

Vibrational modes and changing molecular conformation of perfluororubrene in thin films and solution

F. Anger,¹ R. Scholz,² A. Gerlach,¹ and F. Schreiber¹

¹*Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen, Germany*

²*Institut für Angewandte Photophysik, TU Dresden, 01069 Dresden, Germany*

(Received 13 March 2015; accepted 22 May 2015; published online 9 June 2015)

We investigate the vibrational properties of perfluororubrene (PF-RUB) in thin films on silicon wafers with a native oxide layer as well as on silicon wafers covered with a self-assembled monolayer and in dichloromethane solution. In comparison with computed Raman and IR spectra, we can assign the molecular modes and identify two molecular conformations with twisted and planar tetracene backbones of the molecule. Moreover, we employ Raman imaging techniques to study the morphology and distribution of the molecular conformation in PF-RUB thin films. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4922052>]

I. INTRODUCTION

Amongst semiconducting organic materials, rubrene ($C_{42}H_{28}$, RUB) has attracted significant attention during the last years due to its very high charge carrier mobility^{1–4} and its large exciton diffusion length.^{5–7} One very effective way to tune the electronic properties of a material and at the same time to mitigate the molecular reactivity with oxygen⁸ is fluorination, since fluorine is the most electronegative element.^{9–13} While the optical properties as well as the energy level alignment of perfluororubrene ($C_{42}F_{28}$, PF-RUB) have already been studied,^{12,14,15} a characterization of the molecular vibrations is still lacking. The vibrational modes, however, are fundamental properties of a molecule that play an important role for the understanding of molecular charge carrier transport properties.^{16–20}

In analogy to the rubrene molecule,^{21,22} there are also at least two stable molecular conformations for PF-RUB, either with a planar or with a twisted tetracene backbone (Fig. 1), which result in different optical properties and polaron binding energies.²³ Different single crystal structures formed by rubrene molecules with a planar tetracene backbone were found, for which an orthorhombic packing turned out to be most efficient in terms of charge carrier mobility.^{24–27} For rubrene thin films, a predominance of the energetically favored twisted conformation has been observed directly after growth on silicon substrates with a native oxide layer (SiO_2).²⁸ For the newly synthesized PF-RUB, however, it is not *a priori* clear which molecular conformation prevails in thin films or crystals. Thin films, which are easier to produce than single crystals and indeed preferable for applications, might contain crystallites and/or a fraction of both isomers, which makes it difficult to assign vibrational modes to one of the conformers. On the other hand, samples with mixed conformations provide vibrational information on both twisted and planar molecules.^{29,30} A possibility to influence the thin film growth and also the molecular conformation is the modification of the substrate with a self-assembled monolayer (SAM).^{31–33} In this study, we compare the vibrational properties, i.e., experimental

and computed infrared (IR) and Raman spectra, of the PF-RUB molecules in thin films on SiO_2 and on SAM, and PF-RUB dissolved in CH_2Cl_2 .³⁴

II. EXPERIMENTAL

Thin films of PF-RUB were prepared, respectively, on silicon wafers with a native oxide layer and on silicon wafers covered with a SAM³⁵ consisting of octadecyltrichlorosilane (OTS).³⁶ Prior to deposition, the native silicon oxide wafers were rinsed in acetone, isopropanol, and water in a super-sonic bath for 5 min each. The films were deposited on both substrates at the same time under ultra-high vacuum conditions.^{37,38} During growth, the substrates were kept at room temperature (RT), and the film thickness was grown up to 100 nm at a growth rate of $\sim 2 \text{ \AA/min}$, which corresponds to an evaporation temperature of our Knudsen cell of $T \sim 96 \text{ }^\circ\text{C}$ (comparable rates of hydrogenated RUB require an evaporation temperature of $T \sim 155 \text{ }^\circ\text{C}$). Under these conditions, PF-RUB thin films on native SiO_2 substrates are supposed to grow amorphous.¹² The concentration of the diluted solution of PF-RUB molecules in CH_2Cl_2 was $\sim 2 \text{ mol/l}$.

Raman spectra were acquired using an Horiba Jobin Yvon LabRam HR 800 spectrometer with a CCD-1024 $\times$ 256-OPEN-3S9 as detector. Excitation for Raman was performed using a HeNe-laser at 633 nm with a spot size of $\sim 1 \text{ }\mu\text{m}$. For the reduction of surface inhomogeneity effects of the samples, several spectra were acquired over a representative range and the spectra were integrated. Since the Raman peaks become sharper at low temperatures,³⁹ the thin film samples were cooled down to 77 K during the measurement.

The IR spectra of the thin films and solution were obtained in transmission mode with a Vertex 70 (Bruker) Fourier transform infrared spectrometer with a PMA 50 detector unit attached. In order to avoid back-reflection at the smooth side of the silicon wafer, p-polarized light was sent onto the substrate with an angle of incidence of 74° which is near to the Brewster angle of silicon. The diameter of the IR beam was $\sim 1 \text{ mm}$.

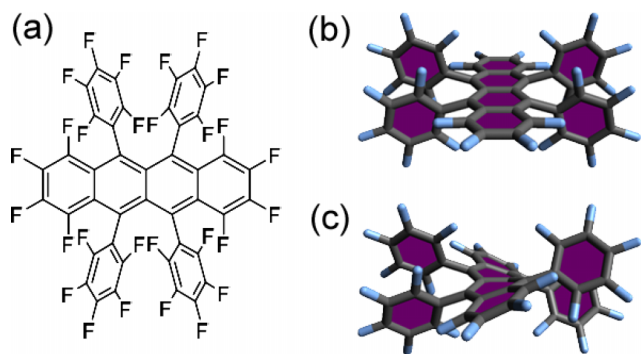


FIG. 1. (a) Chemical structure of PF-RUB. In analogy to rubrene, the molecule can adopt different conformations with either planar or twisted tetracene backbone. Possible molecular symmetries are (b) C_{2h} (planar) or (c) D_2 (twisted), which are found in crystals^{24,26,27} or thin films²⁸ of hydrogenated RUB, respectively. The compound was synthesized and purified by Sakamoto and Suzuki from the Institute for Molecular Science in Okazaki (Japan) using temperature gradient sublimation.

