Electronic Supplementary Material (ESI) for Polymer Chemistry.
This journal is © The Royal Society of Chemistry 2015

Supplementary information

Interactions of a zwitterionic thiophene-based conjugated polymer with surfactants: Fluorescence, electrical conductivity, small-angle X-ray scattering and molecular dynamics simulations

Telma Costa,[a] Diego de Azevedo,[a] Beverly Stewart,[a] Matti Knaapila,[b] Artur J.M. Valente,[a] Mario Kraft,[c] Ullrich Scherf,[c] and Hugh D. Burrows[a]

[a] *Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3004-535 Coimbra, Portugal.*
[b] *Department of Physics, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark.*
[c] *Macromolecular Chemistry Group, Bergische Universität Wuppertal, D-42119 Wuppertal, Germany.*

Table S1. Simulation cell details for all surfactant/zwitterion molecular dynamics for 1:1 ratio P3SBDEAHT:surfactant.

	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**
Surfactant	STS x10	SDS x 10	SOS x 10	$C_{12}E_5$ x10	CTAB x 10	DTAC x 10	CAPB x 10
Zwitterion	P3SBDEAHT × 10	P3SBDEAHT × 10	P3SBDEAHT × 10	P3SBDEAHT × 10	P3SBDEAHT × 10	P3SBDEAHT × 10	P3SBDEAHT × 10
Solvent	10382	10407	10442	16038	10367	10413	10402
Ions	Na x 10	10	Na x 10	-	Cl x 10	Cl x 10	-
Dimensions	7 x 7 x 7	7 x 7 x 7	7 x 7 x 7	7 x 7 x 7	7 x 7 x 7	7 x 7 x 7	7 x7 x7

Table S2. Simulation cell details for all surfactant/zwitterion molecular dynamics for 1:2 ratio P3SBDEAHT:surfactant.

	2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**
Surfactant	STS x20	SDS x 20	SOS x 20	$C_{12}E_5$ x20	CTAB x 20	DTAC x 20	CAPB x 20
Zwitterion	P3SBDEAHT × 10	P3SBDEAHT × 10	P3SBDEAHT × 10	P3SBDEAHT × 10	P3SBDEAHT × 10	P3SBDEAHT × 10	P3SBDEAHT × 10
Solvent	10217	10236	10316	10074	10148	10225	10152
Ions	Na x 20	Na x 20	Na x 20	-	Cl x 20	Cl x 20	-
Dimensions	7 x 7 x 7	7 x 7 x 7	7 x 7 x 7	7 x 7 x 7	7 x 7 x 7	7 x 7 x7	7 x 7 x 7

Table S3. Simulation cell details for all surfactant/zwitterion molecular dynamics for 1:3 ratio P3SBDEAHT:surfactant.

	3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**
Surfactant	STS x30	SDS x 30	SOS x 30	$C_{12}E_5$ x30	CTAB x 30	DTAC x 30	CAPB x 30
Zwitterion	P3SBDEAHT × 10	P3SBDEAHT × 10	P3SBDEAHT × 10	P3SBDEAHT × 10	P3SBDEAHT × 10	P3SBDEAHT × 10	P3SBDEAHT × 10
Solvent	10039	10078	10078	9815	9922	10058	9918
Ions	Na x 30	Na x 30	Na x 30	-	Cl x 30	Cl x 30	-
Dimensions	7 x 7 x7	7 x 7 x 7	7 x 7 x 7	7 x 7 x 7	7 x 7 x 7	7 x 7 x 7	7 x 7 x 7

