

Oxidative-Extractive Desulfurization of Model Fuels Using a Pyridinium Ionic Liquid

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¹H-NMR and ¹³C-NMR analyses of the synthesis ionic liquid [BPy][BF₄]

The ionic liquid [BPy][BF₄] has 14 hydrogens and 9 carbons, and its NMR spectra were reported as chemical shift in ppm (δ) from the internal standard. The results of ¹H-NMR and ¹³C-NMR of [BPy][BF₄] in this work are given in Tables S1 and S2. Our results are consistent with those reported in the open literature,^{1,2} confirming the molecular structure and conformation of [BPy][BF₄].

Table S1: Comparison of ¹H-NMR chemical shifts of [BPy][BF₄] with references

H position	Chemical shift ² (ppm)	Chemical shift (Present work) (ppm)
10; (3H), CH ₃	0.90 (triplet)	0.86 (triplet)
9; (2H), CH ₂	1.30 (multiplet)	1.27 (quartet)
8; (2H), CH ₂	1.90 (multiplet)	1.90 (quartet)
7; (2H), NCH ₂	4.59 (triplet)	4.70 (triplet)
3,5; (2H), aromatic protons	8.14 (multiplet)	8.16 (triplet)
4; (1H), aromatic proton	8.59 (multiplet)	8.62 (triplet)
2,6; (2H), aromatic protons	9.04 (multiplet)	9.16 (doublet)

Table S2: Comparison of ^{13}C -NMR chemical shifts of [BPy][BF₄] with references

C position	Chemical shift ² (ppm)	Chemical shift (Present work) (ppm)
10; (1C), CH ₃	13.23	13.14
9; (1C), CH ₂	18.66	18.60
8; (1C), NCH ₂	32.57	32.57
7; (1C), NCH ₂	60.56	60.45
3,4 (2C), aromatic proton	128.03	127.99
2,6 (2C), aromatic protons	144.58	144.59
4 (1C), aromatic protons	145.43	145.41