The intensity I of the IR spectra was determined using $I = (I_{\text{Sample}} - I_0)/I_0$, where I_{Sample} describes the intensity of the thin film on the substrate (or the molecules dissolved in solution), and I_0 stands for the measured substrate (or the absorption of the solvent) only. Energy regions with strong IR absorption of the solvent CH_2Cl_2 could not be monitored.⁴⁰

The samples were measured with IR and Raman spectroscopies within 4 h after thin film growth. After one day, we discovered a change in the IR and Raman spectra of the PF-RUB thin films deposited on the bare SiO_2 compared to the pristine film. Measurements on the following days thereafter did not reveal further changes in the IR and Raman spectra. From this, we deduce that the thin films deposited on native SiO_2 reached a stable state, about one day after thin film growth. Spectra of thin films on SAMs did not show changes over time. In the following, we will denote data obtained within 4 h after film growth as “pristine” and data obtained after one day or later as “late stage.” Interestingly, we observe a decrease of the photoluminescence (PL) background by a factor of 2 (not shown) for the sample on SiO_2 from the pristine to its late stage. Such an increase in the PL quenching indicates a change of the exciton diffusion length.^{5,41,42} For better evaluation of the spectra, the PL background of the Raman spectra was subtracted after acquisition.

III. RESULTS

We present our findings in three different subsections. First, the experimental and computed IR and Raman spectra are shown and discussed. In the second part, spectra corresponding to molecules with a purely planar and a purely twisted tetracene backbones, respectively, are extracted from the experimental data. Finally, Sec. III C focusses on the correlation of morphology and conformation of the molecules.^{24,43,44} Interestingly, we find a connection between dewetting and a change in the molecular conformation for the thin film on SiO_2 .

A. IR and Raman spectra of PF-RUB

IR and Raman active vibrational modes of two conformations of the isolated PF-RUB molecule that also occur

for hydrogenated RUB^{24,26–28} (D_2 and C_{2h} symmetries with twisted and planar backbones, respectively) were computed with the B3LYP functional and TZVP basis set using Turbomole 6.4.⁴⁵ We find that the twisted D_2 isomer is energetically favored by -0.34 eV against the planar C_{2h} conformation, which is roughly twice as much as in the case of RUB.¹² For better comparison of the computed model with the experimental spectra, the intensity of each mode is represented by a Lorentzian. The energy axis of the computed modes was scaled by a factor of 0.9915, which we found to yield a very good agreement between the theoretical model and experimental values for most modes.⁴⁶ Nevertheless, for particular modes like C-F stretching and few localized C-C stretching modes involving strong fluorine movement, a factor of 0.9860 could be more adequate. The particular type of vibration, which could be identified from the computed modes, is listed in Table I. The values for the different types of vibration (like in-plane bending, out-of-plane bending, and stretching) in Table I correspond roughly to the classical harmonic oscillator model.¹⁵ We find the strongest Raman activity in the range $\tilde{\nu} \sim 1300\text{--}1600\text{ cm}^{-1}$, which agrees well with the spacing of the effective vibronic progression^{15,17,47} observed in absorption spectra of PF-RUB.¹²

Fig. 2(a) shows the fingerprint region of the experimental IR spectra of PF-RUB dissolved in CH_2Cl_2 , on native SiO_2 (pristine and late) and on a SAM covered SiO_2 in comparison with computed spectra (top to bottom). The peaks of the solution spectra are sharper than the peaks from the thin film spectra. Due to the high polarizability of the molecule caused by the large number of negative fluorine atoms, the spectra show strong IR peaks, particularly in the C-F and C-C stretching regions. The computed IR spectra correspond remarkably well to the experimental spectra, and most of the vibrational modes can be identified.

Fig. 2(b) shows the fingerprint region of the experimental Raman spectra of PF-RUB in solution, on native SiO_2 (pristine and late) and on SAM covered SiO_2 in comparison with computed spectra (top to bottom). From a comparison of all samples, the Raman fingerprint of PF-RUB consists of prominent modes in the vicinity of 1315 cm^{-1} , $1520\text{--}1530\text{ cm}^{-1}$, and 1590 cm^{-1} . Peaks in the spectrum of PF-RUB dissolved in CH_2Cl_2 at $\tilde{\nu} \sim 900\text{ cm}^{-1}$, $\sim 1000\text{ cm}^{-1}$, $\sim 1160\text{ cm}^{-1}$, $\sim 1270\text{ cm}^{-1}$, and $\sim 1425\text{ cm}^{-1}$ (b_1 , b_3 – b_5) originate from the solvent.⁴⁰ In the thin film spectra, a rather broad peak in the region of $900\text{--}1000\text{ cm}^{-1}$ (b_2) is related to the SiO_2 substrate.⁴⁸

As resonant and pre-resonant Raman spectra rely on amplitudes of internal vibrations in the relaxed excited geometry

TABLE I. Assignment of the vibrational modes of PF-RUB.

Type of bonding	Type of vibrational mode	Wavenumber $\tilde{\nu}$ (cm^{-1})
Multiple C-C	Skeletal	0...250
C-F	Out-of-plane bending	120...260
C-C	Out-of-plane bending	280...810
C-F	In-plane bending	280...360
C-C	In-plane bending	400...1025
C-F	Stretching	900...1200
C-C	Stretching	1040...1700

