Characterization of Charge-Transfer Kinetics at Organic/Electrode Interfaces Using Potential-modulated Attenuated Total Reflectance (PM-ATR) Spectroscopy

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Potential-modulated attenuated total reflectance (PM-ATR) spectroscopy is a spectroelectrochemical method that utilizes the potential modulation approach and a waveguide ATR geometry. This unique combination enables measurements of electron-transfer (ET) kinetics of monolayer to submonolayer thin films on waveguide electrode surfaces. Selective probing of molecular subpopulations in a film can be achieved by choosing appropriate combinations of applied potential, wavelength, and polarization of light, which allows subpopulation structure to be correlated with ET kinetics. In this review, the basic theory of PM-ATR is introduced, and examples illustrating characterization of the structure and ET kinetics of organic semiconductor monolayers on electrode surfaces are presented, demonstrating the capabilities and applications of the PM-ATR technique.

Keywords Spectroelectrochemistry, attenuated total reflection, optical waveguide, electron-transfer rate, organic electronics, zinc phthalocyanine, perylene diimide, phosphonic acid, indium-tin oxide

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interfaces can be influenced by a number of parameters, including frontier orbital energy offsets, wave function overlap, inherent to these devices. Rates of charge transfer across these transfer across the organic active layer/electrode interfaces and surface energy. These parameters in turn depend on spectroelectrochemistry that u

absorption coefficients of these species differ, the reflectance of a dc potential and an ac potential mod

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ution. The normalized values of Re(Rac) and Im(Rac) are plotted as a function of ω. The rate constant (k) for reversible electron injection into the redox-active film is obtained from the frequency at which Re(Rac) is zero (indicated by the red ellipse). (C) Total internal reflection produces an evanescent field at the waveguide surface. The electric vector of the evanescent field is either parallel to the waveguide plane (transverse electric (TE)) or predominately normal to the waveguide plane (transverse magnetic (TM)). In the experiments described herein, the internal reflection angle (θ) is in the range of 73–75°. (A) Adapted with permission from Ref. 20. (B) Reprinted with permission from Ref. 20. Copyright 2010 American Chemical Society.

2 Theory of PM-ATR

In ER spectroscopy, the intensity of light reflected from an electrode surface is monitored during simultaneous application of a dc potential and an ac potential modulation. The reflectance is a function of the optical constants of the near-surface region of the electrode and therefore is sensitive to the physical/chemical properties of the film.

The applied potential, E, is given by

\[ E = E_{dc} + E_{ac}\sin(\omega t), \]

where \( E_{dc} \) is the dc potential, \( E_{ac} \) is the amplitude of the potential modulation, \( \omega \) is the angular frequency and \( t \) is time. When \( E_{dc} \) is near the formal reduction potential of the redox-active molecular film, potential modulation alters the ratio of the oxidized and reduced species in the film, and when the absorption coefficients of these species differ, the reflectance varies with \( E \). When \( E_{ac} \) is much smaller than \( RT\ln F \) (where \( R \) is the ideal gas constant, \( T \) is the temperature in Kelvin, \( n \) is the number of electrons involved in the redox reaction, and \( F \) is the Faraday constant), the total reflectance, \( R_t \), can be written as

\[ R_t = R_{dc} + R_{ac}\sin(\omega t - \phi), \]

Kuwana and coworkers\(^{1,6} \) pioneered visible wavelength spectroelectrochemistry in both transmission and attenuated total reflectance (ATR) geometries. Subsequent reports by our group\(^{7–9} \) and others\(^{10–12} \) described spectroelectrochemical ATR systems implemented in multi-mode and single-mode waveguide configurations, providing broadband spectral information, sensitivity to submonolayer electroactive films, and chemical selectivity. Potential-modulated attenuated total reflectance (PM-ATR) spectroscopy\(^{13} \) is a unique form of waveguide-based spectroelectrochemistry that utilizes the electroreflectance (ER) spectroscopic approach developed largely by Niki, Sagara, and coworkers.\(^{2,4} \) Combining potential-modulation with the ATR geometry enables the measurement of charge-transfer kinetics of monolayer to submonolayer thin films on waveguide electrodes, with selectivity to molecular subpopulations in the film provided by appropriate choice of the applied potential and the wavelength and polarization of light, as described further below. This method has been applied to study a wide variety of electrode-supported materials, including small molecule and polymeric semiconductors,\(^{13–17} \) proteins,\(^{18} \) inorganic complexes,\(^{19} \) and semiconductor nanocrystals.\(^{20,21} \)

