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APPENDICES

APPENDIX A

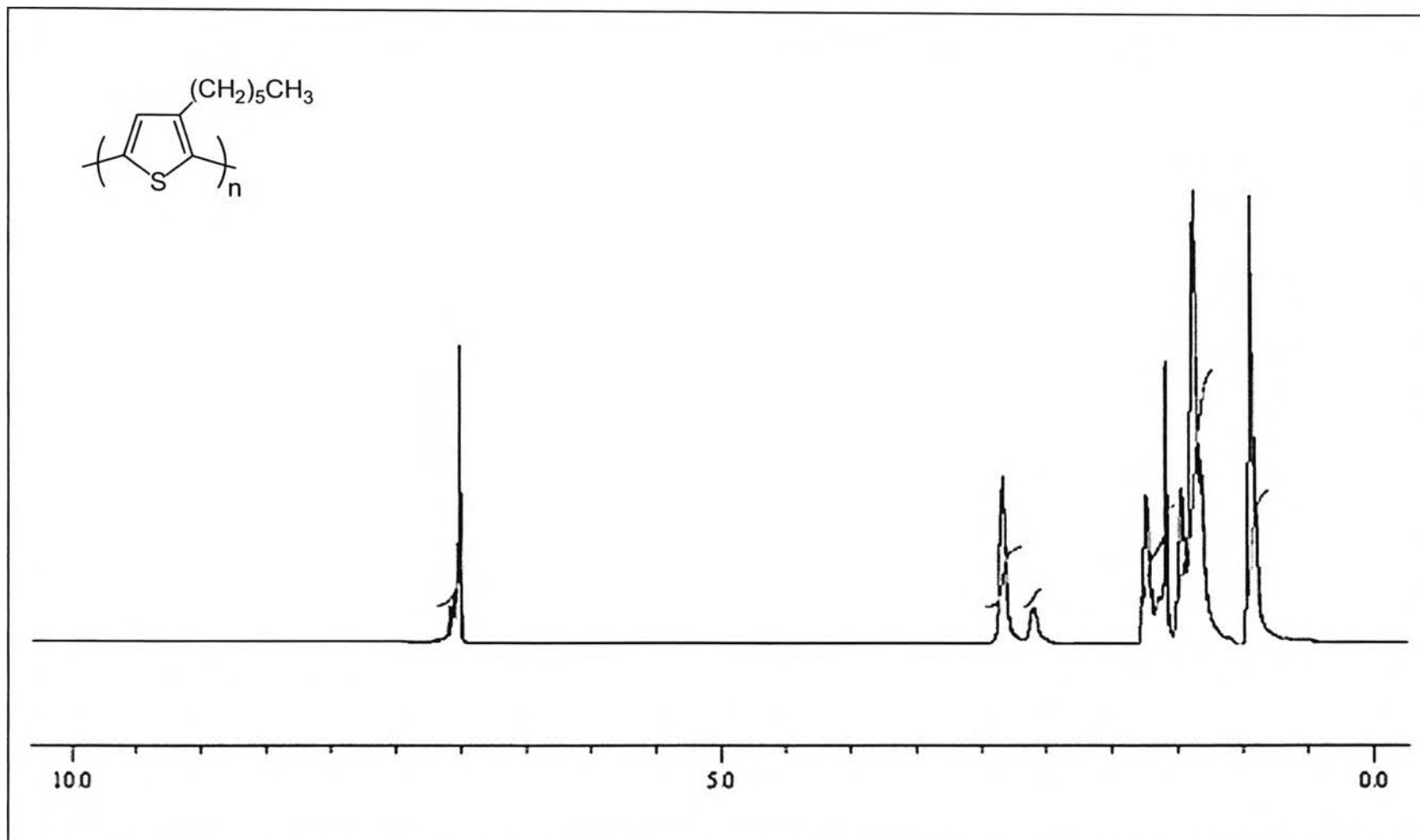


Figure A-1 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of poly(3-hexylthiophene)

