Supporting Information

Benzothiadiazole bridged EDOT based donor-acceptor polymers with tunable optical, electrochemical, morphology and electrochromic performance: effects of solvents and electrolytes

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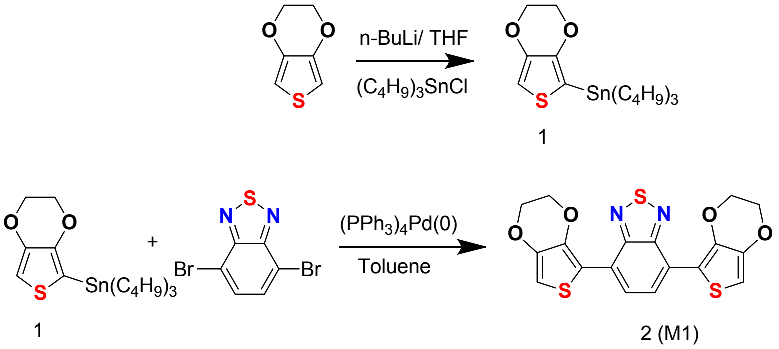
Synthesis of monomer (M1)[1]

The detailed procedure for the synthesis of monomer 4,7-di(2,3-dihydro-thieno[3,4-*b*][1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole is as follows:



Scheme S1. Synthetic route for monomer **M1**

Synthesis of 2-tributylstannyl-3,4-ethylenedioxythiophene (1)

To a solution of 3,4-ethylenedioxythiophene (561 mg, 3.9mmol) in anhydrous tetrahydrofuran (THF) (5ml), a solution of n-butyllithium (3.7 ml, 5.9 mmol,1.6M in hexane) was slowly added under N_2atmosphere at -78 °C. The mixture was then stirred at room temperature for 2 hours to get milk-like mixture. The mixture was then again cooled to -78 °C and tributyltin chloride (1.27 g, 3.9 mmol) was added slowly to it. The reaction mixture was warmed up to room temperature and stirred for 3 hours. After it, the reaction was quenched with water and the organic layer was extracted with diethyl ether (4x50 ml). The organic extract was then dried over Na_2SO_4, filtered and the solvent was evaporated under vaccum to obtain a colorless liquid. The organic residue was then used for the next step without any further purification.

4,7-bis[2-(3,4-ethylenedioxythiophene)]-2,1,3-benzothiadiazole(2, M1)

Tetrakis(triphenylphosphine)palladium (0) (10% mole) was added to a solution of 4,7-dibromo-2,1,3-benzothiadiazole (90 mg, 0.3 mmol) and the above synthesized 2-tributylstannyl-3,4-ethylenedioxythiophene (1) (350 mg, 0.8 mmol) in toluene (10ml). The mixture was refluxed in a N_2 atmosphere for 24 hours and was then cooled to room temperature. The organic residue was then extracted using dichloromethane (DCM) (3x50 ml), wash with H_2O, brine and the organic extract was dried over Na_2SO_4. The excess solvent was evaporated under vaccum using rota-evaporator. The product was further purified by column chromatography eluting with hexane: ethyl acetate (1:2, v/v) to get a red solid in 65% yield (80 mg). ^{1}HNMR ($CDCl_3$, δ): 8.39 (s,2H), 6.56 (s,2H), 4.44-4.41(m,4H), 4.36-4.32 (m,4H). Solubility is too low to obtain a satisfactory ^{13}CNMR.[2]

Table S1. Dielectric constant, density, and viscosity of solvents at 20 °C unless mentioned

Solvents	Dielectric Constant	Density (gcm^{-3})	Viscosity (mPa s)
DCM	9.08	1.325	0.45 (15)
ACN	37.50	0.78	0.37
PC	66.15	1.189	4.9

