Supporting Information

All Solid-state Rechargeable Lithium-Iodine Thin Film Battery Using LiI(3-hydroxypropionitrile)$_2$ as I^- Ion Electrolyte

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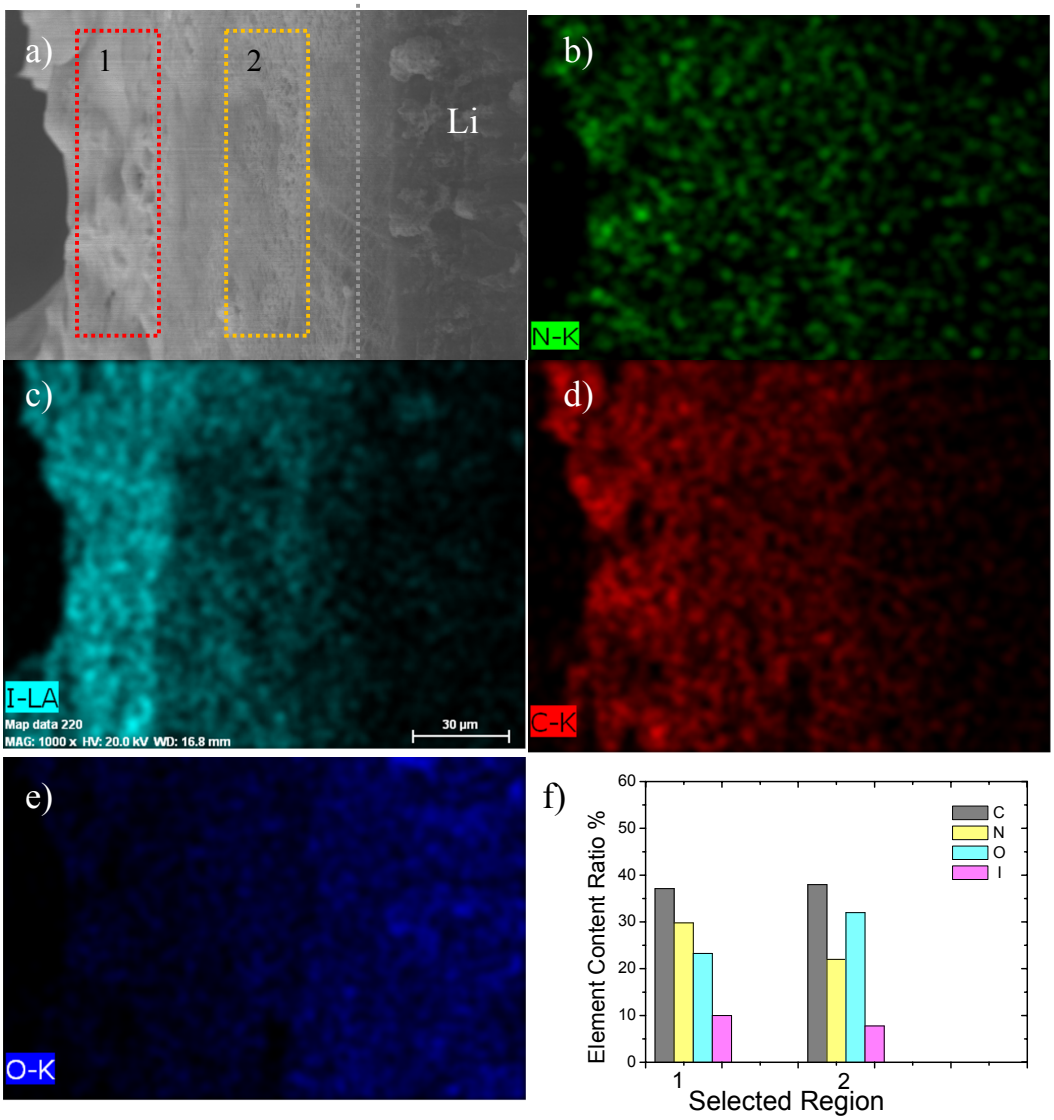

Figure S1. a) Cross-sectional backscattered electron images of Li/LiI(HPN)$_2$/ LiI(HPN)$_2$-I$_2$ cell, and the corresponding energy-dispersive X-ray spectrometry mappings of b) N; c) I; d) C and (e) O; (f)the average molar concentration ratio of I/C/N/O from corresponding EDX spectra in two selected regions(1 and 2).