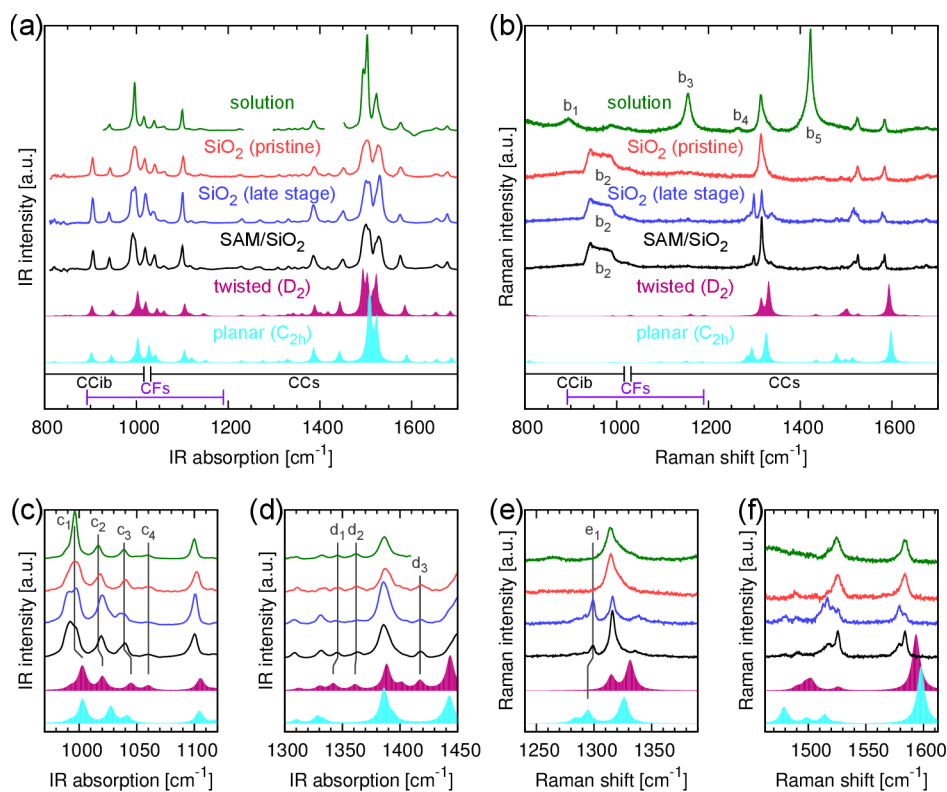


FIG. 2. Experimental vibrational spectra of PF-RUB (lines) and spectra computed by DFT (filled curves). The experimental spectra are obtained from molecules dissolved in CH_2Cl_2 (green line, top), deposited on native SiO_2 in “pristine” (red line) and “late stage” (blue line), as well as on SAM/ SiO_2 (black line, bottom). The theoretical spectra show Lorentzian-shaped modeled curves of the twisted (purple filled) and planar (cyan filled) conformations of the molecule. (a) FT-IR spectra in the fingerprint region of the PF-RUB molecule. (b) Raman spectra of the samples excited at 633 nm. (c) and (d) show a zoom into selected regions of the IR spectra, (e) and (f) of the Raman spectra, respectively. The bars at the bottom of (a) and (b) show the regions of the type of the vibrational mode (“CCib” = C-C in-plane bending, “CCs” = C-C stretching, and “CFs” = C-F stretching). For explanation of the spectra, see text.

of the molecule, only modes of the highest symmetry contribute significantly.⁴⁹ Hence, the number of strongly Raman-active modes remains far below the number of IR-active modes. The computed Raman intensities rely on the ground state geometry of each isomer computed with density functional theory (DFT) using the B3LYP hybrid functional, and on the respective excited state geometry computed with time-dependent DFT, as implemented in Turbomole.^{50,51} These deformations were projected on the complete set of vibrational eigenvectors, allowing to deduce non-vanishing Huang-Rhys factors S_j for internal modes of the highest symmetry, corresponding to the A representation of the D_2 isomer and to A_g for the C_{2h} isomer, respectively. The computed cross sections in the resonant Raman spectra were then obtained as $\sigma_j \propto S_j(\hbar\omega_j)^2$. As evidenced in Figs. 2(b), 2(e), and 2(f), the predominant computed Raman modes around 1300 cm^{-1} and between 1450 cm^{-1} and 1600 cm^{-1} occur in the same region as the measured modes with the largest cross sections of resonant Raman scattering.

Due to the very good agreement between theory and experiment, it is possible to distinguish small differences in the IR spectra. Figs. 2(c) and 2(d) show a zoom into the IR spectra. Since some of the peaks predicted by the theoretical model occur only either for the twisted or for the planar conformation of PF-RUB, it is possible to make an assignment of the spectra. Particularly, the spectrum of the computed twisted conformation shows peaks at 1060 cm^{-1} (c_4), 1340 cm^{-1} (d_1), 1360 cm^{-1} (d_2), and 1420 cm^{-1} (d_3) that do not exist in the spectrum for the planar conformation. Moreover, the computed spectrum, for the twisted conformation, shows slightly different positions of the peaks c_2 and c_3 , involving in particular a wider spacing than for the corresponding peaks in the computed spectrum of the planar conformation in the region of 1020–1050 cm^{-1} .

Comparing the IR solution spectrum with the computed modes (Figs. 2(c) and 2(d)), we find a very good agreement of the peaks c_1 – c_4 , d_1 and d_2 with the twisted conformation.^{29,52} Also, the separation of the peaks c_2 and c_3 corresponds well to the respective computed twisted modes. This confirms the assumption that the majority of molecules in solution adopt an energetically favored twisted conformation.¹²

A zoom of the Raman spectra (Fig. 2(e)) of PF-RUB in solution and thin film on SiO_2 in pristine stage shows one peak at $\tilde{\nu} \sim 1315 \text{ cm}^{-1}$ which has a slight shoulder at $\tilde{\nu} \sim 1325 \text{ cm}^{-1}$. We can identify this peak with a corresponding peak in the computed twisted conformation at 1315 cm^{-1} . The second peak at roughly 1335 cm^{-1} appearing in the theoretical model is obviously strongly suppressed and reduced to a shoulder in the experimental spectra. For the spectra on the SAM and on SiO_2 in late stage, we observe an additional peak e_1 at 1299 cm^{-1} which is near to a computed peak of the planar conformation at 1295 cm^{-1} . Further Raman peaks around 1525 cm^{-1} and 1580 cm^{-1} also coincide roughly with peaks predicted by the computed model. Deviations between computed and measured Raman frequencies remain within the typical scatter of calculated modes obtained with the B3LYP hybrid functional with respect to observed values.

Comparing the Raman spectra of the pristine thin film on SiO_2 with the solution spectra reveals an essentially identical spectrum (Figs. 2(b), 2(e), and 2(f)). This evidences that also in pristine thin films deposited on native silicon, the PF-RUB molecules in the twisted molecular conformation prevail and are most likely disordered. Analogously, the IR spectrum of the PF-RUB thin film on SiO_2 in the pristine stage is similar to the solution spectrum, albeit including a notable peak broadening for the thin film spectrum.

The IR and Raman spectra of PF-RUB molecules deposited on SiO₂ in the late stage and on the SAM show slightly different signatures than the solution or pristine thin film spectra. The peak intensity observed in the IR spectra corresponding to the positions c₄ and d₁-d₃ is less pronounced than for the solution, and both pristine thin film spectra and the peak separation between c₂ and c₃ are different. A reason for this could be the presence of a fraction of molecules with a planar tetracene backbone.^{21,22}

B. Molecular conformation

In order to quantify the ratio of planar and twisted molecules in the respective samples, we perform a more detailed analysis including a decomposition of the spectra of the PF-RUB thin films deposited on SAM ($SAM(\tilde{\nu})$) and on SiO₂ in the late stage ($SIL(\tilde{\nu})$). If the experimental spectra consist of molecules with a fraction α in the planar conformation and another fraction β in the twisted conformation, which have different vibrational modes $A(\tilde{\nu})$ and $B(\tilde{\nu})$, respectively, the experimental spectra $SIL(\tilde{\nu})$ and $SAM(\tilde{\nu})$ are supposed to be a linear combination of both of them. Following this idea, we can describe the spectra of $SIL(\tilde{\nu})$ and $SAM(\tilde{\nu})$ in terms of the basis spectra $A(\tilde{\nu})$ and $B(\tilde{\nu})$ that correspond to the modes of purely planar and purely twisted conformations, respectively,

$$\begin{pmatrix} SIL(\tilde{\nu}) \\ SAM(\tilde{\nu}) \end{pmatrix} = \begin{pmatrix} \alpha_1 & \beta_1 \\ \alpha_2 & \beta_2 \end{pmatrix} \begin{pmatrix} A(\tilde{\nu}) \\ B(\tilde{\nu}) \end{pmatrix}. \quad (1)$$

