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**Supporting Information**

# Bi-functional $Li_2B_{12}H_{12}$ for energy storage and conversion applications: solid-state electrolyte and luminescent down-conversion dye

Joseph A. Teprovich, Jr.,[†]* Hector Colon-Mercado,[†] Aaron L. Washington, II[†] Patrick A. Ward,[†] Scott Greenway,[‡] David M. Missimer,[†] Hope Hartman,[†] Josef Velten,[†] Jonathan H. Christian,[†] and Ragaiy Zidan[†]*

[†]Savannah River National Laboratory, Aiken, SC, 29808, USA

[‡]Greenway Energy LLC, Savannah River Site, 301 Gateway Drive, Aiken, South Carolina 29808, United States

## Materials

$LiBH_4$, decaborane, lithium foil, graphite, polyvinyl alcohol, and acetylene black were used as received and stored inside of an argon filled glovebox with oxygen and water levels below 1 ppm.

## $Li_2B_{12}H_{12}$ synthesis

A slight variation to the thermochemical synthesis of $Li_2B_{12}H_{12}$ was used.[1] $LiBH_4$ (1.0 g) and decaborane (2.807 g) were loaded into a spex mill inside of a glovebox. A 10:1 ball to powder ratio was used with 2 mm stainless steel ball. The sample was spex milled for 5 minutes, then the vial was rotated 180 degrees and spex milled for an additional 5 minutes. The vial was taken back into the glovebox and homogenized with a mortar and pestle. The sample was loaded back into the spex mill vial and this was repeated until 45 minutes of total milling was achieved with sample homogenization inside of the glovebox after every 10 minutes of milling. This ensures a homogenous mixture with minimal heating during the process. Next, 0.3g of the $LiBH_4$-decaborane composite was loaded into a stainless steel reactor with a 3.5 mL volume and sealed with VCR gaskets (Figure S1) in the glovebox. The reactor was then sealed inside a 500 mL volume Parr reactor and removed from the glovebox. The sample was heated to 200 °C and allowed to soak for 18-20 hours. All samples were collected and handled inside of the glovebox once at room temperature. This material is referred to as the as-synthesized sample. The sample called the milled sample was prepared by loading 1.0 g of the as-synthesized $Li_2B_{12}H_{12}$ into a spex mill with a 30:1 ball to powder ratio and milling for 5 minutes. The milling vial was then rotated 180 degrees and spex milled for an additional 5 minutes (10 minutes of total milling). The sample was then collected inside of the glovebox and analyzed by electrochemical and spectroscopic techniques.

## Instrumental Analysis

X-ray diffraction data were collected on a PANalytical X'pert Pro by step scanning over the 2-theta range of 5 to 80 degrees with a step size of 0.0167 degrees and a dwell time of 50.165 sec/step. The large dwell time with short analysis time was achieved using the X'Celerator detector that has a 2.122° (2) active length and operates as if there were an array of over a hundred detectors working simultaneously. All the instrument parameters are listed in Table 1. Compound search-match identification was performed with Jade 2010 software from Materials Data Inc. using the inorganic PDF4 powder diffraction database from the International Centre for Diffraction Data (ICDD).

**TABLE I. Instrument parameters.**

| | |
|---|---|
| Radiation Source | CuK X-ray |
| Source Power | 45 kV, 40 mA |
| Wavelength | 1.5405982 Å |
| Goniometer | PANalytical X'pert Pro |
| Divergence Soller Slit | 0.04 rad |
| Divergence Slit | 1/2° |
| Beam Mask | 10mm |
| Divergence Antiscatter | 1° |
| Specimen Rotation | No |
| Diffracted Beam Antiscatter (short) | 3.4 |
| Diffracted Beam Antiscatter (long) | 5.5 |
| Filter | Nickel |
| Detector | X'Celerator |
| Active Length | 2.122° |
| 2 Range | 5° - 80° |
| Step Interval | 0.0167° (2) |
| Fixed counting Time | 50.165 s/step |

SEM images were acquired using a Hitachi SU8200 Series Ultimate Cold Field Emission SEM with varying accelerating voltages and magnifications. Powder and pressed pellets of the "as-synthesized" and "milled" samples were prepared in an Ar filled glovebox and contained in Ar filled containers until transfer into the instrument. Air exposure during sample insertion was approximately 5 seconds.

Differential scanning calorimetry was performed on a Seteram SENSYS evo DSC using a heating rate of 5 °C/min with a constant flow of argon. The constant volume sample crucibles were sealed under argon in a glovebox.

The spectroscopic properties were obtained using an Agilent Technologies Cary 60 UV-vis and Cary Eclipse Fluorescence Spectrophotometer. A stock solution of 5 mg/mL was prepared and then known amounts were added via a syringe to 2.5mL of water in the cuvette and the concentrations calculated.

Transparent head-up displays were prepared by dissolving 20-60 mg of $Li_2B_{12}H_{12}$ in 60 g of water. Then 3.0 g of PVA (9,000-10,000 MW; 80% hydrolyzed) was added with slow mixing. When the PVA is fully dissolved the solution is then poured onto a glass plate that has a 9”x7” rectangle outlined by duct tape. The solution is allowed to dry naturally to form the film. In more concentrated solutions of $Li_2B_{12}H_{12}$, Triton-X can be added to prevent aggregation of $Li_2B_{12}H_{12}$during the drying process.

Pellets of the materials were prepared by pressing the samples in a hydraulic press at 6 tons of pressure under inert conditions. Each pellet (85−130 mg) was 10 mm in diameter with a thickness between 0.8 and 1.1 mm. All electrochemical testing utilized a Swagelok-type cell. Electrochemical testing was performed using a Bio-Logic VMP3 multichannel potentiostat with a frequency response analyzer. Temperature- dependent studies were performed in an oven with the appropriate electrical connections. For the electrochemical impedance spectroscopy (EIS) and constant current cycling experiments, 10 mm diameter lithium foils were utilized in a symmetric cell setup. The EIS was measured in a frequency range of 1 MHz to 100 Hz. The conductivities were obtained from the diameter of a single arc and the intercept on the $Z_R$ axis in the complex impedance plots.

Constant current cycling was performed in a symmetrical cell with 2 lithium foil electrodes ($Li/Li_2B_{12}H_{12}/Li$) at a current of ±0.1mA.

Cyclic voltammetry was performed with a lithium foil electrode and a Pt disk electrode. The $Li_2B_{12}H_{12}$ was pressed into a pellet with the Pt electrode then the lithium foil electrode was attached to the opposite end ($Li/Li_2B_{12}H_{12}/Pt$).

All solid state cells were assembled by first preparing a composite anode consisting of SFG-10 graphite:$Li_2B_{12}H_{12}$:acetylene black (60:30:10 weight ratio). The components were hand mixed with mortar and pestle. Then 2-5 mg of the composite anode material was placed on top of a nickel foam disk inside of a 10 mm die set. Next 110-130 mg of the milled $Li_2B_{12}H_{12}$ was added on top of the anode composite/nickel foam and pressed at 6 tons to make a solid pellet. A lithium foil electrode was then added to the opposite end and put into a Swagelok type cell for cycling.

