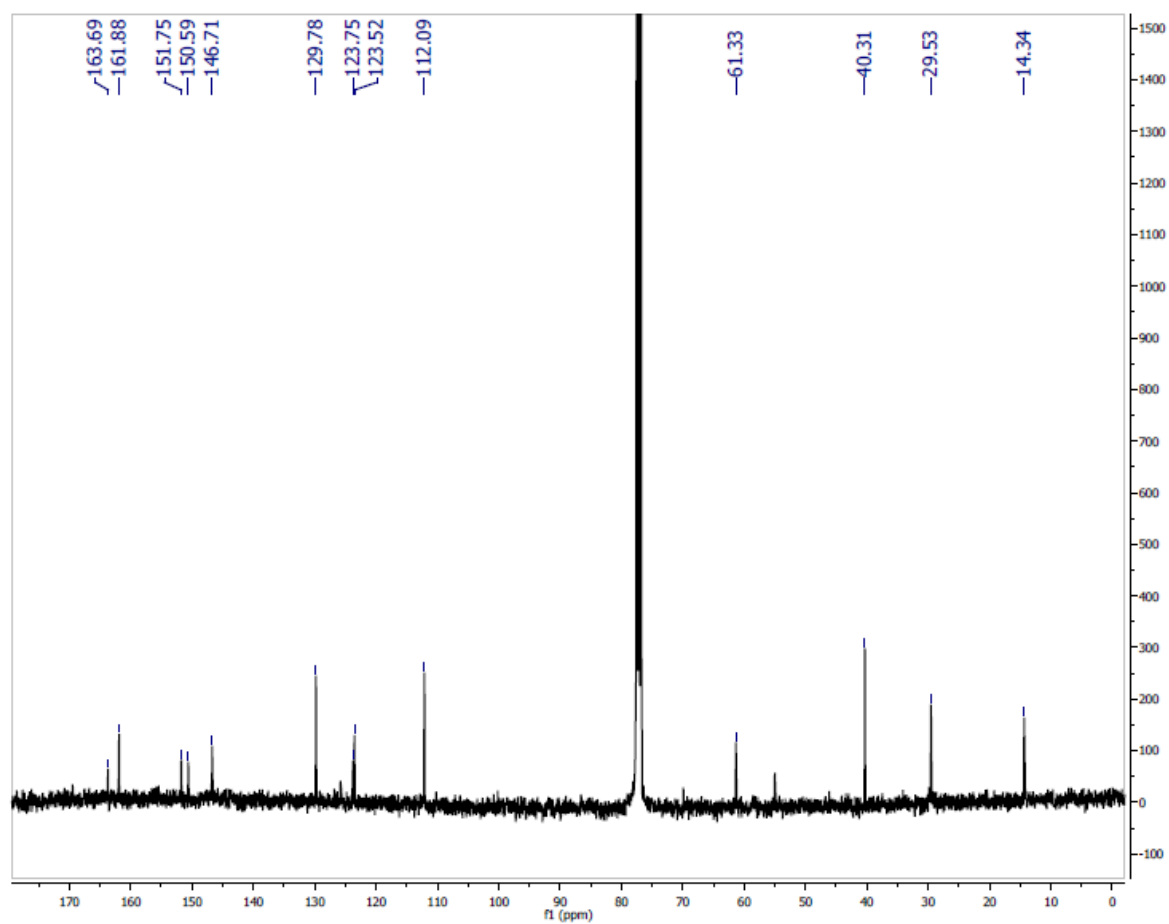
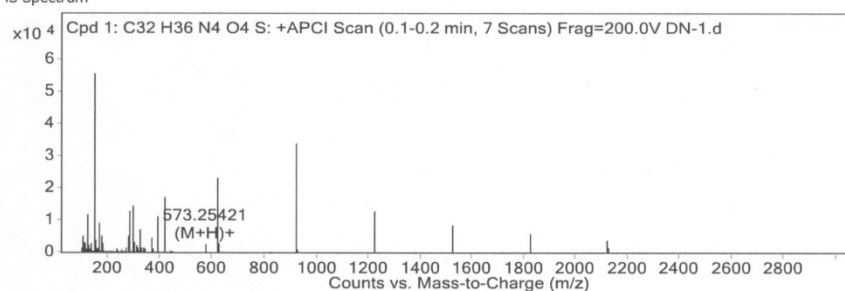