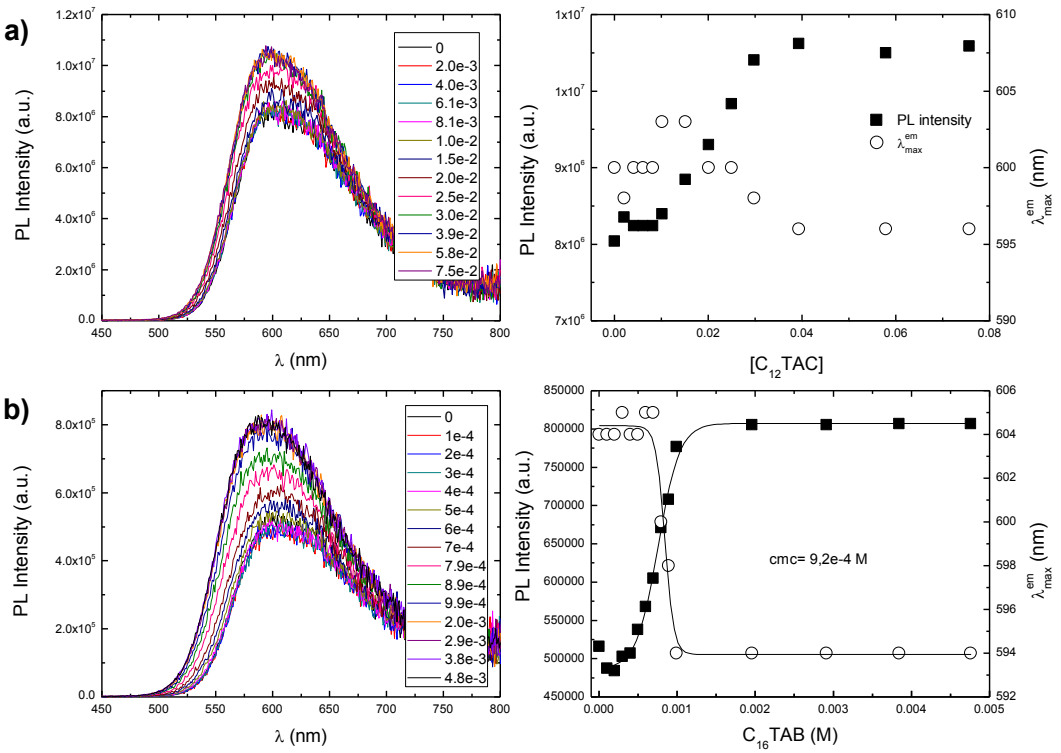


Fig. S1 PL emission spectra (right hand panels) and dependence of the maximum PL intensity and maximum emission wavelength (right hand panels) on the cationic surfactant concentration: a) DTAC and b) CTAB.

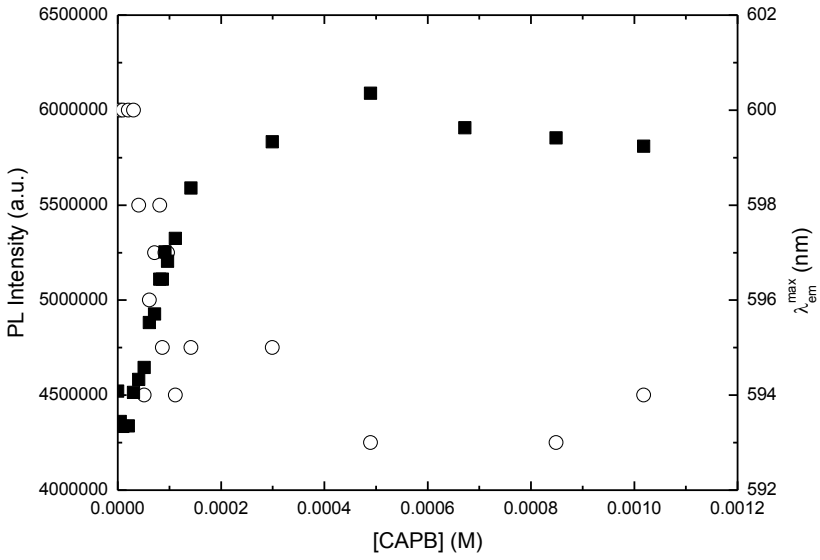


Fig. S2 Dependence of the maximum PL intensity (■) and maximum emission wavelength λ_{em}^{max} (○) of P3SBDEAHT on the CAPB surfactant concentration.

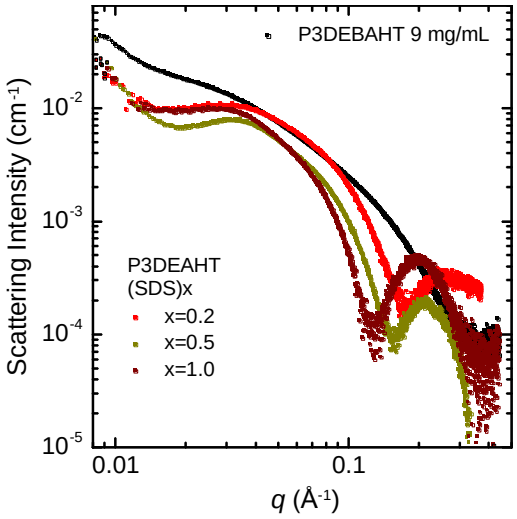


Fig. S3 SAXS data of P3SBDEAHT(CAPB)*x* with *x*=0.2 (red), *x*=0.5 (dark yellow) and *x*=1.0 (wine). Data of 9.06 mg/mL P3SBDEAHT (black) are plotted for comparison. *T*=25 ^{o}C.

