

## Supporting Information

### **Effects of Fluorination on the Electrochromic Performance of Benzothiadiazole-Based Donor-Acceptor Copolymers**

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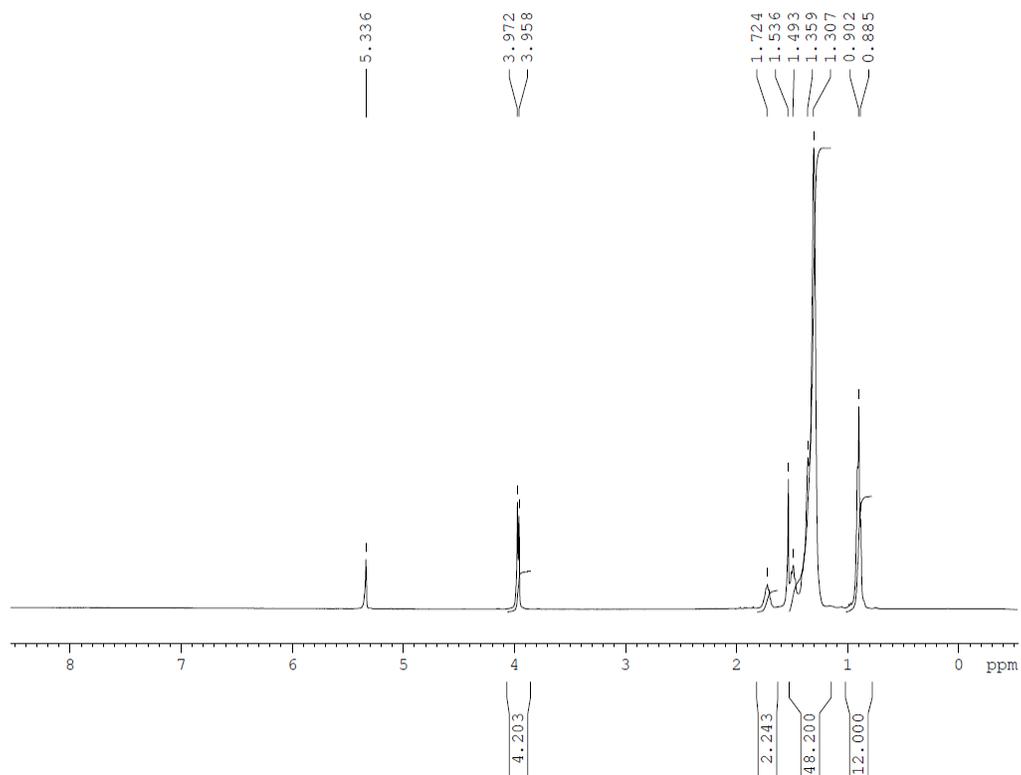
#### **1 NMR of Monomers and Polymers**

#### **2 GPC, TGA and DSC Plots of Polymers**

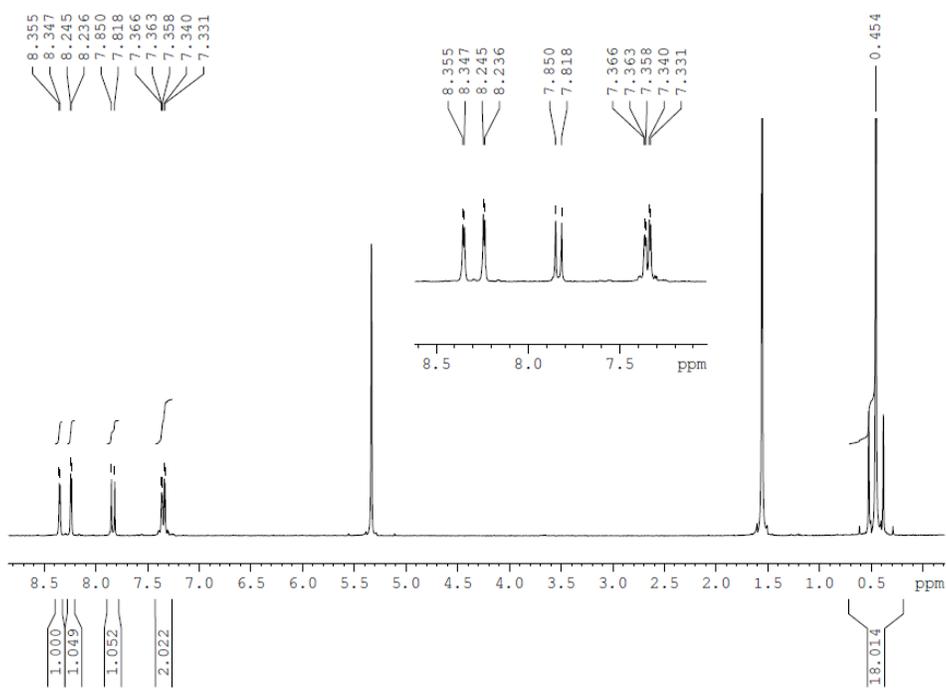
#### **3 Degradation Profile of Electrochromic Devices**

