

Mesoscale Dynamics and Cooperativity of Networking Dendronized Nonlinear Optical Molecular Glasses

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ABSTRACT

First, molecular scale insight into the mobility of a novel class of organic materials for photonic applications with electro-optical activities larger than 300 pm/V is presented. A representative second order nonlinear optical (NLO) material of this class of self-assembling molecular glasses involving quadrupolar phenyl-perfluorophenyl (Ph-Ph^F) interactions is analyzed based on its molecular relaxation phenomena and phase behavior. Thereby, a new and straightforward nanoscale methodology, involving shear modulation force microscopy and intrinsic friction analysis is introduced. It provides both the submolecular enthalpic and entropic dynamics in nanoconstrained systems (e.g., ultrathin films), and thus, insight into local motion of single molecules due to dissociation of Ph-Ph^F pairs as well as the cooperative dynamics of the assembled network. This nanoscale model-independent thermomechanical methodology is shown to be very effective in fundamentally evaluating appropriate poling conditions of organic NLO materials. It promises to be a straightforward analysis tool to guide organic material synthesis from a molecular mobility perspective, particularly for applications that impose nanoscale constraints on the system.

Organic second order nonlinear optical (NLO) materials have shown great potential in photonic applications, such as electro-optical (EO) modulators and frequency-doubling devices, particularly because the electro-optical activity was raised with self-assembled molecular glasses beyond the 300 pm/V mark¹ (Figure 1). With such high EO activity, organic NLO materials significantly exceeded the EO properties of inorganic material, LiNbO₃, currently used for commercial modulator products. The availability of such high EO coefficients enables not only unprecedented performance in conventional device formats, but also the development of new devices such as hybrid modulators and EO polymers integrated with silicon photonics. As an example, a Mach–Zehnder waveguide modulator operation with a half wave voltage of less than 1.0 V, the lowest ever realized, has been recently achieved with organic NLO materials.² On the basis of these recent breakthroughs, a wide range of photonic system applications from external modulators in digital WDM systems, analog modulators for phased array radars and photonic analog/digital converters, to phase modulators for optical gyroscopes are expected to evolve in the near future using organic NLO materials.

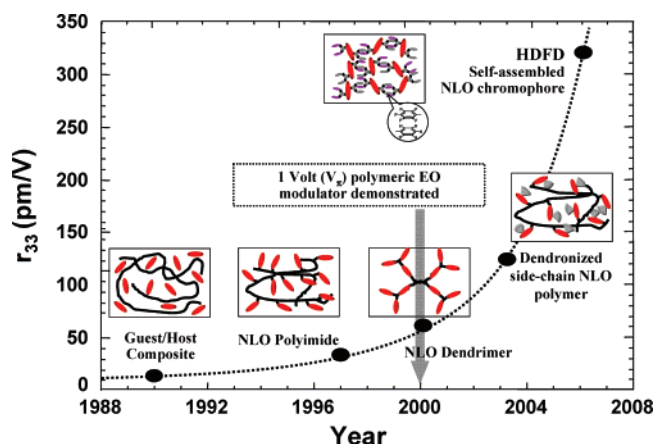


Figure 1. Historical snapshot of the increase of the EO activity (r_{33}) in organic NLO materials.

This remarkable increase in EO activity is attributed to a new class of NLO materials of self-assembling molecular glasses involving quadrupolar phenyl-perfluorophenyl (Ph-Ph^F) interactions. Although self-assemblies from Ph-Ph^F interactions have been reasonably well known in materials chemistry for many years and employed for optoelectronic and liquid crystalline materials,^{3–7} their use in NLO materials has just recently occurred. HFD (with HD for Ph-dendrimer and FD for Ph^F-dendrimer), the most basic representative of

