Supporting Information

Ultrasensitive gaseous NH_3 sensor based on ionic liquid-mediated signal-on electrochemiluminescence

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Coreactant ECL activity comparison between NH_3 and tri-n-propylamine (TPrA)

First, the concentration of NH_3 in the IL was roughly estimated for the case that 50 mL of 5 ppm NH_3 gas was injected into the sensor which used 1 μL IL as the sensing film. The maximum concentration of NH_3 in the IL was calculated to be 0.012 M by assuming that all of the NH_3 in the gas phase (50 mL, 5 ppm) completely dissolved in the 1 mM $Ru(bpy)_3^{2+}$-containing IL. Apparently, the actual concentration of NH_3 in the IL should be lower than 0.012 M, even if the NH_3 was found to easily dissolve in the IL.[1] Then 0.012 M TPrA was dissolved in the 1 mM $Ru(bpy)_3^{2+}$-containing IL for ECL comparison. The ECL responses from the $Ru(bpy)_3^{2+}$-NH_3-IL system and $Ru(bpy)_3^{2+}$-TPrA-IL system were shown in Fig. S1. It can be known from the comparison of the ECL intensities that the coreactant ECL activity of NH_3 in the IL is more 10 times higher of that TPrA in the same medium.

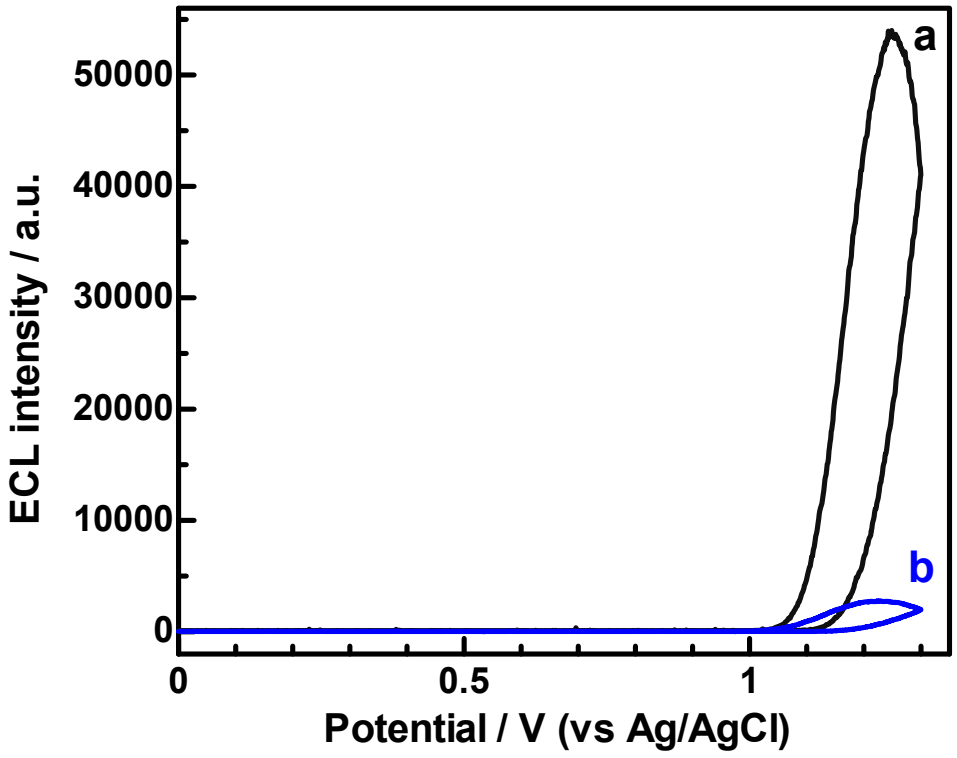

Figure S1. ECL response of 1 mM $Ru(bpy)_3^{2+}$-containing IL film (1 μL) to the coreactants: (a) NH_3 (by injection 50 mL and 5 ppm NH_3/N_2 gas into the sensor, the concentration of NH_3 in the IL film was less than 0.012 M); (b) TPrA (0.012M)

Electrochemical and ECL responses of $Ru(bpy)_3^{2+}$-N_2H_4 system in ionic liquid

In the ECL mechanism of $Ru(bpy)_3^{2+}$-NH_3 system, N_2H_4 is proposed to be the highly reducing intermediate that reduce $Ru(bpy)_3^{3+}$ into the excited state, $Ru(bpy)_3^{2+*}$. To confirm this mechanism, dried N_2H_4 vapor was injected into the ECL sensor that used the 1 mM $Ru(bpy)_3^{2+}$-containing IL film as sensing unit. The dried N_2H_4/N_2 was produced by bubbling N_2 gas into N_2H_4 aqueous solution and drying the obtained N_2H_4 vapor thoroughly with NaOH particles. As shown in section A of Fig. S2, no ECL was found when the $Ru(bpy)_3^{2+}$-IL film was exposed to the dried N_2 gas (curve b), whereas strong ECL emission was observed when the dried N_2H_4 was injected into the sensor (curve a). This experiment shows that the reducing ability of N_2H_4 is strong enough to reduce $Ru(bpy)_3^{3+}$ into $Ru(bpy)_3^{2+*}$, and thus confirms that the ECL reactions of $Ru(bpy)_3^{2+}$-NH_3 system may involve the formation of the highly reducing intermediate, N_2H_4.