#### **4 TD-DFT Calculations**

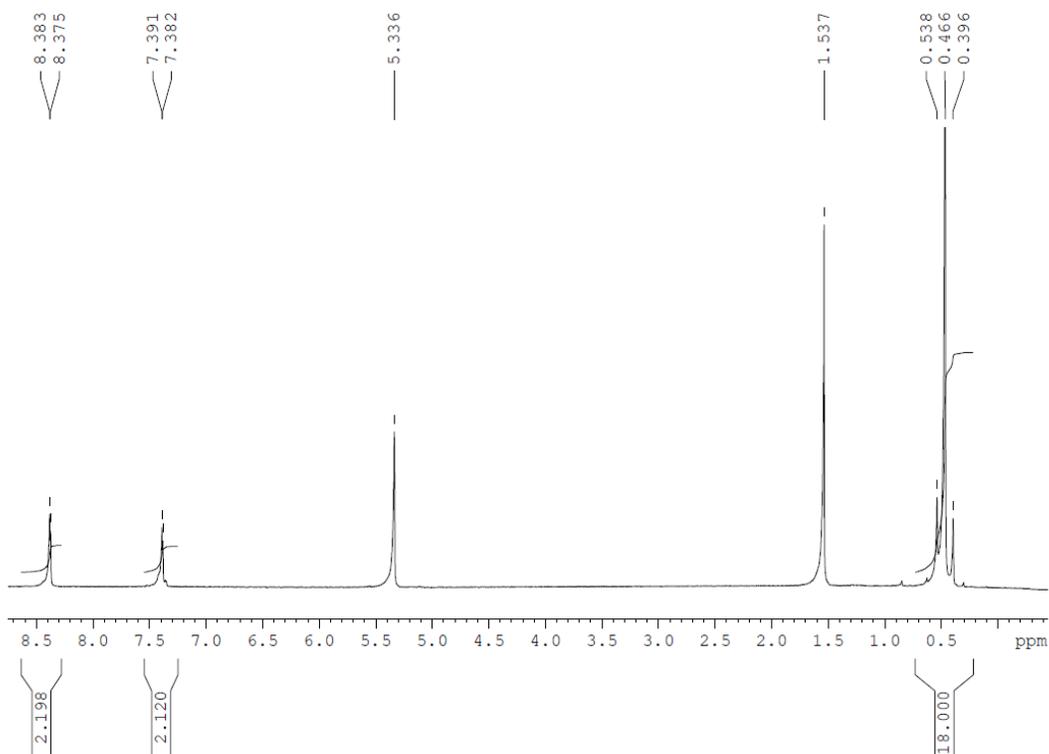
# 1 NMR of Monomers and Polymers



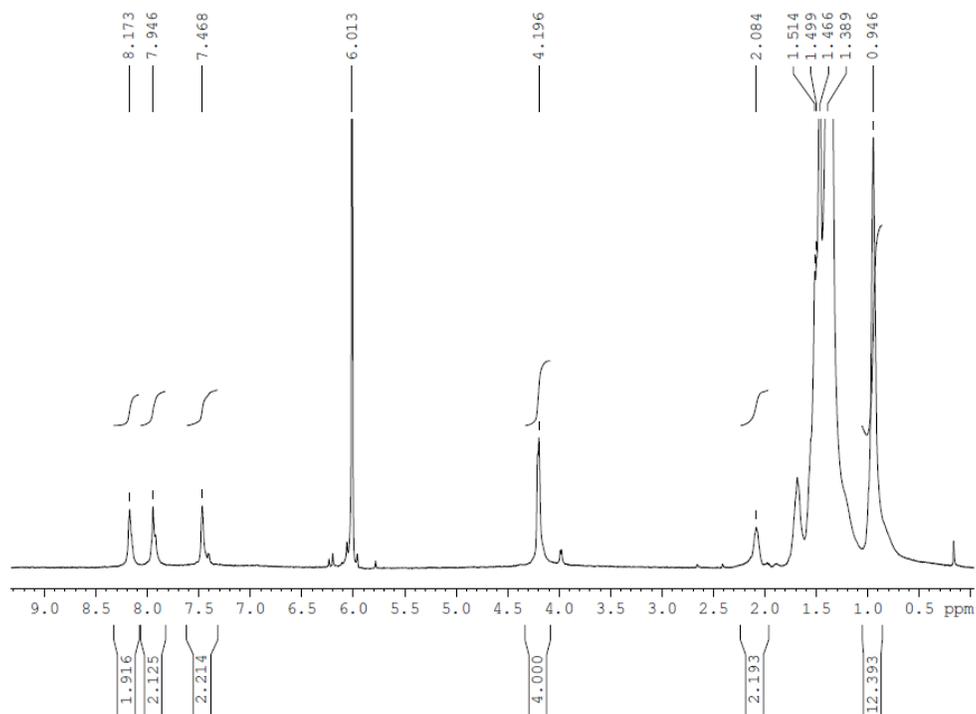
**Figure S1**  $^1\text{H}$  NMR spectrum of compound **2** ( $\text{CD}_2\text{Cl}_2$ , room temperature).



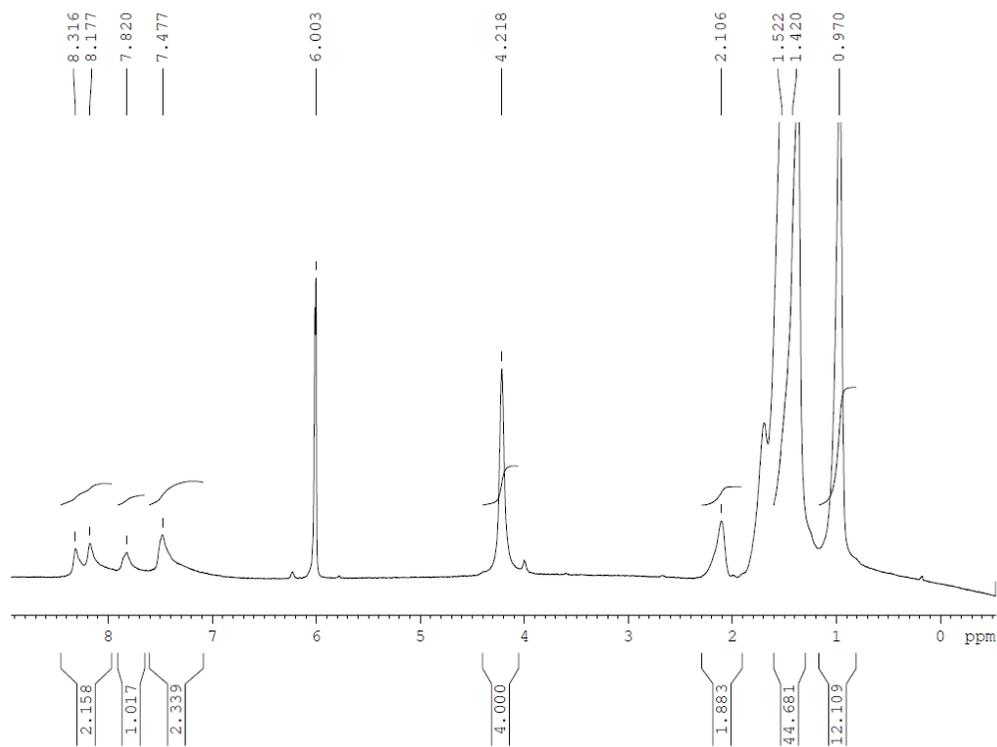
**Figure S2**  $^1\text{H}$  NMR spectrum of compound **4b** ( $\text{CD}_2\text{Cl}_2$ , room temperature).