The overall performance of electronic devices, such as organic photovoltaics (OPVs) and organic light emitting diodes (OLEDs), is dependent in part on the efficiency of charge transfer across the organic active layer/electrode interfaces inherent to these devices. Rates of charge transfer across these interfaces can be influenced by a number of parameters, including frontier orbital energy offsets, wave function overlap, and surface energy. These parameters in turn depend on structural parameters, such as the composition, packing, and orientation of the active layer components, particularly those that comprise the first monolayer adjacent to the electrode.\(^{22–25} \) Tuning the structure of the first monolayer can therefore be used to optimize the efficiency of charge transfer at these interfaces, and ultimately the overall device efficiency. This review describes the use of PM-ATR to characterize the structure and charge-transfer properties of electrode-supported, organic semiconductor monolayers that are used as modifiers to tune the properties of active layer/electrode interfaces in organic electronic devices.
The ET rate constant is calculated from an equivalent circuit, is presented in key references.4,26,27

\[ R_{dc} = \frac{k_s C_{dl}}{\omega_R} \]

where \( R_{dc} \) and \( R_{ac} \) are the dc and ac components of \( R_s \), respectively, and \( \phi \) is the phase angle between \( R_{ac} \) and \( E_{ac} \). When the electrochemical reaction is quasi-reversible, \( \phi \) is a function of the reaction rate, and the apparent electron-transfer (ET) rate constant \( (k_s) \) can be obtained by analysis of the ER response in the frequency domain. Detailed descriptions of the theory of ER and its use for measuring ET rate constants have been presented by Niki, Sagara, and coworkers.4,26,27

ER spectroscopy also can be performed in a transmission geometry, using an optically transparent electrode. However, the sensitivity of both transmission and external reflection ER geometries may be inadequate when the sample is a thin, weakly absorbing molecular film. The sensitivity can be enhanced by using an ATR geometry, wherein the probe beam is internally reflected multiple times through a planar waveguide electrode.13,15,18,20 Compared with transmission and external reflection ER spectroscopy, PM-ATR spectroscopy provides a sensitivity enhancement of ten to several thousand, depending on the geometry of the waveguide electrode. The ATR geometry also provides spatial selectivity because the evanescent wave penetrates only a fraction of the wavelength (\( \lambda \)) into the medium adjacent to the waveguide.

Figure 1A outlines a PM-ATR experiment using a glass slide coated with indium-tin-oxide (ITO) as the waveguide electrode. Light is coupled into and out of the waveguide through two prisms. A standard three-electrode system is used to apply a voltage \( E_{ac} \) to the ITO electrode. Figure 1B shows an example of a complex plane plot obtained from a PM-ATR measurement, where the in-phase (Re(\( R_{ac} \))) and out-of-phase (Im(\( R_{ac} \))) portions of \( R_s \) are plotted as a function of the modulation frequency. The ET rate constant is calculated from \( k_s = \frac{0.56}{C_{dl}} \frac{R_{ac}}{C_{dl}} \), where \( \omega \) is the frequency at which Re(\( R_{ac} \)) = 0, \( R_s \) is the solution resistance, and \( C_{dl} \) is the double layer capacitance. The derivation of the equation, including a description of an equivalent circuit, is presented in key references.4,26,27

A key feature of PM-ATR is that the measurement can be performed using either transverse electric (TE) or transverse magnetic (TM) polarized light (Fig. 1C).15,18 This allows for the selective probing of molecules having absorbance transition dipoles aligned with the electric field vector of the evanescent wave. In an ensemble of molecules with a distribution of molecular orientations, the contribution of each molecule to the ER response is weighted by a factor of cos\(^2\) \( \alpha \), where \( \alpha \) is the angle between the electric field vector and the transition dipole of the molecule. Additional selectivity that allows probing of subpopulations of molecules in a structurally heterogeneous film can be obtained by varying \( E_{ac} \) and the wavelength at which the ER response is measured.15