**Figure S1.** Reactor used for the thermochemical synthesis of $Li_2B_{12}H_{12}$.

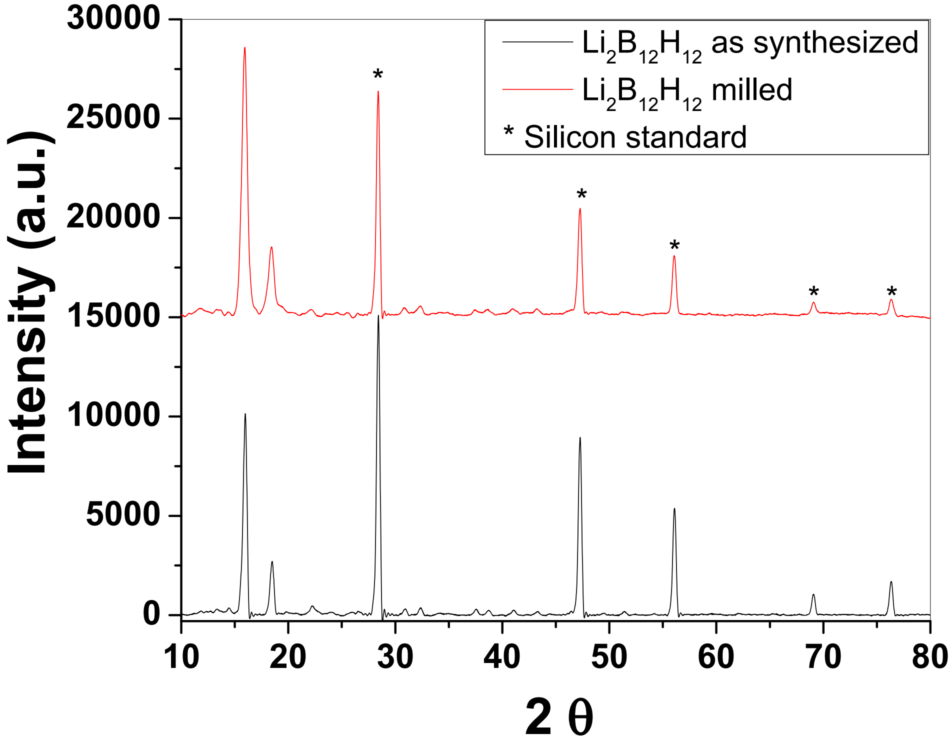

**Figure S2.** XRD spectrum of the as-synthesized (black) and milled (red) $Li_2B_{12}H_{12}$ samples with an added silicon internal standard. The pattern matches the PDF # 04-015-5767.

