

Supplementary information

Origin of Anisotropic Molecular Packing in Vapor-Deposited Alq3 Glasses

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Polarizability tensor calculations

Experimentally we observe nearly zero birefringence in vapor-deposited glasses of Alq3 at all studied substrate temperatures. This is in stark contrast to vapor-deposited glasses of other small molecule organic semiconductors, which depending on the substrate temperature during deposition, can exhibit both significant positive and negative birefringence. To understand this experimental observation, we compute the anisotropic polarizability tensor of Alq3 and TPD with density functional theory (B3LYP/6-31G(d,p)); TPD is a hole transport material whose vapor-deposited glasses show strong birefringence.

Both Alq3 and TPD were geometry optimized at the B3LYP/6-31G(d,p) level of theory. These minimized geometries are then used as input for a polarizability calculation in Gaussian. From these calculations, we obtained the six unique components of the polarizability tensor (values displayed in atomic units).

Upon diagonalizing the polarizability tensors of both molecules, we get the three characteristic eigenvalues of each polarizability tensor (Table S1 and S2). If all eigenvalues are the same, there is no expectation of birefringence as the polarizability tensor is isotropic. For TPD, we get eigenvalues of 675, 446, and 305, which is consistent with the large observed birefringence in previous work. For Alq3, we get eigenvalues of 340, 326, and 320. The drastically reduced anisotropy of the polarizability tensor of Alq3 is one factor responsible for the small observed experimental birefringence.

Table S1. Components of Alq3 polarizability tensor (atomic units):

xx	326.28
yx	6.76
yy	329.25
zx	-2.3
zy	-7.7
zz	331.04

Table S2. Components of TPD polarizability tensor (atomic units):

xx	674.42
yx	-14.09
yy	305.64
zx	0.07
zy	-0.04
zz	445.58

In a second calculation, we project the eigenvector of the largest polarizability eigenvalue of Alq3 onto the molecular coordinate system, and use this vector as the relevant orientation vector for computing the P_2 order of the anisotropic polarizability. This yields the plot in Fig. S1 below, which indicates that the P_2 order of the polarizability tensor at the surface is very small (-0.02), which is the second factor responsible for the absence of birefringence in experiment.

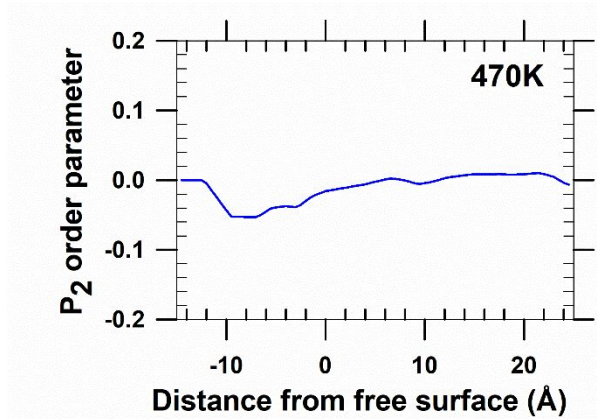


Fig. S1. P_2 order parameter, calculated for the eigenvector associated with the largest eigenvalue of the polarizability tensor, for an Alq3 liquid at 470K plotted as a function of the distance from the free surface.

Comparing peak positions in the plane and out of the plane:

The peak positions in the plane and out of the plane are not the same for vapor deposited Alq3 glasses, as shown in Fig S2. To evaluate the peak positions along Q_z an integration slice of Q from 0.3 to 1.3 \AA^{-1} and χ from 10° to 15° was taken. To evaluate the peak position along Q_{xy} an integration slice of Q from 0.3 to 1.3 \AA^{-1} and χ of 80° to 85° was taken.

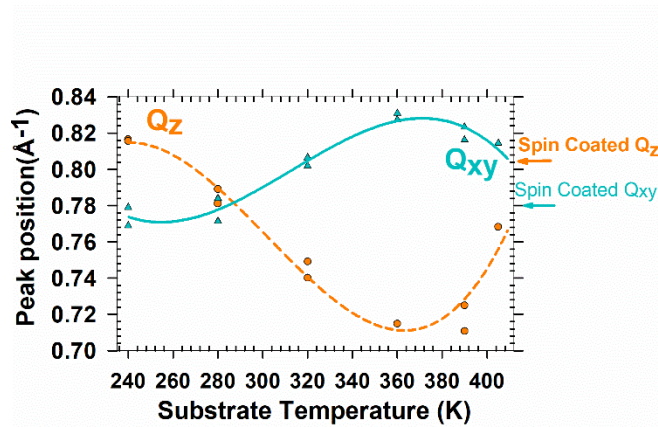


Fig. S2. The peak position in the plane and out of the plane for the scattering feature at $Q \sim 0.75 \text{\AA}^{-1}$. The arrows show the peak positions observed for the spin-coated glass.

