Electronic Supplementary Material (ESI) for RSC Advances

Influence of ionic liquids as solvents for chemical synthesis of poly(3-octylthiophene) with $FeCl_3$

*Tae-Joon Park[a], Yong Seok Kim[b], Eunsung Kan[c], and Sang Hyun Lee[*d]*

[a]*Nano Systems Institute, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 151-744, Korea*

[b]*Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-Gu, Seoul 120-749, Korea*

[c]*Department of Molecular Bioscience and Bioengineering, University of Hawaii at Manoa, Honolulu, HI 96822, USA*

[d]*Department of Microbial Engineering, Konkuk University, Hwayang-Dong, Gwangjin-Gu, Seoul 143-701, Korea*

[*]Corresponding author

Tel: +82-2-2049-6269

Fax: +82-2-3437-8360

E-mail: sanghlee@konkuk.ac.kr

S1. Experimental details

Materials

All ionic liquids (Figure S1) and 3-octylthiophene (3OT) monomer were purchased from Sigma-Aldrich. Ferric chloride (anhydrous $FeCl_3$, Kanto chemical) was used as a catalyst. Thin-layer chromatography (TLC) was carried out using silica gel 60 plates (E. Merck) with fluorescent indicator.

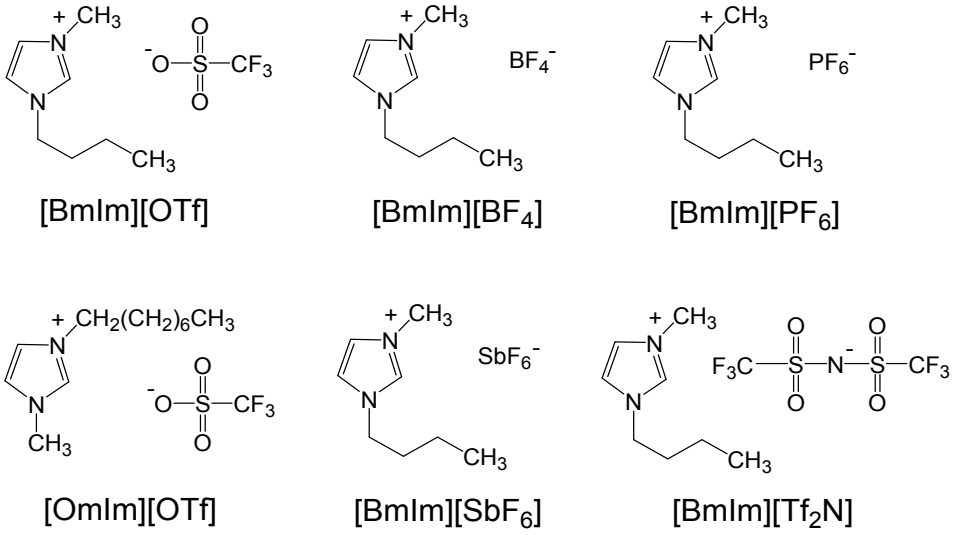

Figure S1. Ionic liquids used for the synthesis of poly(3-octylthiophene) (P3OT).

Synthesis of P3OT

3OT (83 mg, 0.42 mmol) was dropped into a suspension of $FeCl_3$ (273 mg, 1.68 mmol) in the selected ionic liquid (5 g of [BmIm][OTf], [OmIm][OTf], [BmIm][BF_4], [BmIm][Tf_2N], [BmIm][SbF_6], or [BmIm][PF_6]) at 25°C. After the reaction, unreacted ionic liquids and $FeCl_3$ were removed in the aqueous phase after partitioning in a toluene-water system at equilibrium. The reaction mixture was added to a mixture of 150 mL of toluene and 150 mL of water and then shaken for 10 s. The toluene and water phases were then separated at equilibrium and the isolated toluene phase containing dissolved 3OT, oligomers, and P3OT was concentrated by rotary evaporation after removing the aqueous phase. To remove unreacted 3OT (bp: 106-107°C/3 mmHg), this concentrated mixture of 3OT, oligomers, and P3OT was vacuum dried overnight at 50°C in a vacuum oven to obtain the oligomers and P3OT.

Molecular weight and molecular-weight distribution of P3OT

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

S2. Reaction conditions for the synthesis of PTs and PATs

Table S1. The chemical synthesis of PTs and PATs from previous literatures

Polymer	Oxidant	Solvent	Mw	PDI	Yield (%)	Ref.
Poly(thiophene) particles	$AuCl_3$	1-methyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)imide	-	-	-	(13)
	$FeCl_3$		-	-	-	(13)
Poly(terthiophene) particles	$Fe(ClO_4)_3$		-	-	-	(13)
	Fe-tosylate		-	-	-	(13)
	$AgNO_3$		-	-	-	(13)
	$AuCl_3$		-	-	-	(13)
Poly(3-(4-octylphenyl)thiophene	$FeCl_3$	$CHCl_3$	-	-	80	(8)
Poly(3-alkylthiophene) synthesized from 2,5-diiodo-3-alkylthiophene	$Ni(cod)_2/PPh_3$	DMF	30k	4	-	(17)
Poly(thiophene)	$Ni(cod)_2/PPh_3$	DMF	-	-	60 ~ 95	(17)
Films (poly(thiophene),	$MoCl_5$	$CHCl_3$	-	-	-	(7)
poly(furan) or poly(pyrrole))	$RuCl_3$		-	-	-	(7)
	$FeCl_3$		-	-	-	(7)
Poly(3-octylthiophene)	$FeCl_3$	$CHCl_3$	150k	5	-	(18)
Poly(alkylthiophenes)	$FeCl_3$	$CHCl_3$	150k ~ 250k	5	75 ~ 80	(19)
Poly(alkylthiophenes)	$FeCl_3$	$CHCl_3$	204k ~ 398k	1.5 ~ 2.5	60 ~ 97	(20)
Poly(3-octylthiophene)	$FeCl_3$	$CHCl_3$	70k	2.6	70	(21)