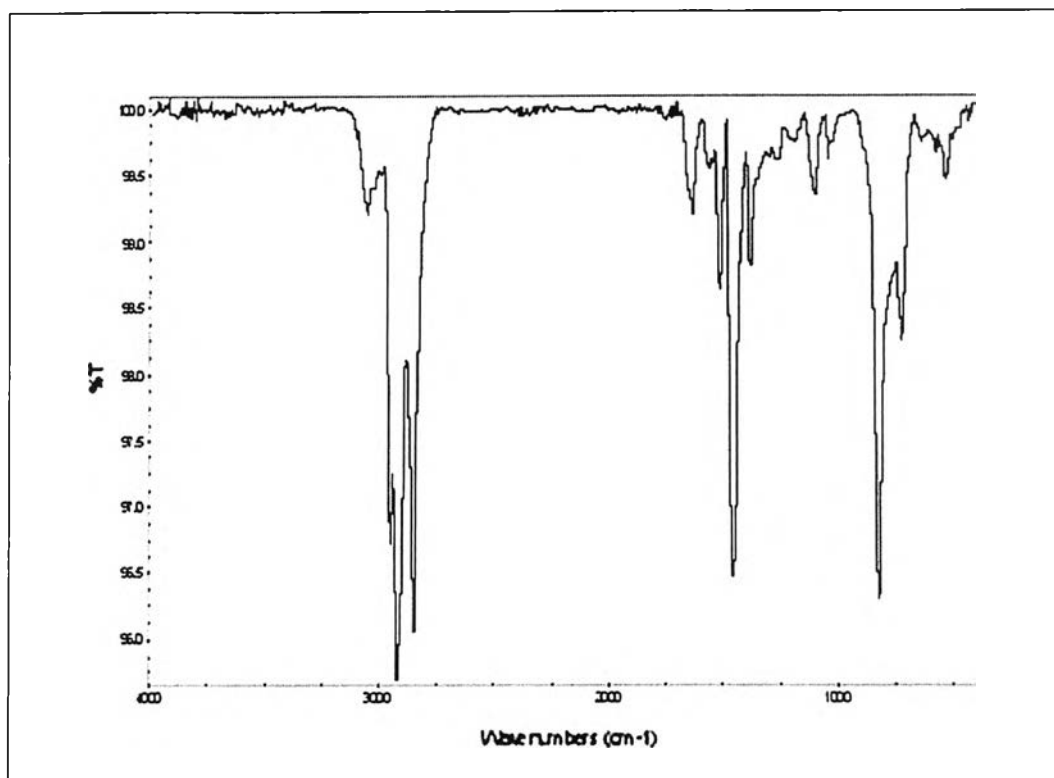


Figure A-2 FT-IR (KBr) spectrum of the oxidized P3HT

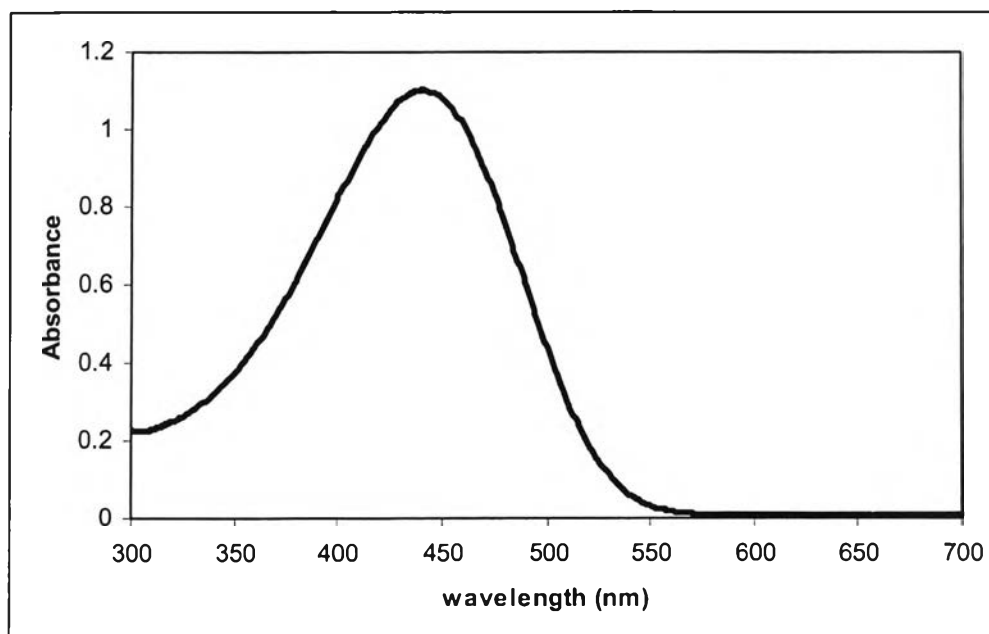


Figure A-3 UV-visible spectrum of P3HT in CHCl₃

APPENDIX B

The Four-point Probe Method for Electrical Conductivity Measurement [8,50]

Four tiny electrodes are arranged in straight line separated at exactly equal distances (d) and touched the surface of the sample to be measured. Then the electrodes are further connected with an electrical circuit equipped with an Amp meter (A) and a Voltmeter (V) (**Figure B-1**). Contacts between the 4 electrodes and the sample surface must be equal. During the measurement, the current (I) is applied through electrode contact 1 to 4, and the potential difference (ΔV) across electrode contacts 2 and 3 is measured. The conductivity of the sample can be calculated from the equation **B-1**

$$\text{Conductivity (S.cm}^{-1}\text{); } \quad \sigma = I/kVt \quad \text{..... (B-1)}$$

Where I is current (A)

k is probe constant (2.418×10^{-4})

V is voltage (volt)

t is film thickness (cm)

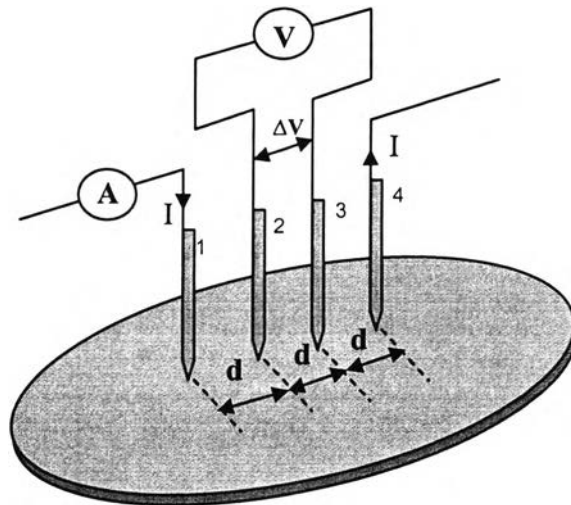


Figure B-1 Conductivity measurement by Four-point Probe method

The accuracy of the conductivity measurement by this method depends on:

- i) the size of the sample, which must be very large compared to the separation distances (d) between the electrodes.
- ii) thickness of the sample, which must be very small compared to the separation distances (d) between the electrodes.

APPENDIX C

Example of the calculation of AC-index

From UV-Visible spectroscopy data;

λ (nm)	Absorbance	λ_i	A_i	$\lambda_i A_i$
		$(\lambda_1 + \lambda_2)/2$	$(A_1 + A_2)/2$	
310	0.208152	310.5	0.208563	64.75
311	0.208974	311.5	0.209521	65.26
312	0.210067	312.5	0.210774	65.86
313	0.21148	313.5	0.212073	66.48
314	0.212667	314.5	0.213511	67.14
315	0.214356	315.5	0.215014	67.83
316	0.215672	316.5	0.216622	68.56
317	0.217572	317.5	0.218448	69.35
318	0.219324	318.5	0.22029	70.16
319	0.221256	319.5	0.222245	71.00
320	0.223233	-	-	-
Sum (310-320 nm)		-	2.14700	676.45

$$\text{AC-index (310-320)} = \frac{\sum \lambda_i A_i}{\sum A_i} = \frac{676.4}{2.147} = 315.0$$

The calculation of %HT

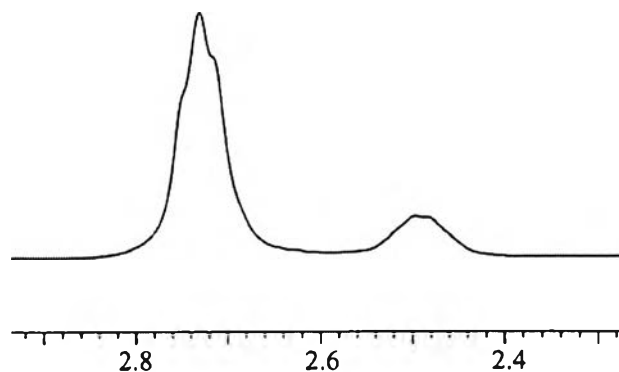


Figure C-1 Part of ^1H NMR spectrum data of CHCl_3 fraction

From ^1H NMR spectral data of P3HT fraction

fraction	HT Area	HH Area	%HT
acetone	1.00	0.74	57.47
hexane	1.00	0.49	67.11
CH_2Cl_2	1.00	0.30	76.92
10% CHCl_3 in CH_2Cl_2	1.00	0.26	79.37
CHCl_3	1.00	0.24	80.65

Example of the calculation of %HT of the acetone fraction;

$$\%HT = \frac{\text{HT Area}}{\text{HT Area} + \text{HH Area}} \times 100 = \frac{1.00}{1.24} \times 100 = 80.65$$

APPENDIX D

Table D-1 λ_{\max} of P3HT fractions ranged by their average molecular weight

Fraction	M_n^*	λ_{\max}
acetone	1,543	393
hexane	6,456	420
CH ₂ Cl ₂ in CH ₂ Cl ₂	26,588	437
10%CHCl ₃	53,255	441
CHCl ₃	67,013	443

*obtained from GPC measurement

Table D-2 %HT of P3HT fractions ranged by their average molecular weight

Fraction	M_n^*	%HT
acetone	1,543	57.47
hexane	6,456	67.11
CH ₂ Cl ₂	26,588	76.92
CH ₂ Cl ₂ in CH ₂ Cl ₂	53,255	79.37
CHCl ₃	67,013	80.65

*obtained from GPC measurement

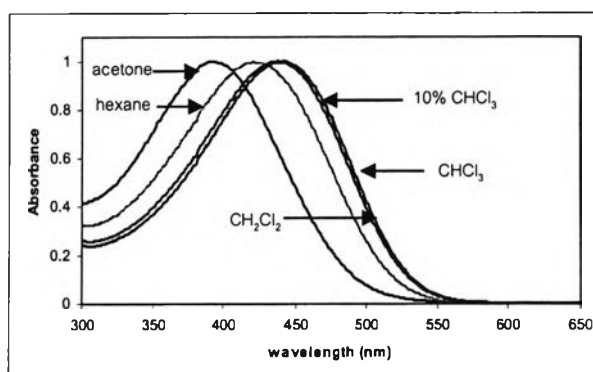


Figure D-1 UV-visible spectra of poly(3-hexylthiophene) fractions ranged by their average molecular weight (**Figure 3.2**).

Table D-3 AC-index values (300-700) of poly(3-hexylthiophene) fractions ranged by their average molecular weight (**Figure D-1**).