On the other hand, the basis spectra $A(\tilde{\nu})$ and $B(\tilde{\nu})$ can be found by inversion of the matrix in Eq. (1),

$$\begin{pmatrix} A(\tilde{\nu}) \\ B(\tilde{\nu}) \end{pmatrix} = \frac{1}{\alpha_1\beta_2 - \alpha_2\beta_1} \begin{pmatrix} \beta_2 & -\beta_1 \\ -\alpha_2 & \alpha_1 \end{pmatrix} \begin{pmatrix} SIL(\tilde{\nu}) \\ SAM(\tilde{\nu}) \end{pmatrix}, \quad (2)$$

which is practically a projection of the spectra $SIL(\tilde{\nu})$ and $SAM(\tilde{\nu})$ onto each other. Note that Eqs. (1) and (2) effectively depend on only two parameters, since the total number of molecules, N , is identical for both films ($\alpha_i + \beta_i = N$) simultaneously deposited. For the same set of parameters ($\alpha_1/N = 0.79$, $\beta_1/N = 0.21$, $\alpha_2/N = 0.32$, and $\beta_2/N = 0.68$), we find basis spectra $A(\tilde{\nu})$ and $B(\tilde{\nu})$ both for IR and for Raman under the constraint that different peaks in $A(\tilde{\nu})$ and $B(\tilde{\nu})$ become minimized but not negative, compare Fig. 3.

Remarkably, a comparison of the IR basis spectra $A(\tilde{\nu})$ and $B(\tilde{\nu})$ with the computed spectra for the planar (C_{2h}) and twisted (D_2) conformations of the free PF-RUB molecule (Figs. 3(a), 3(c), and 3(d)) reveals a very good agreement. From this finding, we conclude that the modeled molecular geometries must be very close to the real conformations of the molecules. Obviously, basis $A(\tilde{\nu})$ corresponds to the planar conformation and basis $B(\tilde{\nu})$ to the twisted conformation, respectively. Analogously, the Raman basis spectrum $B(\tilde{\nu})$ coincides very well with the solution (and the pristine thin film on SiO₂) spectrum of PF-RUB, which is supposed to originate essentially from twisted molecules. Note that the Raman peaks of basis $B(\tilde{\nu})$ appear sharper than in the solution spectrum, while maintaining the same peak area. An overview over the most important vibrational peaks is given in Table II.

This implies the following: (i) We can identify and assign the IR and Raman spectra of basis $A(\tilde{\nu})$ and $B(\tilde{\nu})$ to planar and twisted PF-RUB molecules, respectively. (ii) The intensity ratio of the basis spectra $A(\tilde{\nu})$ and $B(\tilde{\nu})$ can be associated with the fraction of planar to twisted molecules in the thin films. According to the values found for α_i and β_i , the ratio of planar:twisted PF-RUB molecules in the thin film deposited on bare SiO₂ in the late stage corresponds to ~4:1 ($SIL(\tilde{\nu})$), whereas on SAM/SiO₂ ($SAM(\tilde{\nu})$), this ratio changes to ~1:2.

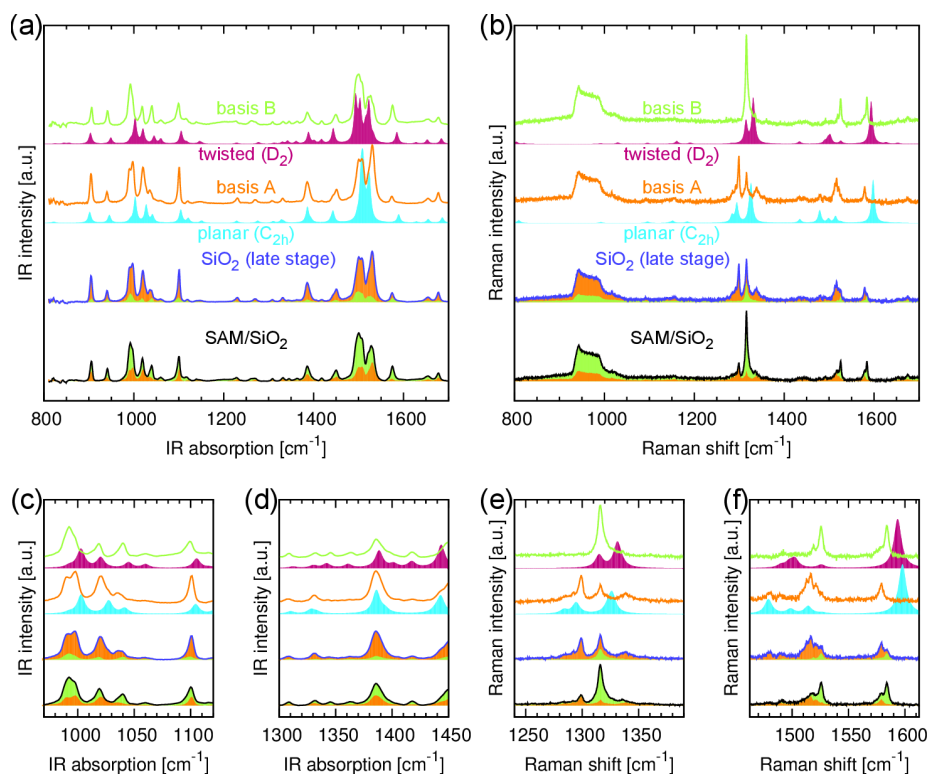


FIG. 3. Decomposition of IR ((a), (c), and (d)) and Raman ((b), (e), and (f)) spectra of PF-RUB on SiO₂ in the late stage (blue line) and on SAM (black line) into basis spectra basis $A(\tilde{\nu})$ (orange line) and basis $B(\tilde{\nu})$ (green line). While for IR, basis $A(\tilde{\nu})$ agrees very well with the computed spectrum for the planar conformation (cyan, filled curve) and basis $B(\tilde{\nu})$ corresponds to the computed spectrum for the twisted conformation (purple, filled curve). The Raman basis $B(\tilde{\nu})$ resembles the solution spectrum of PF-RUB (Fig. 2(b)) with slightly sharpened peaks.

TABLE II. Detailed overview over the most prominent experimentally observed IR and Raman peaks of the basis spectra $A(\tilde{\nu})$ and $B(\tilde{\nu})$ in association with the computed IR and Raman modes for the two isomers (C_{2h} and D_2 geometries) considered for the free PF-RUB molecule. Observed peaks have strong (s) or medium (m) intensity. The energies of the computed modes are multiplied by 0.9915. Raman intensities are normalized to the strongest mode of the respective isomer.