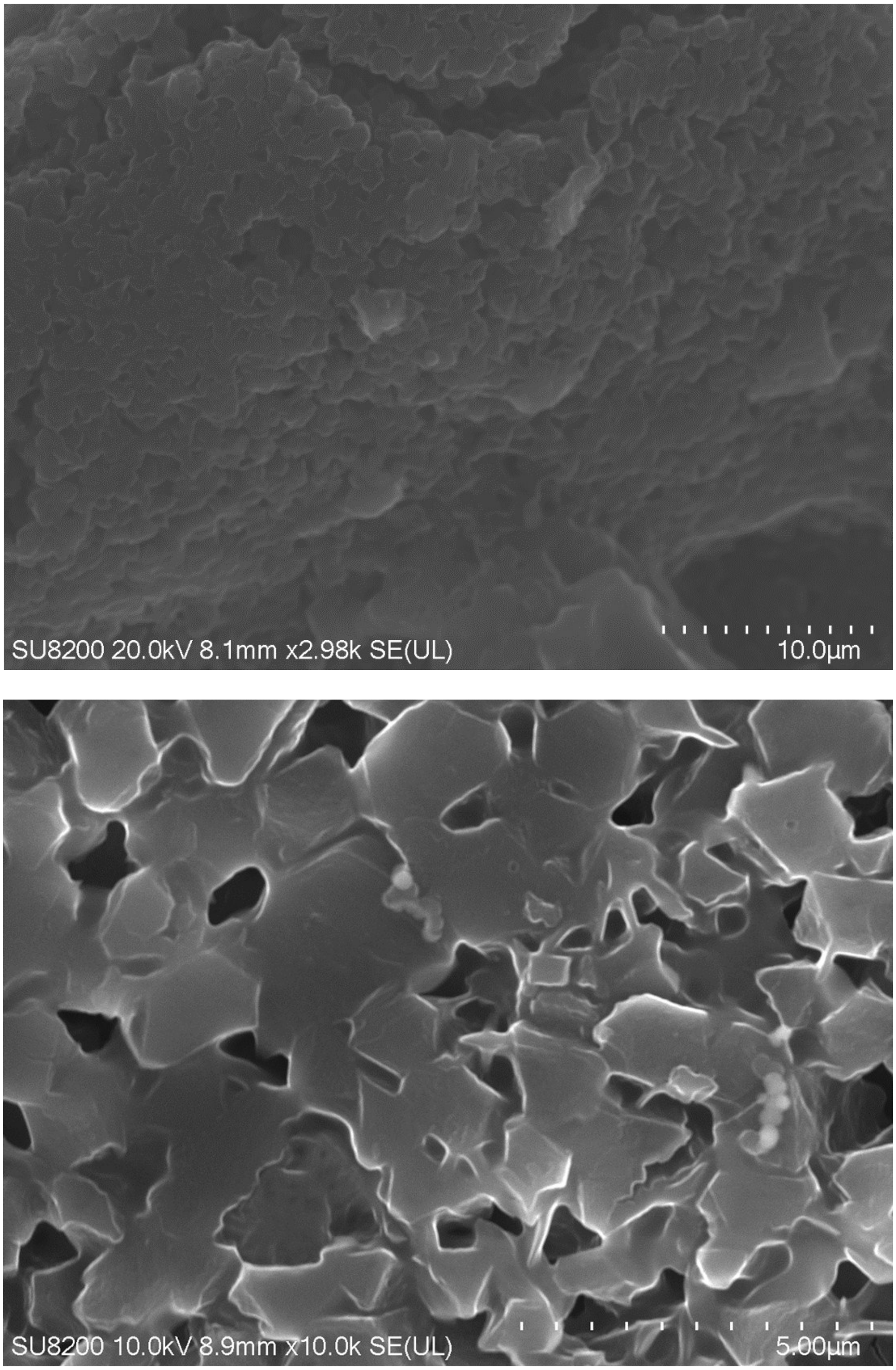

**Figure S3.** SEM images of the as synthesized $Li_2B_{12}H_{12}$

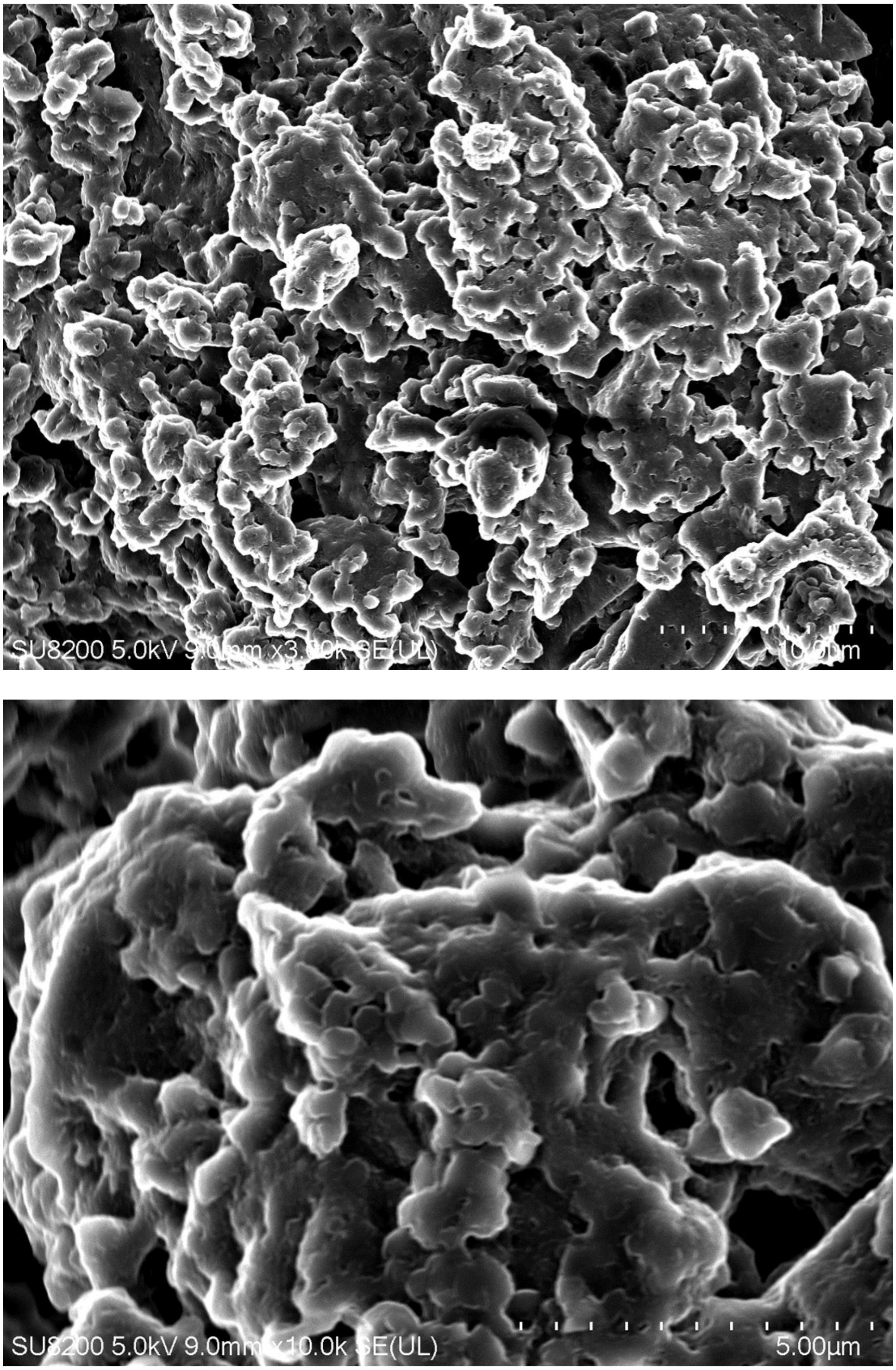

**Figure S4.** (top) SEM image of the milled $Li_2B_{12}H_{12}$, (bottom) zoomed in view of the milled $Li_2B_{12}H_{12}$.