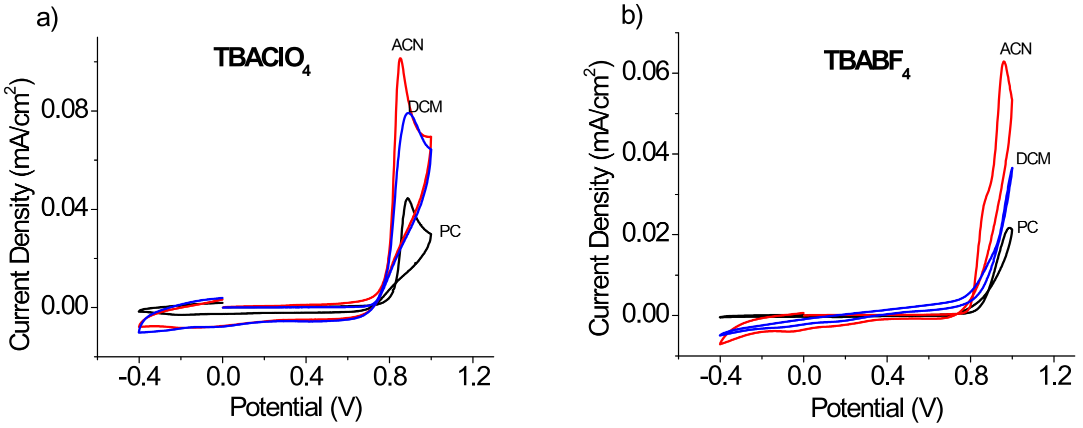


Figure S1. Anodic polarization curves of **M1** in PC, MeCN, and DCM using TBAClO$_4$ and TBABF$_4$ as the supporting electrolyte (0.1 M conc.)