Fraction	M_n^*	AC-index
acetone	1,543	396.7644
hexane	6,456	412.6939
CH ₂ Cl ₂	26,588	425.4063
10%CHCl ₃	53,255	428.1410
CHCl ₃	67,013	428.5281

*obtained from GPC measurement

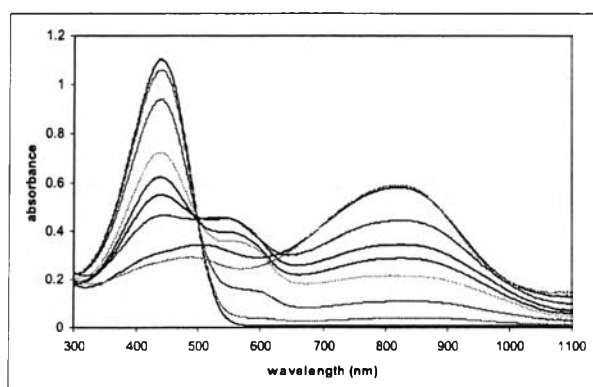
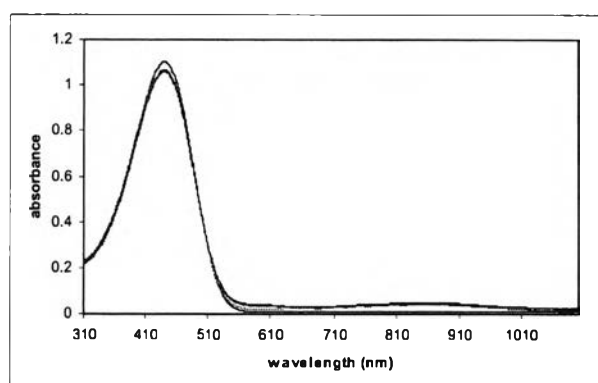


Figure D-2 UV-visible spectra of P3HT doped with Trifluoroacetic acid (TFA) at different equivalent from 0 to 50 min (**Figure 3.9**).

Table D-4 Absorbance values from **Figure D-2**.

Acid $\times 10^3$ (equivalent)	Absorbance		
	440 nm	541 nm	824 nm
0.83	1.0612	0.0652	0.0302
1.67	0.9022	0.1927	0.1081
2.50	0.7615	0.3047	0.1940
3.33	0.6248	0.3839	0.2806
4.17	0.4942	0.4236	0.3744
5.00	0.4211	0.4209	0.4492
6.67	0.3233	0.3525	0.5595
10.00	0.2784	0.2750	0.5788

**Figure D-3** UV-visible spectra of P3HT doped with 0.83×10^3 equivalent of TFA from 0 to 30 min.

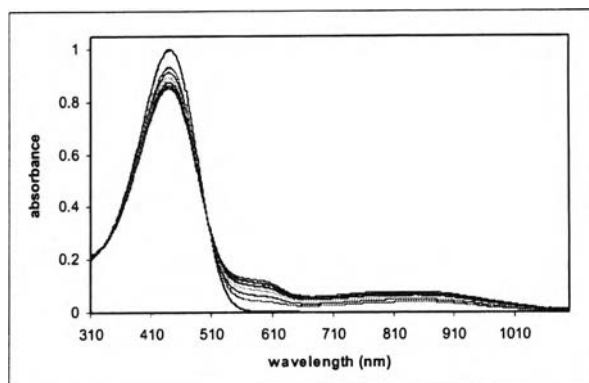


Figure D-4 UV-visible spectra of P3HT doped with 1.67×10^3 equivalent of TFA from 0 to 30 min.

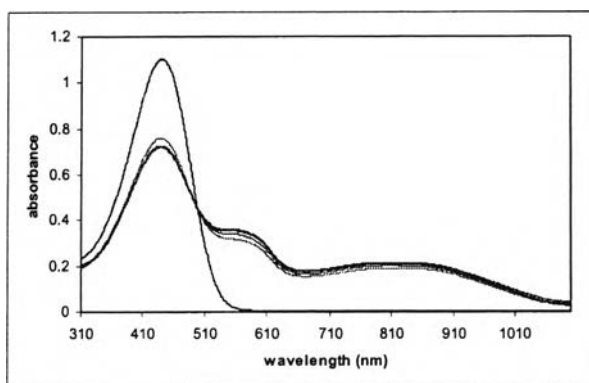


Figure D-5 UV-visible spectra of P3HT doped with 2.50×10^3 equivalent of TFA from 0 to 30 min.

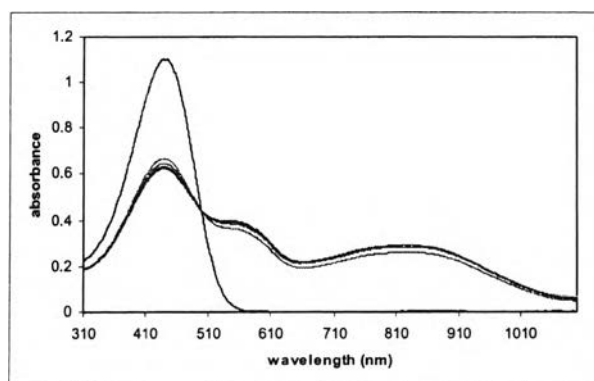


Figure D-6 UV-visible spectra of P3HT doped with 3.33×10^3 equivalent of TFA from 0 to 30 min.

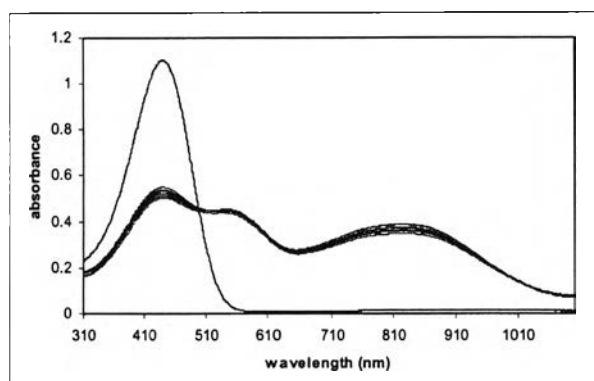


Figure D-7 UV-visible spectra of P3HT doped with 4.17×10^3 equivalent of TFA from 0 to 30 min.

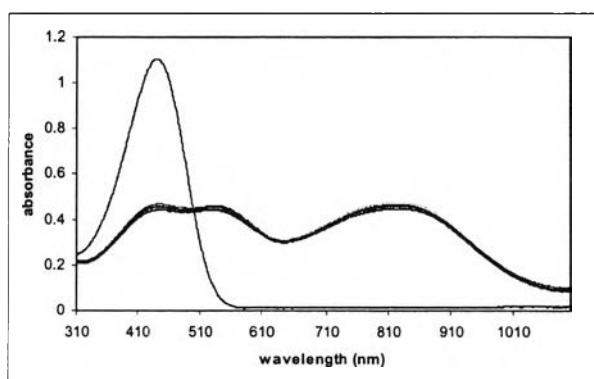


Figure D-8 UV-visible spectra of P3HT doped with 5.00×10^3 equivalent of TFA from 0 to 30 min.

