An Easily Prepared Organic LED Using $[Ru(bpy)_3]^{2+}$

Jonathan Breitzer and Joel Hassenzahl

LED fabrication procedure modified from Frank G. Gao and Allen J. Bard, "Solid-State Organic Light-Emitting Diodes Based on Tris(2,2'-bipyridine)ruthenium(II) Complexes", *Journal of the American Chemical Society*, **122**(30), 7426-7427 (2000)

$[Ru(bpy)_3](BF_4)_2$ synthesis modified from John A. Broomhead and Charles G. Young, *Inorg. Syn*. **28**, 338-340 (1990).

Reactions

$2\ H_2O + NaH_2PO_2 + 12\ bpy + 4\ RuCl_3 \rightarrow 4[Ru(bpy)_3]Cl_2 + 3\ HCl + H_3PO_4 + NaCl$

$[Ru(bpy)_3]Cl_2 + 2\ NaBF_4 \rightarrow [Ru(bpy)_3](BF_4)_2 + 2\ NaCl$

List of materials

Chemicals

Ruthenium(III) chloride trihydrate Aldrich 20,622-9

Sodium tetrafluoroborate Aldrich 20,221-5

Gallium indium eutectic Aldrich 49,542-5 or Alfa Aesar 12478

Hypophosphorous acid, 50 wt % in water Aldrich 21,490-6

2,2'-Dipyridyl Aldrich D21,630-5

Sodium hydroxide

Acetonitrile

Unusual equipment

Tin oxide coated glass. This comes with the ICE Nanocrystalline Solar Cell Kit; the kit has ten pieces and this experiment only requires one. The suppliers are

Hartford Glass Co. Inc.
P. O. Box 613
Hartford City, IN 47348
765/348-1282
765/348-5435 (Fax)
hartglas@netusa1.net

Pilkington, Libbey Owens Ford
811 Madison Ave.
P. O. Box 799

Toledo, OH 43697-0799
419/247-4517

Voltmeter (with leads)

6-volt power supply, such as a lantern battery

Cotton swab

Preparation

These are done by staff prior to the laboratory experiment. This is enough material for about 24 syntheses.

"$RuCl_3$" from commercial $RuCl_3 \cdot 3H_2O$

Place the commercial $RuCl_3 \cdot 3H_2O$ (~3 g) in a mortar and pestle. Place this in an oven (120 to 130 °C) for 3 hours, allow it to cool, and grind it. Place the ground material back in the oven overnight prior to the laboratory experiment. There is most likely some water remaining, as anhydrous $RuCl_3$ is insoluble.

NaH_2PO_2 preparation from H_3PO_2

Hypophosphorous acid is monoprotic (two of the hydrogens are attached directly to phosphorus). It does not fume, but with a pKa of 1.1, it is stronger than phosphoric acid. Use caution when handling, and keep it away from oxidizers (do not store it in a cabinet where the usual mineral acids are kept!)

Measure 10 mL of 50 % H_3PO_2 into a beaker with a stirbar, add 6 mL of water, and begin stirring. *Slowly* add pellets of NaOH until the pH is about 6-8 (wait until the previous pellet dissolves before adding the next). This will require about 3.9 g of NaOH. The final solution is about 6 M in NaH_2PO_2.

Synthesis

Dissolve 0.083 g (0.40 mmol) "$RuCl_3$" in 8 mL of water in a 30-mL beaker equipped with a Teflon-coated stirbar. Add 0.188 g (1.204 mmol) 2,2'-dipyridyl and, using a syringe or Mohr pipet, 0.44 mL of NaH_2PO_2. The liquid will be deep greyish-green. Mark the beaker to indicate the level of liquid, place a watch glass on top of the beaker, and heat so it boils for 30 min. Add water as necessary to bring the level to the mark. The liquid will now be deep orange.

Allow the solution to cool to room temperature. Dissolve 0.333 g of $NaBF_4$ in 1.5 mL of water and add the resulting solution to the orange solution. Solid should form. Heat the mixture until the solid dissolves, adding water as needed. Cool in ice; crystals should form. Collect these by filtration and wash with ethanol. Draw air through the orange solid to dry.

OLED fabrication

Dissolve about 0.01 g of the $[Ru(bpy)_3](BF_4)_2$ in 1 mL of acetonitrile. Determine which side of a piece of ITO coated glass is conductive and make sure it is face up. With a pipet, place about 3 drops of the orange solution on the ITO coated glass and spread it with the pipet tip so that it covers about half of the area. The solution will dry within a minute or so. Place it in the oven (120 °C) for about 10 min. Have the gallium/indium eutectic ready, take the coated glass out of the oven, and spread a few mm^2 of the eutectic onto the dried $[Ru(bpy)_3](BF_4)_2$ film with a cotton swab; this is most easily done while the coated glass is still warm.

In a fairly dark spot, place the assembly on a white sheet of paper, coated side up. Touch the positive lead of a 6-volt power supply directly to the ITO coating (not on the $[Ru(bpy)_3](BF_4)_2$ film). Gently touch the negative lead to the gallium/indium eutectic. The light emission occurs downward from the eutectic, the reflection of which can be observed through the paper. Alternatively, hold the assembly up, back side facing you, and have a partner touch the leads. Observe what part glows.

N.B. An alternative to spreading the eutectic onto the $[Ru(bpy)_3](BF_4)_2$ film is to coat the negative lead with the Ga/In eutectic and gently touch it onto the film. Move it over the surface as needed to maximize brightness, but be sure not to let it touch the tin oxide coated glass itself.