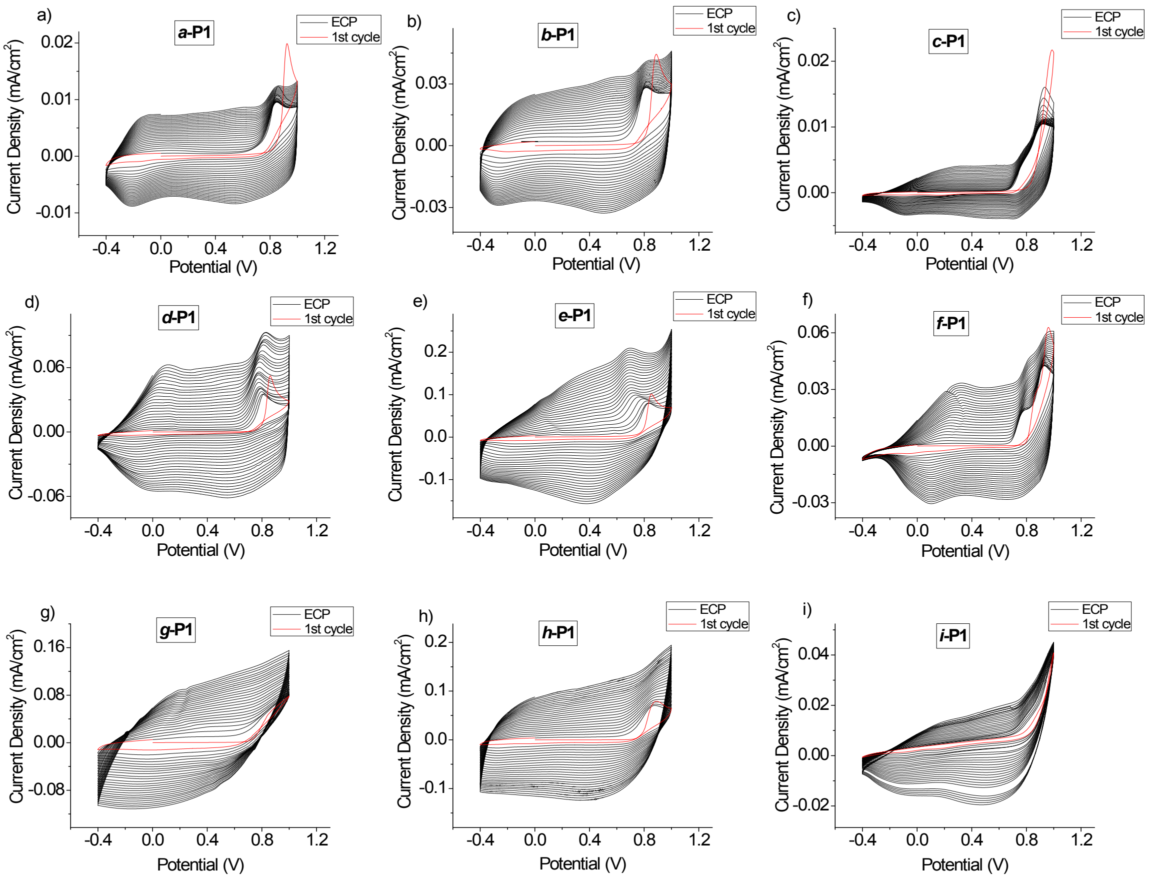


Figure S2.Cyclic voltammograms of the growth of the polymer **P1** on ITO coated glass substrate at 75mV/s for 25 successive cycles using different electrolytes and solvents.