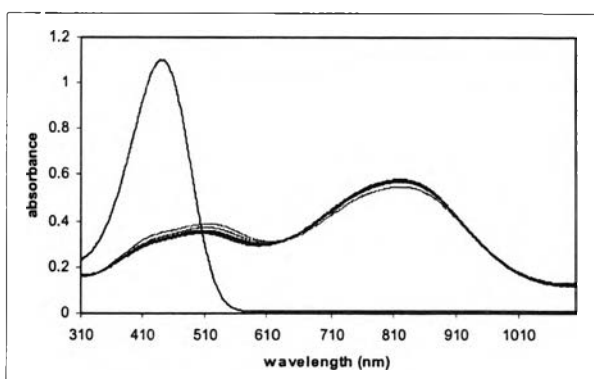


Figure D-9 UV-visible spectra of P3HT doped with 6.67×10^3 equivalent of TFA from 0 to 30 min.

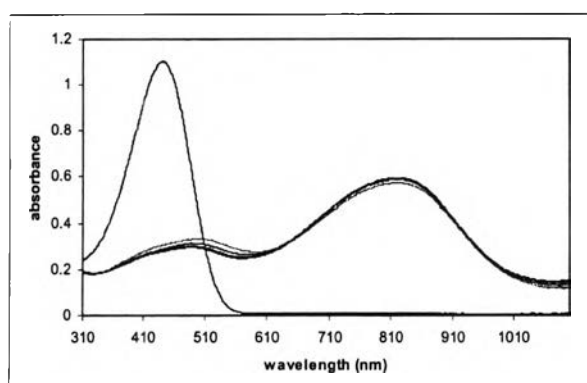


Figure D-10 UV-visible spectra of P3HT doped with 10.00×10^3 equivalent of TFA from 0 to 30 min.

Table D-5 AC-index values (300-1000) of P3HT doped with Trifluoroacetic acid (TFA) from **Figure D-3** – **Figure D-10**.

Acid $\times 10^3$ (equivalent)	AC-index						
	0 min	5 min	10 min	15 min	20 min	25 min	30 min
0.83	437.4747	460.8286	461.6802	463.6449	466.2790	467.7039	462.4023
1.67	434.3392	490.2087	500.7751	508.6624	515.1810	519.1866	515.7822
2.50	434.3392	566.3936	573.9217	579.1621	577.0504	579.6765	580.0662
3.33	430.0447	596.2709	605.5144	608.3463	607.2303	607.5751	609.9711
4.17	441.5246	633.9975	640.8908	637.4657	634.2332	630.4468	626.9141
5.00	444.5107	651.7934	656.1472	663.7614	655.1328	653.8841	650.4358
6.67	436.7996	682.0528	687.3338	688.6044	690.1621	691.0961	691.5434
10.00	435.8958	690.4063	695.7209	698.3548	698.8087	698.8285	699.2273

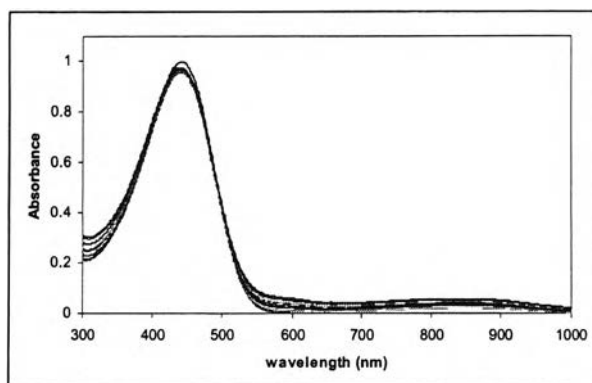


Figure D-11 AC-index curves of P3HT doped with Methanesulfonic acid (MSA) 0.33 equivalent from 0 to 60 min.

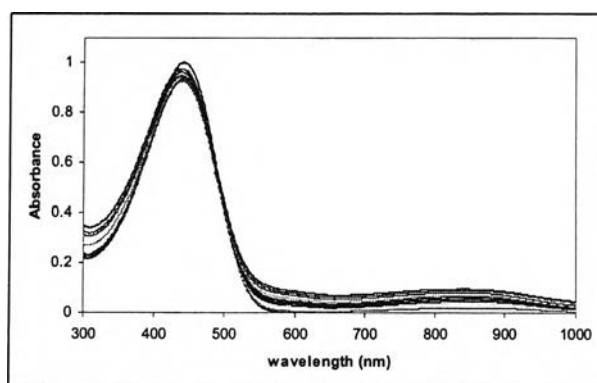


Figure D-12 AC-index curves of P3HT doped with Methanesulfonic acid (MSA) 0.5 equivalent from 0 to 60 min.

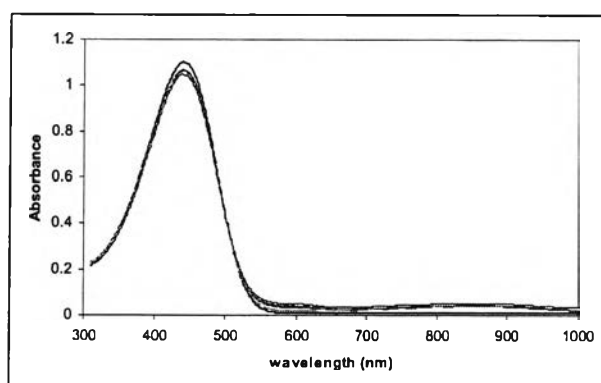


Figure D-13 AC-index curves of P3HT doped with Trifluoroacetic acid (TFA) 0.83 equivalent from 0 to 60 min.

Table D-6 AC-index values (300-1000) of P3HT was doped with MSA and TFA(Figure D-11 –Figure D-13).

Time (min)	Acid ($\times 10^3$ equivalent)		
	MSA (0.33)	MSA (0.50)	TFA (0.83)
0	412.3971	411.1372	411.4747
5	429.4147	429.2044	434.8286
10	432.8958	438.0810	435.6802
15	435.5016	446.2101	437.6449
20	438.9267	450.6951	440.2790
25	441.2799	455.8915	441.7039
30	443.6763	460.1171	442.4023
35	446.1573	463.4258	442.9077
40	447.8854	465.3715	442.5372
45	450.2408	467.5196	444.5464
50	451.7514	469.8038	447.1468
55	452.2505	473.0148	N/A
60	454.4241	474.8630	N/A

N/A = the reaction start from 0 to 50 min

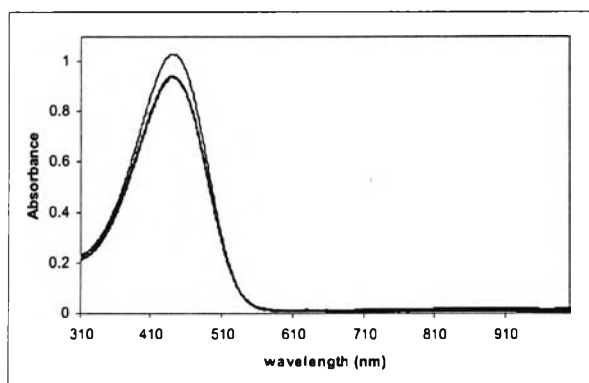


Figure D-14 UV-visible spectra of 0.3 μmol P3HT doped with 3.33×10^3 equivalents of CA + CHCl_3 during 60 min after additions.

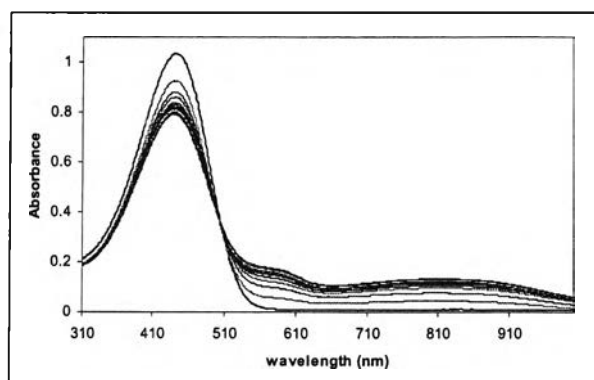


Figure D-15 UV-visible spectra of 0.3 μmol P3HT doped with 3.33×10^3 equivalents of DCA during 60 min after additions.