Vibrational mode C _{2h}		IR			Raman			Vibrational mode D ₂		IR			Raman		
		Computed mode	Basis A		Computed mode	Basis A				Computed mode	Basis B		Computed mode	Basis B	
			Intensity (km/mol)	$\tilde{\nu}$ (cm ⁻¹)		Intensity m, s	Intensity $\propto$				$\tilde{\nu}$ (cm ⁻¹)	Intensity m, s		Intensity (km/mol)	$\tilde{\nu}$ (cm ⁻¹)
$\tilde{\nu}$ (cm ⁻¹)	Symmetry														
214.3	A _g				0.04	215	m	169.9	A				0.01	236	m
								207.9	A			0.04	244	m	
								289.0	A			0.07	284	m	
								377.3	A			0.05	398	m	
								394.5	A			0.03	405	m	
476.9	A _g				0.12	486	m	467.0	A			0.13	463	s	
901.9	A _u	247	905	s				903.4	B ₃	247	906	s			
945.5	B _u	176	940	s				948.8	B ₁	137	941	s			
992.3	A _u	48	990	s											
1002.9	B _u	578	998	s											
1027.4	A _u	395	1020	s				1003.0	B ₂	529	992	s			
1041.5	B _u	163	1035	m				1020.3	B ₃	314	1019	s			
								1045.0	B ₁	168	1040	s			
								1060.1	B ₂	110	1060	m			
1104.4	A _u	296	1101	s				1105.3	B ₃	290	1099	s			
1121.0	B _u	101	1120	m											
1228.8	A _u	48	1230	m											
1275.5	A _u	47	1270	m				1277.4	B ₃	37	1261	m			
1283.8	A _g				0.16	1285	m								
1294.6	A _g				0.44	1299	s								
1310.1	B _u	35	1308	m				1312.2	B ₁	22	1309	m			
1322.4	A _g				0.19	1316	s	1330.4	B ₃	39	1332	m			
1326.4	A _g				0.82	1339	s	1331.1	A				0.99	1316	s
1328.2	A _u	63	1331	m				1334.2	A				0.12	1336	m
								1342.0	B ₁	67	1345	m			
								1361.0	B ₂	53	1363	m			
1386.1	A _u	355	1386	s				1388.5	B ₃	261	1386	s			
								1417.4	B ₂	89	1418	m			
1443.1	A _u	258	1450	s				1443.5	B ₃	327	1449	s			
1479.0	A _g				0.29	1480	m	1493.3	B ₁	948	1500	s			
1506.0	B _u	1022	1501	s				1502.4	A				0.18	1519	m
1510.3	B _u	1051	1507	s				1503.5	B ₂	694	1507	s			
1514.2	A _g				0.15	1516	s	1515.4	B ₂	290	1521	s			
1522.9	A _u	303	1522	s				1523.1	B ₃	855	1527	s			
1524.5	A _u	670	1531	s				1526.0	A				0.07	1526	s
1526.6	A _g				0.02	1521	s	1533.3	B ₃	112	1533	s			

TABLE II. (Continued.)

IR				Raman				IR				Raman			
Vibrational mode C _{2h}		Computed mode	Basis A	Basis A		Computed mode		Basis B		Computed mode		Basis B		Computed mode	
$\tilde{\nu}$ (cm ⁻¹)	Symmetry	Intensity (km/mol)	$\tilde{\nu}$ (cm ⁻¹)	Intensity m, s	$\tilde{\nu}$ (cm ⁻¹)	Intensity α	$\tilde{\nu}$ (cm ⁻¹)	Intensity m, s	$\tilde{\nu}$ (cm ⁻¹)	Intensity (km/mol)	$\tilde{\nu}$ (cm ⁻¹)	Intensity m, s	$\tilde{\nu}$ (cm ⁻¹)	Intensity α	$\tilde{\nu}$ (cm ⁻¹)
1589.2	B _u	184	1574	m	1585.2	1.00	1579	s	1576	259	1576	s	1584	1.00	1584
1597.8	A _g				1593.6								1653	0.03	1653
1654.4	A _u	63	1654	m	1627.0					75	1654	m			
1686.4	A _u	124	1677	s	1652.6						1677	m	1675	0.02	1675
					1652.9					85					
					1684.6										

Remarkably, the substrate apparently influences the molecular conformation still over a long distance, i.e., through the entire thin film with a thickness of 100 nm. This behavior is unexpected, since molecular interactions act on a much shorter length scale.

C. Thin film morphology

Fig. 4 shows an atomic force microscope (AFM) picture of a representative area of the sample with PF-RUB deposited on SiO₂ in the late stage and on SAM. The sample with PF-RUB deposited on SiO₂ in the late stage reveals a large surface roughening of $\sigma = 35$ nm. This is different for the pristine thin film deposited on SiO₂, which is very smooth with $\sigma < 1$ nm (not shown).^{43,53} The PF-RUB film on SAM exhibits a very different surface morphology.³² Most of the sample is covered with a coarse-grained pattern, which under the AFM turns out to consist of steep islands with a height of 200–300 nm and a diameter of up to 5 μ m. Between these islands, there is no or only a very thin film coverage, probably only a wetting layer. Within the coarse-grained pattern, we observe several even bigger grains (height up to 2 μ m) that are surrounded by an emptied feeding zone.

In a further step, we analyze microscopically resolved Raman imaging spectra of the sample with PF-RUB deposited on SAM and on SiO₂ in the late stage. Fig. 5 shows optical microscopy and Raman imaging pictures of the samples. The optical microscopy picture of PF-RUB on SiO₂ (Figs. 5(a) and 5(c)) shows a mostly homogeneous surface, with few differently patterned speckles of 5–20 μ m in diameter. For the sample on the SAM, we find islands as observed in the AFM picture. In order to obtain information about the local molecular conformation and a possible correlation with the morphology, we provide a zoom (red square) into the optical microscopy pictures for both substrates, where we performed Raman imaging. The Raman region of 1250–1400 cm⁻¹ is modeled with several Lorentzians, so the empirically found Raman signature of the twisted and planar conformations can be described. After that, each of the mapped spectra is fitted according to the intensities α_i and β_i for the modeled

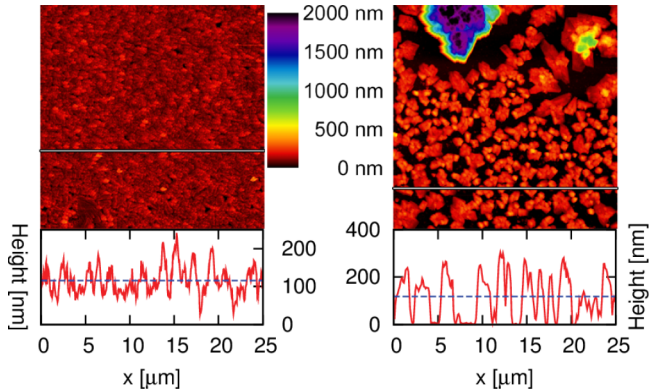


FIG. 4. Representative AFM picture of PF-RUB deposited on SiO₂ in the late stage (left) and on SAM (right). While the surface is roughened for the film on SiO₂ in the late stage, steep islands can be observed for the sample on the SAM. Both films have a thickness of ~ 100 nm and were deposited at the same time under the same conditions. The height profiles below the pictures follow the white line in the respective AFM acquisitions.

