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2 Electronic Supplementary Material (ESI) for Green Chemistry

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4 **Deep Eutectic Solvent Systems for FeCl₃-catalyzed Oxidative**
5 **Polymerization of 3-Octylthiophene**

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21 ***SI. Experimental details***

22

23 **Materials**

24 Choline chloride, urea, glycerol, ethylene glycol, formamide, thiourea, Ferric chloride and 3-
25 octylthiophene (3OT) monomer were purchased from Sigma-Aldrich.

26

27 **Preparation of DES mixtures**

28 DES mixtures were prepared by mixing choline chloride with various HBD partners as shown in
29 our previous article.¹⁰

30

31 **Synthesis of P3OT**

32 FeCl₃ (273 mg, 1.68 mmol) and the selected DES (for example, 5 g of [Ch]Cl:urea) were put into
33 round-bottom flask. Then, 3OT (83 mg, 0.42 mmol) was dropped into a magnetically stirred
34 suspension of FeCl₃ in the selected DES at 25°C or 50°C. After the reaction, DESs and FeCl₃
35 were removed in the aqueous phase after partitioning in a toluene-water system at equilibrium.
36 The reaction mixture was added to a mixture of 200 mL of toluene and 200 mL of water and then
37 shaken for 10 s. The toluene and water phases were then separated at equilibrium and the
38 isolated toluene phase containing dissolved 3OT and P3OT was concentrated by rotary
39 evaporation after removing the aqueous phase. To remove unreacted 3OT (bp: 106-107°C/3
40 mmHg), this concentrated mixture of 3OT and P3OT was vacuum dried overnight at 50°C in a
41 vacuum oven, which resulted in removing 3OT and obtaining P3OT.⁷

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43 **Molecular weight and molecular-weight distribution of P3OT**

44 The weight average molecular weight and number average molecular weight were determined
45 using gel permeation chromatography (GPC, Tosoh Co. EcoSEC HLC-8320 GPC) equipped
46 with columns (Tosoh, 2×TSKgel SuperMultipore HZ-M (4.6 × 150 mm)) and an RI detector
47 using polystyrene standards and tetrahydrofuran (THF) as an eluent at a flow rate of 0.35 mL
48 min⁻¹ and a data module at 40°C. The molecular weights were obtained from the refractive index
49 data, which were analyzed with EcoSEC software.⁷

50 **S2. Yield comparison**

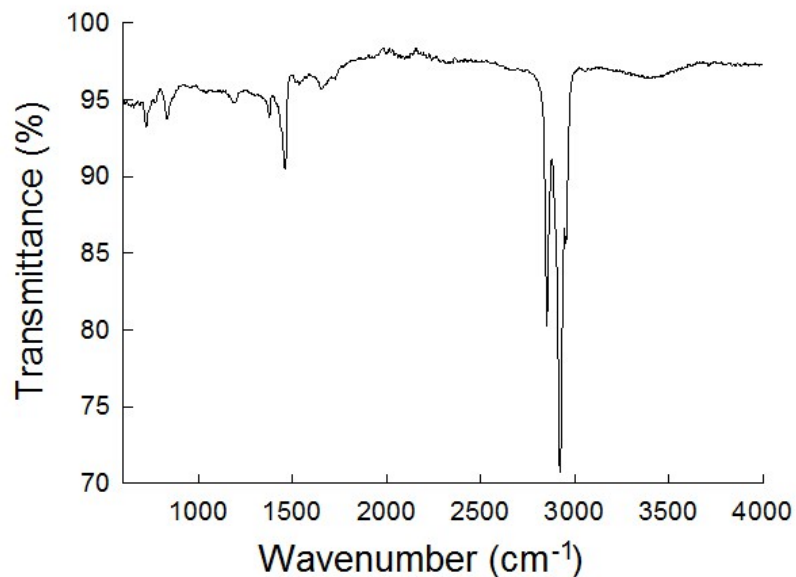
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52 **Table S1.** Yield comparison of P3OT via oxidative polymerization in various DESs.