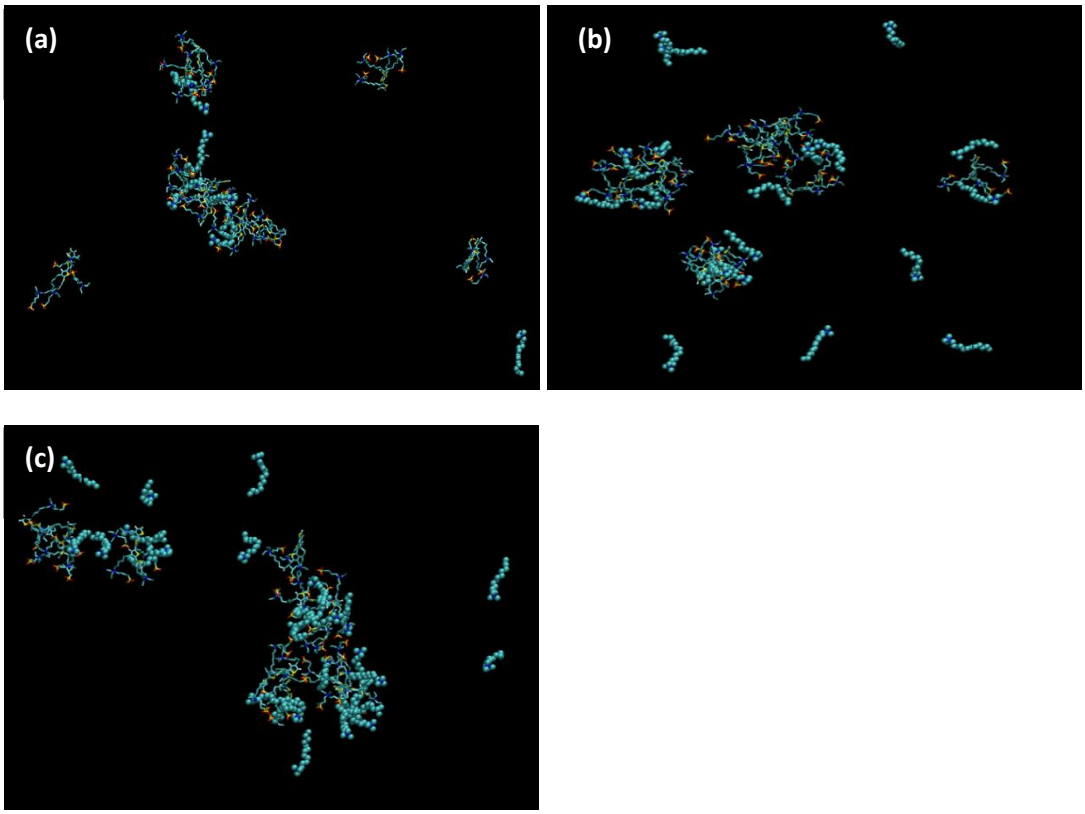


Fig. S4 Simulation cell of P3SBDEAHT and DTAC in (a) 1:1, (b) 1:2 and (c) 1:3 ratios. DTAC shown in van der Waal's representations.

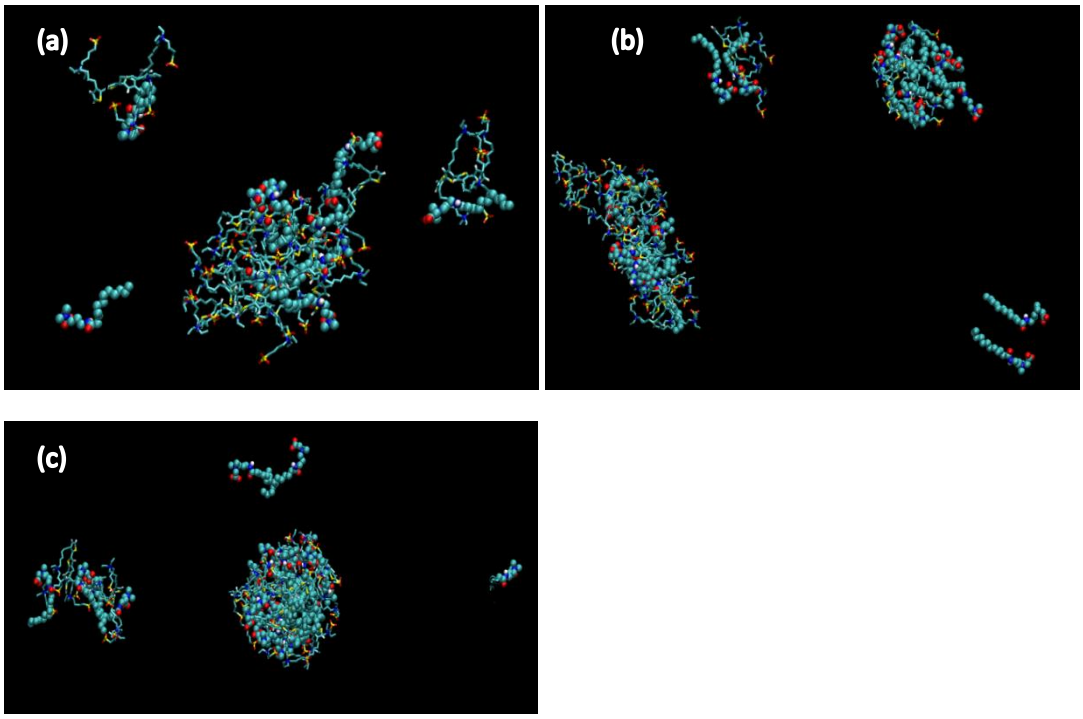


Fig. S5 Simulation cell of P3SBDEAHT and CAPB in (a) 1:1, (b) 1:2 and (c) 1:3 ratios. CAPB shown in van der Waal's representations.

