

Supporting Information

Studies on the Langmuir-Blodgett films of Polythiophene containing mesogenic side chain

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Synthetic procedures of the monomer¹

Synthesis of 4-Formyl phenyl thiophene 3-carboxylate:

Thiophene 3-carboxylic acid (0.078mol), 4-hydroxy benzaldehyde (0.078mol), Dicyclocarbodiimide (0.078mol) dissolved in 25mL of dichloromethane (DCM) and Dimethyl amino pyridine (0.9529g, 0.078mol) was finally added and stirred at room temperature for 24Hrs. The contents were filtered and the organic solution was washed with dil.HCl and 2% KOH solution. The compound was recrystallized in Isopropanol (yield- 62 %.)

¹H NMR (CDCl₃, δ): 10.01(S, 1H), 8.34(Q, 1H), 7.96 (D, 2H), 7.66(D, 1H), 7.4(M, 3H).

¹³C NMR (CDCl₃, δ): 191.0, 160.4, 155.5, 134.7, 134.1, 132.2, 131.4, 128.3, 126.8, 122.6.

ESI-MS Experimental (predicted): 232.72 (232.02)

Synthesis of N- (4- alkoxy Phenyl) acetamide:

N- (4- hydroxy Phenyl) acetamide (0.02mol) dissolved in 100 mL of dimethyl formamide (DMF) and Potassium carbonate (0.02mol) was added and the contents were stirred and heated up to 80°C, Alkyl bromide (0.02mol) was added slowly to the contents and reaction was stirred for 3hrs at 70-80°C. The reaction mixture was poured into cold water and dil. HCl was added and neutralized. The product was filtered and recrystallized using Petroleum ether (yield - 80%)

¹H NMR of PT-C6 (CDCl₃, δ): 7.53(D,1H), 7.36(D,2H), 6.82(D,2H), 3.91(T, 2H), 2.11 (S,3H), 1.75(M,2H), 1.42(M,2H), 1.29(M,8H), 0.87(T,3H).

¹³C NMR of PT-C6 (CDCl₃, δ): 168.5, 130.93, 122,114.8, 68.4, 31.9, 29.4, 29.36, 29.33, 29.1, 24.3, 22.7 and 14.1.

ESI-MS Experimental (predicted): 235.76 (235.16).

Synthesis of 4- alkoxy aniline:

N- (4 - alkoxy Phenyl) acetamide (3.17mmol) was treated with 3N HCl in 50ml of C₂H₅OH and refluxed for 6 hrs. The reaction mixture was poured into water and neutralized using 2% KOH solution the amine obtained was extracted using ether.

¹H NMR of PT-C6 (CDCl₃, δ): 7.0(D, 2H), 6.79(d, 2H), 3.8(T, 2H), 2.02(M, 2H), 1.42(M, 2H), 1.3(M, 4H), 0.87(T, 3H).

¹³C NMR of PT-C6 (CDCl₃, δ): 152.5, 139.8, 116.5, 115.7, 68.8, 32, 29.7, 29.5 and 29.45.

ESI-MS Experimental (predicted): 193.90 (193.29).

Synthesis of 4-{(E)-[(4-alkoxyPhenyl)imino]methyl}phenylthiophene 3- Carboxylate}

4-alkoxy aniline (4.3mmol) and 4-formyl phenyl thiophene 3-carboxylate (4.31mmol) were reacted (detailed multi stage synthetic details are presented in supporting information) in ethanol medium using microwave reactor. The obtained reaction mixture was diluted with methanol and recrystallized using Isopropanol (yield- 62%). The compounds containing hexyloxy and tetradecyloxy groups were labeled as Compound1 and compound2 respectively. The representative NMR data obtained for compound 1 is presented below.

¹H NMR of PT-C6 (CDCl₃, δ): 8.48(S, 1H), 8.3(D, 1H), 7.95(D, 2H), 6.9(D, 2H), 3.97(D, 2H), 1.8(M, 2H), 1.46(M, 2H), 1.3(M, 4H), 0.88(T, 3H).

¹³C NMR of PT-C6 (CDCl₃, δ): 160.7, 158, 157, 152.8 144.5 134.4, 134.3, 132.6, 129, 128.3, 126.6, 122.3 122.1, 115.08, 68.08, 31.4, 19.4 and 13.98.

ESI-MS Experimental (predicted): 408.13 (407.53).

Elemental analysis: C₂₄ H₂₅ N O₃ C: 71.1, H: 6.78, N: 3.84, O: 11.86, S: 7.9

Polymerization: The polymers of PT-C6 and PT-C14 were prepared by electrochemical polymerization in acetonitrile with tetra butyl ammonium perchlorate as the supporting electrolyte with a current density of 2 mA cm⁻². The obtained polymers were washed with cold acetonitrile and dried in Vacuum 50 C. The formed polymers were also confirmed using NMR.

¹H NMR: 8.34, 7.96, 7.38, 7.24, 6.9, 3.3, 2.19 - 0.87.

¹ C. Suryanarayanan, E. Ravindran, S. J. Ananthakrishnan, N. Somanathan and A.B. Mandal, J.Mater. Chem. 2012, 22, 18975.