Solvents	Temp (°C)	Polymerization time	Yield (%)
[Ch]Cl:urea	25	1 h	59
[Ch]Cl:urea	25	4 h	81
[Ch]Cl:urea	25	10 h	100
[Ch]Cl:urea	50	1 h	83
[Ch]Cl:urea	50	2 h	100
[Ch]Cl:urea:thiourea	50	1 h	37
[Ch]Cl:urea:thiourea	50	2 h	87
[Ch]Cl:urea:thiourea	50	3h	100
[Ch]Cl:formamide:thiourea	25	3h	6
[Ch]Cl:formamide:thiourea	25	6h	12
[Ch]Cl:formamide:thiourea	25	10h	16
[Ch]Cl:formamide:thiourea	25	24 h	34
[Ch]Cl:formamide:thiourea	25	48 h	50
[Ch]Cl:formamide:thiourea	50	3 h	15
[Ch]Cl:formamide:thiourea	50	6 h	28
[Ch]Cl:glycerol	25	48 h	8
[Ch]Cl:ethylene glycol	25	48 h	1
[Ch]Cl:urea:glycerol	25	48 h	18
[Ch]Cl:urea:ethylene glycol	25	48 h	24
[Ch]Cl:glycerol:ethylene glycol	25	48 h	6
[Ch]Cl:glycerol:formamide	25	48 h	14
[Ch]Cl:glycerol:thiourea	25	48 h	6
[Ch]Cl:ethyleneglycol:formamide	25	48 h	1
[Ch]Cl:ethyleneglycol:thiourea	25	48 h	18
[BmIm][SbF ₆]	25	6 h	53
[BmIm][SbF ₆]	25	10 h	65
[BmIm][SbF ₆]	50	3 h	45
[BmIm][SbF ₆]	50	6 h	65
CHCl ₃	25	1 h	70
CHCl ₃	25	4 h	79
CHCl ₃	25	10 h	85

53 **S3. FTIR spectra of P3OT**

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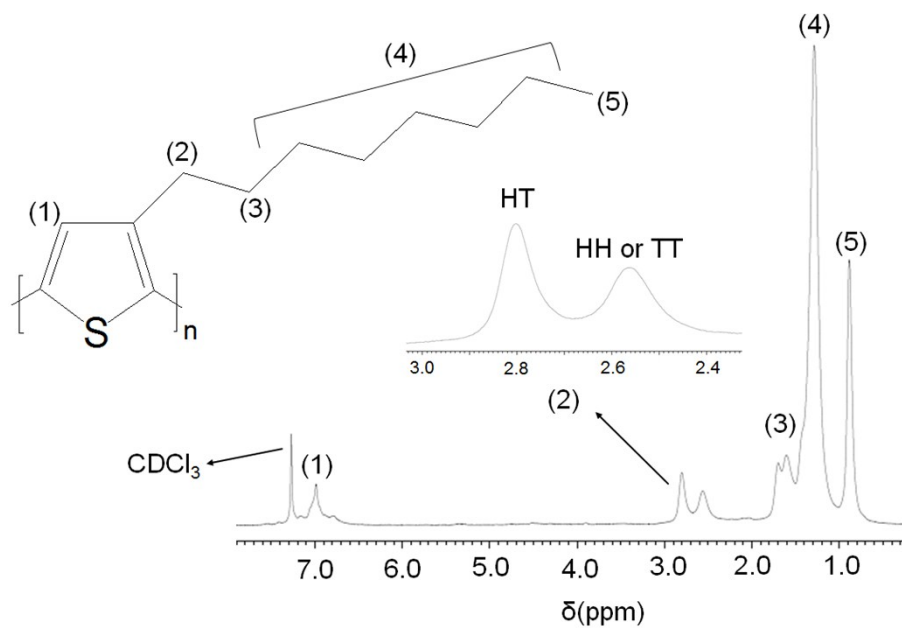
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56 **Figure S1.** FTIR spectra of P3OT

57

58 Figure S1 shows FTIR spectra of P3OT polymerized using [Ch]Cl:urea. In the FTIR spectrum,
59 there were several intensity peaks present in the range of 2800–3000 cm⁻¹, which can be
60 attributed to the C–H stretching modes of alkyl side chain, the range of 1400-1550 cm⁻¹ ascribed
61 to the C=C stretching vibration modes of conjugated backbones, and the aromatic C-H out-of-
62 plain was around 832 cm⁻¹. The peak at 722 cm⁻¹ is attributed to the characteristic absorption of S
63 atom on the polythiophene ring.