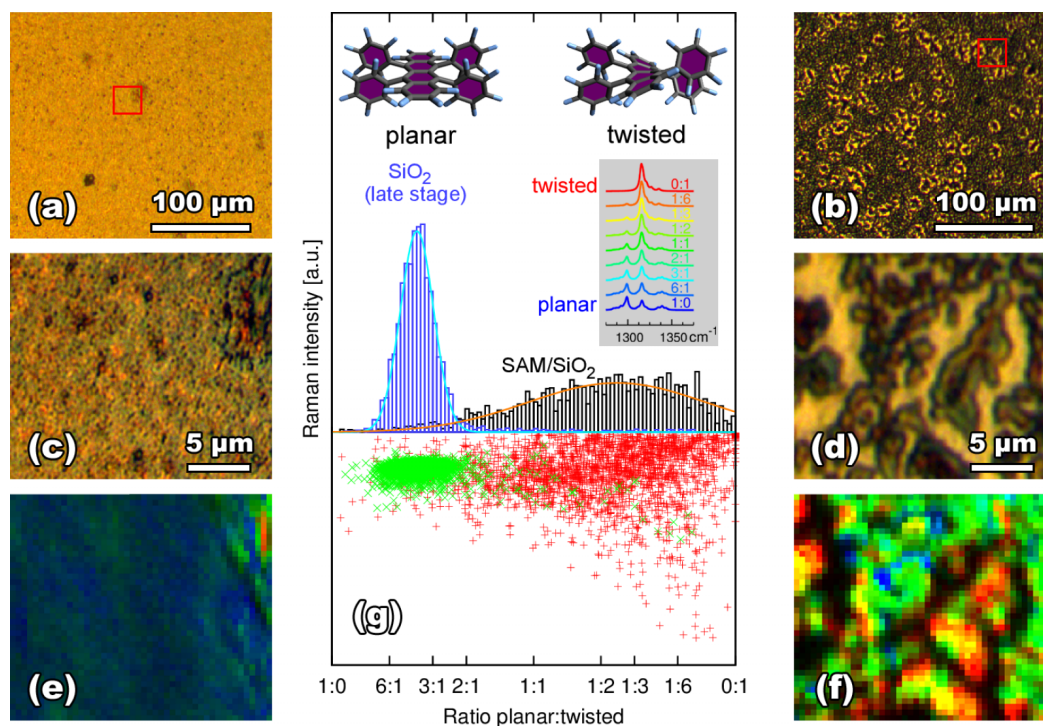


FIG. 5. Microscopic analysis of the distribution of the ratio of planar and twisted PF-RUB molecules in the film on SiO₂ (late stage) and on SAM/SiO₂. (a) and (b) Light microscope picture of PF-RUB on SiO₂ (late stage) and on SAM/SiO₂, respectively. Panels (c) and (d) provide a zoom into the region selected by a red frame in (a) and (b), respectively. (e) and (f) Raman imaging (matrix of 46 px × 40 px) pictures of the peak signature around 1320 cm⁻¹ of PF-RUB on SiO₂ (late stage) and on SAM/SiO₂, respectively. The images (e) and (f) correspond to the zoom of the light microscopy pictures, (c) and (d), respectively. While blue pixels stand for areas of purely planar molecules, red pixels visualize twisted molecules, and green regions are mixtures of both. (g) Evaluation of the Raman imaging pictures. The abscissa reports the fraction of twisted molecules assigned to a specific pixel of the Raman scans in (e) and (f), increasing linearly from left to right. While the distribution of the ratio of planar:twisted molecules of the sample in late stage (blue) is rather narrow, the histogram is broader for the sample on the SAM. Both histograms can be fitted well with a Gaussian. Green “x” and red “+” (bottom) represent the individual pixel intensities from the imaging of SiO₂ late stage and SAM/SiO₂, respectively, plotted on the negative y-axis. Gray box: color coding for the ratio of planar:twisted molecules as used for the imaging pictures.

signature of the twisted and planar conformations, respectively. The resulting fraction $(\alpha_i - \beta_i)/(\alpha_i + \beta_i)$ of the local parameters determines the color coding. While red, blue, and green stand for domains of purely twisted, purely planar, and mixed molecules, respectively, the pixel brightness corresponds to the overall Raman peak intensity $(\alpha_i + \beta_i)$ at a given spot i . As a result of the comparison of Raman imaging with the optical microscopy pictures, we find a correlation between the observed thin film morphology and the conformation of the molecules.

For the thin film deposited on SiO₂ in the late stage, we observe a sharp Gaussian distribution (FWHM = 0.16) with center around 4:1 for the planar:twisted ratio. There are only few speckles with 5–20 μm in diameter that show clear predominance of twisted molecules. This is in sharp contrast to the pristine film, where we observe exclusively molecules in twisted conformation (no imaging provided).

For the thin film on the SAM, we find that the bigger grains surrounded by a feeding zone mostly consist of twisted molecules (red). In contrast to the bigger grains, most of the coarse grained (smaller) islands contain more or less equally (green) blended regions of the two conformations. The ratio of the molecules in planar and twisted conformations follows a Gaussian distribution centered around 1:2, but with much bigger FWHM (0.88) than for the film on bare SiO₂ in the late stage.

Dewetting of RUB thin films is a well-known phenomenon, which is facilitated by the three-dimensional geometry of the molecule.^{24,54} Similarly to hydrogenated RUB, we find that free PF-RUB molecules with twisted backbone are energetically favored compared to the planarized isomer. While thin films of RUB are usually amorphous⁵³ and contain a majority of twisted molecules,⁸ RUB molecules in crystals nevertheless adopt a planar conformation due to a more efficient packing in the crystalline phase.^{24–27} This can be different for RUB derivatives, where crystallization of substituted RUB molecules with twisted molecular backbone has been observed recently.^{55,56} It has been shown that annealing of rubrene thin films on SiO₂^{43,57} or film growth on organics^{32,58,59} can help in parts to overcome the energy barrier needed for a reorientation of the RUB molecules and to stabilize the film by an increase in the degree of crystallization.²⁵

The PF-RUB thin film deposited on native SiO₂ is disordered and very smooth directly after growth, and nearly all molecules exhibit a twisted backbone.¹² Within 24 h after growth, we observe a dewetting of the film and approximately two-thirds of the molecules change their conformation to a planar backbone and the film roughens. In fact, the relatively low evaporation temperature of PF-RUB molecules from our Knudsen cell in comparison to RUB suggests that a reorientation of the PF-RUB molecules in the thin film is promoted already at RT without further annealing. Grazing incidence

X-ray diffraction (GIXD) measurements of these two PF-RUB thin films both on SiO₂ in late stage and on SAM suggest a polycrystalline structure of the thin films.⁶¹ This indicates that the driving force behind the planarization of the PF-RUB molecules occurring in the thin film on SiO₂ is most likely governed by an energy gain due to a more efficient crystal packing. However, directly after growth, the thin film on SAM already contains both conformations of the molecule forming stable clusters on a micrometer scale. Obviously, the SAM leads to a modification of the surface energy which enhances the diffusion of the PF-RUB molecules so that stable crystallite nuclei can be formed.