### 3 PM-ATR Studies of Modifiers of Organic Active Layer/Electrode Interfaces

To enhance the electronic properties of transparent conducting oxide (TCO) electrodes, such as ITO and TiO\(_2\), used in organic electronics devices, modification strategies have been developed to tune the TCO surface composition, surface free energy, work function, and chemical stability. Chemisorption of an organic monolayer via a phosphonic acid (PA) anchoring group is one example that was recently reviewed. Introducing a redox-active moiety into the surface modifier offers the possibility of enhancing the charge-collection efficiency when the redox potential is matched to the relevant charge-transport energy levels. The following sections describe recent studies of redox-active PA modifiers on ITO, focusing on relationships between monolayer structure and charge-transfer kinetics.

#### 3-1 Zinc phthalocyanine modifiers

Lin et al. studied zinc phthalocyanine (ZnPc) monolayers on ITO as modifiers of the interface between the donor layer and the hole collection contact in an OPV.14,15 The monolayer structure, electrochemical properties, and OPV performance of the two modifiers shown in Fig. 2 were compared: ZnPcPA contains an alkyl PA linker in one quadrant and ZnPc(PA)\(_4\) contains four alkyl PA linkers, one in each quadrant. Their structures suggest that immobilization on ITO via the PA anchoring groups would produce films in which the Pc molecular plane is predominately out-of-plane and in-plane, respectively, relative to the ITO surface plane.

The ATR UV-vis spectrum of the ZnPcPA monolayer (Fig. 3A) shows two major absorbance bands which are assigned to monomers (\( \lambda_{max} \approx 680 \text{ nm} \)) and H-aggregates (\( \lambda_{max} \approx 630 \text{ nm} \)). These subpopulations are electrochemically distinct with one-electron oxidation potentials that differ by ca. 200 mV. The presence of both monomeric and aggregated forms contributes...
to a broad distribution of molecular orientations in the film, as indicated by respective mean tilt angles of $33 \pm 1^\circ$ and $57.8 \pm 0.7^\circ$ (measured by polarized ATR UV-vis spectroscopy) between the normal to Pc molecular plane and the normal to the ITO surface plane.\textsuperscript{11} The ATR spectrum of the ZnPc(PA)$_4$ monolayer on ITO (Fig. 3B) shows significantly weaker absorbance at ca. 630 nm compared to the ZnPcPA film, which is indicative of significantly less aggregation. The mean tilt angle of ZnPc(PA)$_4$ molecules is $29 \pm 2^\circ$; this largely in-plane orientation is consistent with the attachment of multiple PA groups per molecule to ITO.\textsuperscript{14} Anchoring \textit{via} multiple PAs is expected to reduce the rotational degrees of freedom and minimize cofacial aggregation, relative to attachment \textit{via} a single PA group in the ZnPcPA film, and produce a largely monomeric film with a narrower orientation distribution. The absence of significant aggregation is supported by the observation of only one oxidation wave, assigned to the monomer, in the cyclic voltammogram of ZnPc(PA)$_4$ on ITO.\textsuperscript{14}

PM-ATR measurements were performed on ZnPcPA films at both the monomer and aggregate absorption maxima and in both TE and TM polarizations, from which the four charge-transfer rate constants listed in Table 1 were obtained.\textsuperscript{15} The four $k_s$ values correspond to different subpopulations of molecules: The TM $k_s$ values are weighted more heavily by molecules tilted out-of-plane whereas those with more in-plane orientations contribute more to the TE $k_s$ value.\textsuperscript{15} The $k_s$ values for aggregated ZnPcPA are 3 - 10 times greater than those measured for the monomeric form, which is attributed to the lower reorganization energy of electron transfer for aggregates relative to monomers.\textsuperscript{15} The aggregate $k_s$ values are polarization-dependent, with the TE value about three times greater than the TM value. Forming a cofacial aggregate with an in-plane orientation implies the presence of one or more gauche defects in the alkyl-PA side chains, and this configuration should produce a shorter tunneling distance for ET to the ITO electrode, resulting in a higher $k_s$ in TE polarization.\textsuperscript{14} In contrast, the monomer $k_s$ values show no dependence on polarization. If the tilt angle distribution of the monomers is narrow, there is no structural basis for a difference in the ET rate, and thus the rate constants measured in both polarizations should be equal. This is the most probable explanation for the polarization-independent results for the monomer.