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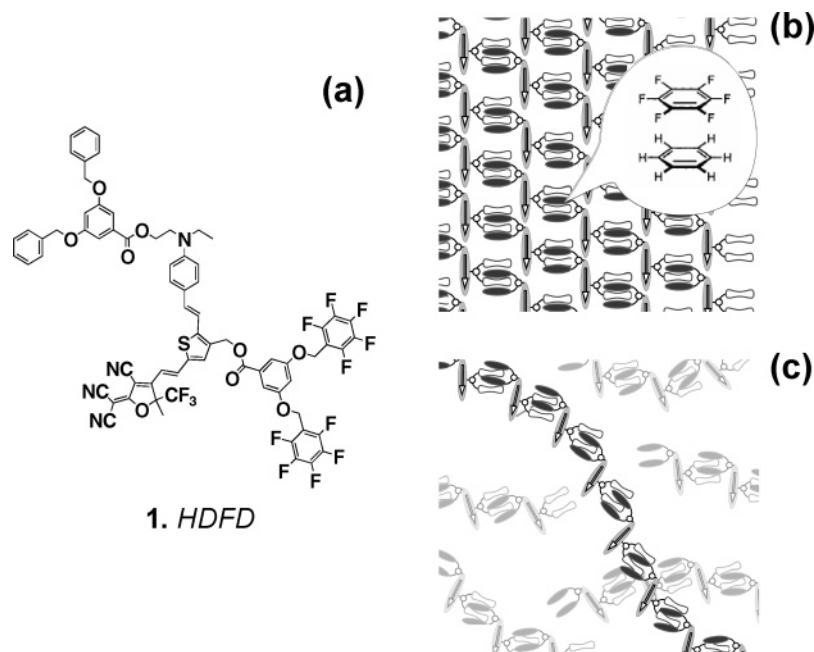


Figure 2. (a) HDFD, a glass-forming chromophore containing a molecule with phenyl and pentafluorophenyl rings incorporated as peripheral dendrons on the π -bridge and the donor-end of the chromophores.¹ (b) Idealized crystalline assembly visualizing compact stacking of the Ph and Ph^F moieties. (c) Realistic “polymerized” self-assembly networking model.

this new class of self-assembling NLO materials,¹ takes advantage of the strong affinity between phenyl (Ph) and perfluorophenyl (Ph^F) moieties, which form face-to-face Ph-Ph^F stacks of alternating hydrocarbon and perfluorinated moieties due to their complementary quadrupole moments.^{8,9} Both Ph and Ph^F moieties are integrated in second generation Frechét-type dendrimers, which then are incorporated as peripheral dendrons on the π -bridge and the donor-end of the NLO chromophores to allow the chromophores to form an ordered network, as illustrated in Figure 2.

As for self-assembled NLO molecular glasses and other advanced multifunctional materials that are composed of intricate molecular building blocks, the challenge is to deduce meaningful molecular scale mobility information to understand the complex relaxation and phase behavior. In the case of organic NLO materials, this is crucial, as the critical processes of achieving a robust acentric alignment strongly depends on the availability of inter- and intramolecular mobilities outside the temperature range of the device operation window. Here, we introduce a nanoscale methodology based on scanning probe microscopy (SPM) that provides direct insight into structural relaxations of NLO molecular glasses that self-assemble due to quadrupolar phenyl-perfluorophenyl (Ph-Ph^F) interactions. This methodology shows great potential to direct material design of sophisticated macromolecules, composites, and nanomaterials in emerging technologies. Furthermore, it provides a means by which the mesoscale dynamics and cooperativity involved in relaxation processes can be captured and quantified in terms of dynamic entropy and enthalpy.

The quest for fundamental material property information is often a question of the availability of appropriate tools to perform the measurements. Phenomenological physical prop-

erty experiments hardly reveal the subtle and distinctive differences in local properties and their process relationships, and mere chemical analysis methods provide an incomplete picture of dynamic processes and constraints. Dealing with organic or biological systems makes us particularly aware of the subtle but important differences. Weak interactions with bonding strengths small compared to kT are of immense importance as they dictate local mobilities. As such, one has to consider to what degree these processes are cooperative on a molecular scale. Highly cooperative phenomena, as those found in glass-forming processes, exhibit unusually large apparent activation energies of up to 100 kcal/mol that are indicative of a high degree of complexity in the motion associated with the relaxation.¹⁰ While noncooperative processes are described in terms of the dynamic enthalpy ΔH^* alone, cooperative processes also include the dynamic entropy, ΔS^* , as given by the activation Gibbs free energy

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (1)$$

As an example, noncooperative side chain polymer relaxations are well described by the dynamic enthalpy with near zero dynamic entropy, while polymer backbone relaxations, observed above the glass transition, are highly cooperative in nature.¹¹ Such weak interactions play an important role in self-assembled NLO molecular glasses.

