

## Supporting Information

### **Enhanced ORR Performance to Electrochemical Lignin Valorization in a Mixture Ionic Liquid/ Organic Solvent Binary Electrolyte**

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## 1. Calculation of viscosity coefficients for [BMIM]BF<sub>4</sub> electrolytes

**Table S1** Values of diffusion coefficient D of Fc and dynamic viscosity  $\eta$  of various electrolytes

Electrolytes	D (cm <sup>2</sup> s <sup>-1</sup> )	$\eta$ (mPa s)
100% [BMIM]BF <sub>4</sub>	2.6661×10 <sup>-7</sup>	104.96
70% [BMIM]BF <sub>4</sub>	1.2864×10 <sup>-6</sup>	21.75
60% [BMIM]BF <sub>4</sub>	3.0153×10 <sup>-6</sup>	9.28
40% [BMIM]BF <sub>4</sub>	7.9970×10 <sup>-6</sup>	3.50
Acetonitrile	-	0.30

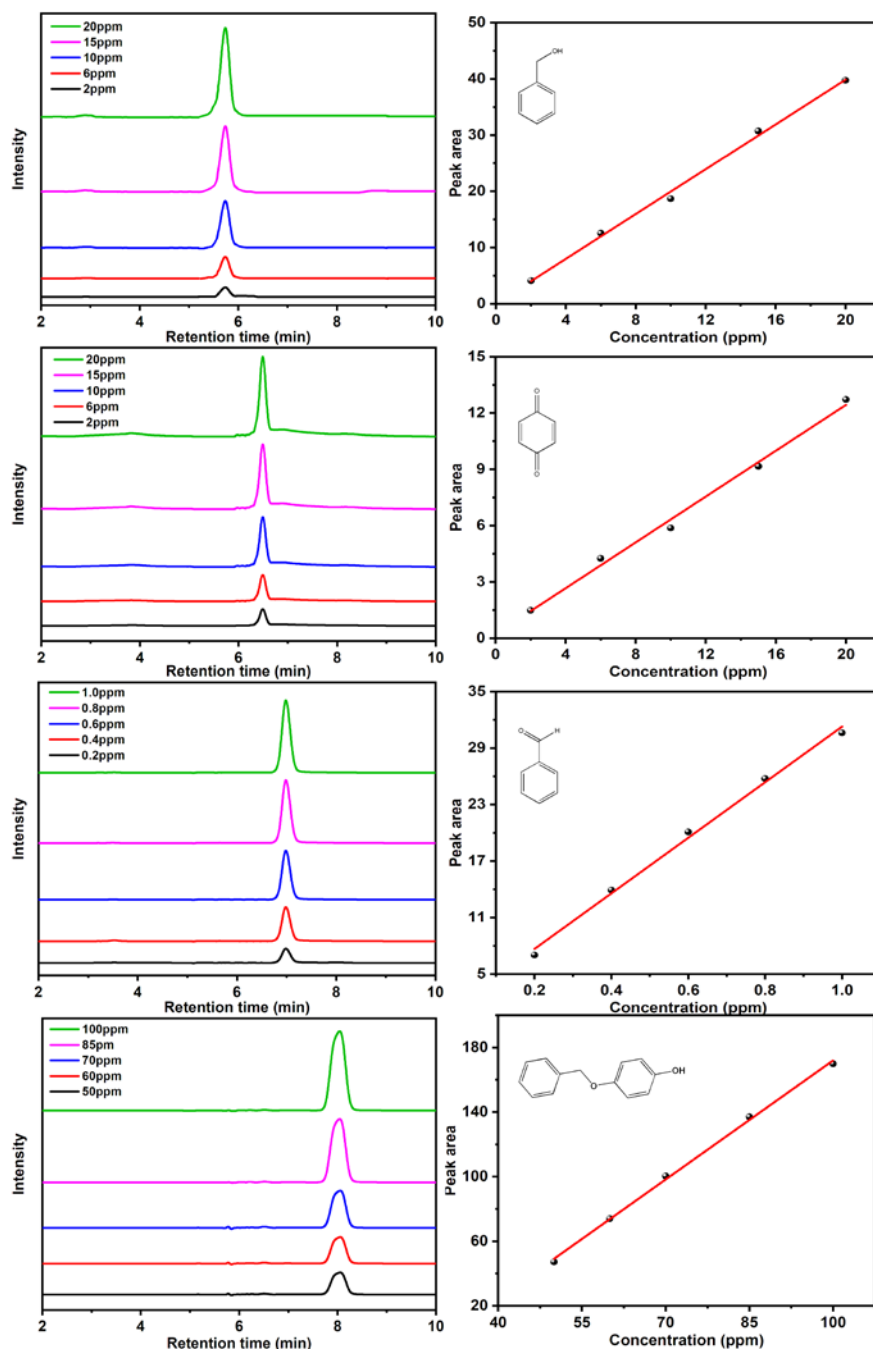
## 2. MD results of O<sub>2</sub> adsorption energy various electrolytes

**Table S2.** The corresponding energy of O<sub>2</sub> in various electrolytes.

Electrolytes	$E_{\text{total}}$ (kJ mol <sup>-1</sup> )	$E_e$ (kJ mol <sup>-1</sup> )	$E_{\text{O}_2}$ (kJ mol <sup>-1</sup> )	$E_{e-\text{O}_2}$ (kJ mol <sup>-1</sup> )
[BMIM]BF <sub>4</sub>	-6794.39	-6778.35	1.57	-17.61
[BMIM]BF <sub>4</sub> /CH <sub>3</sub> CN	-7410.20	-7390.43	1.16	-20.93
CH <sub>3</sub> CN	-2172.69	-2160.13	3.53	-16.10

### 3. Standard curve of products after PBP electrolysis by HPLC

Prepared standard solutions of products with different concentrations to draw the standard curves (as shown in Figure S1). Retention times of benzyl alcohol is 5.8, 1,4-benzoquinone is 6.4 min, benzaldehyde is 7.0 min, and PBP is 8.0 min. It confirms that these two products have good separation effect in electrolytes.



**Figure S1.** The HPLC chromatography and standard curves of various reference materials at different concentrations.

#### 4. The electrical conductivity of different electrolyte systems.

**Table S3.** The electrical conductivity of different electrolytes.

Electrolytes	Conductivity ( $\sigma$ , mS·cm <sup>-1</sup> )
[BMIM]BF <sub>4</sub>	10.43
[BMIM]BF <sub>4</sub> /CH <sub>3</sub> CN (7:3)	44.55
[BMIM]BF <sub>4</sub> /CH <sub>3</sub> CN (4:6)	48.81
[BMIM]BF <sub>4</sub> /CH <sub>3</sub> CN (1:9)	7.85