The $k_s$ values measured for the ZnPc(PA)$_4$ film also show no dependence on polarization (Table 1). This observation is consistent with the spectral and electrochemical data,\textsuperscript{15} indicating that the distribution of ZnPc(PA)$_4$ molecular orientations is relatively narrow. As for the ZnPcPA monomer subpopulation, a narrow tilt angle distribution should not produce a difference in the TE- and TM-polarized rate constants. Importantly, the $k_s$ values for ZnPc(PA)$_4$ are an order of magnitude greater than the highest values measured for ZnPcPA, and are among the highest ever reported for a surface-confined redox couple. The rapid kinetics are attributed to the predominately in-plane orientation. Adsorption of ZnPc(PA)$_4$ to ITO \textit{via} 3 - 4 PA groups per molecule should produce adsorption geometries with short tunneling distances between the ZnPc core and the electrode surface, resulting in rapid charge transfer.\textsuperscript{14} Overall, these studies demonstrate the unique capability of PM-ATR to correlate the structure of subpopulations of molecules in an electrode-supported monolayer with their respective ET rate constants. The selectivity to subpopulations is provided by the combination of the $E_{k_s}$ and the wavelength and polarization of the light propagating in the waveguide.

The impact of the monolayer structure on device performance was assessed by using ZnPc(PA)$_4$ and ZnPcPA as modifiers for hole-harvesting electrode contacts in planar heterojunction OPVs.\textsuperscript{14} The OPV construct was ITO/ZnPc monolayer/20 nm copper phthalocyanine (CuPc)/40 nm C$_{60}$ fullerene/10 nm bathocuproine (BCP)/100 nm Al.

Results from ultraviolet photoelectron spectroscopy showed that the energy level alignment of both ITO/ZnPc(PA)$_4$/CuPc

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Apparent ET rate constants ($k_s$/s$^{-1}$) of ZnPc(PA)$_4$ and ZnPcPA films on ITO measured by PM-ATR$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polarization</td>
<td>ZnPc(PA)$_4$/ITO</td>
</tr>
<tr>
<td></td>
<td>Monomer (690 nm)</td>
</tr>
<tr>
<td>TE</td>
<td>$1.9(\pm0.4)\times10^4$</td>
</tr>
<tr>
<td>TM</td>
<td>$1.8(\pm0.3)\times10^4$</td>
</tr>
</tbody>
</table>

a. Data from Refs. 14 and 15. Experimental conditions are given in the same references.
and ITO/ZnPcPA/CuPc is favorable for hole extraction. The dark and photoresponse characteristics of the two device types are compared in Fig. 4 and Table 2, and significant differences in OPV performance were observed, consistent with the structural differences between the ZnPc(PA)₄ and ZnPcPA monolayers and their respective ET rate constants. Devices constructed on ZnPc(PA)₄ have significantly lower series resistance, higher fill factor, and higher overall power conversion efficiency. The current-voltage curves indicate that devices constructed on ZnPcPA are significantly limited by recombination near the open-circuit voltage. Overall, these results demonstrate how controlling the orientation of a redox-active TCO modifier can lead to improved OPV performance, and provide guidance for further development of new modifiers for charge-harvesting electrical contacts in energy conversion platforms.

3.2 Perylene diimide modifiers

Zheng et al. studied PA-functionalized perylene diimide (PDI-PA) monolayers as modifiers of the active layer/ITO contact in organic electronic devices. Figure 5 shows the PDI-PA modifiers used in their work; the key structural variables are the length of the bridge between the PDI and the PA, to modulate the ET tunneling distance, and the degree of substitution, to tune the extent of PDI-PDI intermolecular interactions. In their initial study, different deposition techniques (solution adsorption (SA) and spin coating (SC)) were used to deposit PDI-phenyl-PA and PDI-diphenyl-PA to create three different types of PDI monolayers: SA PDI-phenyl-PA, SA PDI-diphenyl-PA and SC PDI-phenyl-PA. Polarized ATR UV-vis measurements show that the different deposition methods produce films with different orientations. SC films show a more in-plane orientation with a mean tilt angle between the PDI long axis and ITO surface normal of 45°, whereas the self-assembled films are oriented more out-of-plane with mean tilt angles of 33° and 31° for SA PDI-phenyl-PA and SA PDI-diphenyl-PA, respectively.