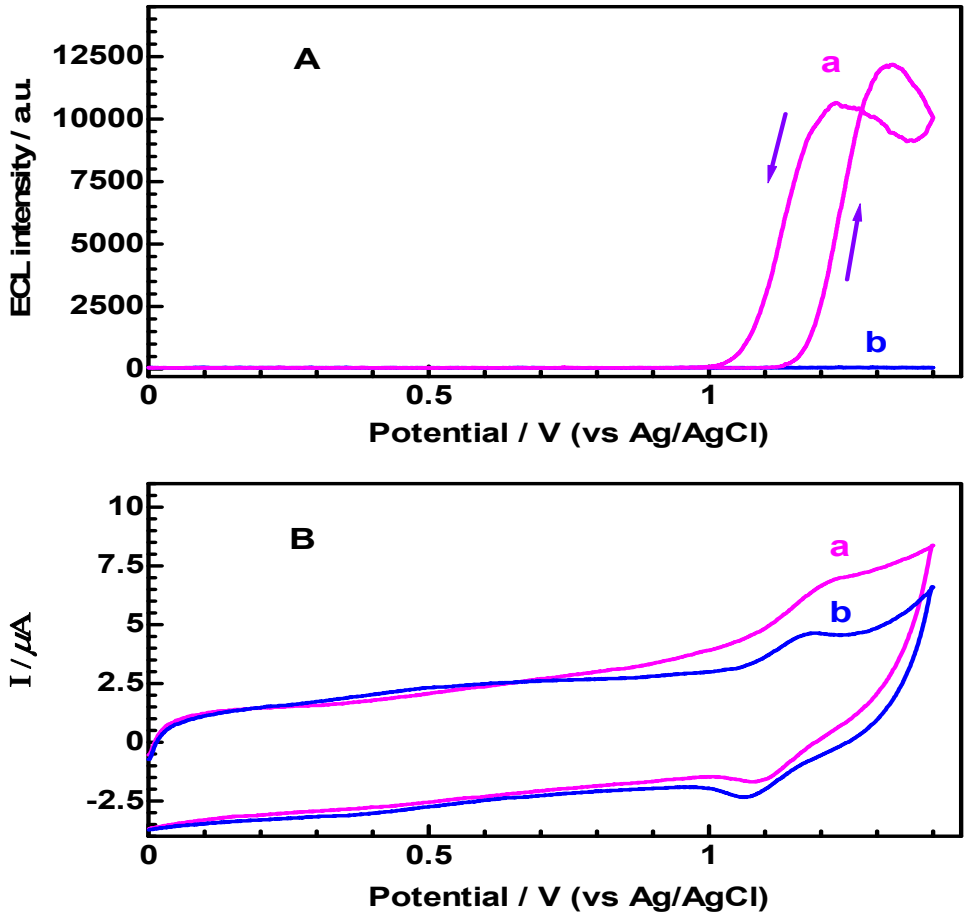

Figure S2. Electrochemiluminescent (A) and electrochemical (B) responses recorded

simultaneously for the $Ru(bpy)_3^{2+}$-containing IL film exposed to (a) dried N_2H_2 gas; (b) dried N_2 vapor.