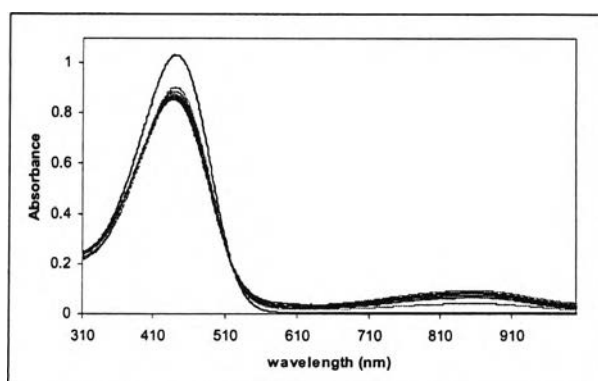


Figure D-16 UV-visible spectra of 0.3 μmol P3HT doped with 3.33×10^3 equivalents of TCA + CHCl_3 during 60 min after additions.

Table D-7 AC-index values (300-1000) of 0.3 μmol P3HT doped with 3.33×10^3 equivalents of acids during 60 min after additions (**Figure D-14 – D-16**).

Time (minute)	Acid (3.33×10^3 equivalent)		
	CA	DCA	TCA
0	432.3603	432.6913	432.2578
5	437.2099	463.5184	469.3110
10	437.5550	489.8643	490.5372
15	437.9362	505.5986	484.9969
20	438.0222	513.5366	485.5133
25	438.4497	519.6574	494.8716
30	438.5387	522.8171	508.6688
35	438.8990	524.8920	499.2394
40	439.0989	526.6683	505.1750
45	439.9834	527.5522	510.7284
50	440.0771	529.1547	512.1274
55	440.5401	530.5845	512.7012
60	440.6843	531.1879	502.2591

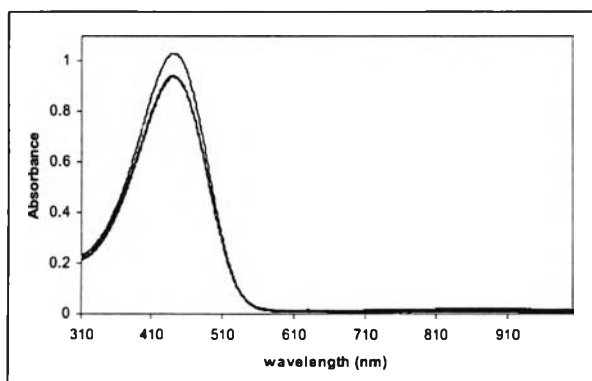


Figure D-17 UV-visible spectra of 0.3 μmol P3HT doped with CA 3.33×10^3 equivalents during 60 min after additions.

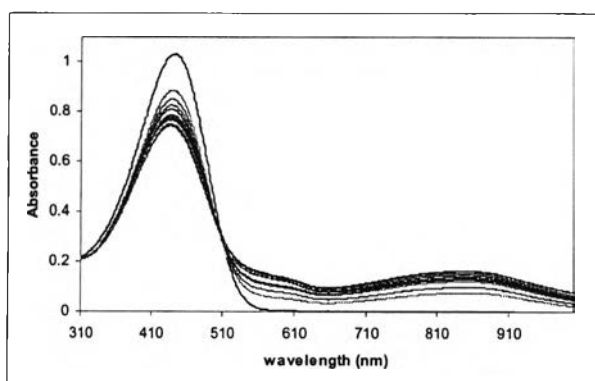


Figure D-18 UV-visible spectra of 0.3 μmol P3HT doped with TCA 3.33×10^3 equivalents during 60 min after additions.

Table D-8 AC-index values (300-1000) of 0.3 μmol P3HT doped with acids 3.33×10^3 equivalents during 60 min after additions (**Figure D-15** and **Figure D-17 – D-18**).

Time (min)	Acid (3.33×10^3 equivalent)		
	CA	DCA	TCA
0	428.5240	425.6913	426.5706
5	440.1182	456.5184	487.8792
10	441.8222	482.8643	505.3875
15	442.5074	498.5986	520.9254
20	443.4451	506.5366	526.5254
25	444.8493	512.6574	532.5966
30	445.6968	514.5091	536.2141
35	446.6525	517.8920	540.3133
40	446.3093	519.6683	543.0997
45	446.7656	520.5522	545.1061
50	446.9275	522.1547	545.7509
55	447.0630	523.5845	549.9638
60	447.1462	524.1879	551.4166

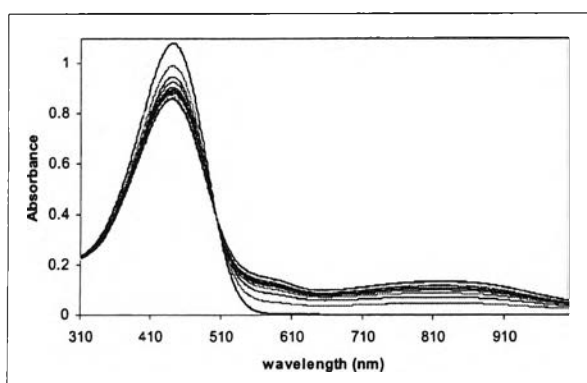


Figure D-19 UV-visible spectra of 0.3 μmol P3HT doped with 3.33×10^3 equivalents DCA during 60 min after additions.

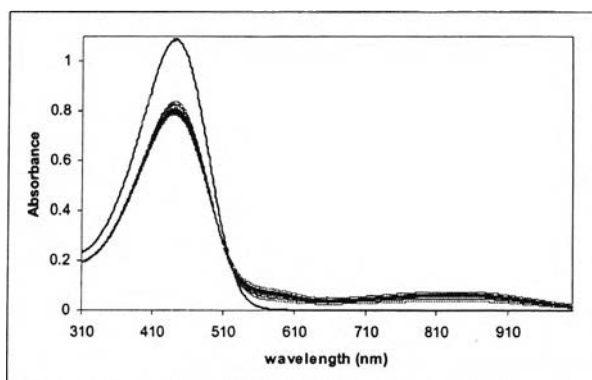


Figure D-20 UV-visible spectra of 0.3 μmol P3HT doped with 3.33×10^3 equivalents DCA + CHCl₃ during 60 min after additions.

Table D-9 AC-index value (300-1000) of 0.3 μmol P3HT doped with DCA 3.33×10^3 equivalents during 60 min after additions (**Figure D-19 – D-20**).

Time (min)	Acid ^a	
	Neat DCA	DCA in CHCl_3
0	416.1040	414.3709
5	453.6230	449.8398
10	472.9912	459.7060
15	484.7963	466.9618
20	493.0547	471.0070
25	497.7657	474.7224
30	502.5262	477.7234
35	506.4206	481.0012
40	508.0521	482.6895
45	509.9334	484.0122
50	512.2841	485.6861
55	515.0731	487.1642
60	515.5896	489.2841

^a acid 3.33×10^3 equivalent = 10 mmol

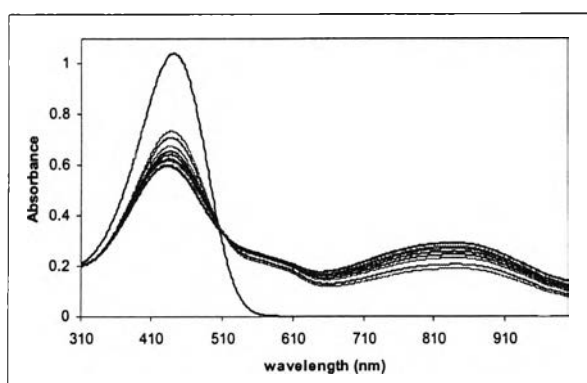


Figure D-21 UV-visible spectra of 0.3 μmol P3HT doped with solution of TCA 3.33×10^3 equivalents in dry CHCl_3 during 60 min after additions.