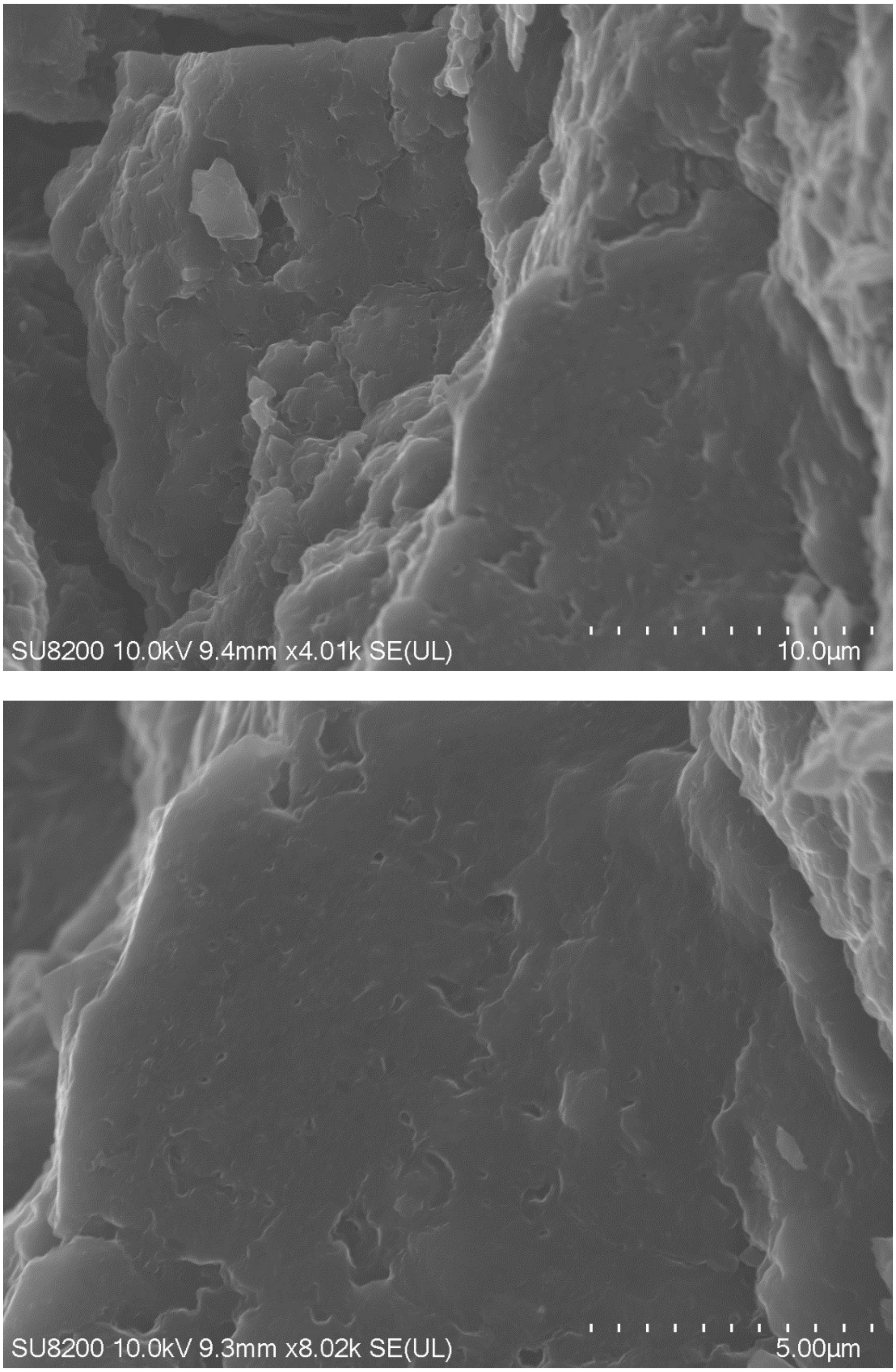

**Figure S5.** SEM images of the milled sample pellet at a broken interface.

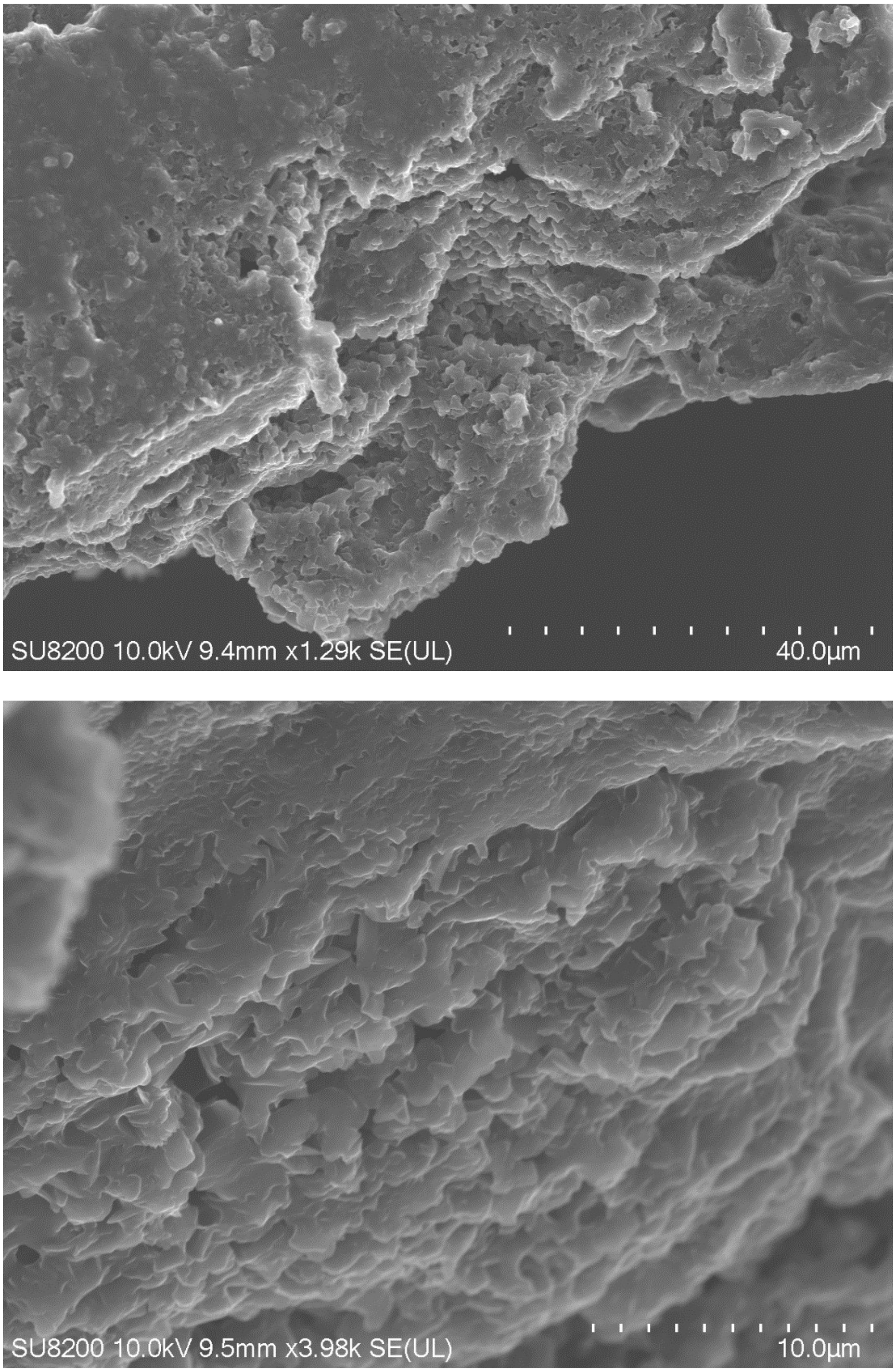

**Figure S6.** SEM images of the “as-synthesized” sample pellet at a broken interface.

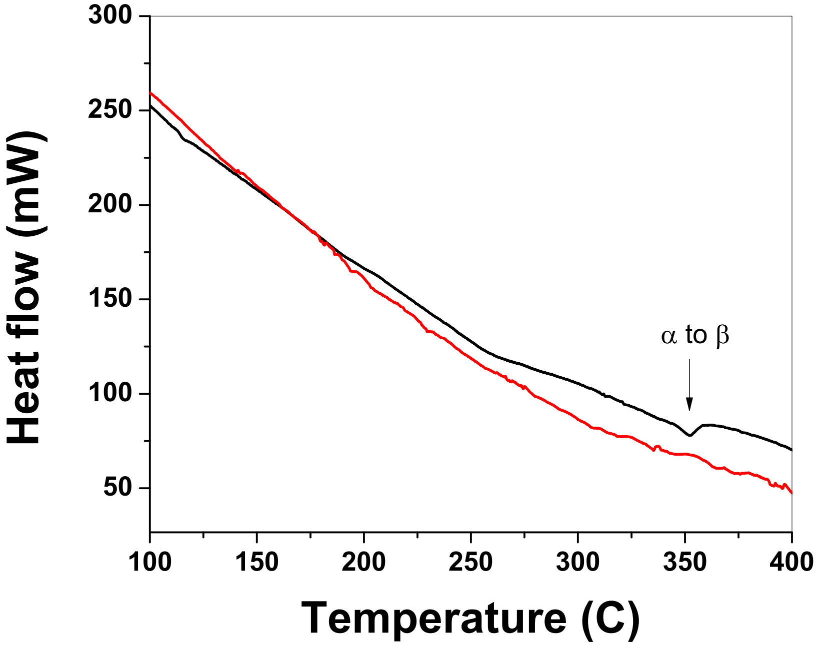

**Figure S7.** DSC of the as-synthesized $Li_2B_{12}H_{12}$ (black) and the milled $Li_2B_{12}H_{12}$ (red) samples.

