Supplemental Information:

Electrochemical Synthesis of Flat-$[\text{Ga}_{1.3-x}\text{In}_x(\mu_3-\text{OH})_6(\mu-\text{OH})_{18}(\text{H}_2\text{O})_{24}(\text{NO}_3)_{15}]$ Clusters as Aqueous Precursors for Solution-Processed Semiconductors


Experimental Methods:

General: All chemicals were used as received, with no further purification: Zn (Alfa Aesar), Ga(NO$_3$)$_3$$\times$H$_2$O (Alfa Aesar), In(NO$_3$)$_3$$\times$H$_2$O (Johnson Matthey Materials Technology), Aluminum (Kurt J. Lesker, 99% Al), DMSO-d$_6$ (Cambridge Isotope Laboratories Inc). The degree of hydration of metal salts was determined by thermogravimetric analysis (TGA). Raman spectroscopic measurements were taken using a WITec alpha 300S. Raman spectra were averaged over 100 acquisitions using a 532 nm excitation wavelength laser that provided 40 mW of power. Samples for transmission electron microscope (TEM) analysis were prepared by focused ion beam milling of device structures utilizing an FEI Helios DualBeam system with a Ga-ion beam. Low-resolution TEM images were acquired using an FEI 80-300 Titan TEM and a 200 kV accelerating voltage. Energy dispersive X-ray spectroscopy (EDX) was taken from the film to confirm mixed-metal content. $^1$H-NMR spectra were obtained on a Bruker 600 MHz spectrometer using Topspin Software. Data was processed in MestReNova. The experiments were run at 298 K in 5 mm tubes (2 mM in DMSO-d$_6$). Electrochemistry was carried out using an Autolab Nova potentiostat. All pH measurements were carried out in-situ using an IQ Instruments GLP series pH ISFET probe.

Electrochemical Synthesis: A three-electrode configuration (Figure S1) was used for the electrochemical cluster synthesis. The working electrode was composed of a Pt wire with a diameter of 0.60 mm and a length of 28.0 cm giving it an area of 5.28 cm$^2$. The counter electrode was composed of a Pt wire with a diameter of 0.60 mm and a length of 7.0 cm giving it an area of 1.32 cm$^2$. Typical current densities ranged from 7 to 15 mA cm$^{-2}$. A Ag/AgCl reference electrode was used for all syntheses.

The working and counter electrodes were placed in the same beaker with the counter electrode enclosed in a medium fritted glass tube (10-20 μm) to confine species generated at the counter electrode from the rest of the solution. The cathodic current passed at the working electrode was assumed to be largely associated with nitrate reduction as discussed in the text. Numerous reduction reactions are possible, given the range of oxidation states accessible to N. The relevant reduction potentials are 0.8-1 V positive of the standard hydrogen electrode. Examples include:
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\begin{align*}
\text{NO}_3^- + 2H^+ + e^- & \rightarrow \frac{1}{2} \text{N}_2\text{O}_4(g) + H_2\text{O} \quad E^o = 0.80 \text{ V vs. NHE} \\
\text{NO}_3^- + 3H^+ + 2e^- & \rightarrow \text{HNO}_2 + H_2\text{O} \quad E^o = 0.94 \text{ V vs. NHE} \\
\text{NO}_3^- + 4H^+ + 3e^- & \rightarrow \text{NO(g)} + 2H_2\text{O} \quad E^o = 0.96 \text{ V vs. NHE} \\
\text{NO}_3^- + 10H^+ + 8e^- & \rightarrow \text{NH}_4^+(g) + 3H_2\text{O} \quad E^o = 0.88 \text{ V vs. NHE}
\end{align*}
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**Figure S1.** Sample image of the electrochemical cell used for the synthesis of clusters. a) Ag/AgCl reference electrode, b) Pt working electrode, c) Pt counter electrode, d) medium-fritted glass tube, e) pH probe. The reaction was performed in an open cell and any gaseous products that may have been formed were not collected.

*Electrochemical Synthesis of flat-Ga_{13}:* A 250 mM Ga cluster solution was prepared by dissolving 2.05 g Ga(NO$_3$)$_3$•$4H_2$O in 25 mL of 18.3 MΩ H$_2$O, and then applying a potential of -1.0 V vs. Ag/AgCl with the solution constantly stirring to remove products from the surface of the working electrode. A small amount of Ga was observed on the working electrode due to the potential being more negative than the Ga standard reduction potential. Electrolysis was terminated after ~2 hr after passing ~420 C of charge. At this point the solution could be used directly for film deposition. For analysis of the cluster solids, the reaction mixture was dried on a transparent glass over the course of 3 days in a watch glass. Scrapings of the dried reaction mixture were rinsed with isopropyl alcohol (IPA) to remove unreacted metal salts.