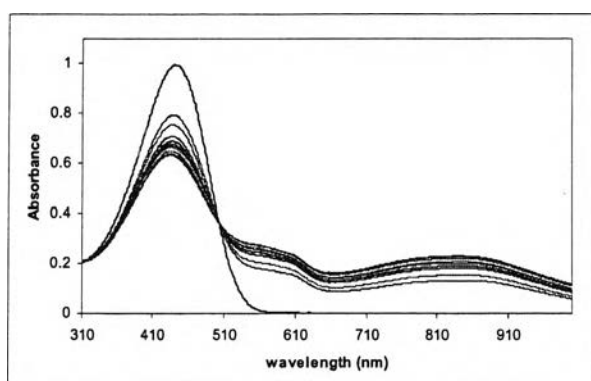


Figure D-22 UV-visible spectra of 0.3 μmol P3HT doped with solid TCA 3.33×10^3 equivalents during 60 min after additions.

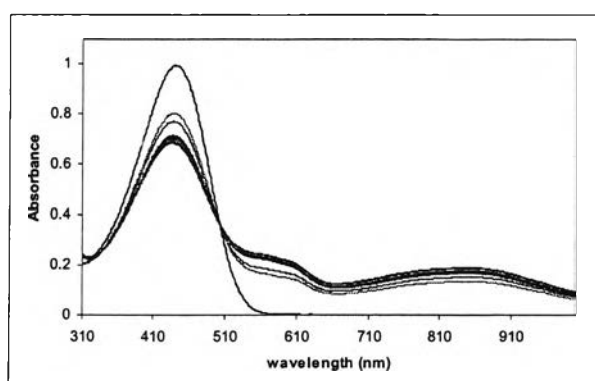


Figure D-23 UV-visible spectra of 0.3 μmol P3HT doped with 3.33×10^3 equivalents TCA+H₂O (10 μL) during 60 min after additions.

Table D-10 AC-index values (300-1000) of 0.3 μmol P3HT doped with TCA 3.33×10^3 equivalents during 60 min after additions (**Figure D-21 – D-23**).

Time (min)	Acid (3.33×10^3 equivalent)		
	TCA in dry CHCl_3	Solid TCA	TCA+ H_2O
0	428.5240	425.6913	426.5706
5	440.1182	456.5184	487.8792
10	441.8222	482.8643	505.3875
15	442.5074	498.5986	520.9254
20	443.4451	506.5366	526.5254
25	444.8493	512.6574	532.5966
30	445.6968	515.8171	536.2141
35	446.6525	517.8920	540.3133
40	446.3093	519.6683	543.0997
45	446.7656	520.5522	545.1061
50	446.9275	522.1547	545.7509
55	447.0630	523.5845	549.9638
60	447.1462	524.1879	551.4166

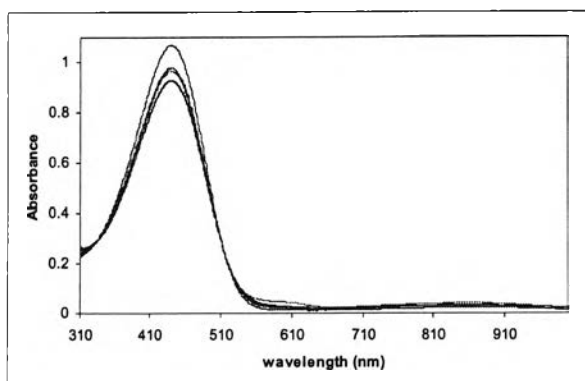


Figure D-24 UV-visible spectra of 0.3 μmol P3HT doped with CA at various equivalent.

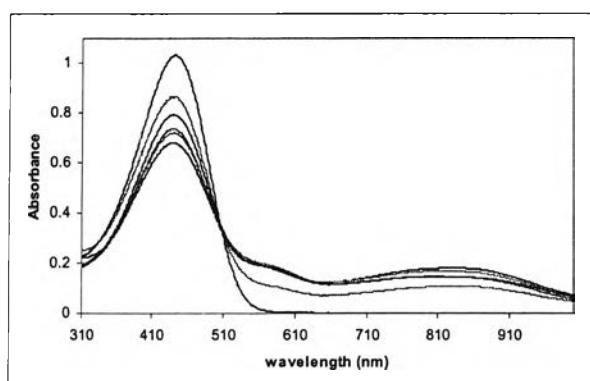


Figure D-25 UV-visible spectra of 0.3 μmol P3HT doped with DCA at various equivalent.

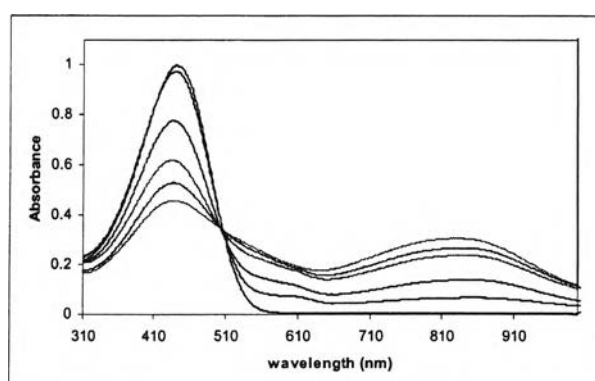


Figure D-26 UV-visible spectra of 0.3 μmol P3HT doped with TCA at various equivalent.

Table D-11 Absorbance at 839 nm of 0.3 μmol P3HT doped with CA, DCA and TCA (**Figure D-24 – D-26**).

Acid $\times 10^3$ (equivalent)	Absorbance		
	CA	DCA	TCA
1.67	N/A	0.040476	0.065843
3.33	0.019957	0.108283	0.140889
5.00	0.025369	0.139051	0.200504
6.67	0.031192	0.159248	0.260341
10.00	0.038551	0.177985	0.301489

N/A = The doping level is too low

Table D-12 AC-index values (300-1000) of 0.3 μmol P3HT doped with CA, DCA and TCA (**Figure D-24 – D-26**).

Acid $\times 10^3$ (equivalent)	AC-index		
	CA	DCA	TCA
1.67	N/A	464.0506	486.0965
3.33	448.4482	514.5091	545.2250
5.00	451.5644	542.6669	576.9026
6.67	456.5185	550.9156	600.8781
10.00	464.3580	563.8801	622.0191

N/A = The doping level is too low

Table D-13 AC-index values (300-1000) of 0.3 μmol P3HT was doped with 3.33×10^3 equivalents of acids ranged in their pK_a values.

Acid	pK_a^*	AC-index	Taken from
TFA	0.52	609.9711	Table D-5
TCA	0.66	545.2250	Table D-12
DCA	1.35	514.5091	Table D-12
CA	2.87	448.4482	Table D-12

* From Ref....