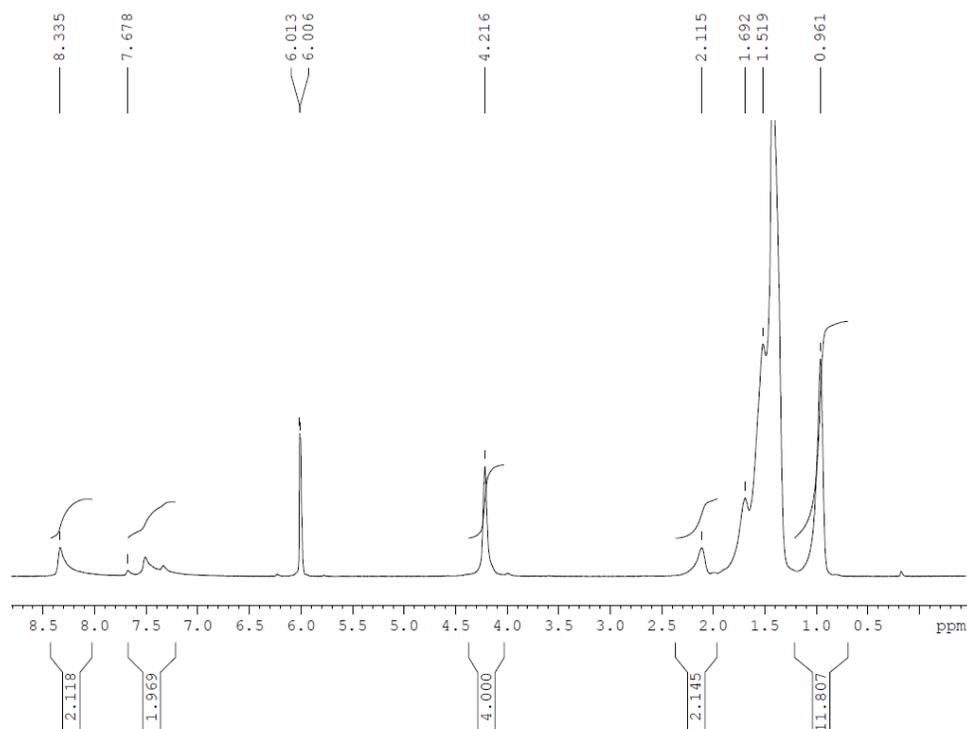
**Figure S3**  $^1\text{H}$  NMR spectrum of compound **4c** ( $\text{CD}_2\text{Cl}_2$ , room temperature).