The electrolytes *of LiI(HPN)$_2$* preparation method is similar to report previously elsewhere(B. Xue, Z. W. Fu, H. Li, X. Z. Liu, S. C. Cheng, J. Yao, D. M. Li, L. Q. Chen, Q. B. Meng, *J. Am. Soc. Chem.* **2006**, 128,8720-8721.). The LiI(HPN)$_2$-ethylacetate saturated solution was prepared by adding 0.1 g LiI(HPN)$_2$ into 2 ml ethylacetate (a few LiI(HPN)$_2$ was salted out) in the glove box for the film fabrication of LiI(HPN)$_2$. In a typical process, this solution was firstly coated on the surface of the lithium foil (purity 99.999%) at 50 ^{o}C. After drying, the surface of LiI(HPN)$_2$ film was exposed to the I$_2$ vapor that sublimed from I$_2$ crystals in a vial at room temperature. The distance between the substrate and the I$_2$ crystals was about 6 cm. After exposure to I$_2$ vapor for 8 seconds, a battery consisting of Li/LiI(HPN)$_2$/I$_2$-LiI(HPN)$_2$ was formed. As shown in Figure S1, the fresh cell includes two layers: the lithium foil is at the right side of the dotted line. The

$LiI(HPN)_2$ electrolyte and a complex mixture of iodine and $LiI(HPN)_2$ consisting of of N, C, I, O elements as cathode is at the left side of the dotted line. The thickness of solid electrolyte and parts of reacted produce with iodine is about ~100 μm. Existence of trace amount of oxygen and nitrogen in the lithium foil should be attributed to the oxidation and nitridation of lithium contacted with air during sample transfer. The chemical reaction of I_2 vapor with $LiI(HPN)_2$ can be investigated by measuring EDX spectra in selected area. As shown in Figure S1 (f), the average molar concentration ratios of I/C/N/O are 10: 37: 29: 23 and 8:38:22:32 in two selected regions 1 and 2. Apparently, the iodine concentration in selected region 1 is higher than that in region 2. The composition of I_2-$LiI(HPN)_2$ in region 1 is estimated to be 0.33: 1 using I/C=10:37.