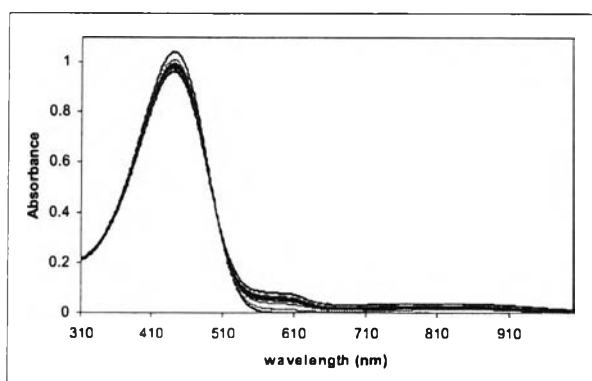


Figure D-27 UV-visible spectra of 0.3 μmol P3HT doped with 3.33×10^3 equivalents of $\text{TsOH H}_2\text{O}$ during 60 min after additions.

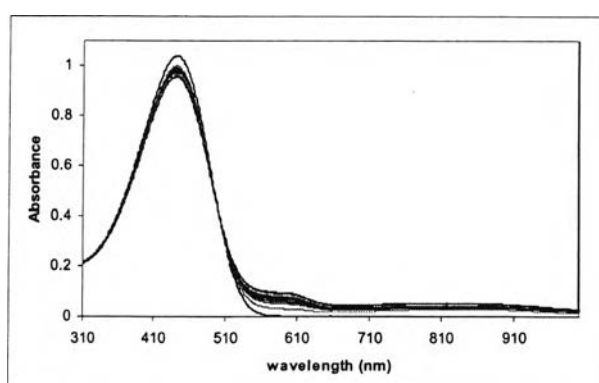


Figure D-28 UV-visible spectra of 0.3 μmol P3HT doped with 3.33×10^3 equivalents of anhydrous TsOH during 60 min after additions.

Table D-14 AC-index values (300-1000) of 0.3 μmol P3HT doped with 3.33×10^3 equivalents of acids (**Figure D-27 – D-28** and **Figure D-6**).

Time (min)	Acid (0.83×10^3 equivalent)		
	TsOH:H ₂ O	TsOH	TFA
0	422.4162	423.8164	411.4747
5	435.6683	452.0778	434.8286
10	443.7124	459.9755	435.6802
15	448.3751	462.1294	437.6449
20	451.3146	465.438	440.2790
25	452.3469	467.4506	441.7039
30	455.4948	468.9674	442.4023
35	456.6336	470.1514	442.9077
40	459.4915	472.8372	442.5372
45	461.7853	474.5435	444.5464
50	462.5267	475.3275	447.1468
55	464.7539	477.1935	-
60	465.3681	478.2440	-

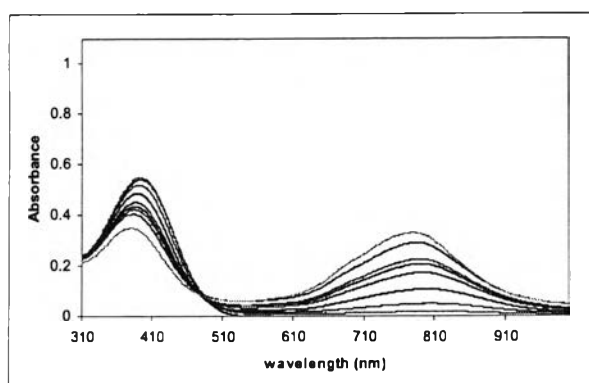


Figure D-29 UV-visible spectra of acetone fraction of P3HT extraction doped with 3.33×10^3 equivalents of TFA from 0 to 60 min.

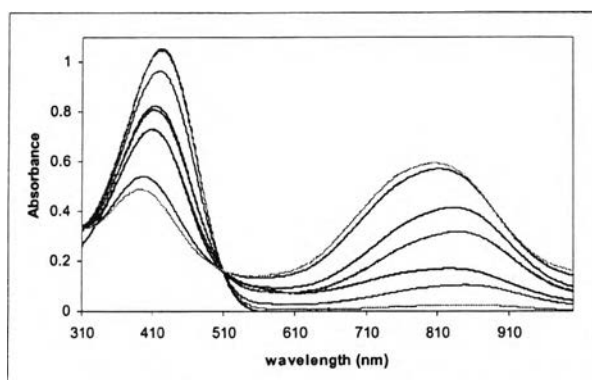


Figure D-30 UV-visible spectra of hexane fraction of P3HT extraction doped with 3.33×10^3 equivalents of TFA from 0 to 60 min.

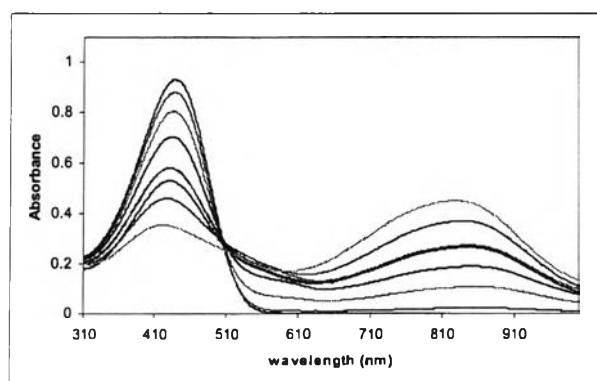


Figure D-31 UV-visible spectra of CH_2Cl_2 fraction of P3HT extraction doped with 3.33×10^3 equivalents of TFA from 0 to 60 min.

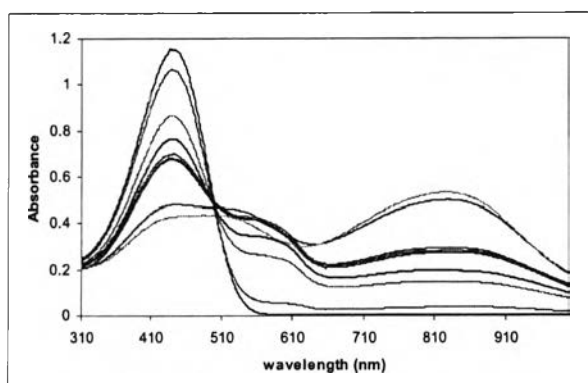


Figure D-32 UV-visible spectra of 10%CHCl₃ in CH₂Cl₂ fraction of P3HT extraction doped with 3.33×10^3 equivalents of TFA from 0 to 60 min.

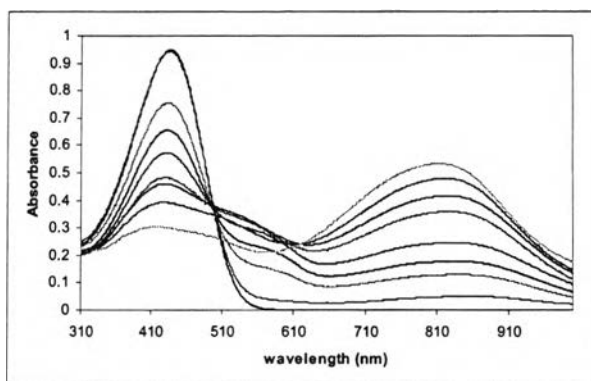


Figure D-33 UV-visible spectra of CHCl₃ fraction of P3HT extraction doped with 3.33×10^3 equivalents of TFA from 0 to 60 min.

Table D-15 AC-index values (300-1000) of poly(3-hexylthiophene) fractions upon doping with Trifluoroacetic acid (TFA) (**Figure D-29 – D-33**).