**Figure S4**  $^1\text{H}$  NMR spectrum of PDAT-DTBT ( $\text{C}_2\text{D}_2\text{Cl}_4$ , 120  $^\circ\text{C}$ ).

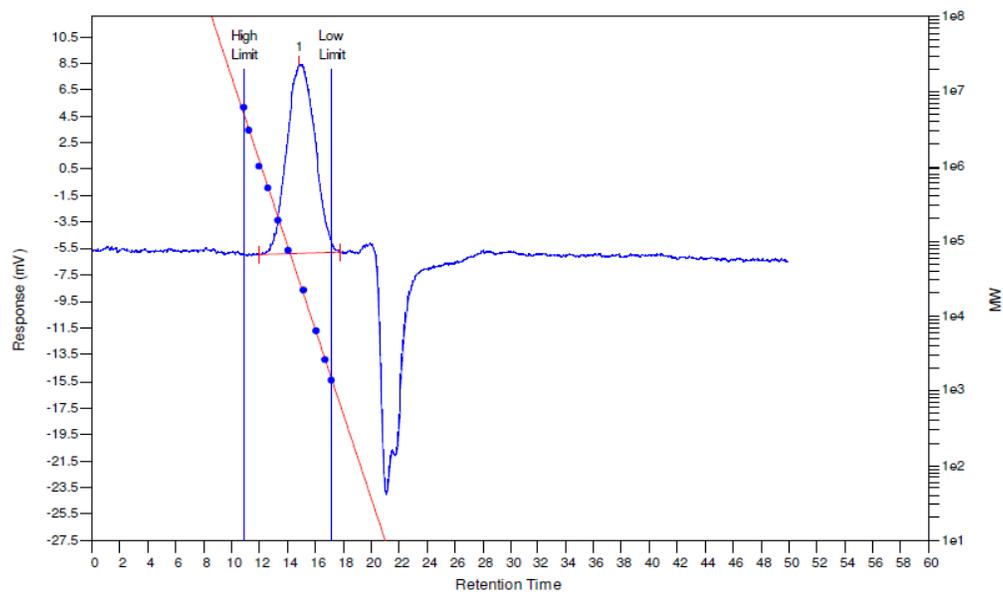


**Figure S5**  $^1\text{H}$  NMR spectrum of PDAT-DTBT-F ( $\text{C}_2\text{D}_2\text{Cl}_4$ , 120  $^\circ\text{C}$ ).



**Figure S6**  $^1\text{H}$  NMR spectrum of **PDAT-DTBT-2F** ( $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $120\text{ }^\circ\text{C}$ ).

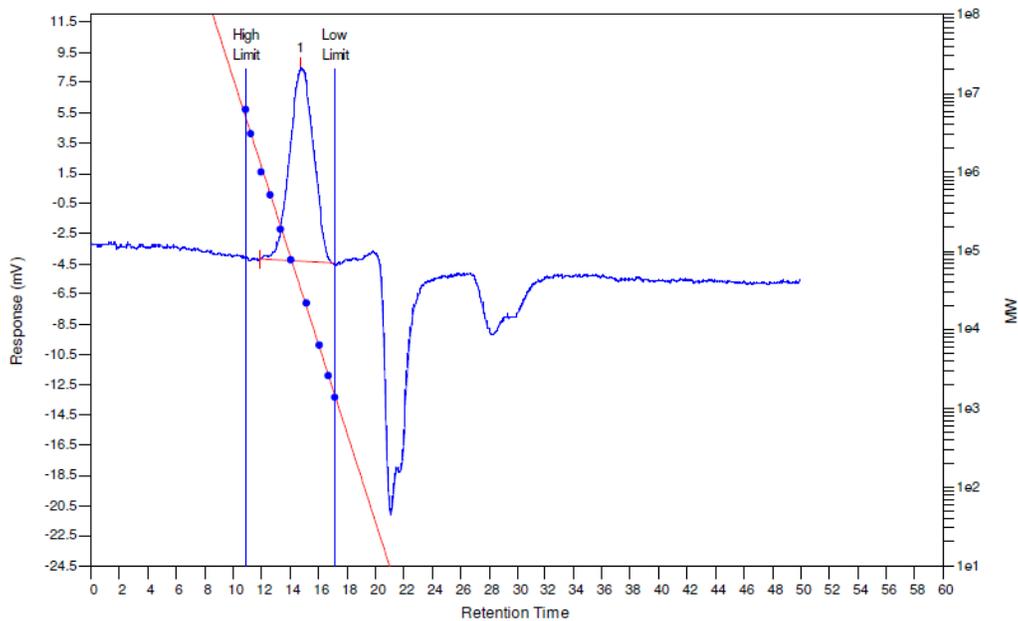
## 2 GPC, TGA and DSC Plots of Polymers



### MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	31181	12934	48352	143431	306204	40171	3.73836

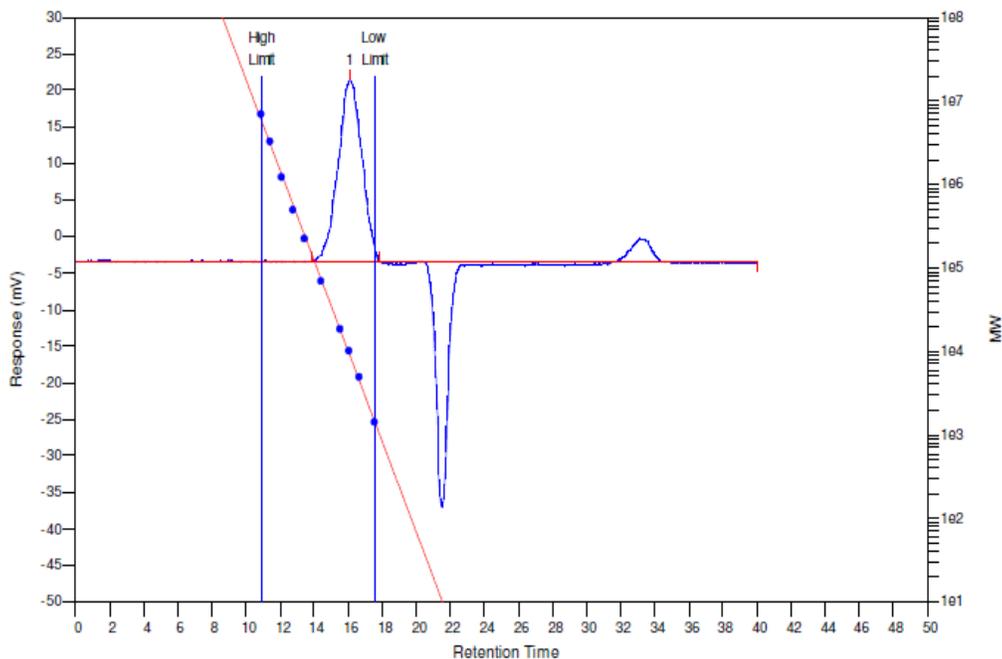
**Figure S7** GPC chromatogram of **PDAT-DTBT**.