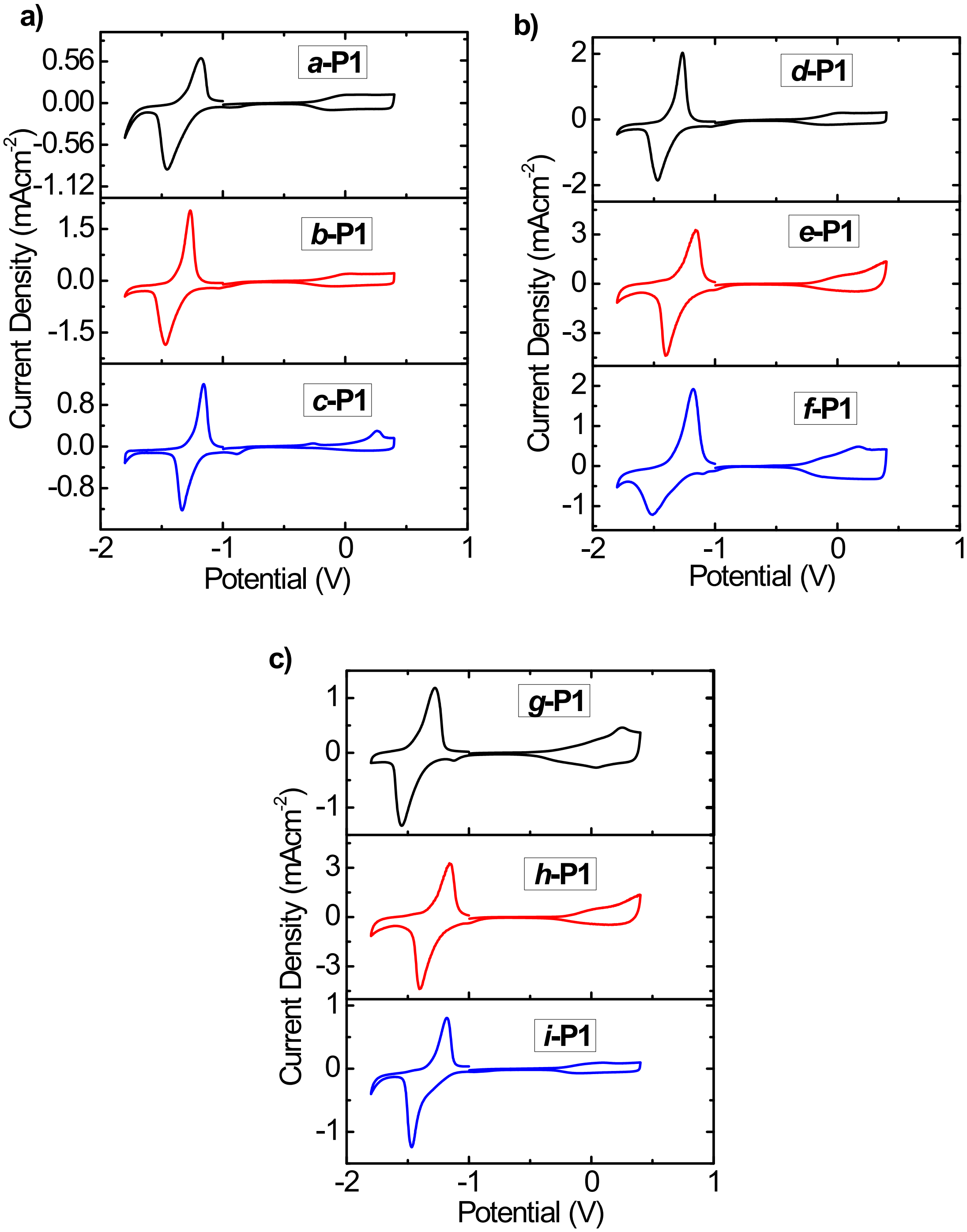
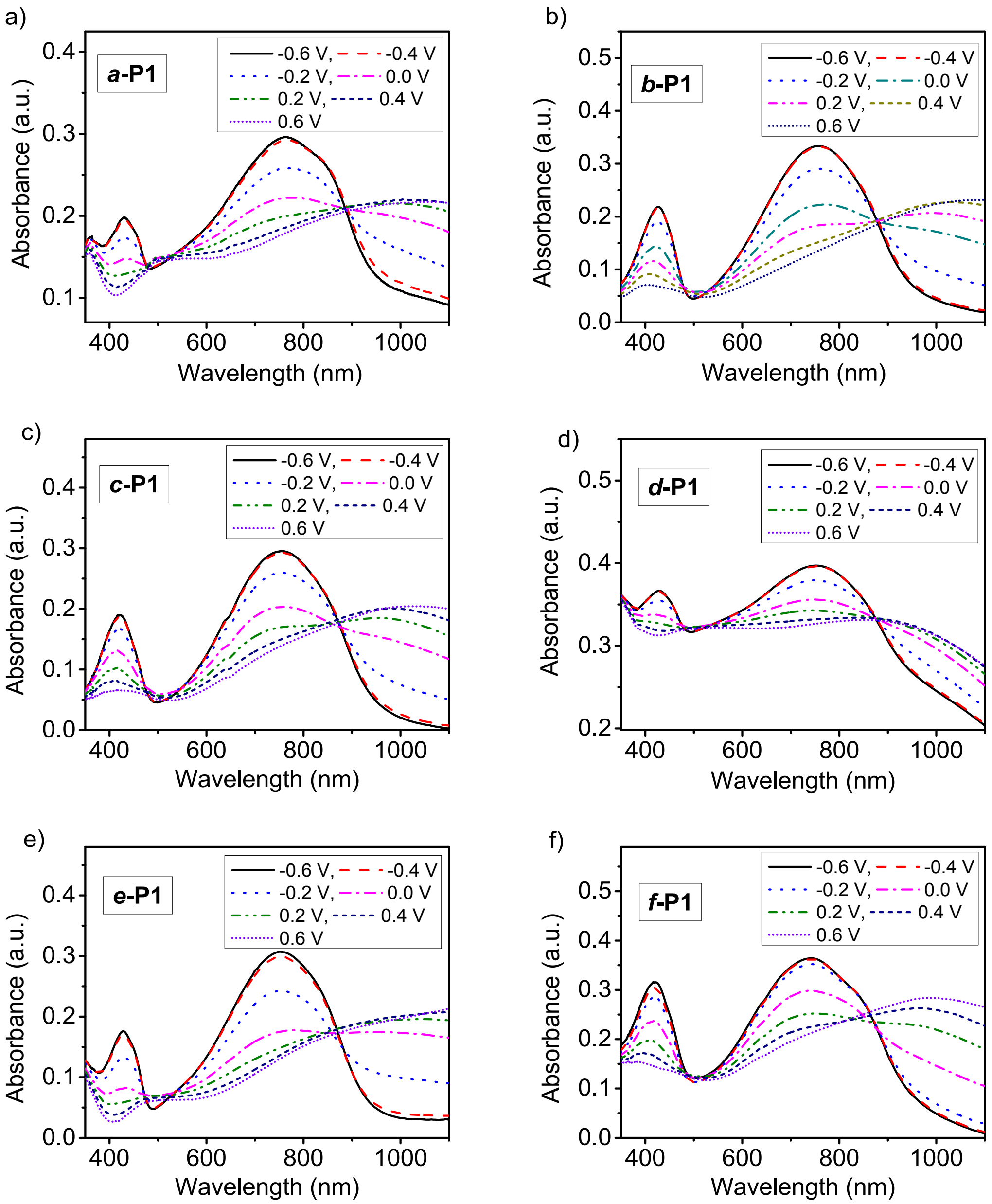