IV. CONCLUSION

In summary, we obtained both Raman and IR spectra of PF-RUB thin films on bare silicon wafers with native dioxide layer, SAM covered wafers, and in solution. We identified and assigned the experimental vibrational peaks in detail to computed modes of isomers with twisted and planar tetracene backbones. Moreover, we could show that not only particular vibrational modes of the experimental spectra correspond to either the twisted or planar conformation of the molecule but also we could decompose the experimental spectra into fractions derived from twisted and planar molecules. Using Raman imaging, we distinguished different regions of the thin films with respect to the ratio of planar and twisted molecules on a micrometer scale and found significant differences between PF-RUB on native silicon dioxide (SiO₂) and PF-RUB on SAM/SiO₂. The exploration of the vibrational properties of PF-RUB is of fundamental interest and will contribute to a more general understanding of the charge carrier mobility in fluorinated rubrene derivatives.

ACKNOWLEDGMENTS

We thank Y. Sakamoto and T. Suzuki for providing the material. We gratefully thank the bwGRiD project⁶⁰ for the computational resources. We thank A. Lange for introduction to the bwGRiD batch system and R. M. J. Jacobs for valuable advice on the IR setup. Financial support by the seventh framework programme (FP7) of the European Union and the DFG is gratefully acknowledged.

¹V. Podzorov, E. Menard, A. Borisov, V. Kiryukhin, J. A. Rogers, and M. E. Gershenson, *Phys. Rev. Lett.* **93**, 086602 (2004).

²V. C. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R. L. Willett, T. Someya, M. E. Gershenson, and J. A. Rogers, *Science* **303**, 1644 (2004).

³J. Takeya, M. Yamagishi, Y. Tominari, R. Hirahara, Y. Nakazawa, T. Nishikawa, T. Kawase, T. Shimoda, and S. Ogawa, *Appl. Phys. Lett.* **90**, 102120 (2007).

⁴J. Takeya, J. Kato, K. Hara, M. Yamagishi, R. Hirahara, K. Yamada, Y. Nakazawa, S. Ikehata, K. Tsukagoshi, Y. Aoyagi, T. Takenobu, and Y. Iwasa, *Phys. Rev. Lett.* **98**, 196804 (2007).

⁵H. Najafov, B. Lee, Q. Zhou, L. C. Feldman, and V. Podzorov, *Nat. Mater.* **9**, 938 (2010).

⁶P. Irkhin and I. Biaggio, *Phys. Rev. Lett.* **107**, 017402 (2011).

⁷B. Verreert, P. Heremans, A. Stesmans, and B. P. Rand, *Adv. Mater.* **25**, 5504 (2013).

⁸M. Kytka, A. Gerlach, J. Kováč, and F. Schreiber, *Appl. Phys. Lett.* **90**, 131911 (2007).

⁹S. Uttiya, L. Raimondo, M. Campione, L. Miozzo, A. Yassar, M. Moret, E. Fumagalli, A. Borghesi, and A. Sassella, *Synth. Met.* **161**, 2603 (2012).

¹⁰M. C. R. Delgado, K. R. Pigg, D. A. da Silva Filho, N. E. Gruhn, Y. Sakamoto, T. Suzuki, R. M. Osuna, J. Casado, V. Hernández, J. Teodomiro, L. Navarrete, N. G. Martinelli, J. Cornil, R. S. Sánchez-Carrera, V. Coropceanu, and J.-L. Brédas, *J. Am. Chem. Soc.* **131**, 1502 (2009).

¹¹S. Kera, S. Hosoumi, K. Sato, H. Fukagawa, S.-i. Nagamatsu, Y. Sakamoto, T. Suzuki, H. Huang, W. Chen, A. T. S. Wee, V. Coropceanu, and N. Ueno, *J. Phys. Chem. C* **117**, 22428 (2013).

¹²F. Anger, R. Scholz, E. Adamski, K. Broch, A. Gerlach, Y. Sakamoto, T. Suzuki, and F. Schreiber, *Appl. Phys. Lett.* **102**, 013308 (2013).

¹³A. Hinderhofer, U. Heinemeyer, A. Gerlach, S. Kowarik, R. M. J. Jacobs, Y. Sakamoto, T. Suzuki, and F. Schreiber, *J. Chem. Phys.* **127**, 194705(1) (2007).

¹⁴F. Anger, H. Glowatzki, A. Franco-Cañellas, C. Bürker, A. Gerlach, R. Scholz, Y. Sakamoto, T. Suzuki, N. Koch, and F. Schreiber, *J. Phys. Chem. C* **119**, 6769 (2015).

¹⁵T. Petrenko, O. Krylova, F. Neese, and M. Sokolowski, *New J. Phys.* **11**, 015001 (2009).

¹⁶A. Troisi, *Adv. Mater.* **19**, 2000 (2007).

¹⁷D. A. da Silva Filho, E.-G. Kim, and J.-L. Brédas, *Adv. Mater.* **17**, 1072 (2005).

¹⁸A. Girlando, L. Grisanti, M. Masino, I. Bilotti, A. Brillante, R. G. Della Valle, and E. Venuti, *Phys. Rev. B* **82**, 035208 (2010).

¹⁹E. Venuti, I. Bilotti, R. G. Della Valle, A. Brillante, P. Ranzieri, M. Masino, and A. Girlando, *J. Phys. Chem. C* **112**, 17416 (2008).

²⁰M. Fischer, M. Dressel, B. Gompf, A. K. Tripathi, and J. Pflaum, *Appl. Phys. Lett.* **89**, 182103 (2006).

²¹A. S. Paraskar, A. R. Reddy, A. Patra, Y. H. Wijsboom, O. Gidron, L. J. W. Shimon, G. Leitius, and M. Bendikov, *Chem.-Eur. J.* **14**, 10639 (2008).