**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	33992	19989	55596	182608	488040	46870	2.78133

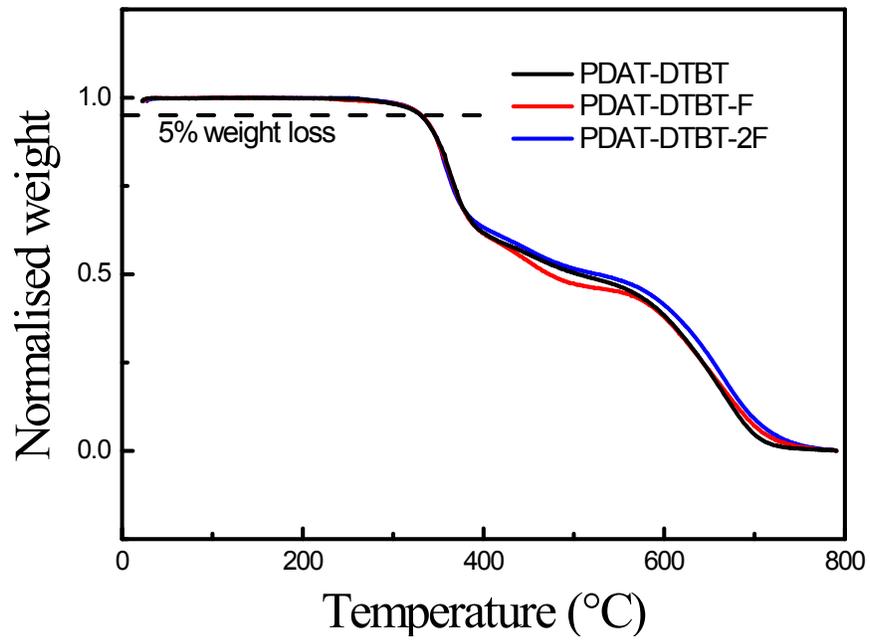
**Figure S8** GPC chromatogram of PDAT-DTBT-F.



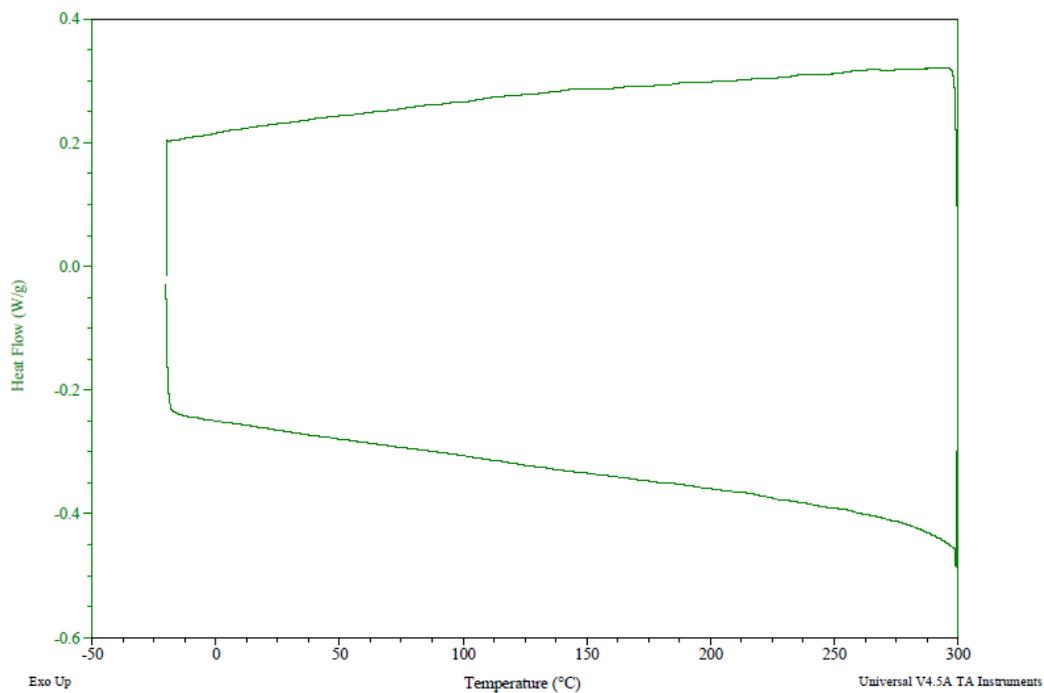
**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	9097	6695	12572	23757	40610	11398	1.87782