PM-ATR measurements of kₛ for the three different types of films are listed in Table 3. The kₛ value for the SA PDI-phenyl-PA film is about 3-fold greater than that for the SA PDI-diphenyl-PA film which is due to the shorter bridge and consequent shorter tunneling distance (r) between the PDI core and the electrode. Assuming a through-bond tunneling mechanism for charge transfer, and the dependence of the ET rate constant (kₚₗ) on r given by kₚₗ = k₀e⁻βᵣ (where k₀ is the extrapolated value of the rate constant for r = 0 and βᵣ is the exponential decay coefficient), an estimate for βᵣ of 0.28 Å⁻¹

<table>
<thead>
<tr>
<th>ZnPc layer</th>
<th>Fill factor</th>
<th>Rₛ/Ω cm²</th>
<th>η, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnPcPA</td>
<td>0.28 ± 0.01</td>
<td>52 ± 8</td>
<td>0.60 ± 0.05</td>
</tr>
<tr>
<td>ZnPc(PA)₄</td>
<td>0.57 ± 0.01</td>
<td>0.81 ± 0.08</td>
<td>1.47 ± 0.05</td>
</tr>
</tbody>
</table>

a. Rₛ is series resistance and η is overall power conversion efficiency. Minor differences in open-circuit voltage, short-circuit current, and shunt resistance were measured, see Ref. 14.
Table 3 Apparent ET rate constants of PDI-PA films on ITO measured by PM-ATR

<table>
<thead>
<tr>
<th>PDI-PA film</th>
<th>$k_{s^{-1}}$</th>
</tr>
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<tbody>
<tr>
<td>SA PDI-phenyl-PA</td>
<td>1.4(±0.3)×10^4</td>
</tr>
<tr>
<td>SA PDI-diphenyl-PA</td>
<td>0.5(±0.2)×10^4</td>
</tr>
<tr>
<td>SC PDI-phenyl-PA</td>
<td>5(±2)×10^4</td>
</tr>
<tr>
<td>(Phenyl)$_2$-PDI-PA</td>
<td>0.19(±0.07)×10^4</td>
</tr>
<tr>
<td>(Terphenyl)$_2$-PDI-PA</td>
<td>0.12(±0.01)×10^4</td>
</tr>
<tr>
<td>(Terphenyl)$_2$-PDI-IP-PA</td>
<td>0.10(±0.03)×10^4</td>
</tr>
</tbody>
</table>

a. Data from Refs. 16 and 17. Experimental conditions are given in the same references.

is obtained which is consistent with calculated and measured values reported for electron transfer through unsaturated bridges.32 Although the through-bond tunneling distance in SC PDI-phenyl-PA and SA PDI-phenyl-PA films is predicted to be equal, the $k_s$ value for SC film is about 4-fold greater. The difference in the tilt angle, however, indicates a difference in the film structure and possibly an altered distribution of PA binding modes resulting from SC vs. SA deposition. Aggregation may have also played a role; based on the ATR UV-vis spectra, the SC film is more aggregated than both SA films.

The effects of PDI aggregation on the ET kinetics were the subject of a subsequent study.17 A series of PDI-PA molecules, (phenyl)$_2$-PDI-PA, (terphenyl)$_2$-PDI-PA, and (terphenyl)$_2$-PDI-IP-PA (Fig. 5), was designed to have different degrees of aggregation when deposited as monolayers on ITO, based on differences in the structure and size of the substituents at the imide positions. These three molecules were deposited on ITO using the SA method and their properties were compared along with those of the SA PDI-phenyl-PA. PDI aggregation causes broadening of the visible absorbance bands and can be assessed by the relative intensity of the 0-0 and 0-1 vibronic bands, with a 0-0/0-1 band ratio close to 1.6 considered to be monomeric.34 Although the ATR UV-vis spectra (Fig. 6) shows that aggregation exists in all four films, the degree varied. The 0-0/0-1 band ratio increases from 0.36 for the PDI-phenyl-PA film to 0.98 for the (terphenyl)$_2$-PDI-IP-PA film, showing an inverse correlation between the size/number of the substituents and the degree of aggregation. This finding is supported by complementary measurements, including electroactive PDI surface coverage, PDI tilt angle, and total internal reflection fluorescence spectra.17