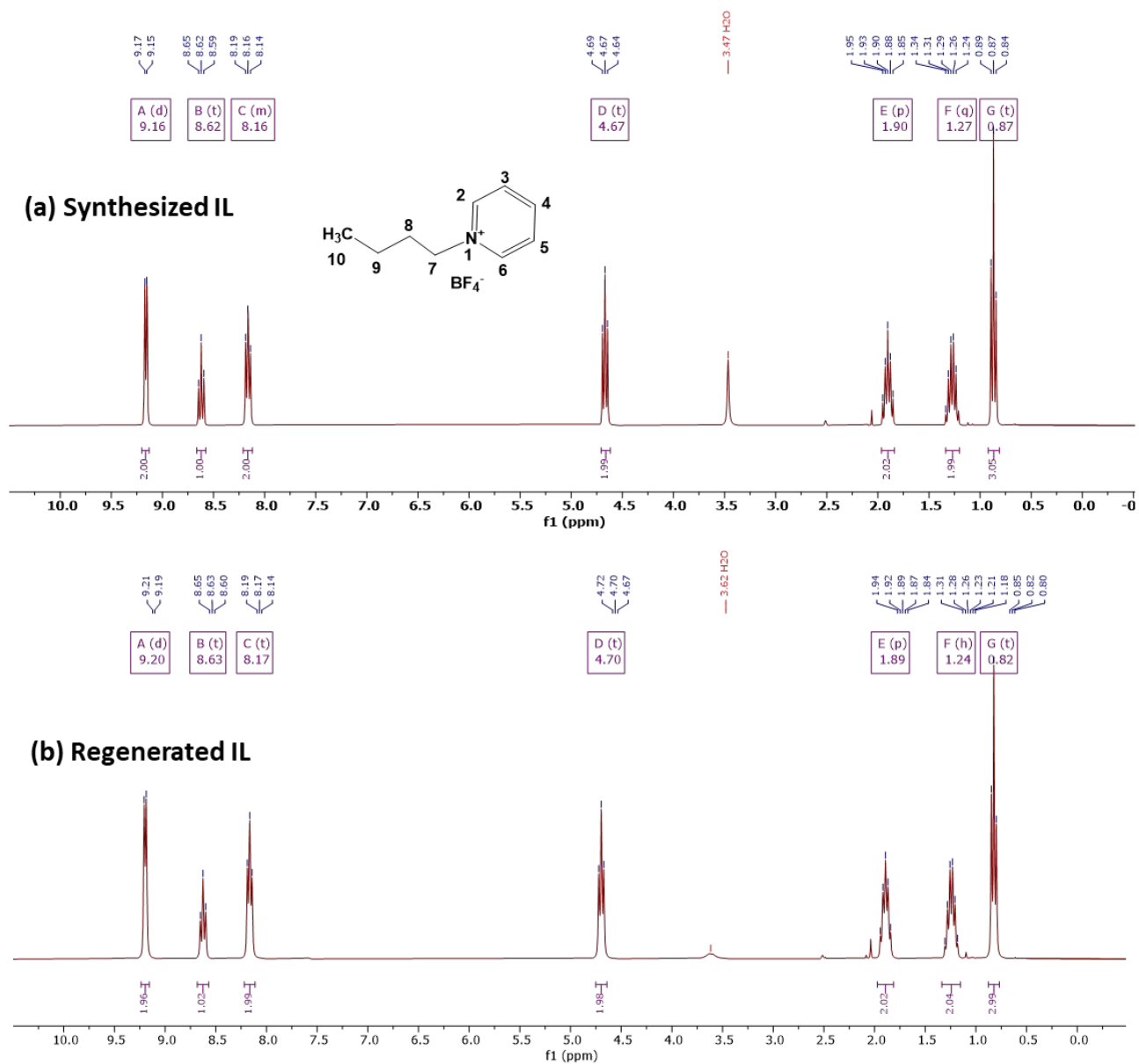


Figure S1: $^1\text{H-NMR}$ (300 MHz, $\text{DMSO-}d_6$) spectrums of (a) the synthesized and (b) regenerated ionic liquid (IL) $[\text{BPy}][\text{BF}_4]$.