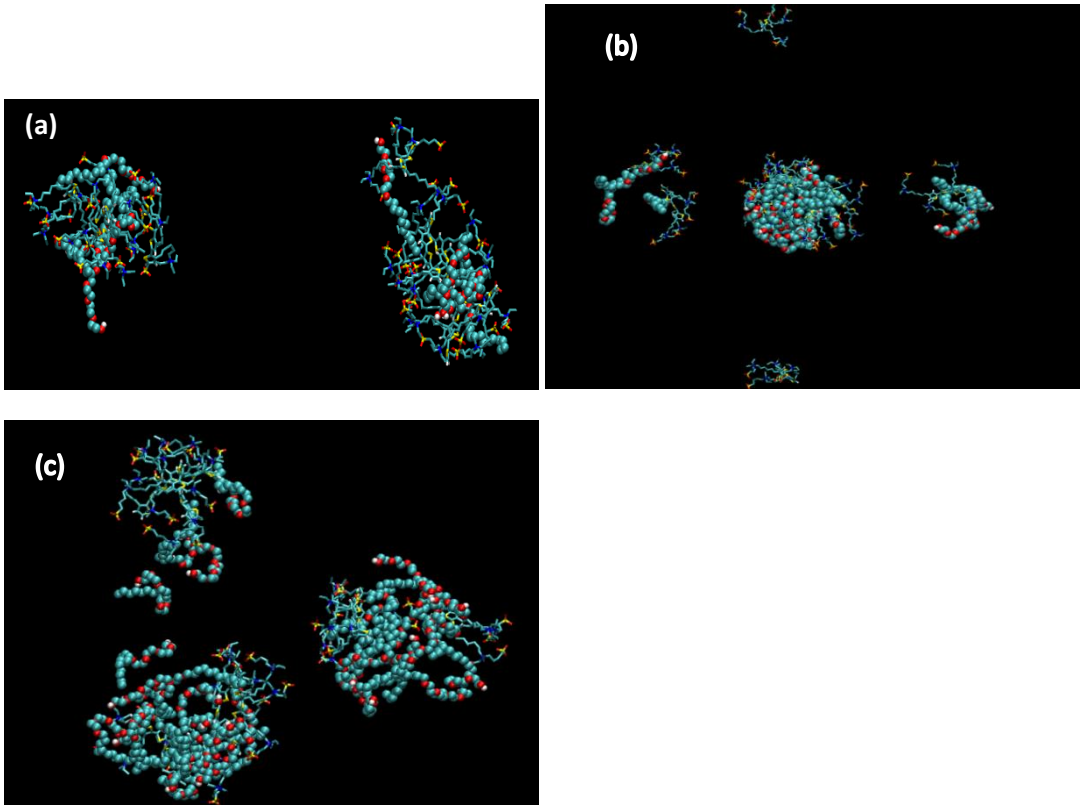
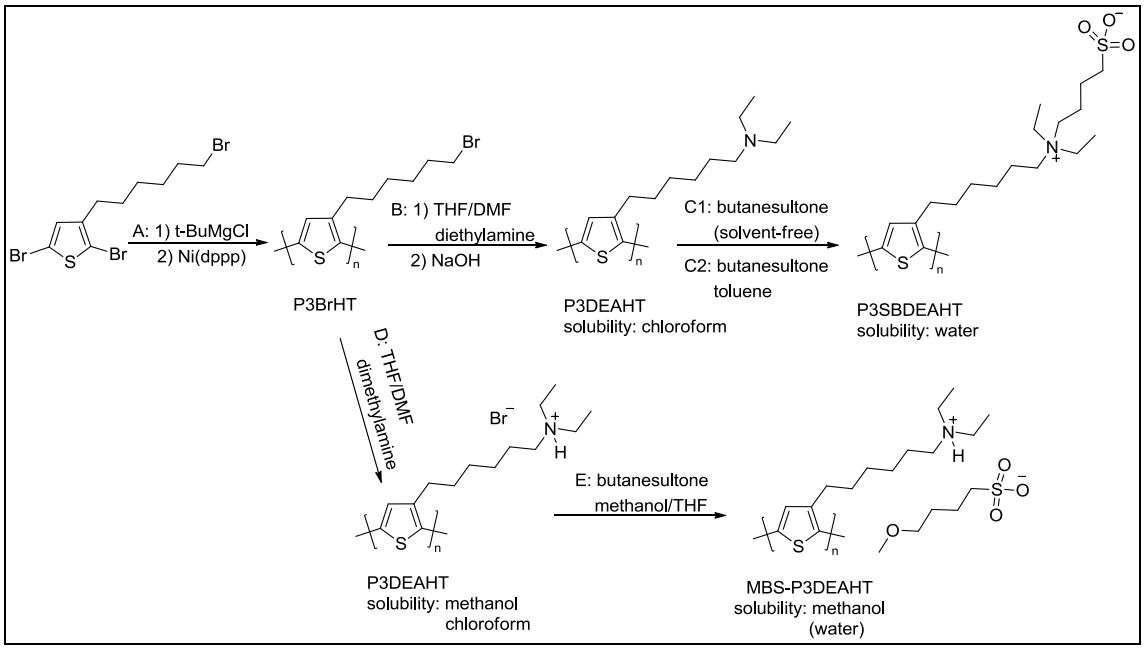


Fig. S6 Simulation cell of P3SBDEAHT and $C_{12}E_5$ in (a) 1:1, (b) 1:2 and (c) 1:3 ratios. $C_{12}E_5$ shown in van der Waal's representations.

Polymer synthesis

The synthesis route for the zwitterionic poly[3-(N-(4-sulfonato-1-butyl)-N,N-diethylammonium)hexyl-2,5-thiophene] (P3SBDEAHT) includes a two-step postpolymerization functionalization of the neutral precursor polymer P3BrHT.