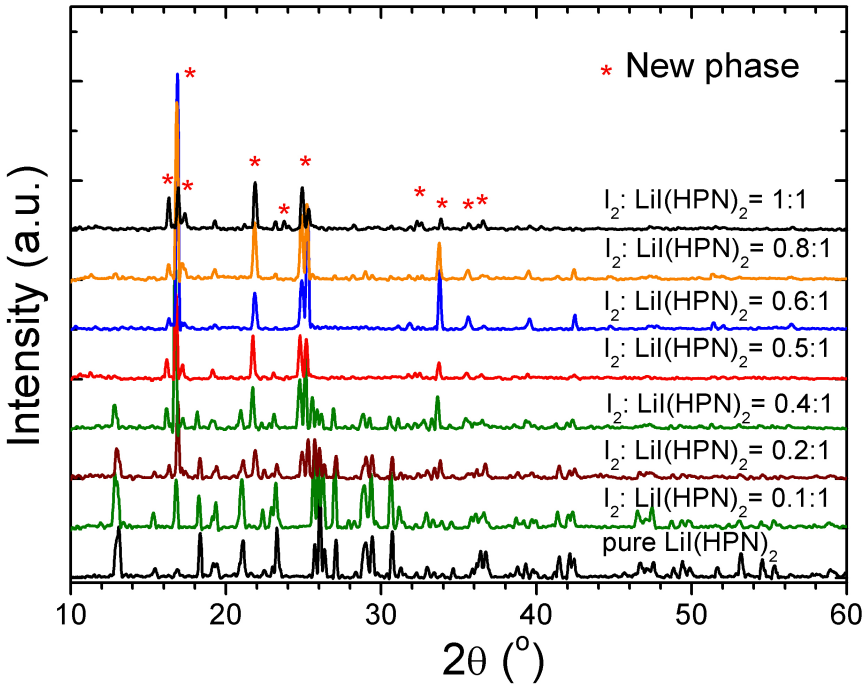

Figure S2 XRD patterns of a complex mixture of iodine and $LiI(HPN)_2$ with different molar ratio of $I_2/LiI(HPN)_2$. XRD pattern of the pure electrolyte $LiI(HPN)_2$ is included for comparison.

Several peaks at 13.1°, 18.4°, 21.1°, 23.3°, 25.9°, 27.0°, 29.0°, 29.3°, 30.7°, 36.3°, 36.8°, 41.4°, and 42.1° are in good agreement with the diffraction peaks of single crystal $LiI(HPN)_2$. (See Ref. [8], H. X. Wang, Z.X. Wang, H. Li, Q. B. Meng, L. Q. Chen, Electrochimica Acta 52 (2007) 2039-2044)). The new diffraction peaks (marked with star) appear after addition of iodine. The crystal structure of new phase will be resolved in future.

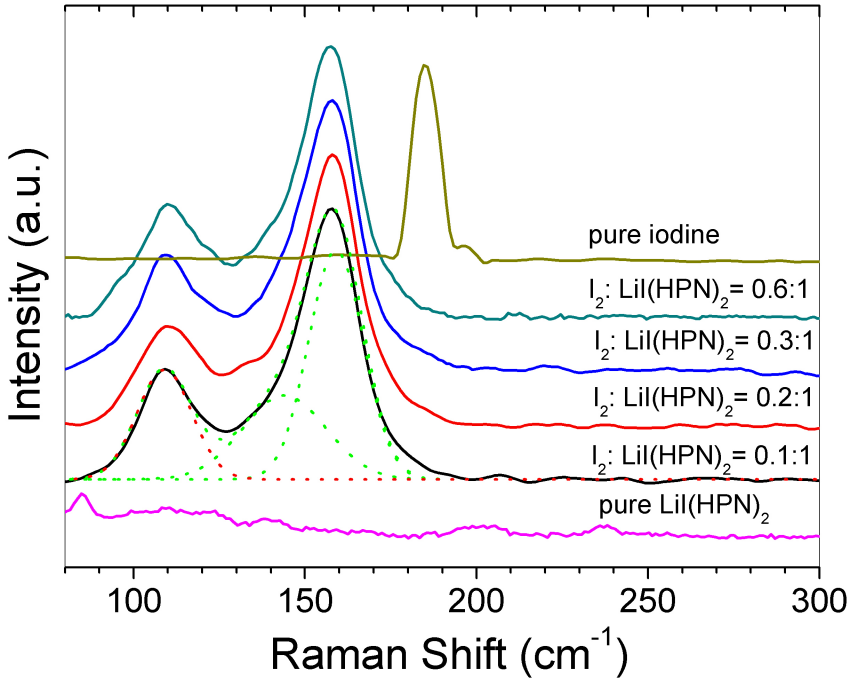

Figure S3 Raman spectra of the pure iodine, pure electrolyte $LiI(HPN)_2$ and a complex mixture of iodine and $LiI(HPN)_2$ with different molar ratio of I_2/$LiI(HPN)_2$.