Figure S3. Cyclic voltammograms of **P1**on Pt disc at 75mV/s in monomer free MeCN solvent (polymer deposited for 25 successive cycles using different electrolytes and solvents).


a)
a-P1
-0.6 V, -0.4 V
-0.2 V, 0.0 V
0.2 V, 0.4 V
0.6 V
Absorbance (a.u.)
0.1
0.2
0.3
0.4
Wavelength (nm)
400
600
800
1000
b)
b-P1
-0.6 V, -0.4 V
-0.2 V, 0.0 V
0.2 V, 0.4 V
0.6 V
Absorbance (a.u.)
0.0
0.1
0.2
0.3
0.4
0.5
Wavelength (nm)
400
600
800
1000
c)
c-P1
-0.6 V, -0.4 V
-0.2 V, 0.0 V
0.2 V, 0.4 V
0.6 V
Absorbance (a.u.)
0.0
0.1
0.2
0.3
0.4
Wavelength (nm)
400
600
800
1000
d)
d-P1
-0.6 V, -0.4 V
-0.2 V, 0.0 V
0.2 V, 0.4 V
0.6 V
Absorbance (a.u.)
0.2
0.3
0.4
0.5
Wavelength (nm)
400
600
800
1000
e)
e-P1
-0.6 V, -0.4 V
-0.2 V, 0.0 V
0.2 V, 0.4 V
0.6 V
Absorbance (a.u.)
0.0
0.1
0.2
0.3
0.4
Wavelength (nm)
400
600
800
1000
f)
f-P1
-0.6 V, -0.4 V
-0.2 V, 0.0 V
0.2 V, 0.4 V
0.6 V
Absorbance (a.u.)
0.0
0.1
0.2
0.3
0.4
0.5
Wavelength (nm)
400
600
800
1000