Equivalent of TFA	AC-index				
	acetone	hexane	CH ₂ Cl ₂	10%CHCl ₃ in CH ₂ Cl ₂	CHCl ₃
0.83	42.4853	127.4820	234.6406	336.0090	452.1820
1.67	78.9246	170.6588	285.3921	411.5250	501.9117
2.50	130.0584	218.9323	332.3331	458.3915	553.9949
3.33	173.8261	274.6370	371.3321	485.2187	588.4372
4.17	191.2169	305.1422	413.2579	513.1743	605.5824
5.00	201.3074	321.1182	426.6231	526.7586	625.2518
6.67	226.2689	347.1784	441.6231	534.6742	642.1380
10.0	245.1729	361.1750	461.9120	545.7355	661.9849

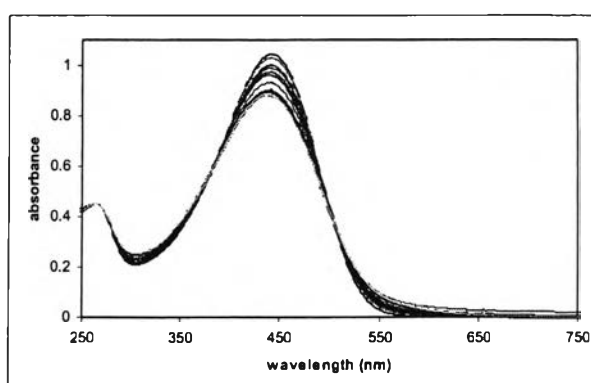


Figure D-34 UV-visible spectra of P3HT oxidized by H₂O₂/TFA from 10 to 120 min oxidation (**Figure 3.24**).

Table D-16 AC-index values (300-1000) of P3HT oxidized by H₂O₂/TFA (mole ratio P3HT : H₂O₂ : TFA = 0.15 : 37.5 : 3.72) (**Figure D-34**).

Time (min)	AC-index
0	429.9495
10	430.9494
20	428.7297
30	419.1585
40	422.3664
50	422.5488
60	437.6197
70	433.9138
80	430.9159
90	431.7829
100	433.1720
120	434.5505

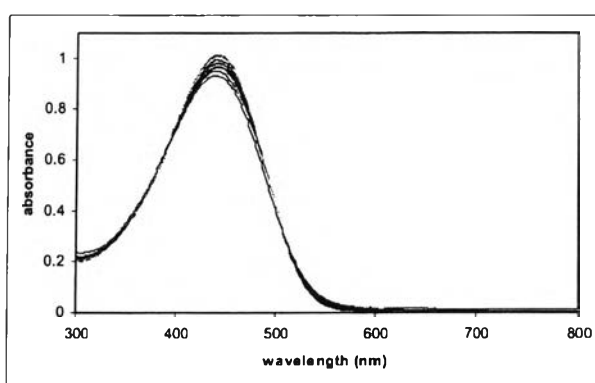


Figure D-35 UV-visible spectra of P3HT oxidized by UHP/TFA (mole ratio P3HT : UHP : TFA = 0.15 : 37.5 : 3.72)

Table D-17 AC-index values (300-1000) of P3HT oxidized by UHP/TFA (mole ratio P3HT : UHP : TFA = 0.15 : 37.5 : 3.72) (**Figure D-35**).

Time (minute)	AC-index
0	432.3968
10	433.6759
20	429.4626
30	422.1387
40	421.2483
50	432.0799
60	444.6514
70	435.2715
80	435.4717
90	435.1354
100	436.1366
120	434.1125

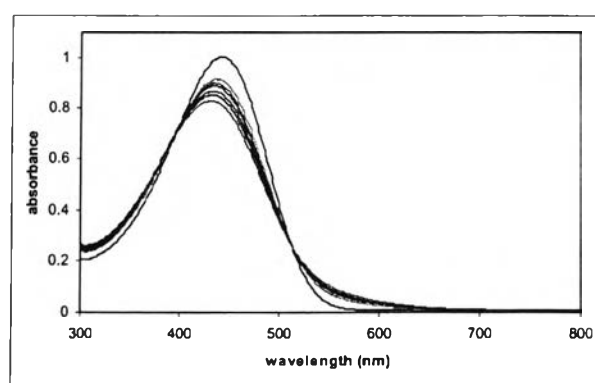


Figure D-36 UV-visible spectra of P3HT oxidized by UHP/TFA at 55°C (mole ratio P3HT : UHP : TFA = 0.05 : 0.10 : 0.20).

Table D-18 AC-index value (300-1000) of P3HT oxidized by UHP/TFA at 55°C (mole ratio P3HT : UHP : TFA = 0.05 : 0.10 : 0.20) (**Figure D-36**).

Time (min)	AC-index
0	421.1955
30	418.2387
60	426.0418
90	425.7929
120	416.9836
150	417.9814
180	419.1055

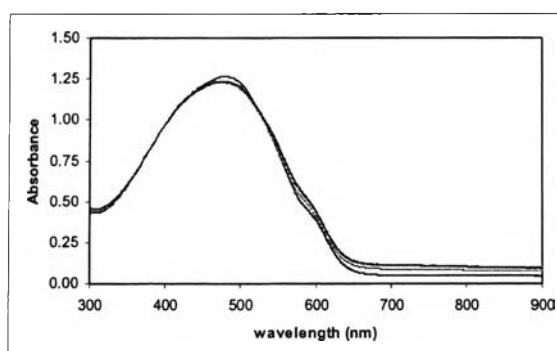


Figure D-37 UV-visible spectra of P3HT solvato-controlled doped by MSA and thiophene. Measuring the absorption after heating at 60 °C every 10 min intervals until 100 min (mole ratio P3HT : MSA : thiophene = 0.1 : 0.05 : 0.1)

Table D-19 AC-index values (300-1000) of P3HT solvato-controlled doped by MSA and thiophene (mole ratio P3HT : MSA : thiophene = 0.1 : 0.05 : 0.1) (Figure D-37).

Time (min)	AC-index
0	463.8285
10	466.2778
20	467.3017
30	467.8795
40	468.1866
50	468.3787
60	468.4875
70	468.5604
80	468.6029
90	468.6258
100	468.6311



Table D-20 Conductivity of 0.45 mM P3HT doped by TFA.

TFA $\times 10^3$ (equivalent)	Conductivity
0.83	0.0
1.67	0.1
2.50	0.2
3.33	0.3
4.17	0.4
5.00	0.5
6.67	0.6
10.00	0.7

Table D-21 Conductivity of P3HT doped by TFA in various concentrations.

TFA $\times 10^3$ (equivalent)	Conductivity of P3HT				
	0.45 mM	0.33 mM	6.67 mM	10.00 mM	16.67 mM
0.83	0.00	0.10	0.30	0.40	0.60
1.67	0.10	0.20	0.45	0.60	1.00
2.50	0.20	0.30	0.60	0.85	1.40
3.33	0.30	0.40	0.75	1.15	1.70
4.17	0.40	0.50	0.90	1.40	1.90
5.00	0.50	0.60	1.05	1.65	2.10
6.67	0.60	0.70	1.20	1.90	2.30
10.00	0.70	0.80	1.40	2.10	2.50

Table D-22 Conductivity of 0.05 mM P3HT fractions.

TFA $\times 10^3$ (equivalent)	Conductivity				
	acetone	hexane	CH ₂ Cl ₂	10%CHCl ₃	CHCl ₃
0.83	0.2	0.2	0.0	0.0	0.0
1.67	0.3	0.3	0.1	0.1	0.1
2.50	0.4	0.4	0.2	0.2	0.2
3.33	0.5	0.5	0.3	0.3	0.3
4.17	0.6	0.6	0.4	0.4	0.4
5.00	0.7	0.7	0.5	0.5	0.5
6.67	0.8	0.8	0.6	0.6	0.6
10.00	0.9	0.9	0.7	0.7	0.7

VITA

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