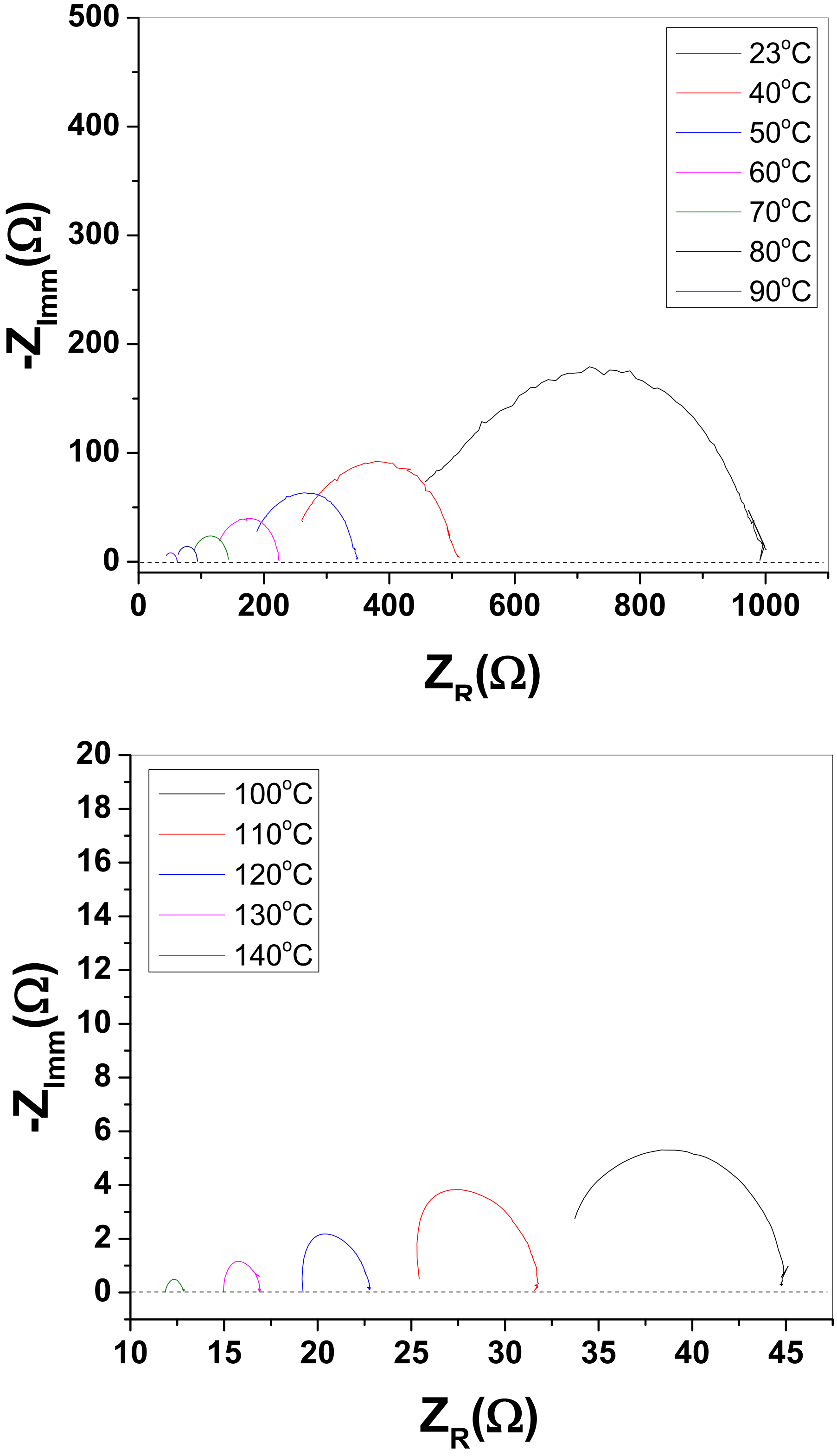

**Figure S8.** EIS for the Li/$Li_2B_{12}H_{12}$ (milled)/Li symmetrical cell, (top) 23-90 °C and (bottom) 100-140 °C.

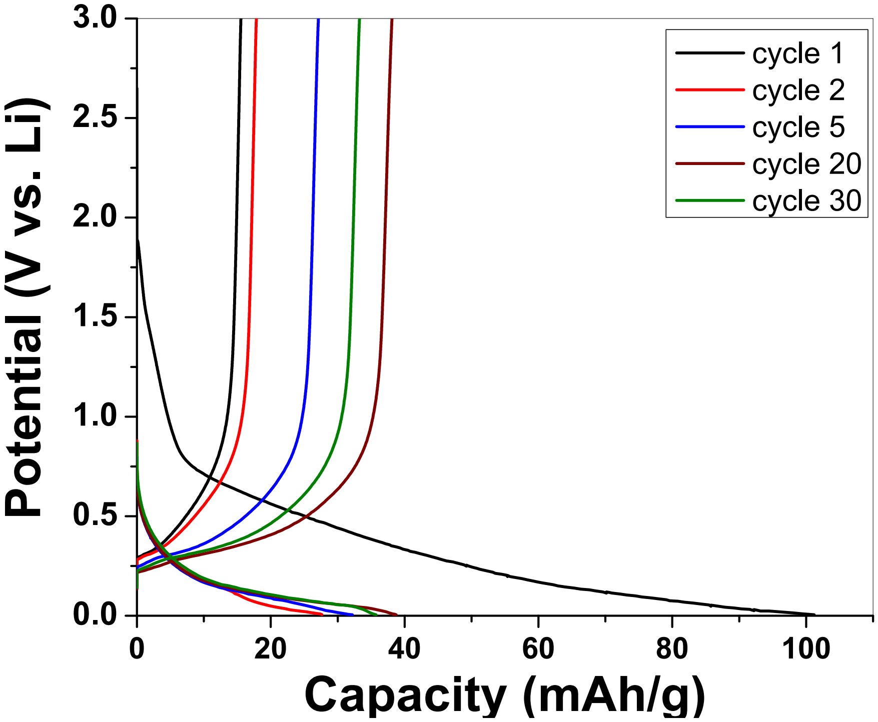

**Figure S9.** Charge-discharge curves for the Li/$Li_2B_{12}H_{12}$/graphite solid-state cell cycled at 30°C and a 0.1C discharge rate.