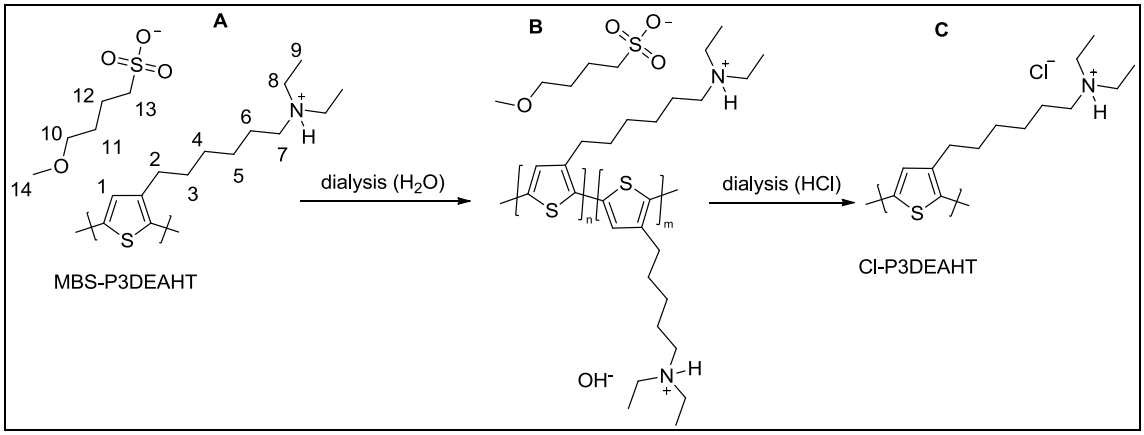
Well-known P3BrHT as non-ionic, non-polar precursor polymer is made in a so-called Grignard metathesis polymerization (GRIM) procedure (A). In the first polymer-analogous reaction step (B), the bromine function of P3BrHT is converted into a diethylamino function by S_N2-type substitution with diethylamine and subsequent formation of the free amine by treatment with NaOH. The second polymer-analogous reaction step (C) involves a ring-opening addition reaction of butanesultone to the diethylamino function in the side chain of P3DEAHT. This reaction proceeds under aprotic reaction conditions, either in an aprotic solvent as toluene or, more effectively, under solvent-free conditions. The complete synthetic route is outlined in Scheme S1.



Scheme S1. Synthesis of the zwitterionic P3SBDEAHT as well as the cationic MBS-P3DEAHT

The polymer analogous substitution with diethylamine leads predominantly to the formation of protonated ammonium groups (D). We observed that the complete

deprotonation of P3DEAHT is of great importance, since the subsequent reaction of protonated P3DEAHT with butanesultone, under the reaction conditions described in reference[12], leads to the formation of poly[3-(N,N-diethylammonium)hexyl-2,5-thiophene] 4-methoxybutane-1-sulfonate MBS-P3DEAHT as cationic polyelectrolyte (reaction step E). Here, a nucleophilic attack of MeOH at the butanesultone takes place. The formation of cationic MBS-P3DEAHT could be confirmed by NMR-measurements in MeOD before and after dialysis (cut-off of the membrane: 3500 g/mol). Fig. S7 shows the corresponding NMR spectra. Before dialysis, all signals of the cationic polyelectrolyte and counterion can be determined (**A**). It should be noted that the signal 14 of the methoxy-group is not depicted, since it overlaps with the solvent signal. But it can be observed in other solvents as DMSO-d6. The signals of the sulfonate cation (10-13) are reduced after dialysis treatment against MeOH/water 1:1, due to ongoing counterion exchange (**B**). The sulfonate species can be completely removed by dialysis against aqueous hydrochloric acid (**C**).



