Amorphous-to-crystalline transition and photoluminescence switching in guest-absorbing metal-organic network thin films

Amr Ghazy,[a] Muhammad Safdar,[a] Mika Lastusaari[b] and Maarit Karppinen*[a]

[a] Department of Chemistry and Materials Science, Aalto University, FI-00076 Espoo, Finland
[b] Department of Chemistry, University of Turku, FI-20014 Turku, Finland
Email: maarit.karppinen@aalto.fi

Experimental details:

ALD/MLD Process development: In our neodymium terephthalate (Nd-TP) ALD/MLD process, we employed in-house synthesized $Nd(thd)_3$ complex (thd = 2,2,6,6-tetramethyl-3,5-heptanedione) as a metal precursor, and terephthalic acid (1,4-benzenedicarboxylic acid; Tokyo Chemical Industry Co., Ltd.) as an organic precursor. Film depositions were carried out in a commercial flow-type hot-wall ALD reactor (F-120 by ASM Microchemistry Ltd.). The reactor pressure was maintained between 2-4 mbar and nitrogen (>99.999%; Schmidlin UHPN 3000 N2 generator) was used both as the purging and carrier gas. The samples were deposited on Si(100) substrates (25 × 25 mm^2). Metal and organic precursors were kept as solids in open glass crucibles inside the reactor at 150 °C and 185 °C, respectively. The pulse/purge length for the inorganic precursor was 4 s/4 s, while for the organic precursor 7.5 s/25 s, respectively.

Humidity and heat treatments were performed for thin-film samples, to study the water absorption/desorption characteristics. In the humidity treatment, thin-film samples were stored in a glass box with concentrated sodium chloride salt solution that gives 75% relative humidity (RH). The relative humidity of the laboratory air was approximately 30%. For the thermal treatment, the sample was heated in a muffle furnace (Nabertherm LT 9/11) in air at 150 °C overnight.

Characterization: The crystallinity of the films was studied using grazing incidence X-ray diffraction (GIXRD; X'Pert Pro MPD, PANalytical; Cu K_α) measurements, while the thickness of the films was determined using X-ray reflectivity (XRR) using the same equipment. The step size was 0.02 degrees in GIXRD, while the time per step was set at 16.5 seconds and 3.5 seconds in GIXRD and XRR, respectively. Density of the films was calculated using the critical angle θ_c, obtained from the XRR patterns, as follows: $\rho_e = (\theta_c^2 \pi)/(\lambda^2 r_e)$, where ρ_e is the mean electron density, λ is the X-ray wavelength and r_e is the classical electron radius. By assuming the elemental composition is that of pure Nd-TP, that is, $Nd_2C_{24}H_{12}O_{12}$, the mass density can be estimated from $\rho_m = (\rho_e A)/(N_A Z)$, where A is the average molar mass, N_A is Avogadro constant and Z is the average atomic number. PANalytical X'Pert Reflectivity software was used for extracting film thicknesses and fitting surface roughness data using the determined density and thickness values.

Chemical composition and bonding were studied by Fourier transform infrared (FTIR) spectroscopy. The measurements were carried out in transmission mode with a Bruker Alpha II FTIR spectrometer in the range of 500-4000 cm^{-1}.

Photoluminescence luminescence measurements were carried with an Avantes Avaspec HS-TEC CCD spectrometer at room temperature using a data collection time of 30 s with 2 averages. The excitation source was a Lotis TII LS-2134UTF Nd:YAG laser operated at 266 nm. A Newport 10LF10-266 line pass filter was used for the excitation and a Standa KS-11 high pass filter (cutoff at 650 nm) was used to filter the excitation from the detector.