²²D. Käfer, L. Ruppel, G. Witte, and C. Wöll, *Phys. Rev. Lett.* **95**, 166602 (2005).

²³S. Duhm, Q. Xin, S. Hosoumi, H. Fukagawa, K. Sato, N. Ueno, and S. Kera, *Adv. Mater.* **24**, 901 (2012).

²⁴D. Käfer and G. Witte, *Phys. Chem. Chem. Phys.* **7**, 2850 (2005).

²⁵L. Huang, Q. Liao, Q. Shi, H. Fu, J. Mab, and J. Yao, *J. Mater. Chem.* **20**, 159 (2010).

²⁶T. Matsukawa, M. Yoshimura, M. Uchiyama, M. Yamagishi, A. Nakao, Y. Takahashi, J. Takeya, Y. Kitaoka, Y. Mori, and T. Sasaki, *Jpn. J. Appl. Phys.* **49**, 085502 (2010).

²⁷M. E. Helou, O. Medenbach, and G. Witte, *Cryst. Growth Des.* **10**, 3496 (2010).

²⁸M. Kytka, L. Gisslen, A. Gerlach, U. Heinemeyer, J. Kováč, R. Scholz, and F. Schreiber, *J. Chem. Phys.* **130**, 214507 (2009).

²⁹C. H. Choi and M. Kertesz, *Macromolecules* **30**, 620 (1997).

³⁰C. H. Choi, M. Kertesz, M.-I. Boyer, M. Cochet, S. Quillard, G. Louarn, and S. Lefrant, *Chem. Mater.* **11**, 855 (1999).

³¹Z. Li, J. Du, Q. Tang, F. Wang, J.-B. Xu, J. C. Yu, and Q. Miao, *Adv. Mater.* **22**, 3242 (2010).

³²C. H. Hsu, J. Deng, C. R. Staddon, and P. H. Beton, *Appl. Phys. Lett.* **91**, 193505 (2007).

³³C. Zhang, C. Du, H. Yan, S. Yuan, and L. Chi, *RSC Adv.* **3**, 15404 (2013).

³⁴T. Breuer, M. A. Celik, P. Jakob, R. Tonner, and G. Witte, *J. Phys. Chem. C* **116**, 14491 (2012).

³⁵F. Schreiber, *Prog. Surf. Sci.* **65**, 151 (2000).

³⁶F. Schreiber, *J. Phys.: Condens. Matter* **16**, R881 (2004).

³⁷G. Witte and C. Wöll, *J. Mater. Res.* **19**, 1889 (2004).

³⁸F. Schreiber, *Phys. Status Solidi A* **201**, 1037 (2004).

³⁹Z. Q. Ren, L. E. McNeil, S. Liu, and C. Kloc, *Phys. Rev. B* **80**, 245211 (2009).

⁴⁰*Infrared and Raman Spectra of Polyatomic Molecules*, edited by G. Herzberg (D. Van Nostrand Company, Inc., Princeton, New Jersey, New York, 1945).

⁴¹T. K. Mullenbach, K. A. McGarry, W. A. Luhman, C. J. Douglas, and R. J. Holmes, *Adv. Mater.* **25**, 3689 (2013).

⁴²P. Irkhin, A. Rysanyanskiy, M. Koehler, and I. Biaggio, *Phys. Rev. B* **86**, 085143 (2012).

⁴³S.-W. Park, J.-M. Choi, K. H. Lee, H. W. Yeom, S. Im, and Y. K. Lee, *J. Phys. Chem. B* **114**, 5661 (2010).

⁴⁴R. J. Thompson, B. Yadin, Z. J. Grout, S. Hudziak, C. L. Kloc, O. Mitrofanov, and N. J. Curson, *Appl. Phys. Lett.* **98**, 053302 (2011).

- ⁴⁵TURBOMOLE V6.4 2012, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; Available from <http://www.turbomole.com>.
- ⁴⁶Y. Yamakita, J. Kimura, and K. Ohno, *J. Chem. Phys.* **126**, 064904 (2007).
- ⁴⁷U. Heinemeyer, R. Scholz, L. Gisslén, M. I. Alonso, J. O. Ossó, M. Garriga, A. Hinderhofer, M. Kytka, S. Kowarik, A. Gerlach, and F. Schreiber, *Phys. Rev. B* **78**, 085210 (2008).
- ⁴⁸P. A. Temple and C. E. Hathaway, *Phys. Rev. B* **7**, 3685 (1973).
- ⁴⁹R. Scholz, L. Gisslén, B.-E. Schuster, M. B. Casu, T. Chassé, U. Heinemeyer, and F. Schreiber, *J. Chem. Phys.* **134**, 014504 (2011).
- ⁵⁰O. Treutler and R. Ahlrichs, *J. Chem. Phys.* **102**, 346 (1995).
- ⁵¹K. Eichkorn, F. Weigend, O. Treutler, and R. Ahlrichs, *Theor. Chem. Acc.* **97**, 119 (1997).
- ⁵²L. Cuff and M. Kertesz, *Macromolecules* **27**, 762 (1994).
- ⁵³S. Kowarik, A. Gerlach, S. Sellner, F. Schreiber, J. Pflaum, L. Cavalcanti, and O. Kononov, *Phys. Chem. Chem. Phys.* **8**, 1834 (2006).
- ⁵⁴P. R. Ribič and G. Bratina, *Surf. Sci.* **602**, 1368 (2008).
- ⁵⁵M. Mamada, H. Katagiri, T. Sakanoue, and S. Tokito, *Cryst. Growth Des.* **15**, 442 (2015).
- ⁵⁶K. A. McGarry, W. Xie, C. Sutton, C. Risko, Y. Wu, V. G. Young, J.-L. Brédas, C. D. Frisbie, and C. J. Douglas, *Chem. Mater.* **25**, 2254 (2013).
- ⁵⁷M. Nothaft and J. Pflaum, *Phys. Status Solidi B* **245**, 788 (2008).
- ⁵⁸L. Raimondo, E. Fumagalli, M. Moret, M. Campione, A. Borghesi, and A. Sassella, *J. Phys. Chem. C* **117**, 13981 (2013).
- ⁵⁹E. Fumagalli, M. Campione, L. Raimondo, A. Sassella, M. Moret, L. Barba, and G. Arrighetti, *J. Synchrotron Radiat.* **19**, 682 (2012).
- ⁶⁰bwGRiD (<http://www.bw-grid.de>), member of the German D-Grid initiative, funded by the Ministry for Education and Research (Bundesministerium für Bildung und Forschung) and the Ministry for Science, Research, and Arts Baden-Württemberg (Ministerium für Wissenschaft, Forschung und Kunst Baden-Württemberg).
- ⁶¹See supplementary material at <http://dx.doi.org/10.1063/1.4922052> for grazing incidence X-ray diffraction measurements.