Supplementary Material (ESI) for Polymer Chemistry

A Fluorescent All-Fluorene Polyazomethine – Towards Soluble Conjugated Polymers Exhibiting High Fluorescence and Electrochromic Properties

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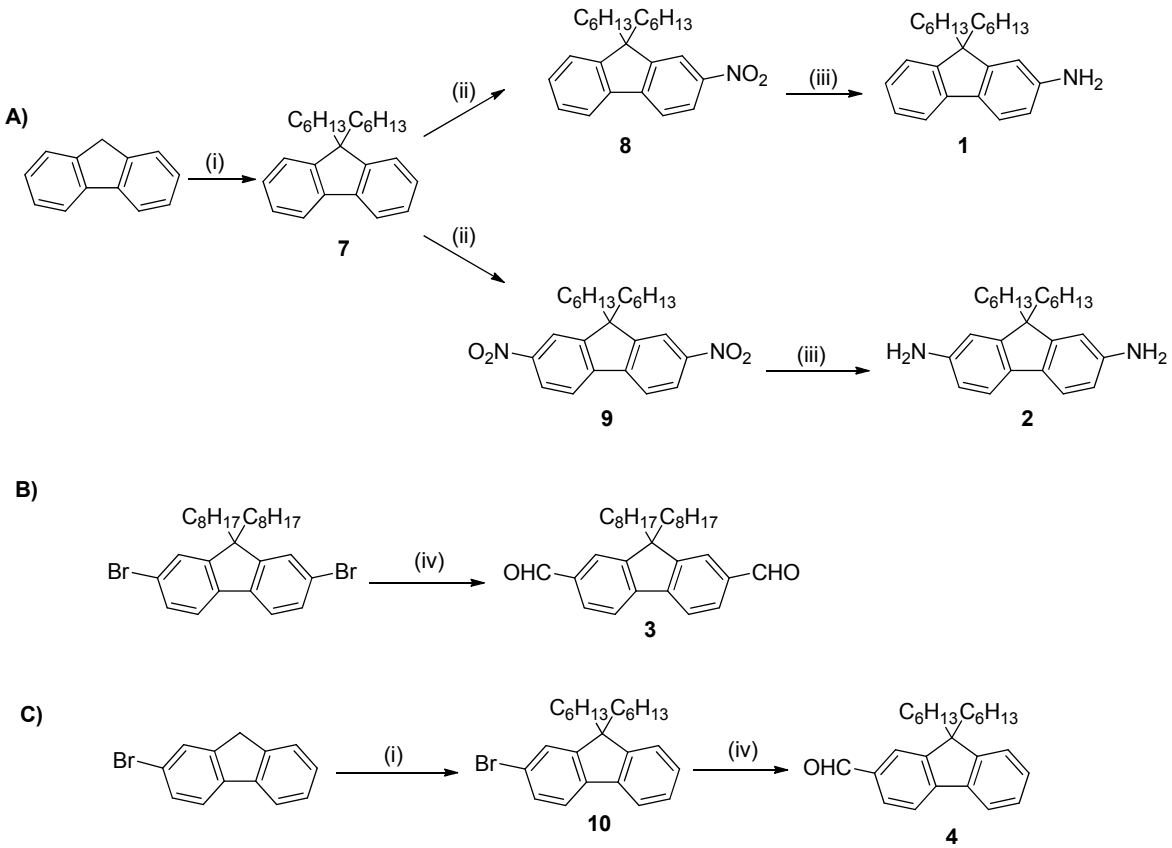
The syntheses of the monomers required for preparing the alternating copolymer **6** are outlined in Scheme 1. Commercially available fluorene was alkylated with 1-bromohexane, followed by nitration in refluxing nitric acid. The mixture of mono- and dinitrated derivatives was separated and each nitro-derivative was separately reduced to afford the corresponding aminofluorene **1** and **2**, respectively, by catalytic reduction with Pd/C and hydrazine monohydrate. The dialdehyde **3** was prepared from the corresponding 2,7-dibromo-9,9-dioctylfluorene, using butyl-lithium in a mixture of DMF in THF according to known methods.[17] Meanwhile, the monoaldehyde **4** was prepared from 2-bromofluorene that was alkylated with 1-bromohexane with 50 % NaOH followed by standard formylation with butyl-lithium and THF/DMF.