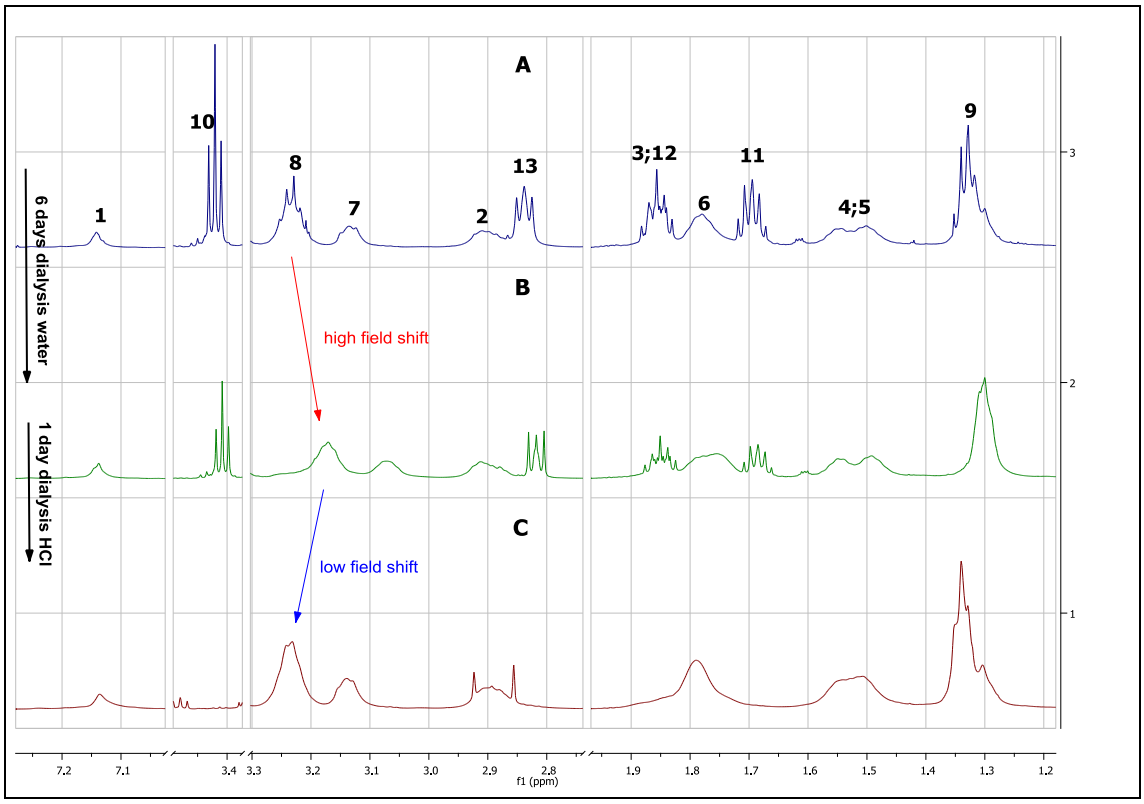


Fig. S7 NMR-spectra of MBS-P3DEAHT before and after dialysis treatment

Because of these findings we strongly recommend to perform ring-opening additions of butanesultone to tertiary amines under aprotic and non-nucleophilic conditions, especially in the case of polymer-analogous reactions. For P3SBDEAHT the most effective reaction was carried out under solvent-free conditions.

The NMR spectra of the "regular" reaction products P3DEAHT (neutral aminohexyl-substituted polythiophene; solvent: $CDCl_3$) and P3SBDEAHT (zwitterionic polyelectrolyte; solvent: DMSO-d6/D_2O 8:1) are shown in Figs. S8 and S9..

