



## Supporting Online Material for

### **Organic Glasses with Exceptional Thermodynamic and Kinetic Stability**

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## **Supplemental Material**

### **Materials**

1,3-bis-(1-naphthyl)-5-(2-naphthyl)benzene (also referred to as  $\alpha\alpha\beta$ -tris-naphthylbenzene, tris(naphthylbenzene), or TNB), along with its partially deuterium substituted analog, were synthesized using procedures analogous to those described previously (*1*). Indomethacin (IMC) was purchased commercially (Aldrich), and used without further purification. IMC is hygroscopic, and care was taken to maintain sample dryness. The structures of d-TNB and IMC are shown in Fig. S1.

Note that the literature prior to 1996 contains several papers characterizing a substance identified as 1,3,5-tri- $\alpha$ -naphthylbenzene. Whitaker and McMahon established that these earlier studies were almost certainly performed on  $\alpha\alpha\beta$ -TNB (*1*).

### **Methods**

#### **Vapor Deposition**

Physical vapor deposition was used to create glasses of IMC, and of h-TNB and d-TNB (*2*). Samples were prepared by deposition onto a silicon wafer or DSC pan at a controlled temperature. The substrate temperature was held constant during deposition using a Lakeshore 340 controller with platinum RTD sensors. Deposition rates varied from 0.1 to 5 nm/s. Deposition occurred from crystalline material in a heated crucible located 3 – 30 cm from the substrates. The background pressure in the chamber was  $< 10^{-7}$  torr.

The purities of vapor deposited IMC and TNB films were assessed by DSC for samples directly deposited into DSC pans. For IMC films, two distinct melting point temperatures ( $424.5 \pm 1$  K and  $431.9 \pm 1$  K) were observed corresponding to the  $\alpha$  and  $\gamma$  polymorphs, respectively. Analysis of TNB films resulted in a melting point temperature of  $468.6 \pm 1$  K. Our measured melting points are consistent with previously reported values (*1, 3*). Comparison of vapor deposited films to samples that were directly weighed into DSC pans resulted in melting point and glass transition temperatures that are independent of preparation method (within 1.5 K).

Vapor-deposited TNB and IMC glasses were at least 99% amorphous, as judged by their transparent visual appearance. Samples left at room temperature for months developed white crystalline spots which grew slowly with time. Other indications of the amorphous nature of the vapor-deposited films include: 1) the density which decreases upon annealing above  $T_g$  (see Fig. 2); 2) the diffusion that occurs after the long induction time shown in Fig. 4B; and 3) the large enthalpy relaxation signal near the conventional  $T_g$ , shown in Fig. 1A. Preliminary wide angle x-ray scattering of vapor-deposited IMC films show no indications of the sharp lines indicative of crystalline IMC.

For neutron reflectivity measurements, multilayer thin films of h-TNB and d-TNB were deposited onto 76 mm diameter, 3 mm thick silicon wafers (Wafer World and Virginia Semiconductor). The silicon was used as received, with the native oxide coating. The deposition rate was typically 0.1 nm/s. Prior to deposition, the substrate was spin-coated with a 10 nm polystyrene layer (Polymer Source,  $\sim 10^6$  g/mol), which acted to minimize crystallization and dewetting of the TNB film during annealing. The polystyrene was a mixture of protio and perdeuterio chains, in order to approximately match the neutron scattering length density of the first h-TNB layer. Following deposition, the samples were slowly cooled and held at room temperature for 1 to 5 days before neutron reflectivity measurements.

### **Heat Capacity Measurements**

Heat capacity measurements were done on a TA Instruments Q1000 differential scanning calorimeter. Each curve was obtained by heating  $\sim 3$  mg of material in a sealed aluminum pan at 10 K/min. After heating above the melting point, the sample was cooled at 40 K/min and rescanned, giving results for the liquid-cooled material, which we also describe as the “ordinary glass”. The DSC instrument was calibrated using an indium standard.

### **Density Measurements**

The data in Fig. 2 were determined from x-ray reflectivity measurements made on as-prepared films of TNB and on the same films after thermal equilibration above  $T_g$ . All x-ray data was taken at room temperature. Fits to this data provided direct measurements of film thickness. Since the area of the film was the same before and after annealing, the ratio of the densities equals the inverse of the ratio of the thicknesses, and this is reported in Fig. 2.