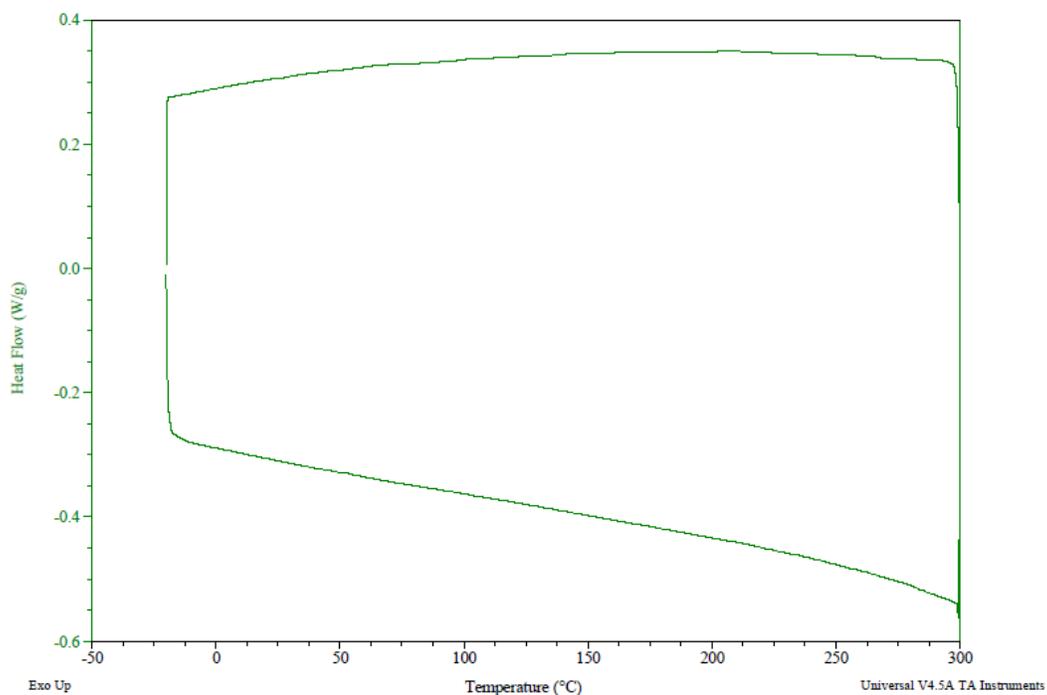
**Figure S9** GPC chromatogram of PDAT-DTBT-2F.