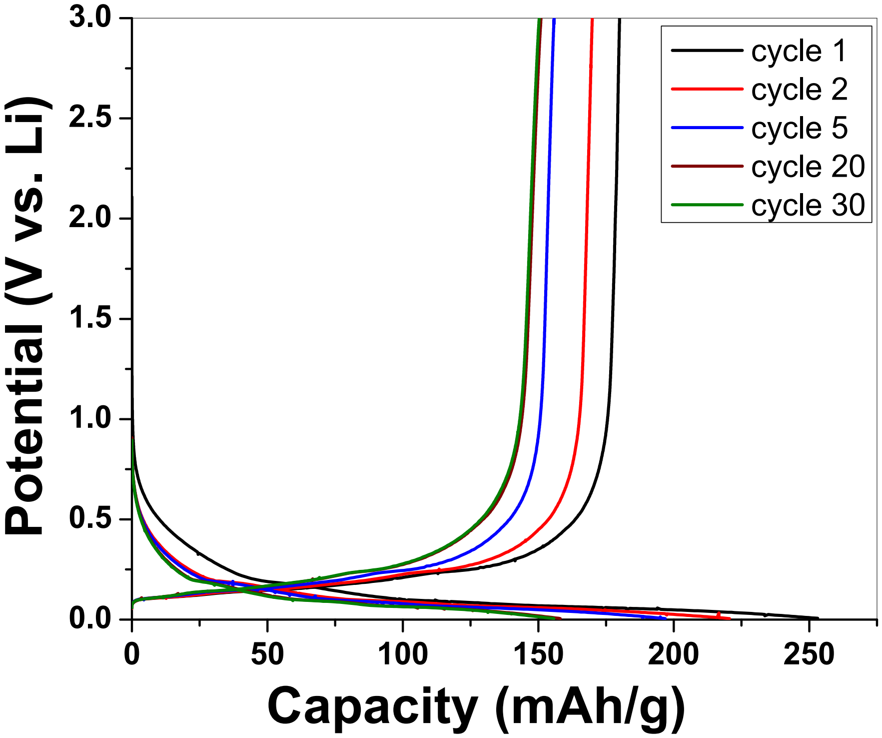

**Figure S10.** Charge-discharge curves for the Li/$Li_2B_{12}H_{12}$/graphite solid-state cell cycled at 60°C and a 0.1C discharge rate.

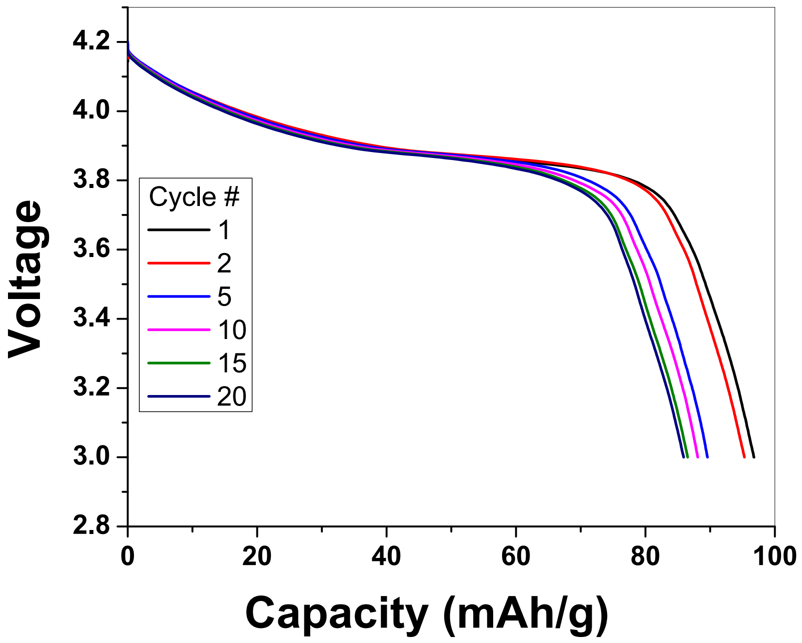

**Figure S11**. Cycling performance of a full cell using the liquid electrolyte $LiPF_6$ in the following cell set-up (Li/$LiPF_6$-EC-DMC/$LiCoO_2$-Acetylene black carbon (90:10 wt %)).

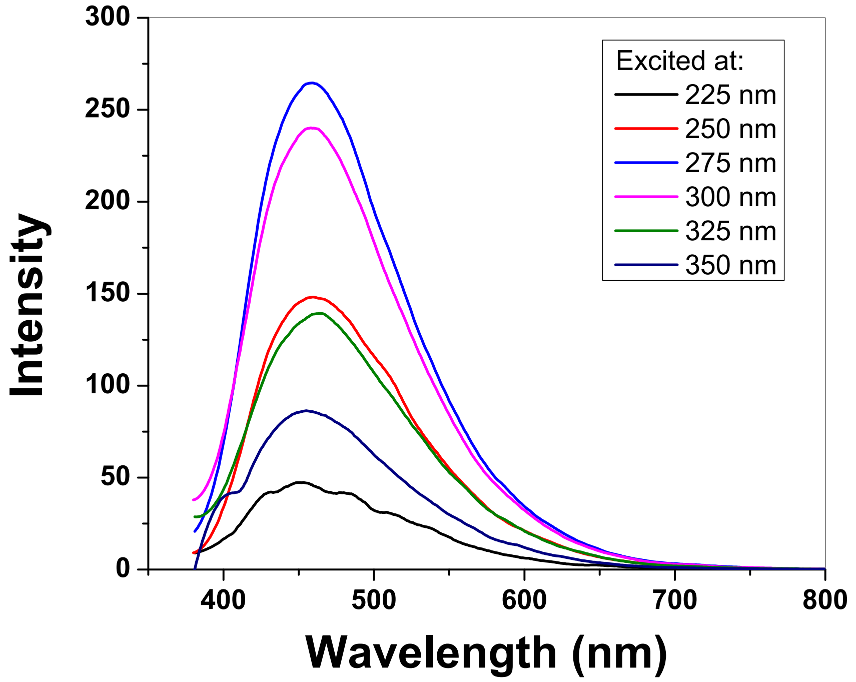

**Figure S12.** Emission spectrum of the aqueous $Li_2B_{12}H_{12}$ solution excited at the indicated wavelengths.

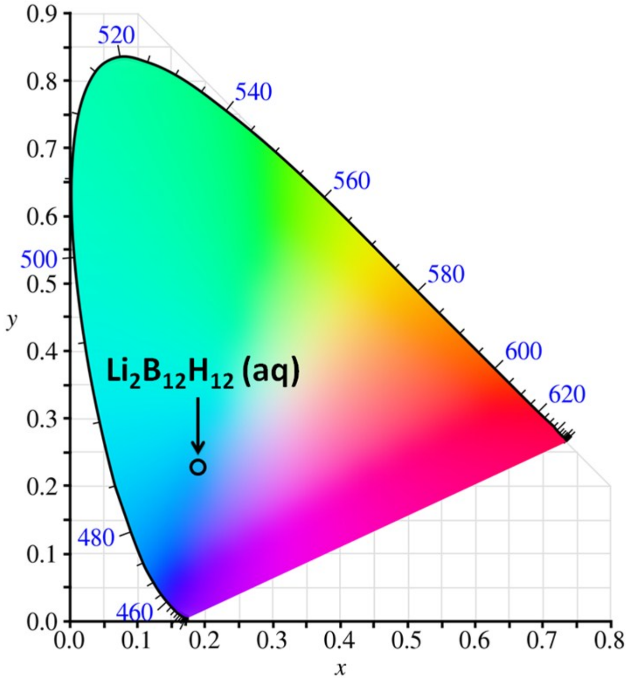

**Figure S13.** The CIE (Commission Internationale de l'éclairage) index points for an aqueous solution of $Li_2B_{12}H_{12}$ were calculated from the PL spectrum excited at 285 nm. The CIE coordinates (0.19, 0.23) are plotted on the CIE 1930 chromacity chart. The calculated color is in excellent agreement with the color observed in the Figure 4 inset.