Figure S13. ^{13}C NMR of pristine 7 obtained by constitutional component exchange from 1 and 6.

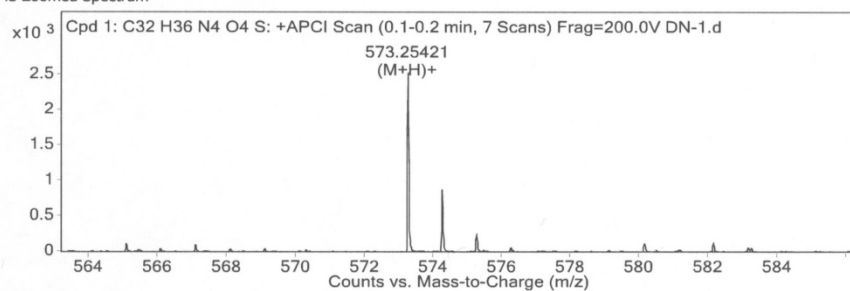
Analysis Report

Data File DN-1.d **Sample Name** DN-1
User Name Karine **Acq Method** APCI_POS_DIR.m
Acquired Time 9/26/2012 9:24:35 AM **DA Method** HRMS.m
Comment

MS Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

| Ion | Formula | Abund | Observed m/z | Calc m/z | Diff(ppm) |
|--------|---|----------|--------------|----------|-----------|
| | | 58353.33 | 149.02514 | | |
| (M+H)+ | C ₃₂ H ₃₇ N ₄ O ₄ S | 2539.96 | 573.25421 | 573.253 | 1.2 |

Figure S14. High resolution mass spectrum of **7** obtained by constitutional component exchange from **1** and **6**.

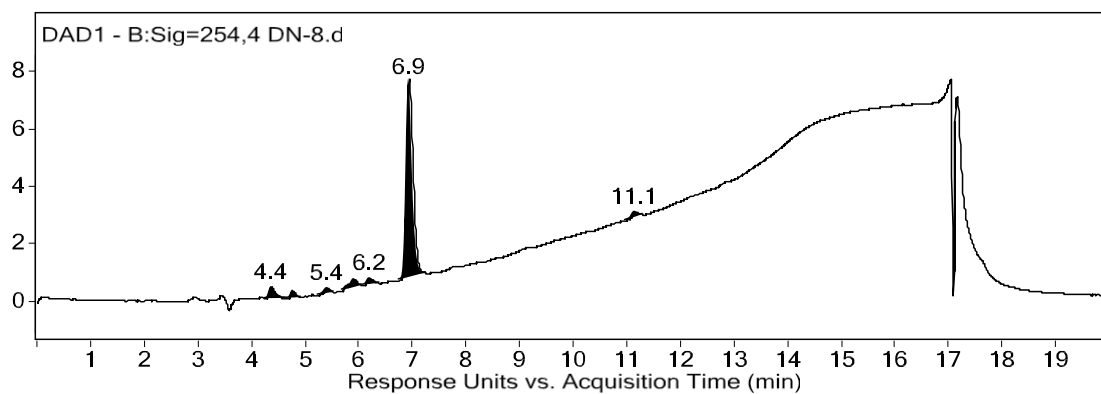


Figure S15. Liquid chromatograph monitored at 254 nm of dichloromethane washings obtained from component exchange of **3** with an excess of **6**. The peak at 6.9 min corresponds to unreacted **6**.