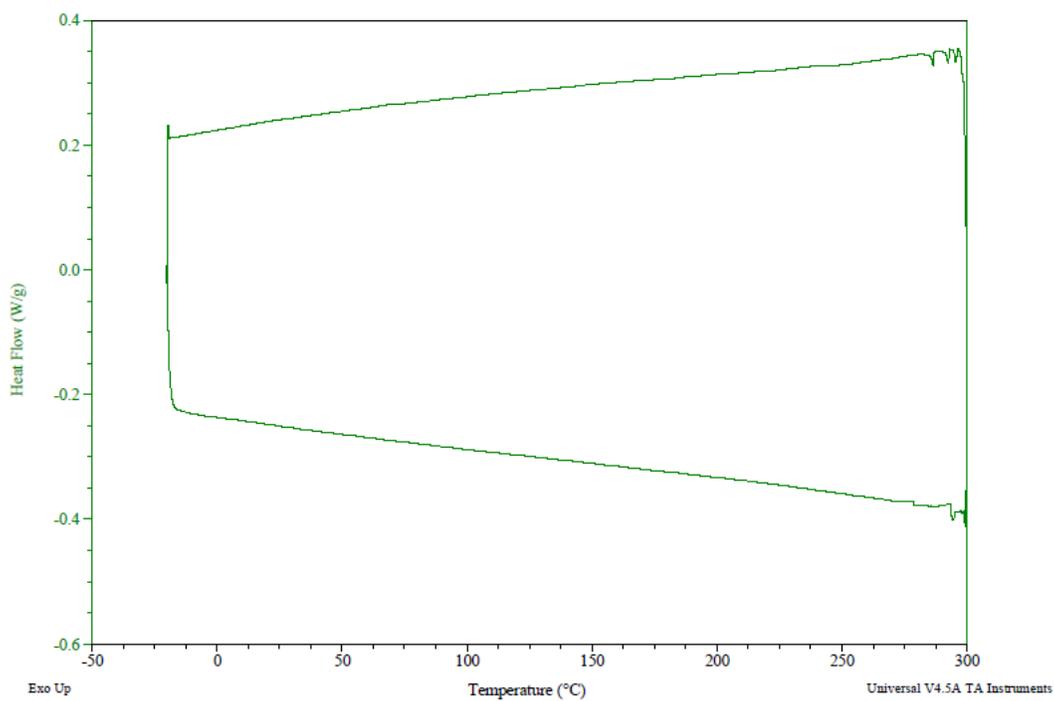
**Figure S10** Thermograms of PDAT-DTBT, PDAT-DTBT-F and PDAT-DTBT-2F.



**Figure S11** DSC plot of PDAT-DTBT.

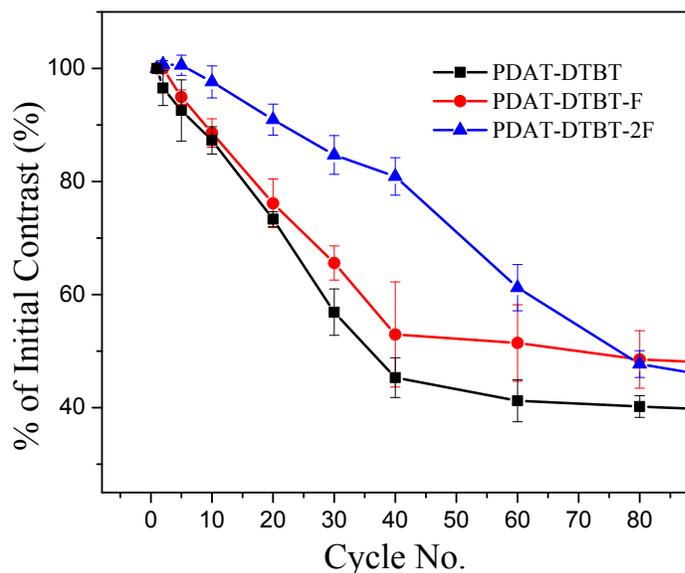


**Figure S12** DSC plot of PDAT-DTBT-F.



**Figure S13** DSC plot of PDAT-DTBT-2F.

### 3 Degradation Profile of Electrochromic Devices



**Figure S14** Degradation profiles of **PDAT-DTBT**, **PDAT-DTBT-F** and **PDAT-DTBT-2F** devices during the ‘burn-in’ period. The devices were switched at 15 s cycles between +1.6 and -1.6 V at 1500 nm. Data was obtained based on 3 repeated trials.

### 4 TD-DFT Calculations

**Table S1.** DFT calculations of **PDAT-DTBT**, **PDAT-DTBT-F** and **PDAT-DTBT-2F** dimer.

Model	HOMO (eV)	LUMO (eV)	LH gap (eV)
PDAT-DTBT	-4.668	-2.705	1.963
PDAT-DTBT-F	-4.694	-2.780	1.914
PDAT-DTBT-2F	-4.754	-2.782	1.972