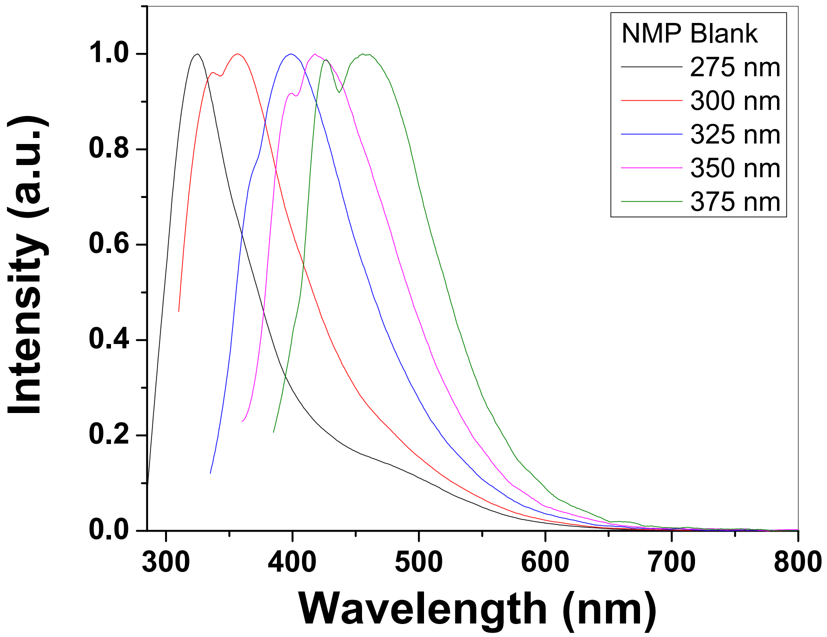

**Figure 14.** Emission spectrum of pure NMP at various excitation wavelengths.

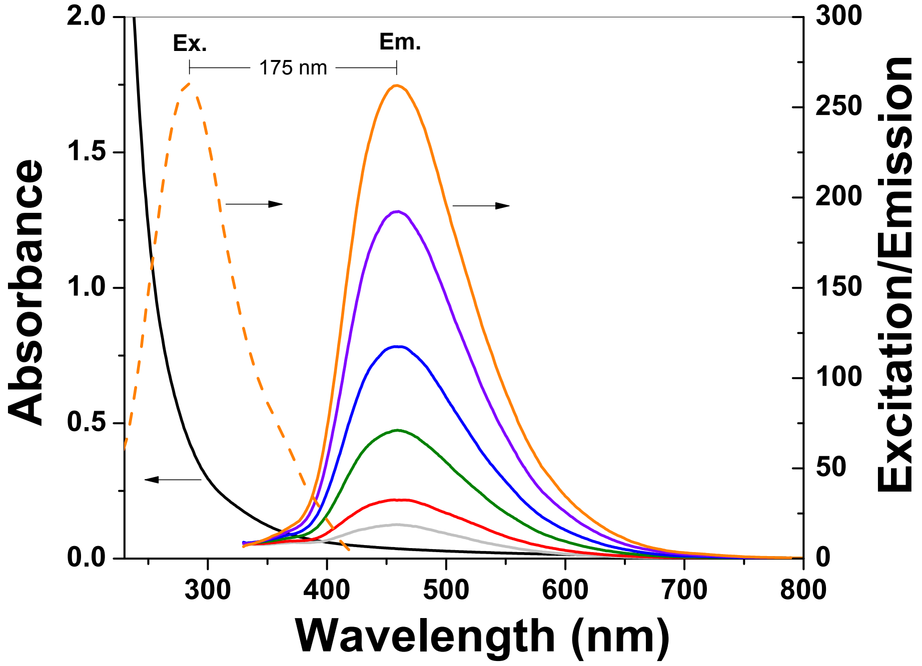

**Figure 15.** UV-vis (solid black), excitation (dash black), and emission (grey- 0.0076 mg/mL, red- 0.015 mg/mL, green- 0.038 mg/mL, blue- 0.074 mg/mL, purple- 0.143 mg/mL, and orange- 0.266 mg/mL) spectrum of $Li_2B_{12}H_{12}$ in water.