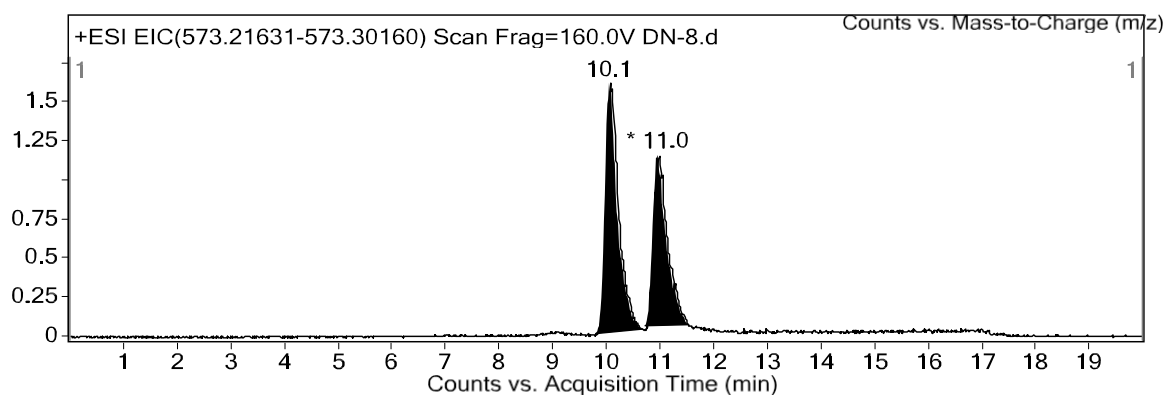


Figure S16. Liquid chromatograph monitored by total ion count at $m/z=573$ of dichloromethane washings obtained from component exchange of **3** with an excess of **6**.

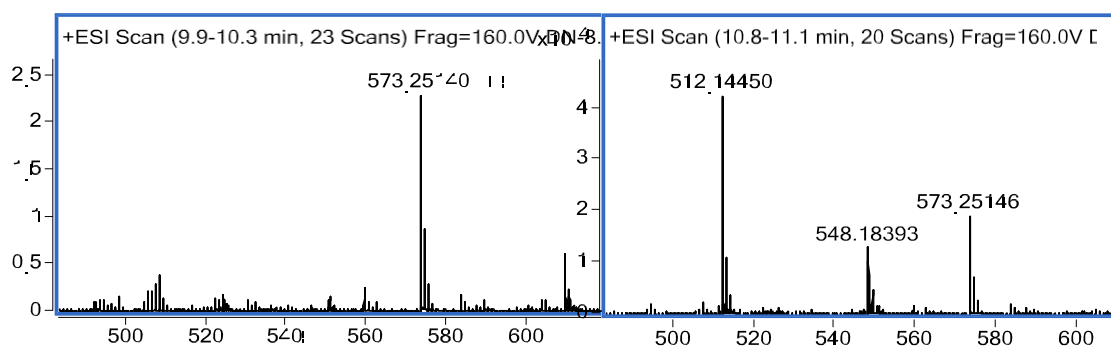


Figure S17. ESI mass spectrum of the peaks from Figure S16 corresponding to **7**.