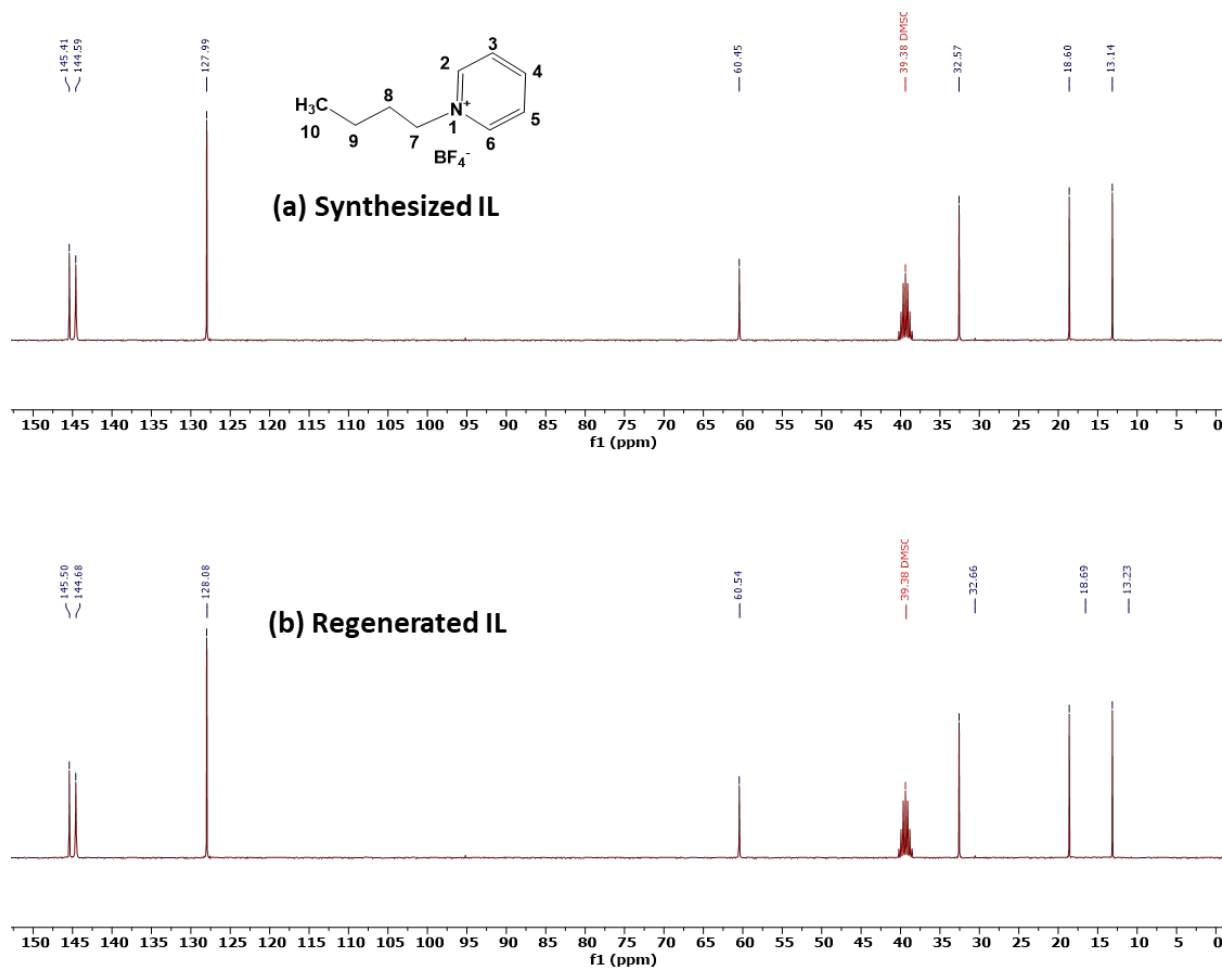


Figure S2: ¹³C-NMR (75 MHz, DMSO-*d*₆) spectrums of (a) the synthesized and (b) regenerated ionic liquid (IL) [BPy][BF₄].