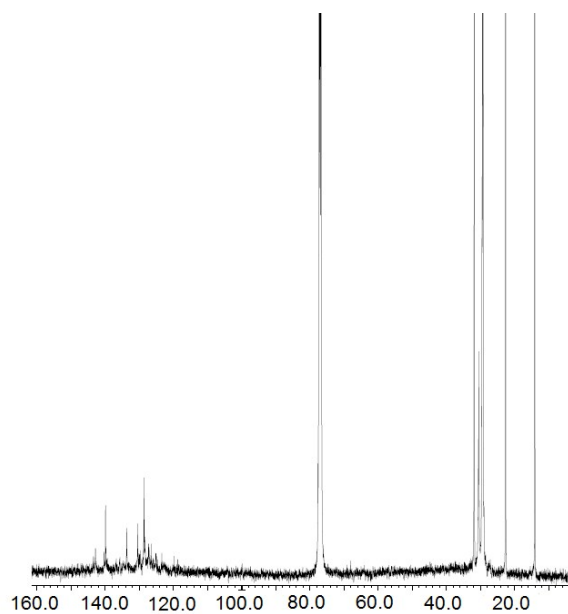
64 **S4. NMR spectroscopy of P3OT**



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(a)



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(b)

69 **Figure S2.** Representative (a) ¹H NMR spectrum and (b) ¹³C NMR spectrum of P3OT prepared
70 using [Ch]Cl:urea.