Figure 2a provides the chemical structure of HDFD. On the basis of the quadrupolar Ph-Ph^F interaction and a measured ultrahigh EO activities of over 300 pm/V,¹ one is tempted to visualize the self-aggregation processes as highly ordered (Figure 2b). However, X-ray analysis indicates that the structure is amorphous. Thus, the orientational stability

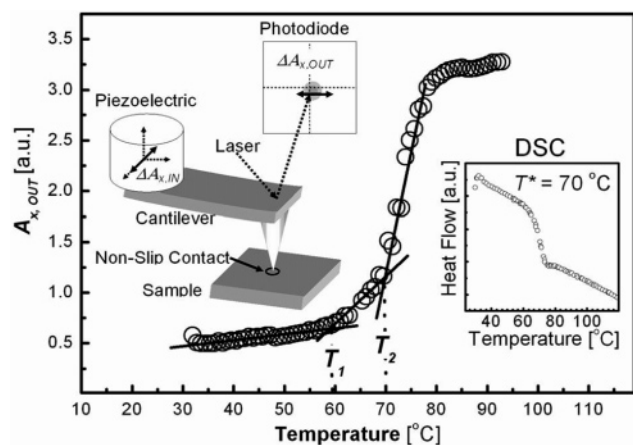


Figure 3. TM temperature profile of a 340 nm thick HDFD film on ITO exhibiting two transitions at T_1 and T_2 . Left inset: Principle of SM-FM. Right inset: DSC thermogram of HDFD.

in this system originates from a mesoscale structural alignment, that is, a networking system that resembles a polymer chain (Figure 2c). The obtained high acentric order of the chromophores after electric field poling suggests a network system that, contrary to conventional polymers, is highly temperature susceptible. Chains can be either broken, reconnected, or can form new connections under appropriate temperature conditions. This highly complex dynamic system exhibits intermolecular relaxations with enthalpic activation barriers and cooperative phenomena. To investigate the subtle dynamics and energetics of the HDFD condensed phases, we utilized a microscopic methodology involving SPM wherein the SPM cantilever is used (1) as a thermomechanical (TM) sensor to detect critical temperature transition values and (2) to record the energetics of inter- and intramolecular mobilities within distinct equilibrium phases.

A TM temperature profile of a 340 nm thick film (50 °C annealed and vacuum-dried for 12 h) of HDFD is provided along with a differential scanning calorimetry (DSC) thermogram in Figure 3. HDFD was spin-cast onto indium tin oxide (ITO)-coated glass substrates from a filtered 5% HDFD solution dissolved in 1,1,2-trichloroethane. The $A_{x,OUT}$ signal in the TM temperature profile represents the shear modulation response to a sinusoidal mechanical disturbance (1–10 nm) of the HDFD surface by a non-scanning SPM tip held at constant load (10–100 nN). This analysis method, also referred to as shear modulation force microscopy (SM-FM),^{12–14} is depicted in the inset of Figure 3. The probing tip is laterally modulated with a “no-slip” nanometer amplitude, $A_{x,IN}$. The modulation response, $A_{x,OUT}$, is analyzed using a two-channel lock-in amplifier, comparing the response signal to the input signal. The modulation response is a measure of the contact stiffness,¹⁴ and therefore thermally activated transitions in the material can be determined from “kinks” in the response curve, as found in for HDFD in Figure 3. SM-FM, as with any scanning probe microscopy-based method, is highly surface sensitive with subsurface information playing a role to a maximum depth of a few tens of nanometers. For homogeneous organic systems, such as HDFD, near surface thermomechanical properties were found to be in good correspondence with bulk measure-

ments.¹⁵ In polymers, phase relaxations are indicative of side-chain relaxations (secondary transitions) or backbone relaxations (glass transition). In contrast to polymer systems, this study revealed that for HDFD molecular self-assembling glasses, the thermal transitions pinpoint bond formations and multiscale coordination (assembly or order–disorder transitions).

The TM profile exhibits three temperature regimes separated by the transition temperatures $T_1 = 59 \pm 2$ °C and $T_2 = 70 \pm 2$ °C. Note, the second transition corresponds to the transition at $T^* = 70 \pm 3$ °C observed in the DSC analysis at a 10 °C/min of heating rate under nitrogen (Figure 3 inset) and is the only one of the two detectable with this classical thermoanalytical heat capacitance method. All heating cycles during the DSC analysis exhibited an amorphous behavior of HDFD, that is, no melting peaks were observed. This result is in agreement with our X-ray diffraction analysis of spin-coated HDFD films. The HDFD films showed a thermodynamically stable amorphous state above T_2 up to the decomposition temperature of around 200 °C.