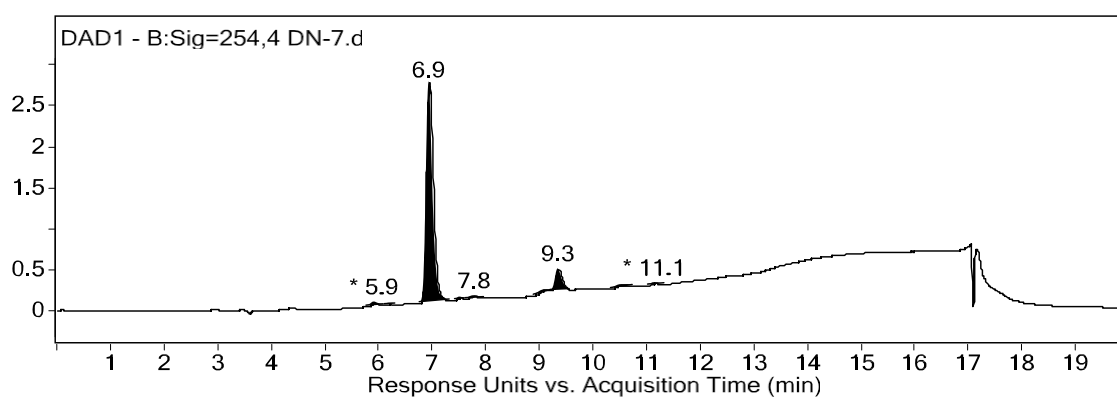


Figure S18. Liquid chromatograph monitored at 254 nm of dichloromethane washings obtained from component exchange of **5** with an excess of **6**. The peak at 6.9 min corresponds to unreacted **6**.

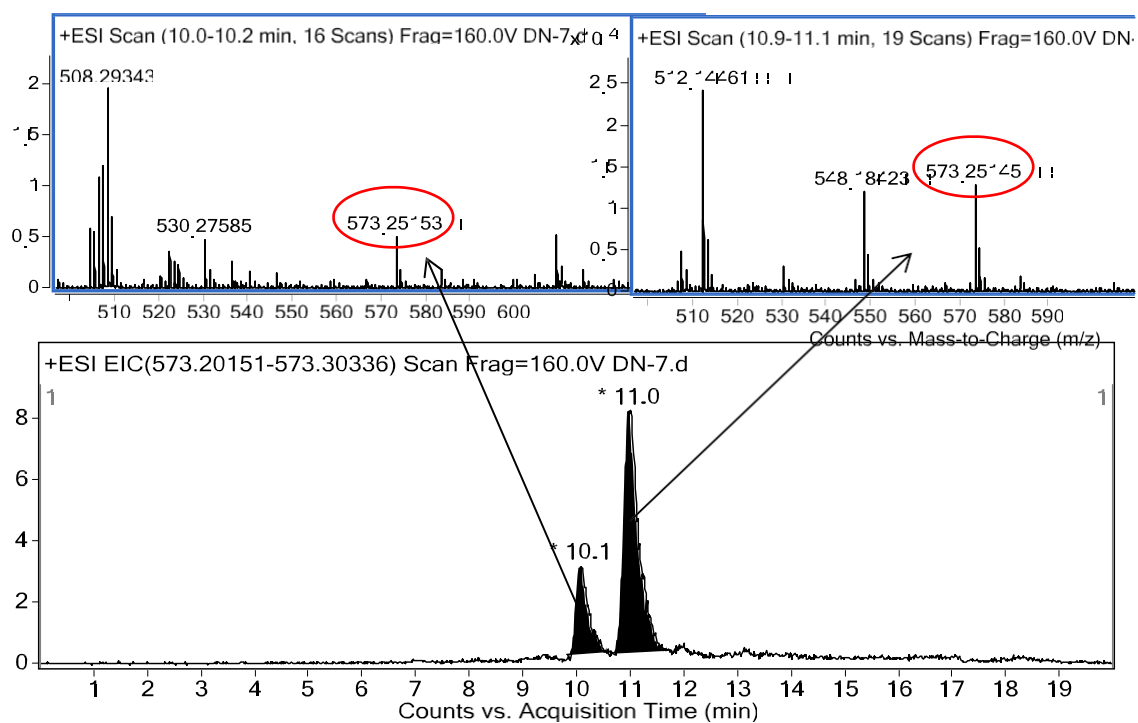


Figure S19. ESI mass spectra of the peaks at 10.1 (left) and 11.0 (right) min. retention time (top) from the liquid chromatograph monitored as a function of total ion count (bottom).