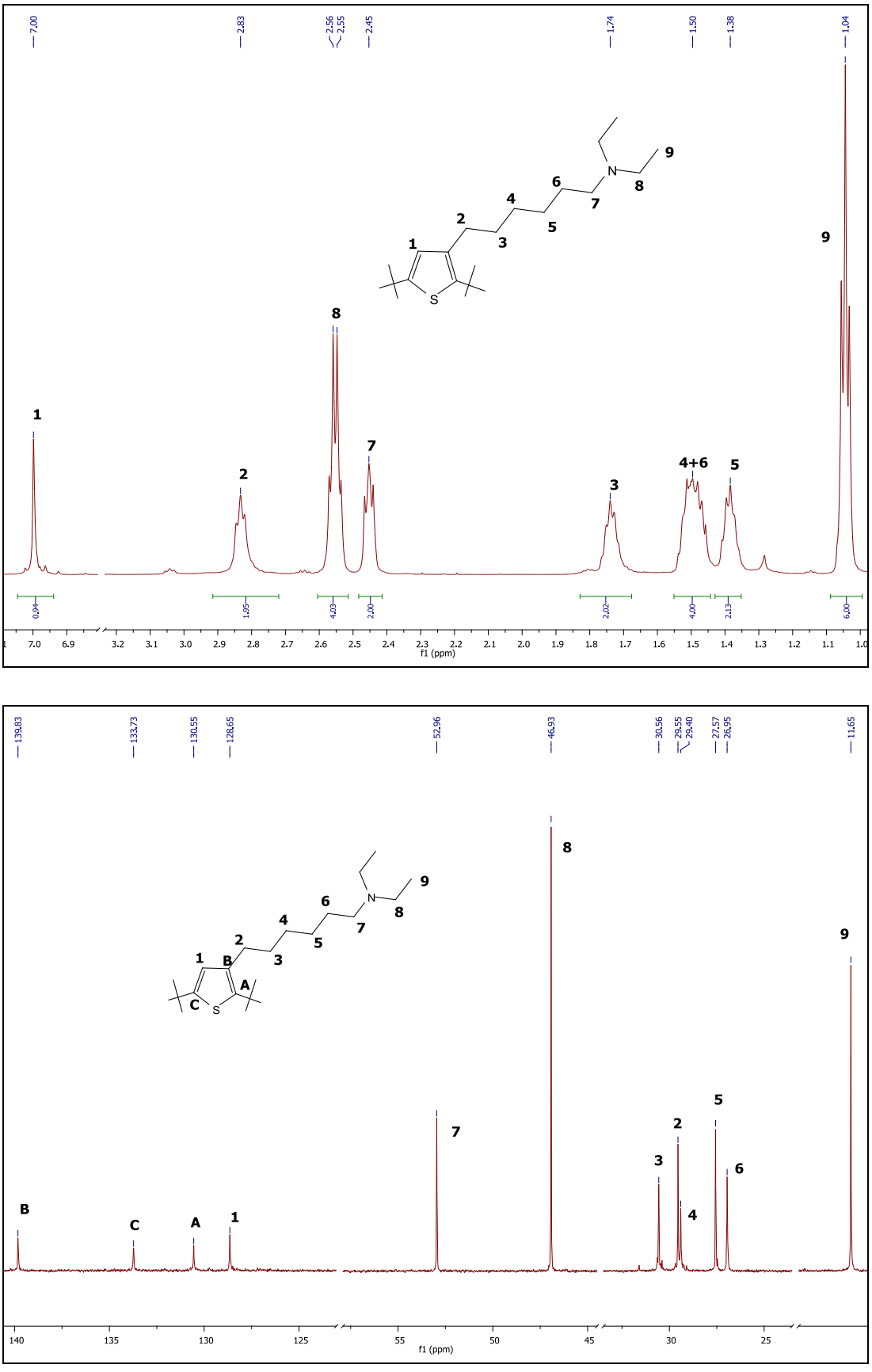


Fig. S8 ^{1}H- (top) and ^{13}C-NMR (bottom) spectra of P3DEAHT

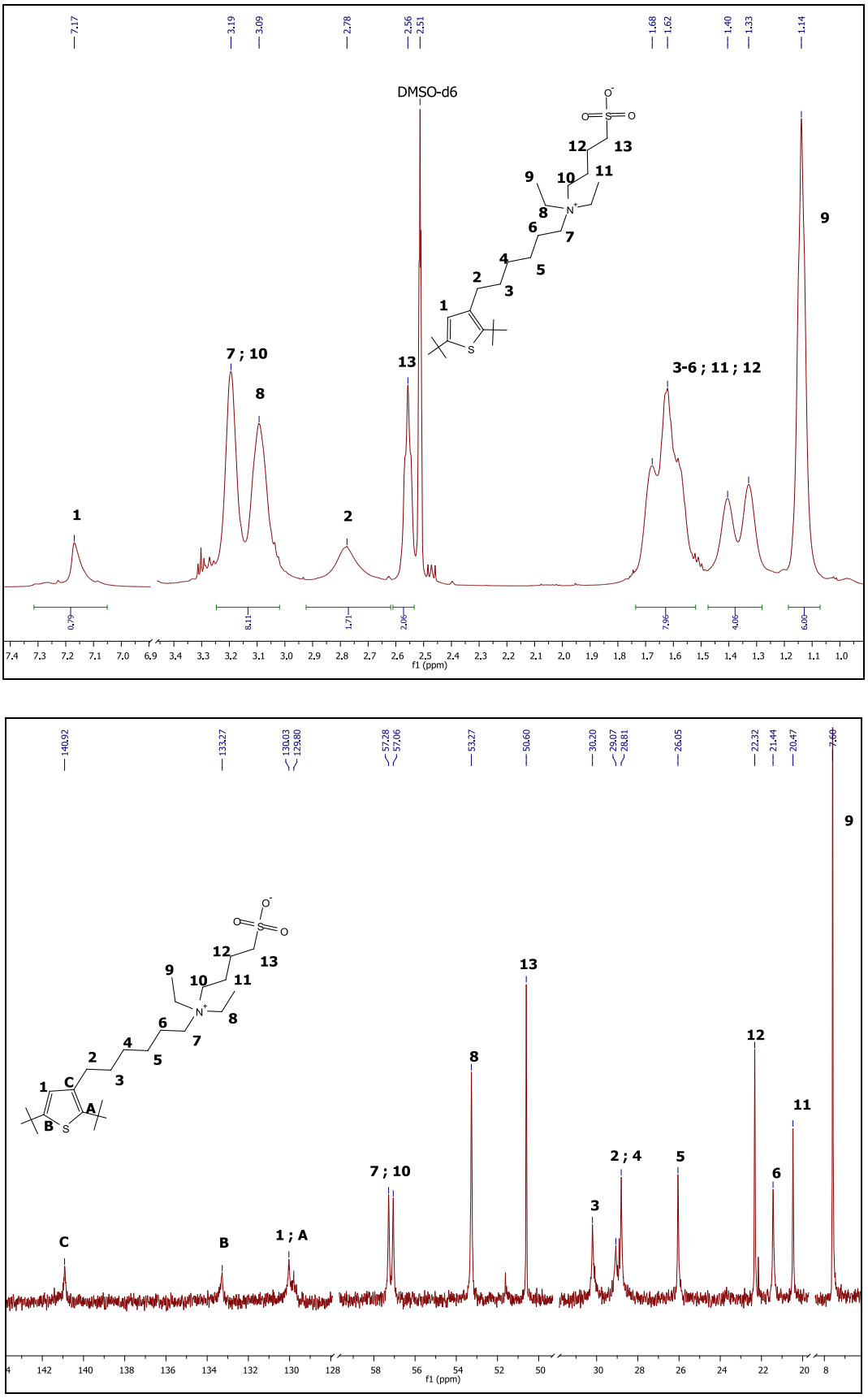


Fig. S9 ^{1}H- (top) and ^{13}C-NMR (bottom) spectra of P3SBDEAHT

Poly[3-(6-bromohexyl)thiophene] (P3BrHT)

3 g (7.41 mmol) of 2,5-dibromo-3-(6-bromohexyl)thiophene are placed into a Schlenk vessel and dissolved in 60 mL of dry THF under inert conditions. After injection of one equivalent of tert.-BuMgCl in the absence of light the vessel is sealed and heated at 80 °C for 2 hours. Following this, 48 mg (0.09 mmol) Ni(dppp)Cl_2 are added to the cooled solution and the reaction mixture is stirred for further 30 min at room temperature. The polymerization is stopped by addition of 30 ml 2 M aqueous HCl. The mixture is stirred for additioinal two hours and the polymer is subsequently precipitated into cold methanol. The raw product is filtered and purified by solvent extraction with MeOH, hexane, ethylacetate and dichloromethane. The dicholormethane fraction is concentrated by evaporation and re-precipitated into methanol. After drying, 710 mg (39 %) polymer are isolated.