*Electrochemical Synthesis of flat-Ga$_{13-x}$In$_x$ (x = 5, 4):* A 340 mM (total metal content) 6:7 In:Ga solution was prepared by dissolving appropriate amounts of Ga(NO$_3$)$_3$ and In(NO$_3$)$_3$ in 25 mL of 18.3 MΩ H$_2$O. The working electrode potential was set to -0.49 V vs. Ag/AgCl. The potential was less negative than in the case of the pure Ga cluster synthesis as the potential was practically limited by the less-negative reduction potential of In (-0.58 vs Ag/AgCl) compared to Ga (-0.77
vs Ag/AgCl). The electrolysis was terminated after ~2 hr after passing ~390 C of charge. Aliquots of solution (3-4 mL) were placed in an evaporating dish (for analysis) while the remainder of the solution was used for thin-film deposition and processing. Drying and washing of the solid was carried out in the same manner as with Ga$_{13}$ clusters. Ga$_{13-x}$In$_x$ clusters were also synthesized using Zn metal as reductant, as reported previously,$^1$ and were used as standards for comparison with electrochemically produced clusters.

![Figure S2](image)

**Figure S2.** pH as a function of total cathodic charge passed through a 50 ml 0.34 M solution of 7:6 Ga:In nitrate in water. The starting salt solution has a pH of 1.83 and begins to buffer around a pH of 2 as cluster formation in the solution occurs.

*Nuclear Magnetic Resonance:* $^1$H-NMR was conducted on the isolated products of both electrochemical syntheses (Figure S3). The spectra obtained from these experiments were compared to known samples (Figure S4). Similar to Ga$_{13}$, NMR data indicates that the mixed clusters are dynamic in solution; however, one day after dissolution distinct “fingerprint” regions emerge for each species. Heterometallic clusters can most easily be differentiated by comparing the $^1$H signals between 6.5 ppm and 6.8 ppm (Figure S4). Proton signals appear farther downfield with increased In:Ga ratios. The this trend provides a simple tool for the determination of metal ratios in In:Ga heterometallic clusters.
Figure S3. $^1$H NMR spectrum of raw, electrochemically-synthesized Ga$_{13}$. Note the three large peaks at values just greater than 7 ppm correspond to ammonium ion being present in the sample. The fingerprint region is between 6.5 and 6.9 ppm.

Figure S4. $^1$H NMR fingerprint region of various M$_{13}$ clusters synthesized by the Zn-reduction method, illustrating the definitive characteristics of each substitution (from Ref. S2). The composition was determined for each sample from the single-crystal structure also obtained. This data is included here to demonstrate that the fingerprint region of the $^1$H NMR spectra are indeed indicative of the Ga-In ratio in the cluster.
**Film and Electrical Characterization:** Thin film transistors (TFTs) were fabricated by delivering the unpurified electrochemical solutions through a 0.45 µm PTFE filter onto 100 nm thermally grown SiO$_2$ on p$^+$-Si (resistivity $\sim 0.007$ Ω cm) with a Cr/Au ohmic back contact (Hewlett Packard). Substrates were subjected to an oxygen plasma etch cleaning (150 W RF field, 120 s, 300 mTorr, 74.6 sccm O$_2$) in a March CS-1701 plasma etcher prior to solution deposition. Films were spin-cast at 3000 RPM for 30 s, and immediately transferred to a 300 °C hotplate for 1 min. The thin films were then annealed under air in a furnace at 550 °C for 2 hr. The TFT devices consist of the following structures: channel dimension= 1000 µm x 500 µm, channel width (W)= 1000 µm, and channel length (L)= 150 µm. Current-voltage behavior was measured with two Keithley 2400 SMUs joined via Labview using a 1 V step size and 200 ms dwell time. Device performance was assessed through analysis of channel average mobility ($\mu_{\text{ave}}$), turn-on voltage ($V_{\text{on}}$), and drain current on-to-off ratio ($I_{\text{on}}/I_{\text{off}}$) measurements.

![Energy dispersive x-ray spectroscopy measurements](image)

**Figure S5.** Energy dispersive x-ray spectroscopy measurements of the film presented in Figure 4a confirming the presence of Ga, In and O in the final material.

**References:**