The solid line in Fig. 2 indicates the predicted value of  $\rho_{VD}/\rho_o$  in the hypothetical situation where vapor deposition produces an equilibrium liquid at the deposition temperature. Magill and Plazek (4) report the liquid density at higher temperatures and this was extrapolated to obtain  $\rho_{VD}$  for this purpose. In order to plot the line in Fig. 2, we also need an absolute value for the density of the liquid-cooled material ( $\rho_o$ ). We assume that our samples have the equilibrium liquid density after extensive annealing above  $T_g$ . Thus we use the equilibrium liquid density at 346 K and the glassy thermal expansion coefficient reported by Magill and Plazek (4) to calculate  $\rho_o$ . In this last step, we assume that samples cooled quickly on a silicon substrate have the same density as that obtained by quickly cooling a bulk liquid. The former process produces a slightly anisotropic glass (due to the thermal expansion mismatch between Si and TNB) but this should have a small effect on the density.

Fictive temperatures can be assigned to the as-deposited films on the basis of their densities. The values can be found using Fig. 2, by horizontally shifting the points to overlap with the line shown.

## **Neutron Reflectivity Measurements**

Fig. 3 shows neutron reflectivity data for as-deposited samples prepared by vapor deposition at a range of substrate temperatures. This data was measured at room temperature. The amplitude of the peaks is governed by the sharpness of the interfaces, while the position in  $q$ -space is determined by the length scale being probed:  $q = 2\pi/\lambda$ . The fundamental wavelength is equal to the thickness of the repeating element, in this case a single h-TNB/d-TNB bilayer of typically 60 nm, while the higher harmonics probe the structural order on progressively shorter length scales. The first and third harmonics are shifted to slightly higher  $q$  values than would be anticipated based upon the equation above, due to the presence of the critical edge of the silicon substrate at  $q \approx 0.01 \text{ \AA}^{-1}$  (2).

Neutron reflectivity experiments were conducted at the NIST Center for Neutron Research at the National Institute of Standards and Technology (NCNR-NIST). The NG7 horizontal reflectometer utilized a  $4.76 \text{ \AA}$  collimated neutron beam, with a wavelength divergence of  $0.18 \text{ \AA}$ . The angular divergence of the beam was varied through the reflectivity scan and this provided a relative  $q$  resolution  $\Delta q/q = 0.04$  ( $q = 4\pi \sin \theta/\lambda$ , where  $\theta$  is the incident and final angle with respect to the surface of the film, and where here  $\lambda$  is the neutron wavelength). For Fig. 4, reflectivity measurements were performed during annealing by heating the sample in an in-line oven. The temperature was held constant to within  $\pm 0.1 \text{ K}$  during the annealing process, which ranged up to 30 hours. Scans were made over a  $q$  range from  $0.01 \text{ \AA}^{-1}$  to a maximum of  $0.13 \text{ \AA}^{-1}$ , with a typical duration of 30 minutes per scan. An analysis software package called Reffit, provided by NIST, was used to analyze the neutron reflectivity data.

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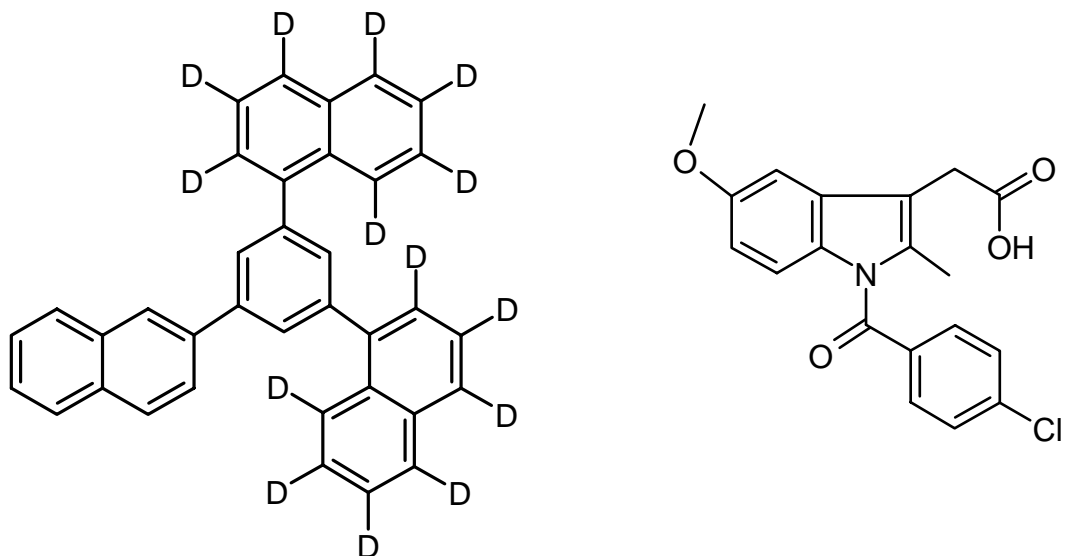


Fig. S1. Schematic drawing of d-TNB (left,  $C_{36}H_{10}D_{14}$ ) and indomethacin (right,  $C_{19}H_{16}ClNO_4$ ).

### References

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