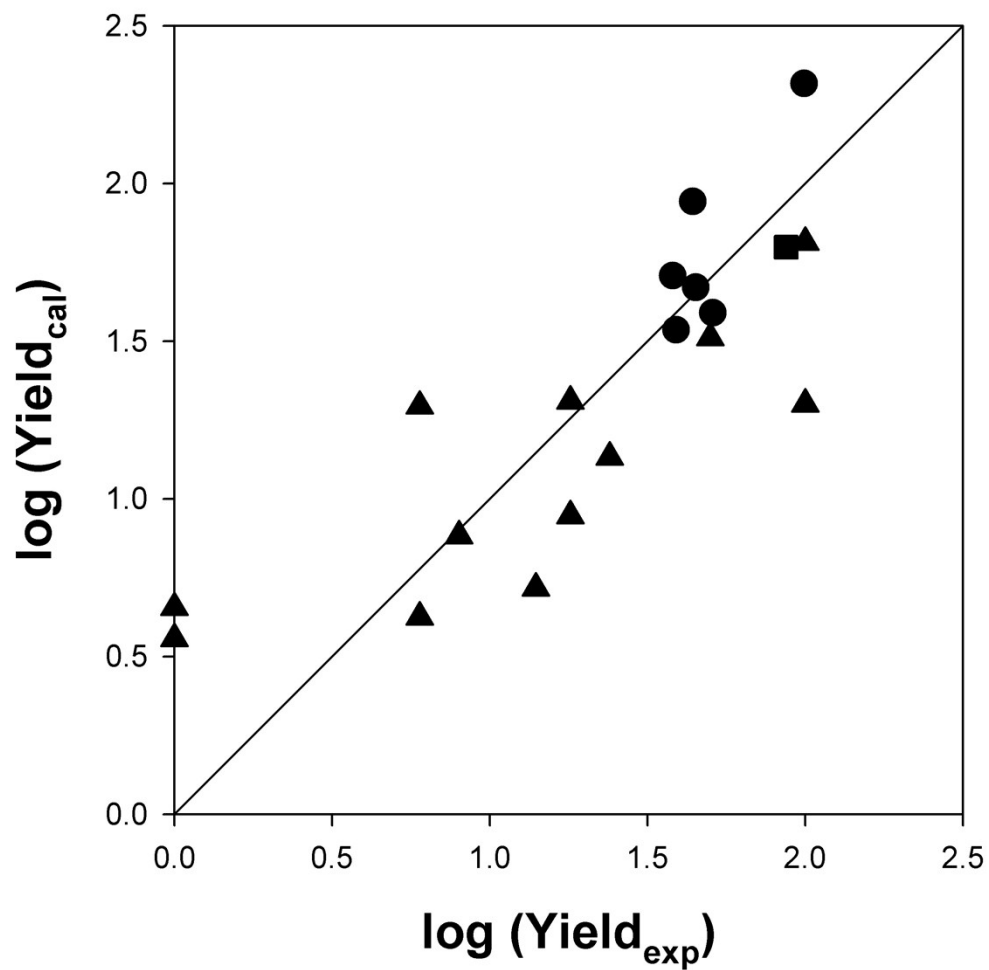
71 Figure S2 (a) represents ^1H NMR spectrum of P3OT polymerized using [Ch]Cl:urea. For a
72 quantitative determination of the regioregularity degrees, ^1H NMR spectra were recorded for all
73 samples in CDCl_3 solutions. A single peak at around 6.9 ppm is attributed to the aromatic proton
74 at position 4 of the thiophene ring. The peaks appearing between 0.7 and 1.8 ppm are attributed
75 to the methyl and six of the methylene groups of the side-chain. The signal of methylene linked
76 to thiophene ring is affected by the regioregularity of the polymer. The methylene signal of the
77 head-to-tail (HT) dyad appears at 2.80 ppm and the methylene of the head-to-head (HH) or tail-
78 to-tail (TT) dyad at 2.57 ppm. The regioregularity degree was calculated by the ratio of these 1)
79 HT peak and 2) HH or TT peak area. The HT content was calculated to be 55%. Figure S2 (b)
80 shows the full ^{13}C spectrum for our P3OT. The alkyl region only shows eight absorptions
81 corresponding to the octyl side chain at 14.2, 22.7, 29.3, 29.5, 29.6, 30.5, 30.7 and 31.9 ppm.^{S1-S4}

82 ***S5. PDI comparison***

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84 **Table S2.** PDI comparison of PATs from previous literatures in various solvents

No.	Polymer	Oxidant	Solvent	Polymerization time	Temp (°C)	PDI	Yield (%)	Ref.
1	Poly(3-octylthiophene)	FeCl ₃	[Ch]Cl:U	1h	25	6.7	59	This study
2	Poly(3-octylthiophene)	FeCl ₃	[Ch]Cl:U	10h	25	12.9	100	This study
3	Poly(3-octylthiophene)	FeCl ₃	CHCl ₃	1h	25	5.8	70	This study
4	Poly(3-octylthiophene)	FeCl ₃	CHCl ₃	48h	25	12.9	87	This study
5	Poly(3-hexylthiophene)	FeCl ₃	Acetone	1~6 h	0	3.4~5.0	72~76	(S5)
6	Poly(3-hexylthiophene)	FeCl ₃	Benzene	2h	23	5.3	47	(S6)
7	Poly(3-hexylthiophene)	FeCl ₃	Toluene	2h	23	4.5	39	(S6)
8	Poly(3-hexylthiophene)	FeCl ₃	Xylene	2h	23	2.1	11	(S6)
9	Poly(3-hexylthiophene)	FeCl ₃	CHCl ₃	2h	23	3.5	53	(S6)
10	Poly(3-octylthiophene)	FeCl ₃	CHCl ₃	2~24h	25	4.5~10.9	75~80	(S7)
11	Poly(3-decylthiophenes)	FeCl ₃	CHCl ₃	2~24h	25	5.5~8.0	75~80	(S7)



90 **Figure S3.** Calculated values of log (yield) against experimental values of log (yield). ▲: DESs,

91 ●: ILs, and ■: chloroform.

92 **References**

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