S3. Effect of solvents on $FeCl_3$-catalyzed oxidative polymerization

Table S2. Effect of solvent properties on $FeCl_3$-catalyzed polymerization of 3OT

Solvents	β (ref. 24, 25)	Solubility of $FeCl_3$ (ref. 4)	Polymerization (ref. 4)
$CHCl_3$	0.10	Not completely	Yes
Toluene	0.11	Not completely	Yes
CCl_4	0.00	None	Yes
Pentane	0.00	None	Yes
Hexane	0.00	None	Yes
Diethylether	0.47	Completely	No
Xylene	0.20	Completely	No
Acetone	0.43	Completely	No
Formic acid	0.38	Completely	No

S4. Photoluminescence properties of P3OT

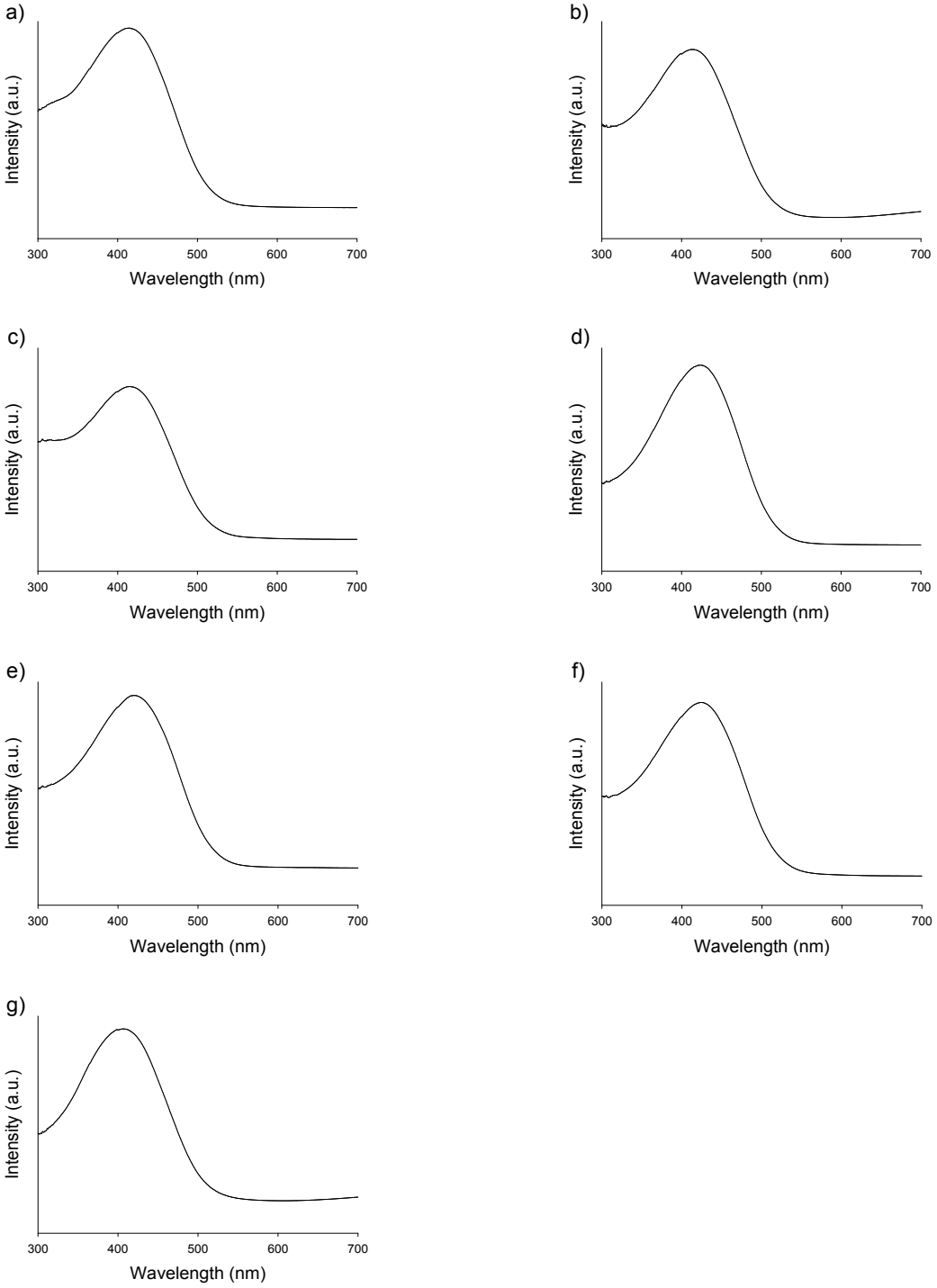

Figure S2. UV-vis absorption spectra of P3OT synthesized via $FeCl_3$-catalyzed oxidative polymerization with (a) [BmIm][SbF_6], (b) [BmIm][Tf_2N], (c) [BmIm][PF_6], (d) [BmIm][BF_4], (e) [OmIm][OTf], (f) [BmIm][OTf], and (g) $CHCl_3$.

UV-visible absorbance spectra were obtained with a double-beam UV-visible spectrophotometer (UV-2101, Shimadzu) and photoluminescence spectra were recorded with a spectrofluorophotometer (RF-5301PC, Shimadzu, Japan). Excitation was incident at an angle of 0° to the front face of the sample, and the emission was recorded in reflection mode at an angle of 90° with respect to the surface normal.