Scheme 1. Synthetic route for monomers: (i) 1-bromohexane, 50 % NaOH in DMSO room temperature, 4 days; (ii) HNO_3, reflux, 2h; (iii) 10% Pd/C reflux THF/EtOH followed by hydrazine monohydrate, room temperature, overnight; (iv) BuLi, -78 °C, THF followed by DMF, room temperature, overnight.

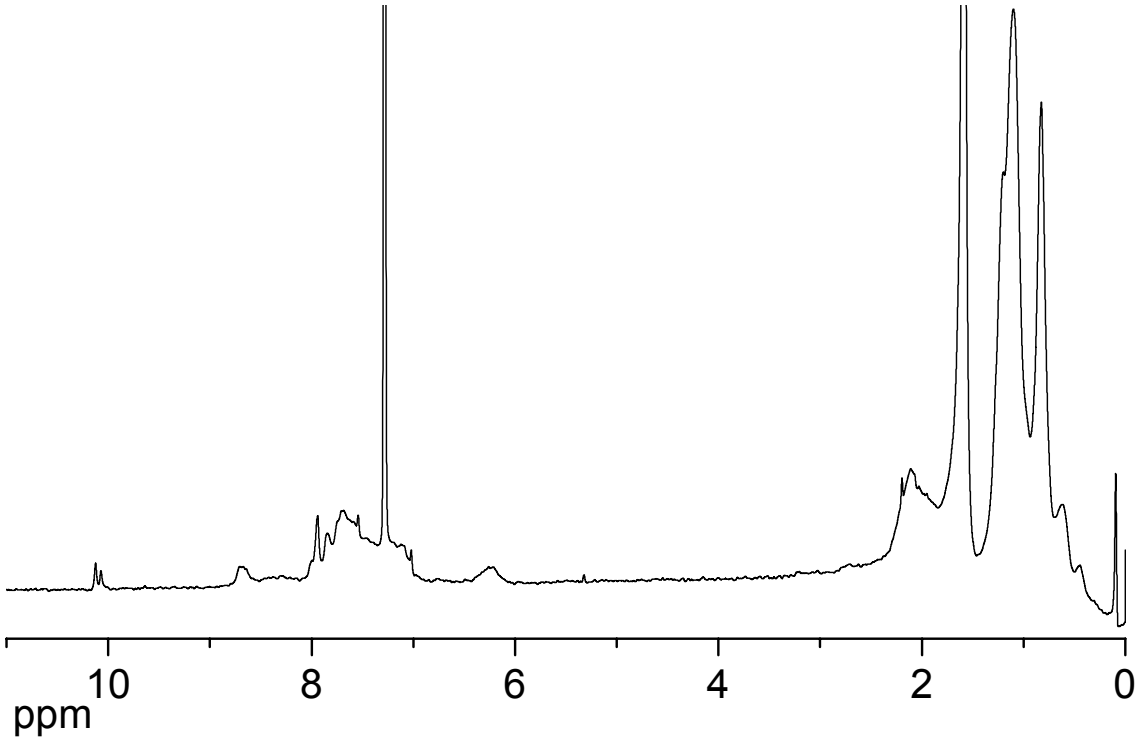


Figure 1. ^{1}H NMR spectrum of **6** in $CDCl_3$

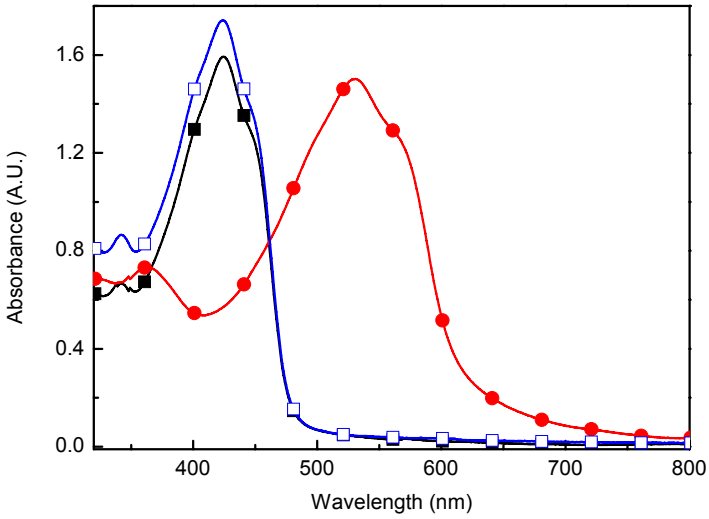


Figure 2. Absorbance spectra of **6** (●), oxidized with $FeCl_3$ (■), followed by neutralization with hydrazine hydrate (□) in dichloromethane.