Table S1. Parameters calculated from hysteresis experiments at different area per repeat unit levels obtained for PT-C6 and PT-C14.

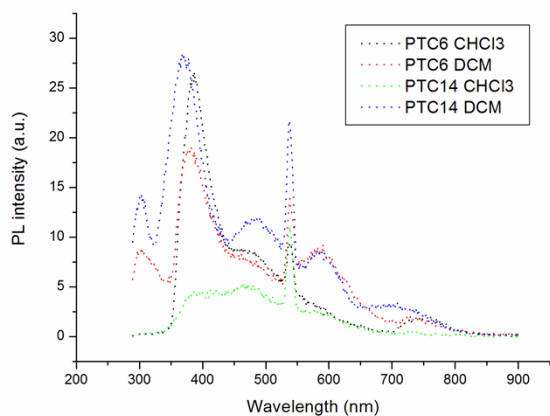
Sample code	Hysteresis ratio		Permanent Set	
	First cycle	Second cycle	First cycle	Second cycle
PT-C6 CHCl₃	55.86	43.36	19.79	20.6
PT-C6 CH₂Cl₂	40.88	38.54	13.78	20.75
PT-C14 CHCl₃	58.37	53.95	28.19	37.59
PT-C14 CH₂Cl₂	53.14	46.31	23.7	11.64

The stability of the Langmuir films has been tested using the hysteresis analysis well below the collapse pressure of the film, where the transfer to solid surfaces was done.

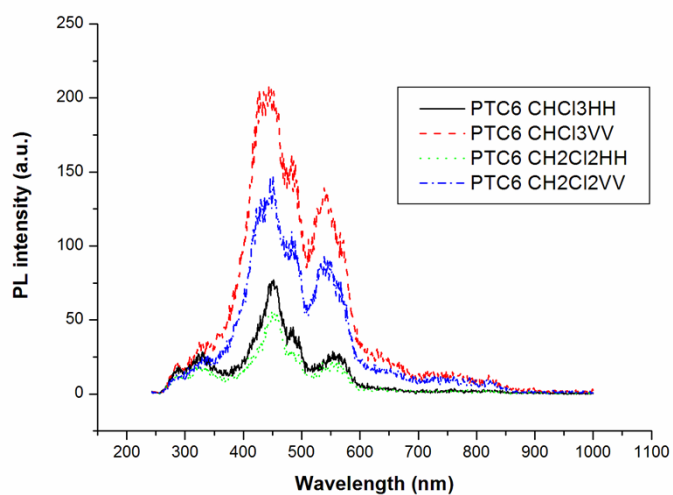
S2 The rate of change of area per unit time from the hysteresis analysis

Sample	CH ₂ CL ₂		CHCl ₃	
	1st Cycle	2nd Cycle	1st Cycle	2nd Cycle
PTC6	0.9	0.59	0.97	0.77
PTC14	0.85	0.6	0.89	0.77

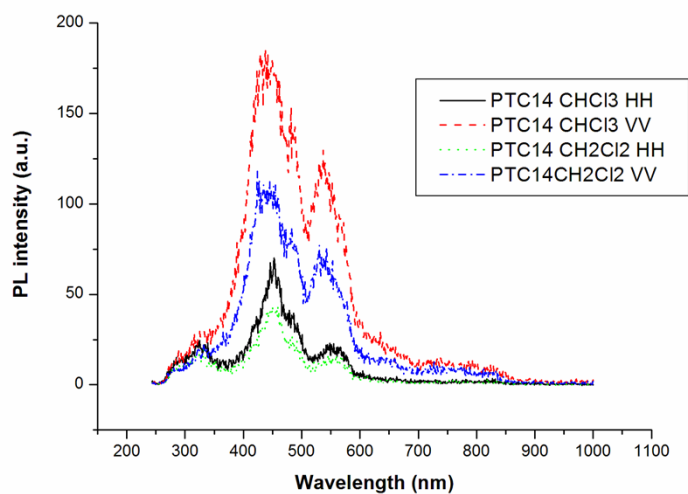
The rate of change of area for a neat film on compression and expansion should be same. However, any hysteresis curve is expected to have lost some amount of film material based on the property of the material. The material is stable as Langmuir films.



S3 PL spectra of PTC6 and PTC14 in CHCl_3 and CH_2Cl_2 solutions



S4 PL spectra of spin coated films of PTC6



S5 PL spectra of spin coated films of PTC14

Table S6. Linear dichroism from polarised Photo luminescence spectra.

Sample code			UV	Blue	Green	Red
LB film	PT-C6	CH ₂ Cl ₂	0.856	0.357	0.171	0.190
		CHCl ₃	0.714	0.296	0.128	0.192
	PT-C14	CH ₂ Cl ₂	0.719	0.303	0.170	0.163
		CHCl ₃	0.707	0.288	0.158	0.193
Spin coated film	PT-C6	CH ₂ Cl ₂	0.876	0.384	0.198	0.271
		CHCl ₃	0.814	0.366	0.168	0.210
	PT-C14	CH ₂ Cl ₂	0.864	0.390	0.182	0.238
		CHCl ₃	0.738	0.368	0.140	0.232