GPC: (THF) M_n [g/mol] = 11500; M_w [g/mol] = 12700; PD = 1.10.

^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ 7.00 (s, 1 H), 3.45 (t, *J* = 6.7 Hz, 2 H), 2.90 -2.70 (m, 2 H), 1.97 – 1.83 (m, 2 H), 1.80 – 1.67 (m, 2 H), 1.56 – 1.37 (m, 4 H).

^{13}C NMR (101 MHz, $C_2D_2Cl_4$) δ 140.0; 133.9; 130.7; 128.9; 34.8; 33.0; 30.6; 29.6; 28.9; 28.3.

elementary analysis: $(C_{10}H_{13}BrS)_n$; calculated (%): C 48.99; S 13.08; H 5.34; measured (%): C 48.89; S 13.15; H 5.43.

TGA: first degradation step: 384 °C (41 %); second degradation step: 468 °C (34 %).

DSC: T_m = 143 °C, 149 °C.

absorption: $CHCl_3$ solution: λ_{max}^{Abs} [nm] = 446; film (spincoating from $CHCl_3$ solution): λ_{max}^{Abs} [nm] = 518.

emission: $CHCl_3$ solution (λ_{exc} = 440 nm): λ_{max}^{Em} [nm] = 573; film (spincoating from $CHCl_3$ solution): λ_{max}^{Em} [nm] = 649.

Poly[3-(6-(N,N-diethylamine)hexyl)thiophene] (P3DEAHT):

200 mg (0.82 mmol) of P3BrHT are dissolved in 6 mL of dry THF under inert gas conditions. After injection of 5 mL of DMF and 4 mL (38 mmol) of diethylamine at 50 °C the Schlenk tube is sealed and the reaction mixture stirred at 80 °C over night.

Following this, the mixture is dialyzed, first against methanol/THF (1/1, v/v) and second against aqueous NaOH solution (0.4 M). The solid formed after removal of the water is separated by filtration, washed with water and washed out of the filter by chloroform. Evaporation to dryness leads to 186 mg (0.78 mmol; 95 %) of a black-reddish solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.00 (s, 1 H), 2.89 – 2.75 (m, 2 H), 2.54 (q, *J* = 7.1 Hz, 4 H), 2.48 – 2.36 (m, 2 H), 1.78 – 1.7 (m, 2 H), 1.54 – 1.44 (m, 4 H), 1.42 – 1.34 (m, 2 H), 1.03 (t, *J* = 7.0 Hz, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 139.8; 133.7; 130.6; 128.7; 53.0; 46.9; 30.6; 29.6; 29.4; 27.6; 27.0; 11.7.

elementary analysis: $(C_{14}H_{23}NS)_n$; calculated (%): C 70.83; H 9.77; N 5.90; S 13.51; measured (%): C 70.10; H 9.58; N 5.59; S 13.45.

TGA: first degradation step: 414 °C (30 %); second degradation step; 472°C (42 %); third degradation step; 794 °C (16%).

DSC: $T_{recryst.}$ = 0.5 °C, T_m = 89.8 °C

absorption: $CHCl_3$ solution: λ_{max}^{Abs} [nm] = 441.

emission: $CHCl_3$ solution (λ_{exc} = 400 nm): λ_{max}^{Em} [nm] = 572.

Poly[3-(N-(4-sulfonato-1-butyl)-N,N-diethylammonium)hexyl-2,5-thiophene] (P3SBDEAHT):

136 mg (0.57 mmol) of P3DEAHT are melted at 110 °C in a Schlenk tube under inert gas conditions. 8 mL (78 mmol) of 1,4-butanesultone are injected into the polymer melt and the mixture is stirred at 90 °C over three days. After cooling down to room temperature the liquid is decanted from the solid phase. The solid residue is washed with THF and dissolved in water. The aqueous polymer solution is purified by dialysis (cut-off limit of the membrane: 3500 g/mol), first against methanol/water and second against methanol for two days. The solid after removal of the water is separated and Soxhlet extracted with methanol (six hours) and chloroform (overnight). The resulting solid is washed out of the Soxhlet tube with water and concentrated under reduced pressure. The highly concentrated polymer solution is transferred into a plastic tube and

evaporated to dryness under high vacuum (10^{-3} mbar). 104 mg (0.28 mmol; 49 %) of a red solid are isolated.

^{1}H NMR (400 MHz, DMSO) δ 7.15 (s, 1 H), 3.36 – 2.89 (m, 8 H), 2.90 – 2.64 (m, 2 H), 2.56 (s, 2 H), 1.82 – 1.23 (m, 12 H), 1.13 (s, 6 H).

^{13}C NMR (151 MHz, DMSO) δ 140.9; 133.3; 130.0; 129.8; 57.3; 57.1; 53.3; 50.6; 30.2; 29.1; 28.8; 26.1; 22.3; 21.4; 20.5; 7.6.

elementary analysis: $(C_{18}H_{31}NO_3S_2)_n$; calculated (%): C 57.87; H 8.36; N 3.75; S 17.17; measured (%): C 56.48; H 10.68; N 3.67; S 17.44.

TGA: first degradation step: 284 °C (13 %); second degradation step: 364°C (35 %); third degradation step; 468 °C (29%).