FTIR results

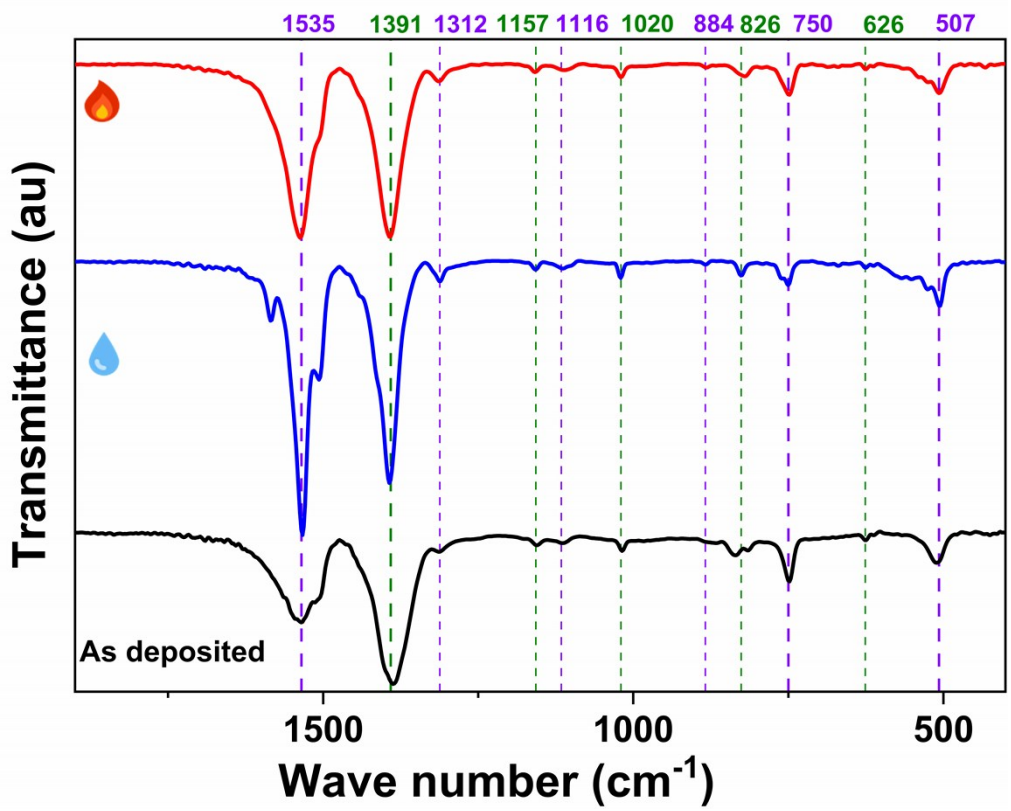

Figure 1 FTIR peaks for the as deposited sample (back), humidity-treated sample (blue) and heat-treated sample (red) with labeled peaks.

FTIR results confirmed the absence of the free carboxylic acid groups as there is no peaks around 1700 cm^{-1}. The peaks around 1535 cm^{-1} and 1397 cm^{-1} confirm the bonded carboxylate peaks of the terephthalic acid as they are attributed to the asymmetric and symmetric stretching of the carboxylate group, respectively. The separation between these bands remained at ca. 150 cm^{-1}, confirming the bridging type mode of the carboxylate groups. The peaks at 507 cm^{-1}, 626 cm^{-1} and 750 cm^{-1} are attributed to the carboxylate group rocking, bending and in-plane deformation, respectively. The peaks around 826 cm-1 and 884 cm-1 are attributed to the CH bond out of plane deformation, while the peaks at 1020 cm^{-1}, 1116 cm^{-1} and1157 cm^{-1} are attributed to the CH bond in-plane deformation. While the 1312 cm^{-1} peak represents the benzene ring stretching.[1,2]

Table 1 FTIR peak assignments.

Wave no. / cm^{-1}	Bond	Assignment
507	COO^-	Rocking
626		Bending
750		In-plane deformation
826	CH	Out of plane deformation
884		
1020		In-plane deformation
1116		
1157		
1312	Ar. Ring	Stretching
1397	COO^-	Symmetric stretching
1535		Asymmetric stretching

1 C. A. Téllez S., E. Hollauer, M. A. Mondragon and V. M. Castaño, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, 2001, **57**, 993–1007.

2 H. T. Varghese, C. Y. Panicker, D. Philip, K. Sreevalsan and V. Anithakumary, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, 2007, **68**, 817–822.