There is no band for pure $Li(HPN)_2$ in the range of 100 to 300 cm^{-1}. Raman spectrum of pure I_2 (Lab Grade, Aldon Corp.) is used for comparison. A peak at 185 cm^{-1} can be indexed to the vibration assignment of I-I bonds. (See, Ref. [7], Weinstein, L.; Yourey, W.; Gural, J.; Amatucci, G.G., Electrochemical Impedance Spectroscopy of Electrochemically Self-Assembled Lithium-Iodine Batteries, *J. Electrochem. Soc.* **2008**, 155, A590-A598, [a] Stangar, U.L.; Orel, B.; Vuk, A.S.; Sagon, G.; Colomban, P.; Stathatos, E.; Lianos, P., In Situ Resonance Raman Microspectroscopy of a Solid-State Dye-Sensitized Photoelectrochemical Cell, *J. Electrochem. Soc.* **2002**, 149, E413-E423, [b] Howard, W.F.; Andrews, L.; *J. Raman Spectrosc.*, **1974**, 2, 447-462).
It is found that no any peaks from the Raman shift of I_2 is observed for the mixture of iodine and $Li(HPN)_2$. This indicates clearly that a mixture of $LiI(HPN)_2$ with iodine is not a physical mixture and iodine should react with $Li(HPN)_2$. Previous studies showed that the weak band at 107 cm^{-1} and a strongly band at 163 cm^{-1} in (trimesic acid $H_2O)_{10}HI_5$ can be attributed to be that characteristic of a I^{3-} ν_1 and I^{5-} ν_1 vibrations, respectively (See Masagi Mizuno, Jiro Tanaka, Issei Harada, *J. Phys. Chem.* **1981**, 85, 1789-1794) . In the PVP-I_n^- complex, the peak at 115 cm^{-1} and 173 cm^{-1} are assigned to I^{3-} ν_1 and I^{5-} ν_1 vibrations (See L. Weinstein, W. Yourey, J. Gural, and G. G. Amatucci, *Journal of The Electrochemical Society,* **2008**, 155, A590-A598). The I^{3-} ν_3 band at 144 cm^{-1} is clearly observed as a shoulder on the main I^{5-} peak, which can be deconvoluted as shown in Figure. A clear assignment of Raman bands in Figure S4 need clear information of the coordination of iodine in $LiI(HPN)_2$ and possible crystal structure, which will be studied further. Above preliminary results indicate clearly the formation of certain $LiI(HPN)_2$-I_n complex.

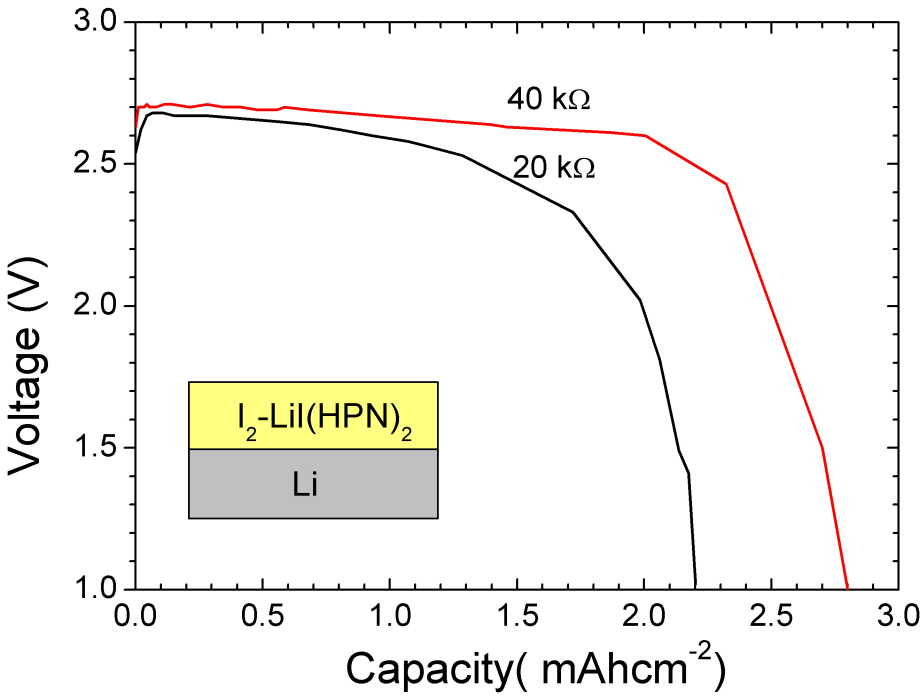

Figure S4. The discharging curves of an Li/I_2-LiI$(HPN)_2$ battery using a 20 kΩ and 40 kΩ loading.

