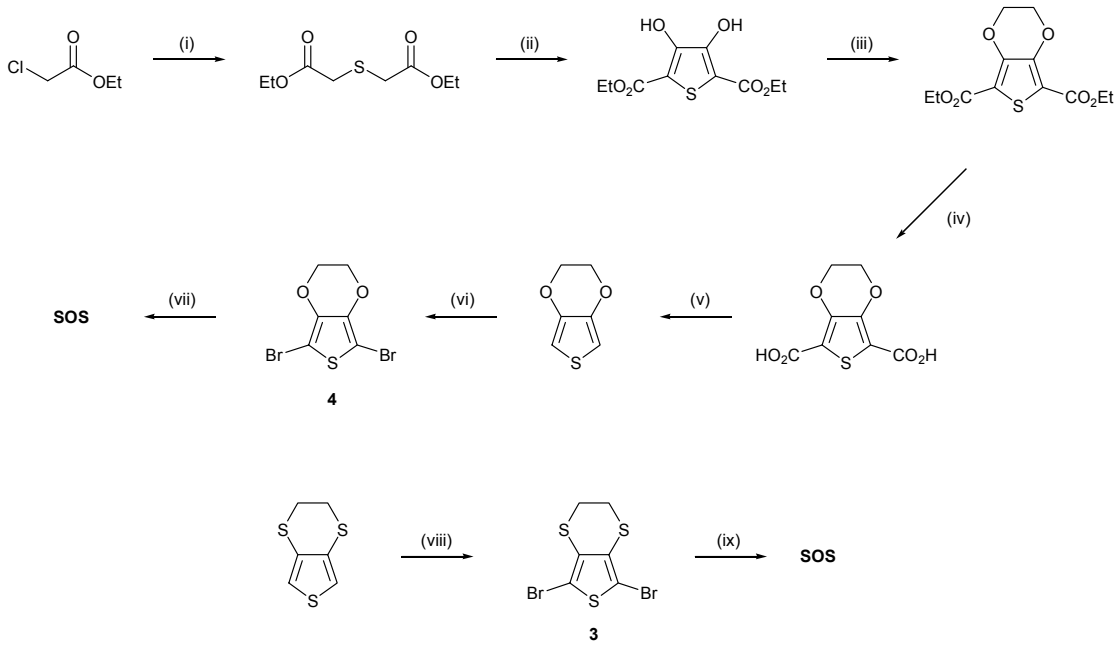
Supplementary material (ESI) for Journal of Materials Chemistry

Supplementary Information

Synthesis of EDOT

Many synthetic routes to EDOT (and its derivatives), have been reported,[1] including the single step synthesis of the 3,4-dimethoxythiophene precursor[2] which can lead directly to EDOT as shown recently by Hellberg *et al*.[3] In this work, we have used a five step route as illustrated in Scheme 1. An acetone solution of ethyl chloroacetate was treated with sodium sulfide nonahydrate yielding the diester in 83%.[4] The diester was added to an ethanolic solution of sodium ethoxide and left for 30 minutes. Following this, diethyl oxalate was added and the mixture refluxed overnight. The dihydroxythiophene product was formed as a white solid in good yield (66%). A Mitsunobu coupling was the choice of reaction for the next step.[5] The thiophene, ethylene glycol and triphenyl phosphine were dissolved in dry THF under a nitrogen atmosphere; DEAD was then added very slowly so as not to raise the temperature more than a few degrees as yields are noticeably reduced if the temperature is not closely controlled. After complete addition of DEAD, the mixture was allowed to reflux overnight which gave the etherified product in 43% yield. Saponification of the 3,4-ethylenedioxy bridged thiophene took place by refluxing with potassium hydroxide in a solution of ethanol; this afforded the dicarboxylic acid in 95% yield. The diacid was decarboxylated by heating in quinoline and a quantity of copper (II) oxide to yield EDOT in 68% yield.



Scheme 1 *Reagents and conditions*: (i) $Na_2S.9H_2O$, acetone, 60 ºC, 3 h; (ii) NaOEt, 0.5 h, $(CO_2Et)_2$, reflux, 18 h, 2M HCl; (iii) PPh_3, ethylene glycol, DEAD, reflux, 18 h; (iv) KOH, EtOH, reflux, 3 h; (v) Cu(II)O, quinoline, 200 ºC, 5 h; (vi) NBS, DCM:AcOH (3:1), 0 ºC, 3 h, in the dark; (vii) EDTT, LDA, $ZnCl_2$, $Pd(PPh_3)_4$; (viii) NBS, DCM:AcOH (3:1), 0 ºC, 3 h, in the dark; (ix) EDOT, LDA, $ZnCl_2$, $Pd(PPh_3)_4$.

References

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