The $k_s$ values measured by PM-ATR show that faster ET kinetics are correlated with a higher degree of PDI aggregation (Table 3). This trend is hypothesized to be due to an enhanced rate of intermolecular electron self-exchange between surface-bound PDI$^-$ and PDI species. Conductive-tip atomic force microscopy has been used to map the electrical properties of ITO; the results show that the conductivity of the electrode surface is spatially heterogeneous on the nm length scale, and this heterogeneity has been correlated with electrochemical properties and OPV performance.36–37 We hypothesize that PDI-PA$_n$ bound to the more electrically conductive regions ("hot spots")37 on ITO undergo more rapid ET than PDI-PA$_n$ bound to less conductive regions. In the latter case, the dominant mechanism for ET is likely to involve both lateral self-exchange and exchange between a PDI and ITO at a "hot spot". The closer spacing of the PDI cores in a more highly aggregated film is predicted to enhance the self-exchange rate, resulting in a higher apparent $k_s$. Overall, the results of these two studies demonstrate how the structure of PDI-based modifiers can be varied to control the kinetics of reversible ET at PDI/ITO interfaces.

4 Conclusion

"Molecular engineering" of an interface using an organic monolayer usually implies structural control, i.e., a major objective is to create a structurally uniform interface that yields spatially uniform functional properties. However, deposition of an organic modifier on the chemically and structurally heterogeneous surface of a TCO electrode often produces a structurally heterogeneous interface, and studying structure-function relationships at such interfaces can consequently be difficult. The studies described herein demonstrate the unique capabilities of PM-ATR for probing structurally heterogeneous TCO/organic interfaces. The choice of the $E_a$, the wavelength, and the polarization of the light propagating in the waveguide provide for selective probing of molecular subpopulations in these films, and obtaining kinetic information assignable to these subpopulations.

Compared to more conventional voltammetric methods, PM-ATR offers higher selectivity and improved sensitivity, and expanding the wavelength range to the near infrared region or using fluorescence detection39 are feasible approaches to enhance both the information content and selectivity. However it should be noted that since $E_a$ is typically only 10 - 50 mV RMS, only the molecules that can be oxidized or reduced within $E_a \pm E_c$ contribute to the measured $R_{ac}$. Thus the $k_s$ value is obtained from a minor fraction (ca. 10%) of the electroactive subpopulation (or film), specifically the minor fraction that equilibrates most rapidly with the modulated electrode potential. As a consequence, a $k_s$ measured by PM-ATR may differ from an ET rate constant measured by cyclic voltammetry which operates over a larger potential range and addresses electroactive molecules that are oxidized/reduced at higher overpotentials.

Measurement of ET rate constants for kinetically rapid redox couples by PM-ATR is ultimately limited by the RC time constant of the electrochemical cell. However, the drive to fabricate a cell with a smaller RC time constant must be balanced by the need for an optical path length that provides sufficient sensitivity to perform the measurement. In ATR, the path length is proportional to the number of total internal

Fig. 6 ATR spectra of PDI-PA films on ITO measured in TM polarization: PDI-phenyl-PA (black), (phenyl)$_2$-PDI-PA film (red), (terphenyl)$_2$-PDI-PA (blue), and (terphenyl)$_2$-PDI-IP-PA (green). The surface coverage of each film was ca. one monolayer. The spectra were acquired at open circuit with the films in contact with acetonitrile containing 0.1 M tetrabutylammonium perchlorate. Adapted with permission from Ref. 17. Copyright 2016 American Chemical Society.
reflections and a greater number of internal reflections implies a larger electrochemical cell volume. A solution to this tradeoff is to use a thinner waveguide, and extending this strategy to the single-mode regime has been demonstrated.  

5 Acknowledgements

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6 References

31. The tilt angles for the monomers and aggregates are very different; this means that the overall orientation distribution is broad. The values ±1° and ±0.7° are the standard deviations of the respective mean tilt angles and thus are not indicative of the breadth of the molecular orientation distribution.