The primary batteries of Li/I_2-LiI$(HPN)_2$ were constructed as following. Li plate (purity 99.999%) with a thickness of 0.5 mm (1.0 cm^2) was used as an anode directly. The finely ground powders of iodine (purity 99.99%) and LiI$(HPN)_2$ with a molar ratio of 0.5:1 were mixed mechanically and pressed into a columnar electrode (diameter=11.3 mm, thickness= 0.5 mm) as cathode. The cells were assembled and measured in an Ar-filled dry glove box. No separator or electrolyte was used in this case. The operating voltage is relative flat at the 40 kΩ discharge curve until the cathode is depleted in iodine. The operation of this battery indicates that the I_2-LiI$(HPN)_2$ can be used as cathode material for lithium-iodine batteries, similar as I_2-P_2VP cathode. It has to be mentioned that this battery cannot be discharged galvanostatistically at a current density of 1 μAcm^{-2} using CHI660A electrochemical workstation.

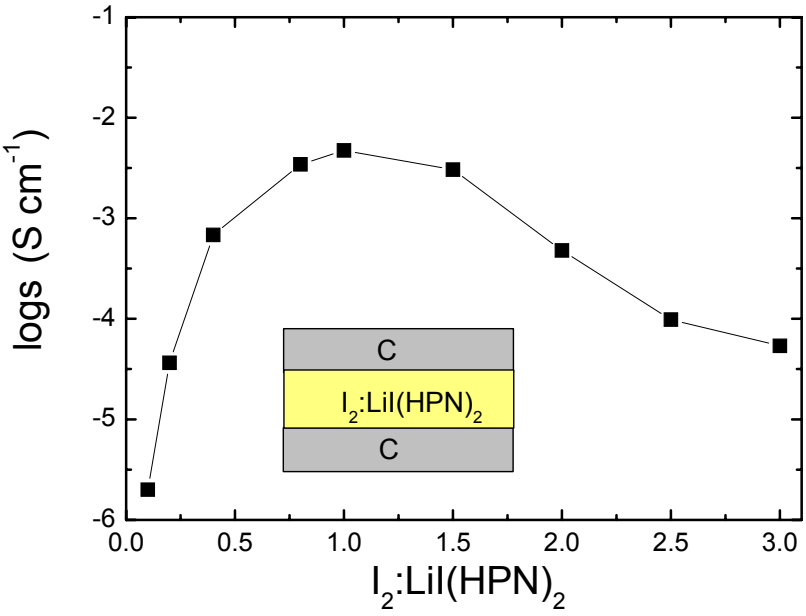

Figure S5 Conductivity of a complex mixture of iodine and $LiI(HPN)_2$ with different molar ratio of $I_2/LiI(HPN)_2$.

Conductivity measurement was carried out by using the sandwiching with two carbon electrodes and one columnar electrode of I_2:$LiI(HPN)_2$, which were obtained by cold pressing iodine (purity 99.99%) and $LiI(HPN)_2$ with different molar ratio. The conductivity of I_2:$LiI(HPN)_2$ was calculated by the known area and the thickness as well as the examined resistance of C/ I_2:$LiI(HPN)_2$/C by a CHI660A electrochemical workstation. It can be found that the conductivity drastically decrease from 10^{-2} Scm^{-1} to 10^{-5} S/cm^{-1} with the value of I_2:$LiI(HPN)_2$ from 1.0 to 0.1