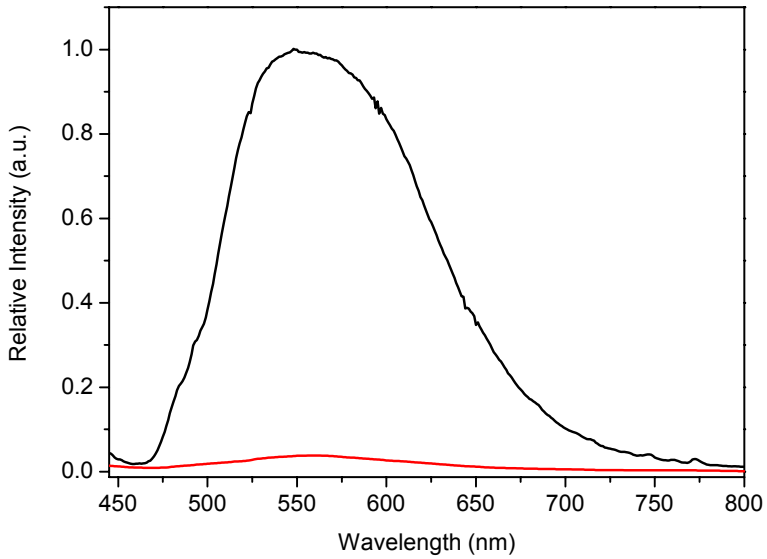


Figure 3. Fluorescence spectra of **6** at room temperature (red) and 77 K (black) in 2-methylcyclohexane.

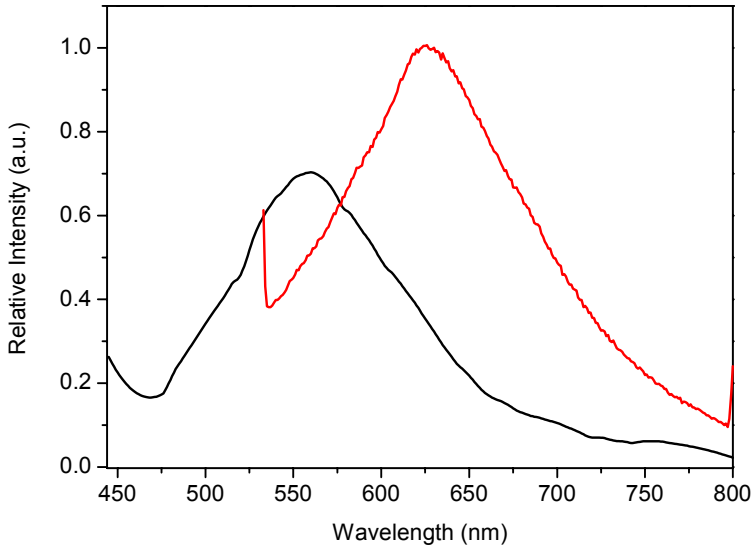


Figure 4. Fluorescence spectra of **6** at room temperature (black) and protonated (red) in 2-methylcyclohexane.

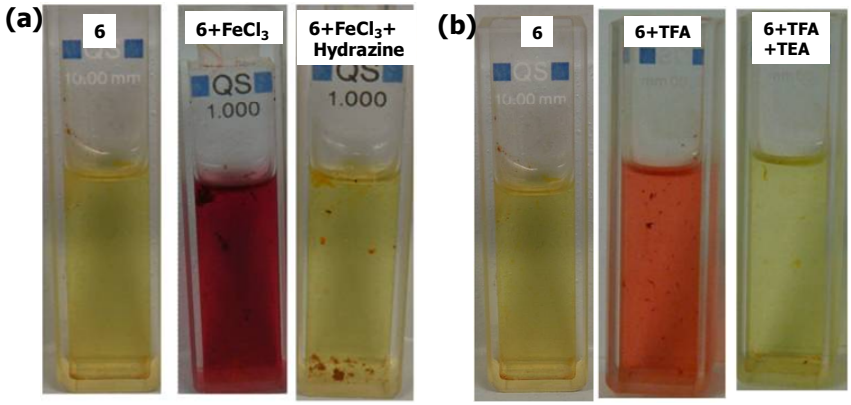


Figure 5. Photographs of **6** in dichloromethane (left) with: A) $FeCl_3$ added (middle) followed by the addition of hydrazine hydrate (right) and B) with the addition of TFA (middle) followed by the addition of TEA (right).