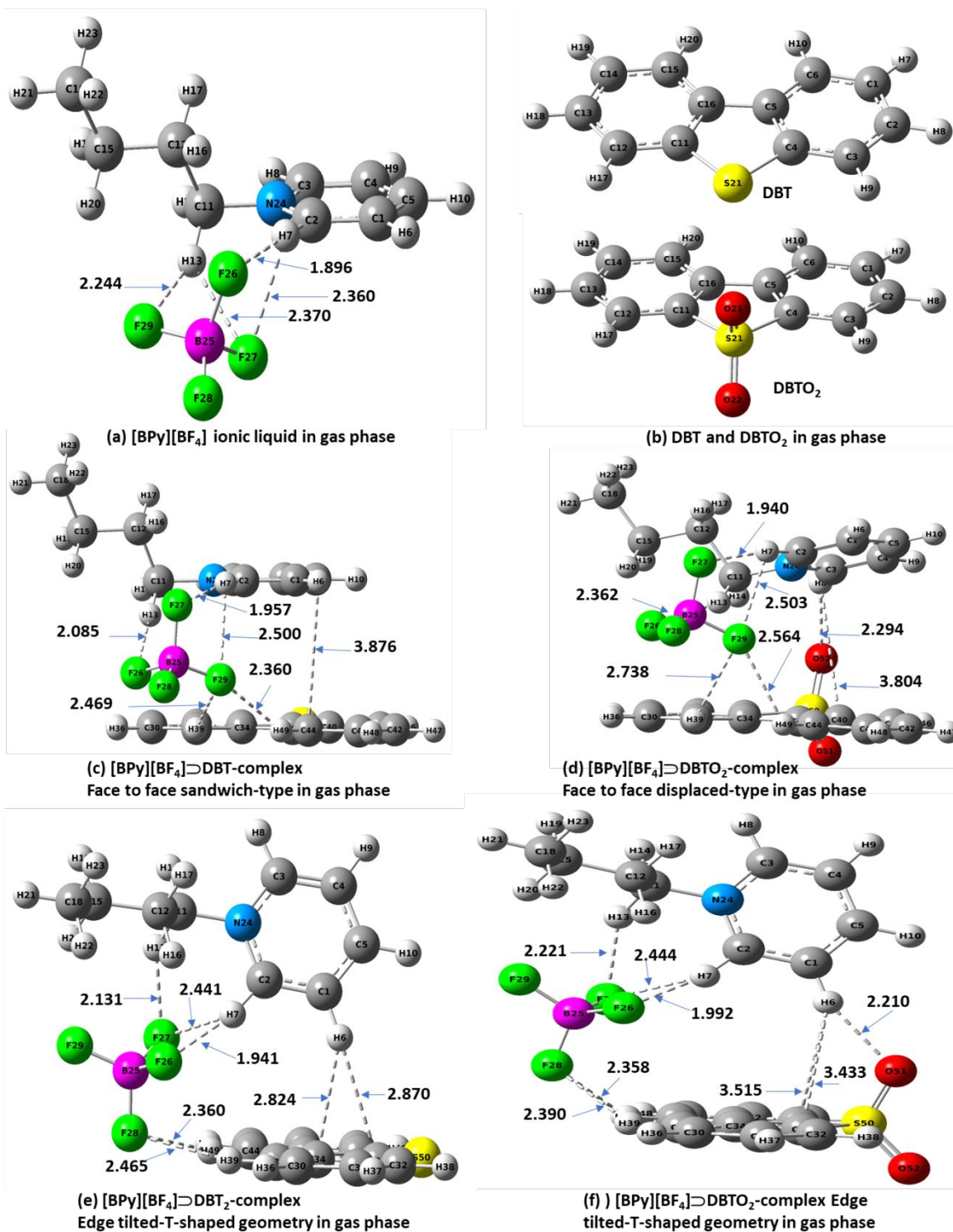


Figure S3. The geometry optimized structures of (a) [BPy][BF₄]; (b) dibenzothiophene (DBT), dibenzothiophene sulfone (DBTO₂); (c) & (e) ([BPy][BF₄]⊃DBT; and (d) & (f) ([BPy][BF₄]⊃DBTO₂) in gas phase. Color code: carbon = grey; hydrogen= white; nitrogen= blue; oxygen = red; sulfur = yellow, boron = magenta and fluorine = green.

FT-IR analysis of [BPy][BF₄]

Molecular structure of [BPy][BF₄] was characterized by FT-IR with the IR spectrum of [BPy][BF₄] being shown in Figure S4. Small band at 3618 cm⁻¹ is characteristic of traces of water present in the sample. The peaks at 3071 and 2937 cm⁻¹ are indicative of C–H stretching vibrations, representing hybridizations of sp² (aromatic) and sp³ (aliphatic) respectively. Peaks at 1709 and 1636 cm⁻¹ are the characteristic overtone bands for aromatic rings. Bands at 1583, 1489 and 1468 cm⁻¹ are attributed to the aromatic C=C stretching vibrations. In the region of the fingerprint, there are flexion bands for sp³ C–H at 1455 and 1364 cm⁻¹. Peaks at 1223, 1174, 1047 and 1034 cm⁻¹ are due to the coalescence of aromatic stretching and sp³ C–H bending, whereas sharp peaks at 771 and 685 cm⁻¹ are assigned to the aromatic sp² C–H bending. The IR data of [BPy][BF₄] synthesized in this work are consistent with those reported elsewhere.²

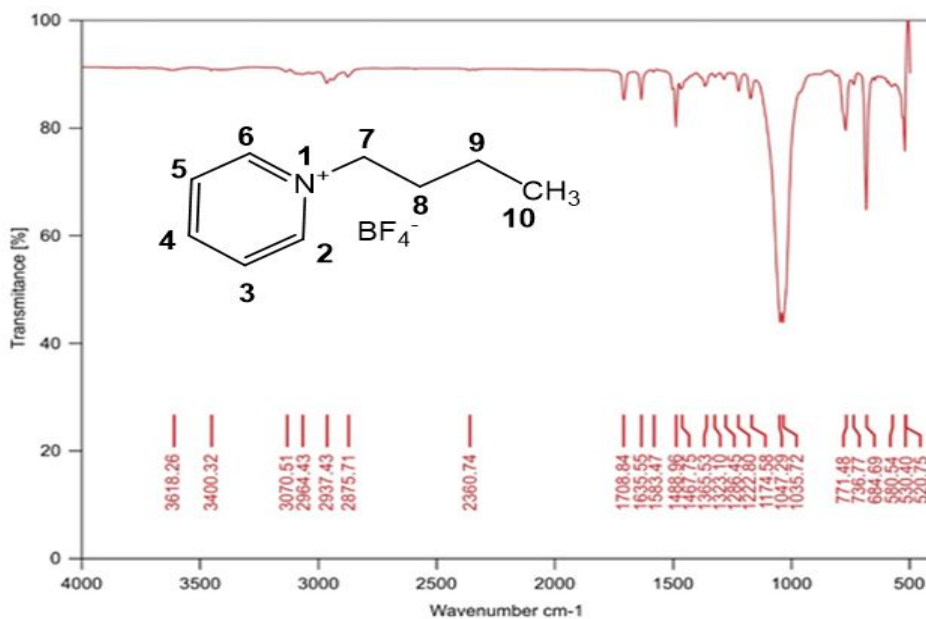


Figure S4. FT-IR spectrum of [BPy]BF₄

References:

- (1) D. Zhao, Y. Wang, E. Duan, Oxidative desulfurization of fuel oil by pyridinium-based ionic liquids, *Molecules* **2009**, *14*, 4351–4357.
- (2) M. Enayati, H. Faghihian, *N*-butyl-pyridinium tetrafluoroborate as a highly efficient ionic liquid for removal of dibenzothiophene from organic solutions, *J. Fuel Chem. Technol.* **2015**, *43*, 195–201.