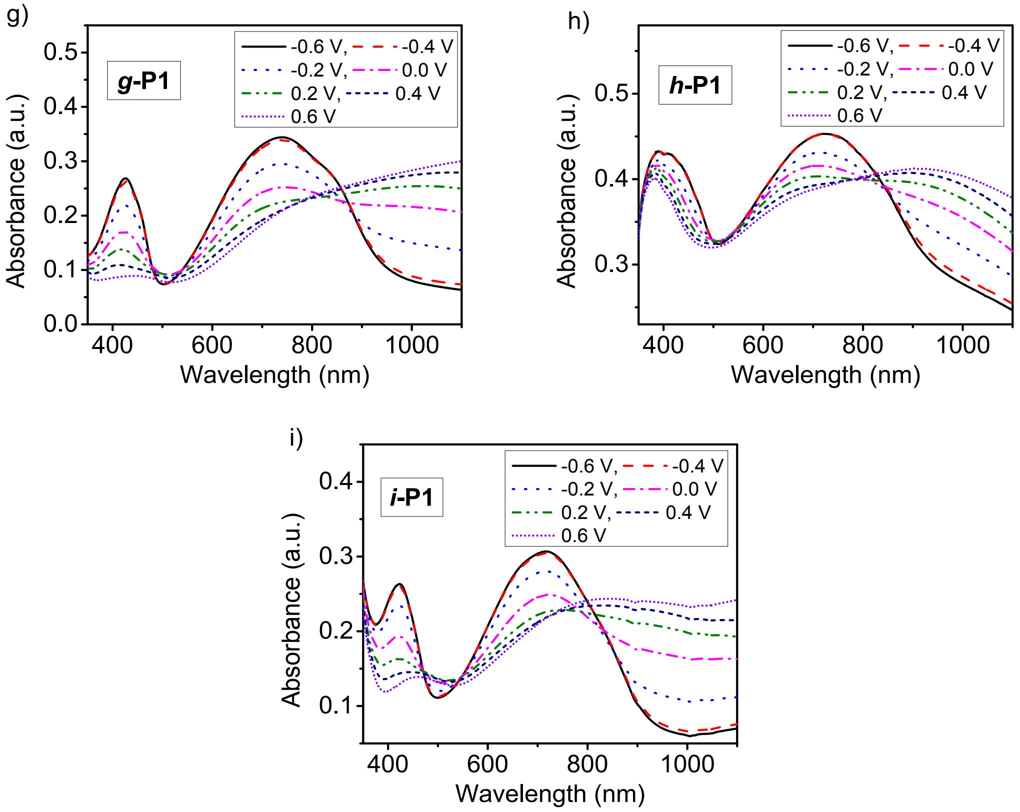


Figure S4. Spectroelectrochemical graphs of polymer a) ***a*-P1**, b) ***b*-P1**, c) ***c*-P1**, d) ***d*-P1**, e) ***e*-P1**, f) ***f*-P1**, g) ***g*-P1**, h) ***h*-P1** and i) ***i*-P1**