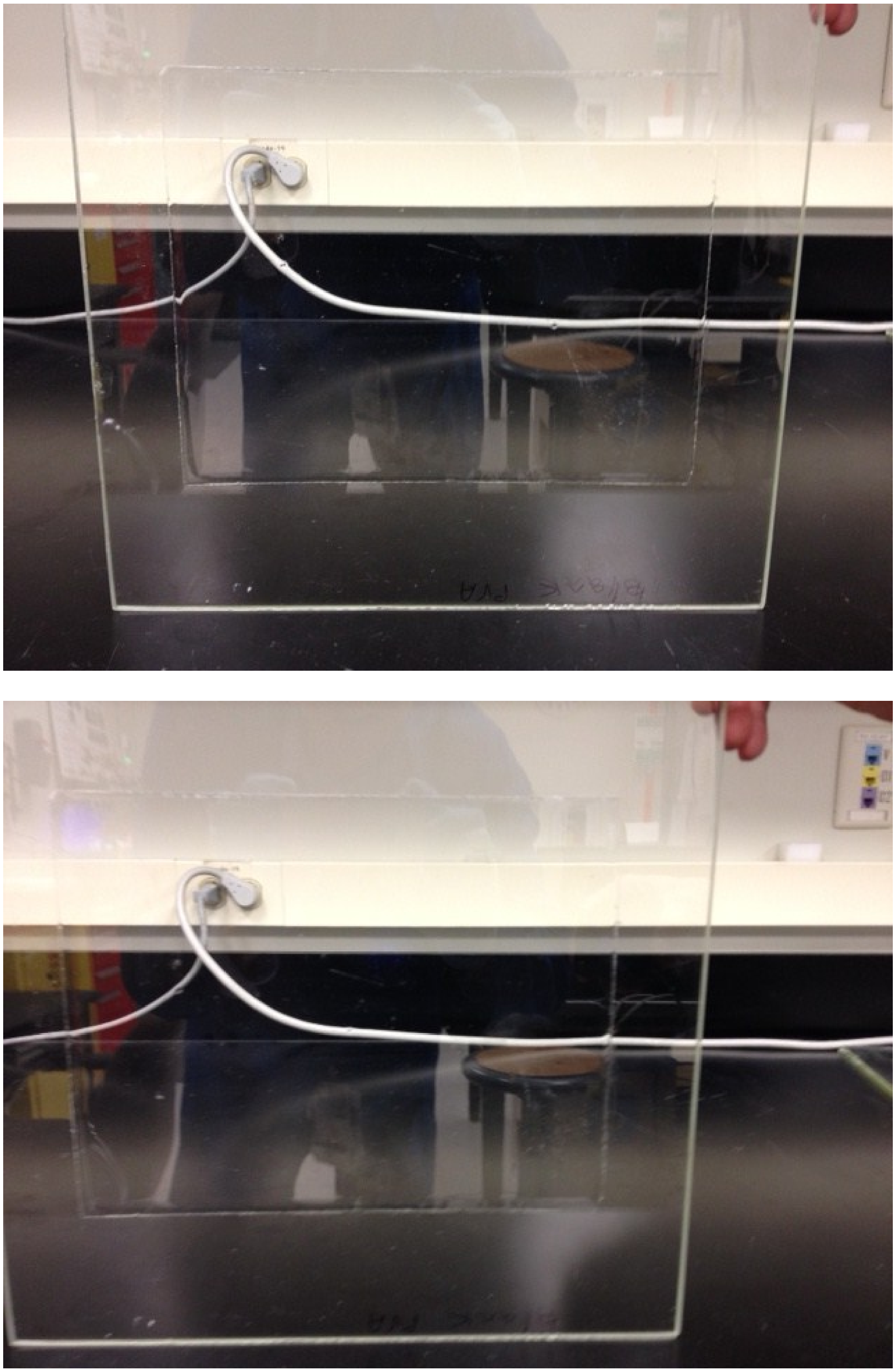

**Figure S16.** (top) PVA blank film without $Li_2B_{12}H_{12}$, (bottom) blank PVA without $Li_2B_{12}H_{12}$ exposed to the UV-LED projection source.

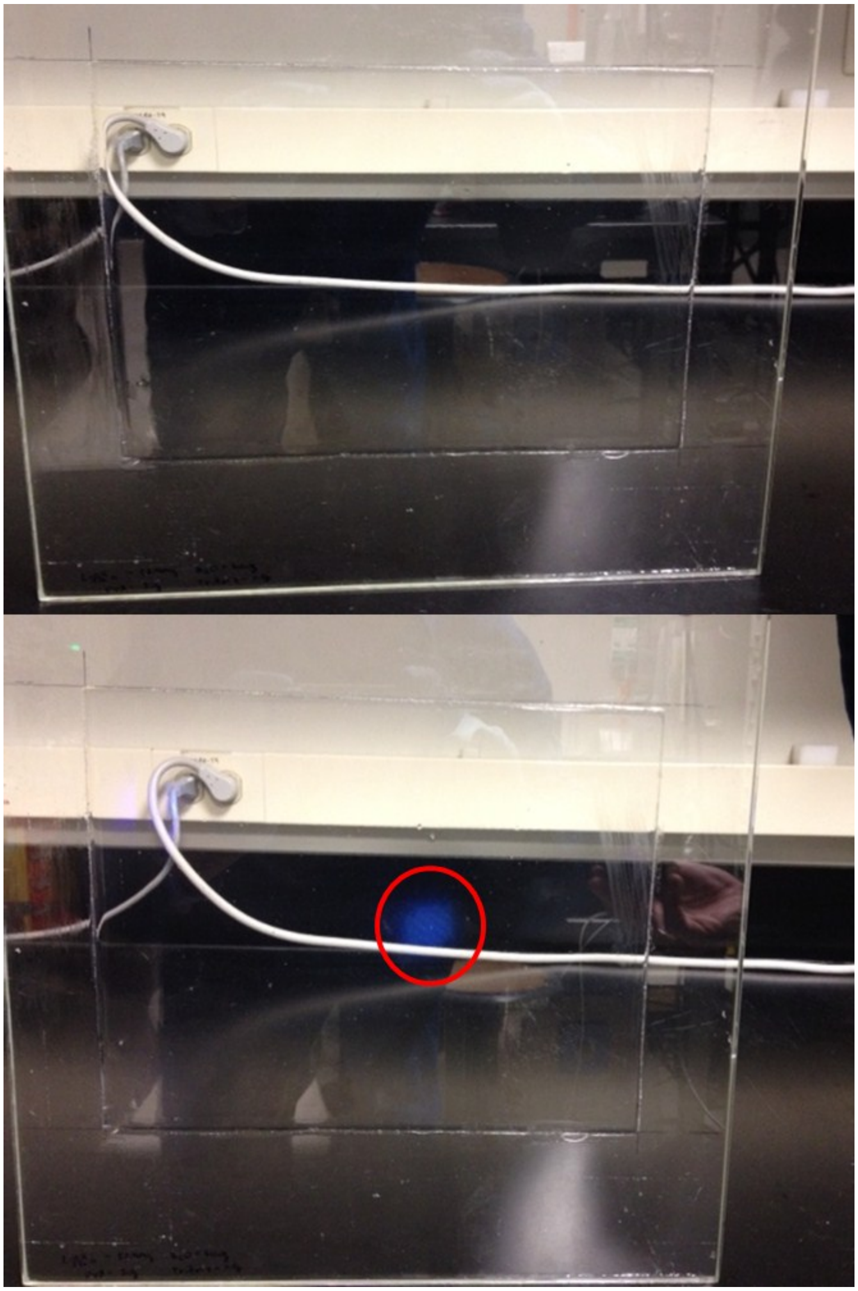

**Figure S17.** (top) PVA film with $Li_2B_{12}H_{12}$, (bottom) PVA with $Li_2B_{12}H_{12}$ exposed to the UV-LED projection source in normal room light. Red circle highlights the projected image.

**Figure S18.** (top) PVA blank film without $Li_2B_{12}H_{12}$ exposed to the UV-LED projection source in the dark (bottom) comparison of the blank PVA film without $Li_2B_{12}H_{12}$ with the $Li_2B_{12}H_{12}$ infused PVA film when exposed to the UV-LED projection source in the dark. The blank PVA film on the glass plate is located in front of the $Li_2B_{12}H_{12}$ infused PVA on glass plate. The project image is circled in green for the blank and red for the $Li_2B_{12}H_{12}$ and clearly shows down conversion of the UV source to visible light.

1. "Facile Solvent-Free Synthesis of Anhydrous Alkali MetalDodecaborate M2B12H12 (M = Li, Na, K)" *J. Phys. Chem. C*, **2014**, *118*, 6084-6089, Liqing He, Hai-Wen Li, Son-Jong Hwang, and Etsuo Akiba