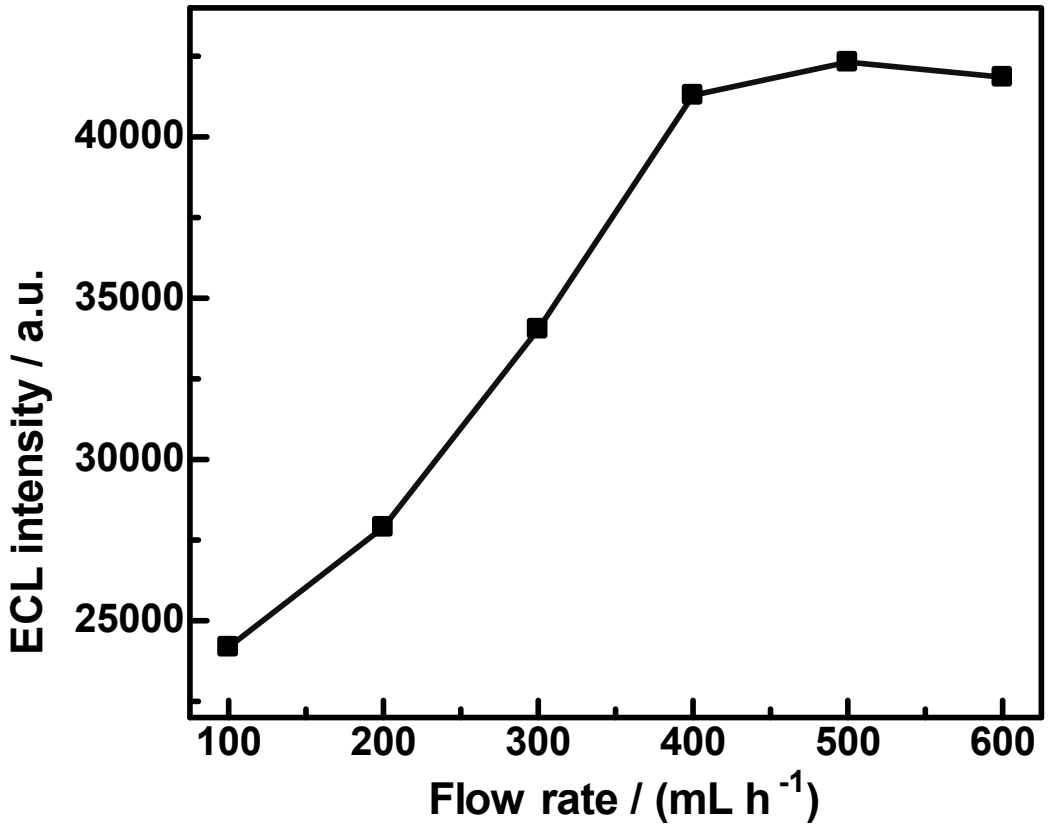

Figure S3. Influence of NH_3 gas flow rate on the ECL intensity of the NH_3 sensor to 1 ppm NH_3.

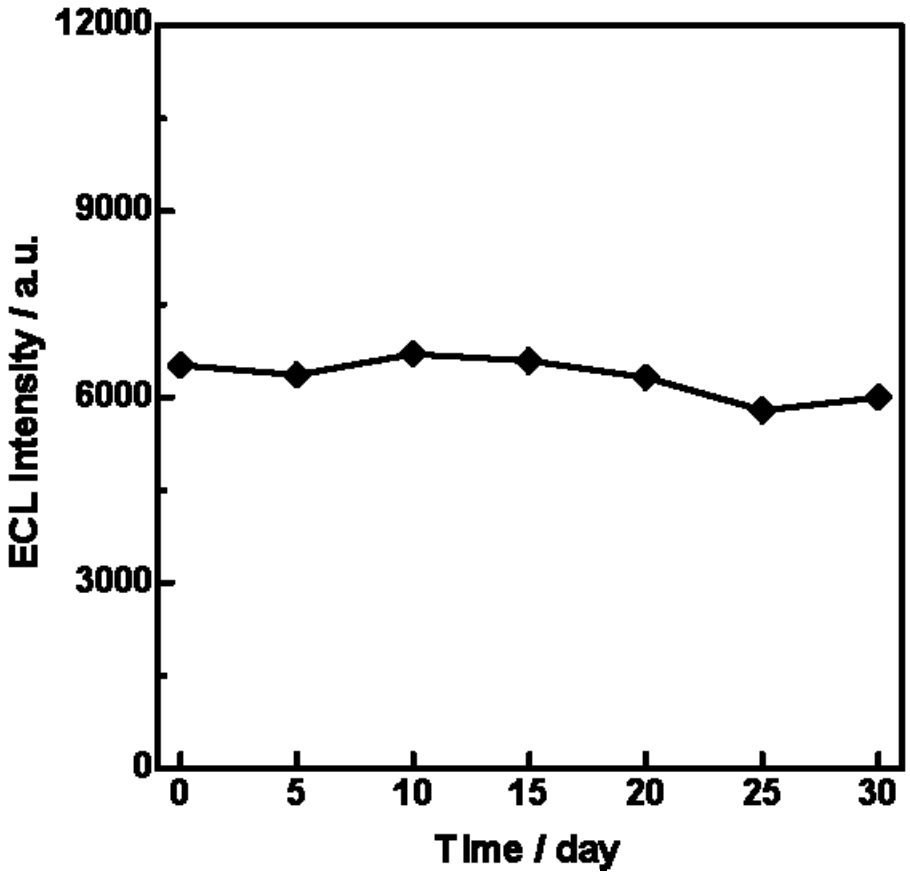

Figure S4. Long-term stability observed for the as-developed ECL sensor for 10 ppb NH_3.

References

[1] A. Yokozeki, M. B. Shiflett, *Ind. Eng. Chem. Res.* **2007**, *46*, 1605-1610.