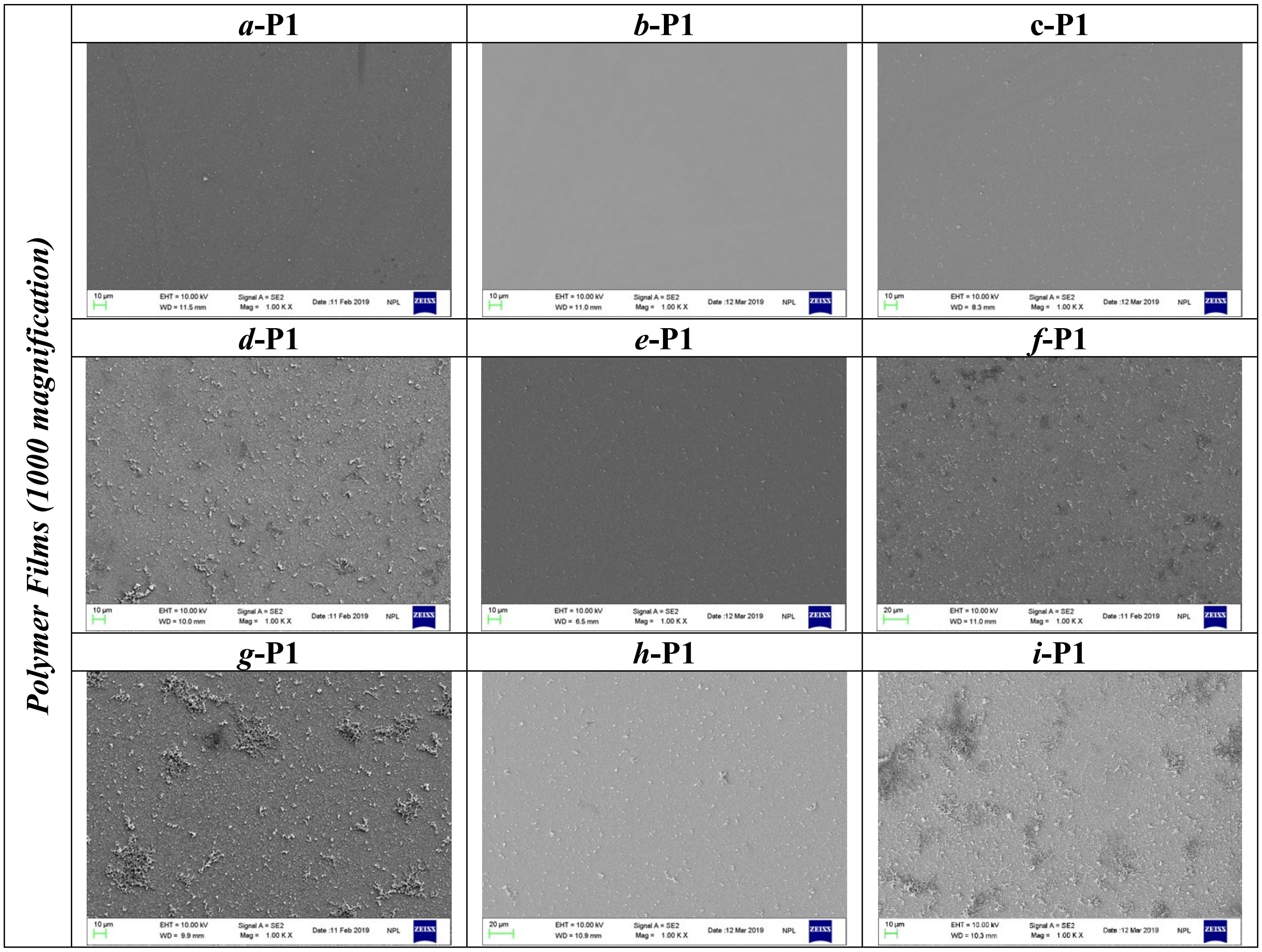


Figure S5.FE-SEM images of polymer films at 1000 magnification (measured at EHT of 10.0 keV).

Table S2. Electrochromic properties of **P1** polymer samples deposited using different electrolytes and solvents measured at different wavelengths (calculated for 95% switching).

Polymers	***Wavelength (nm)***	τ_{oxi} *(s)*[a]	τ_{red} *(s)*[a]	$\Delta T\%$[b]	$\eta_{oxd}(cm^2/C)$[c]	$\eta_{red}(cm^2/C)$[c]
***a*-P1**	1100	1.3	0.8	61.4	211	203
	752	2.6	1.3	35.4	185	189
	431	4.3	2.1	28.3	175	174
***b*-P1**	1100	2.6	0.8	65.3	264	202

	760	1.3	1.3	32.1	182	189
	426	3.0	1.9	29.3	156	156
***c*-P1**	1100	2.6	0.4	50.1	248	208
	757	0.4	0.4	20.1	125	124
	422	0.4	0.8	17.3	119	117
***d*-P1**	1100	1.7	1.7	47.6	179	174
	755	0.4	0.4	19.9	54	54
	430	2.5	0.9	22.5	98	93
***e*-P1**	1100	1.2	0.6	55.6	185	175
	754	0.4	0.4	20.6	103	106
	428	1.3	0.9	33.1	121	122
***f*-P1**	1100	0.7	0.5	41.1	183	178
	745	0.4	0.4	14.5	77	77
	420	0.8	0.4	9.5	42	32
***g*-P1**	1100	3.0	2.6	41.6	149	157
	738	0.8	0.4	16.5	88	89
	426	3.0	1.7	29.2	112	118
***h*-P1**	1100	1.6	2.3	44.0	155	181
	724	1.2	0.9	22.2	121	118
	390	2.6	0.6	18.3	68	62
***i*-P1**	1100	1.7	0.8	32.0	122	174
	720	1.2	0.7	9.4	90	90
	423	-	-	-	-	-

[a] *Response time calculated for both oxidation and reduction process*
[b] *Optical contrast of the films (-1.0 V to 1.0 V)*
[c] *Coloration efficiency calculated during both charge ejection and injection*

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[1] W. Y. Wong, X. Wang, H. L. Zhang, K.Y. Cheung, M.K. Fung, A. B. Djurisic, and W. K. Chan, *J. Organomet. Chem.*, 2008, **693**, 3603-3612.

[2] X. Wang, K. Wang, and M. Wang, *Polym. Chem.*, 2015, **6**, 1846-1855.