Dipole moment vector

Shown in Fig S3 is the dipole moment vector of Alq3 along with its molecular structure. It is apparent from this three-dimensional representation of the molecular structure of Alq3 that it is quasi-spheroidal.

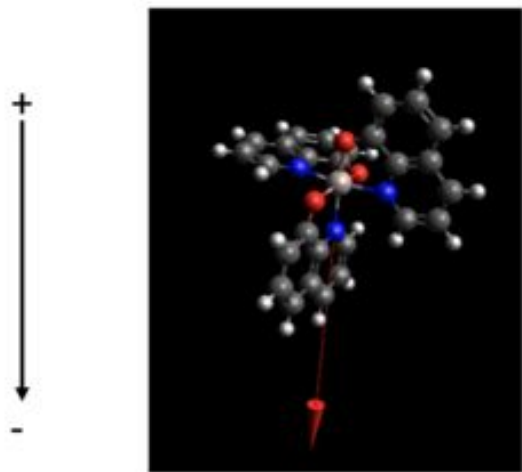


Fig. S3: The dipole moment vector of Alq3 is shown below along with a three-dimensional representation of the Alq3 molecule.

Sine-corrected scattering intensities

The sine-weighted scattering intensities are often plotted to qualitatively assess the orientation dependence of packing. The sine-weighted intensities for Alq3 glasses prepared at $T_{\text{sub}}=280\text{K}$ and 405K are shown below. The dashed line shows the calculated intensity for an isotropic glass. The data have been normalized to the intensity at $\chi=85^\circ$.

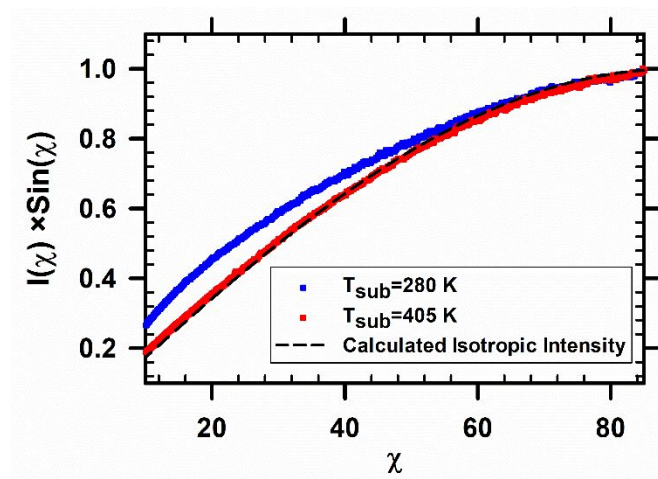


Fig S4: The sine-corrected intensities for Alq3 glasses vapor-deposited at $T_{\text{sub}}=280\text{K}$ (blue) and $T_{\text{sub}}=405\text{K}$ (red). The calculated intensity for an isotropic distribution is shown for reference

(dashed line). The scattered intensity for both the glasses have been normalized by their respective intensity at $\chi=85^\circ$. The deposition rate for both these glasses was roughly $\sim 0.2\text{nm/s}$.

S_{GIWAXS} for two deposition rates:

The order parameter S_{GIWAXS} is shown below for two different deposition rates. The observed shift in the high temperature regime is qualitatively consistent with the surface equilibration mechanism.

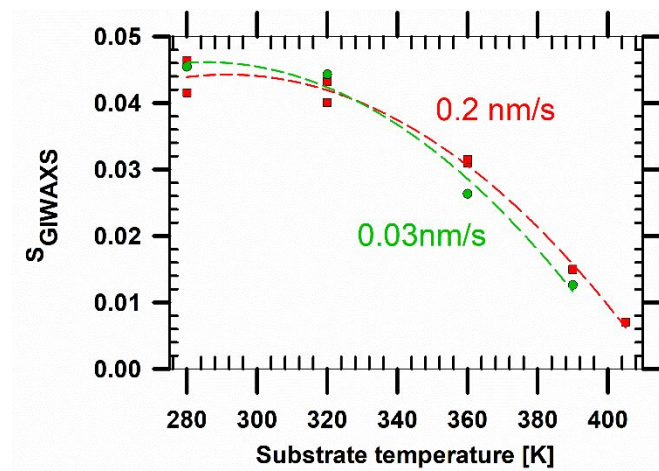


Fig S5: The order parameter S_{GIWAXS} is shown as a function of substrate temperature, for deposition rates of $\sim 0.2\text{ nm/s}$ (red) and 0.03 nm/s (green).