To obtain information about molecular mobilities within the three distinct equilibrium phases described by the TM profile in Figure 3, we employed a thermomechanical spectroscopic sliding method that is referred to in the literature as intrinsic friction analysis (IFA).^{16,17} It is based on the well-established lateral force microscopy that has demonstrated a probing sensitivity down to the subnanometer scale.^{17–19} IFA probes the interaction of condensed material phases with a velocity-dependent external mechanical lateral stress-field on the nanoscale. The local isothermal stress response, that is, the friction force $F_F(v)|_T$ provides a thermomechanical spectrum that originates from thermal fluctuations within the sample. Thermal fluctuations generally arise from the reorientation of individual molecules or from rotations of submolecular units and are strongly dependent on the relaxation mechanism. Like dielectric resonance spectroscopy (DRS) and contrary to conventional spectroscopy methods such as vibrational spectroscopy and NMR, we will show here that IFA is directly sensitive to cooperative phenomena caused by intermolecular interactions.

The friction isotherms $F_F(v)|_T$ are treated based on the theory of time–temperature equivalence.^{20,21} All isotherm curves are superimposed to an arbitrary reference isotherm by shifting them with horizontal distances $\ln(a_T)$, where a_T is the thermal shift factor (Figure 4a). We found that in the case of purely enthalpic isolated relaxation process with well-defined activation barriers, for example, phenyl side-chain relaxations in polystyrene,¹⁶ horizontal shifts suffice to generate a master curve. In the case of coupled processes that contain a cooperative entropic energy component, vertical shifts also have to be undertaken to superimpose the spectra to a single master curve, as depicted in Figure 4a with the force shift ΔF_F . Figure 4b shows the resulting master curve for HDFD after appropriate horizontal and vertical shifting.

The master curve of Figure 4b involved three sets of thermal shift factors. The transition temperatures at $T_1 = 59$ °C and $T_2 = 70$ °C, obtained by SM-FM (Figure 3), made it apparent that horizontal shifts had to be undertaken

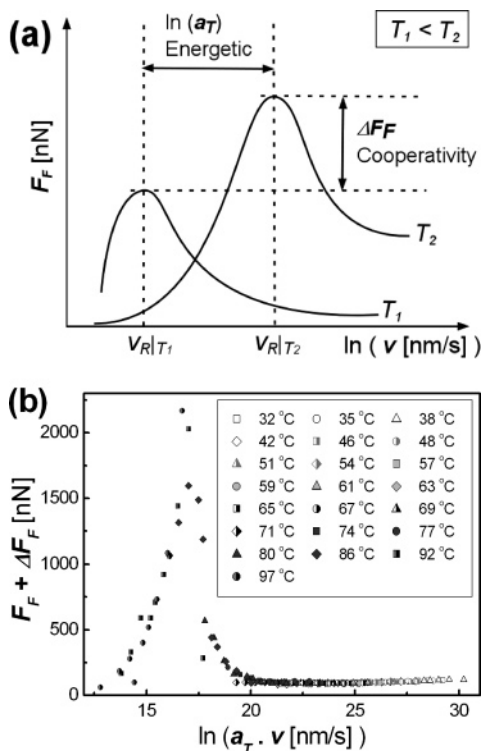


Figure 4. (a) IFA loss curve analysis with decoupled energetic (enthalpic) and cooperative (entropic) contributions. (b) HDFD $F_F(v)$ isotherms superimposed with vertical and horizontal shifts to a single master curve.

separately within these boundaries of phase/structural equilibrium. The master curve was finally established by shifting vertically where necessary.

While horizontal shifts provide insight into the energetics, vertical shifts offer a way to quantify the degree of cooperativity. In Figure 5a, the lateral time–temperature-shift factor, a_T , supplies three apparent activation energies of 23, 44, and 71 kcal/mol. The degree of vertical shifting, that is, the degree of cooperativity is inferred from Figure 5b. The onset of vertical shifting, that is, the deviation from a purely enthalpic process, corresponds to the first transition at T_1 and is significantly enhanced above the second transition at T_2 . Thus, the energy values above T_1 of 44 and 71 kcal/mol contain entropic energy contributions that are caused by cooperative effects.

To evaluate the entropic energy contribution, we employ a method by Starkweather that provides a baseline for analyzing cooperativity on the basis of apparent Arrhenius activation energies.^{10,11} Founded on this work, the apparent activation energy can be determined from

$$E_a = RT[1 + \ln(kT/2\pi hf_R)] + T\Delta S^* \quad (2)$$

where k and h are Boltzmann's constant and Planck's constant, respectively, f_R is the frequency at which the relaxation peak is observed, and ΔS^* is the entropic activation. For illustrative purposes and also to justify our approach, we first utilized spectroscopy data from a recent study of polystyrene by Sills et al. that involved both IFA and DRS.¹⁷ In this

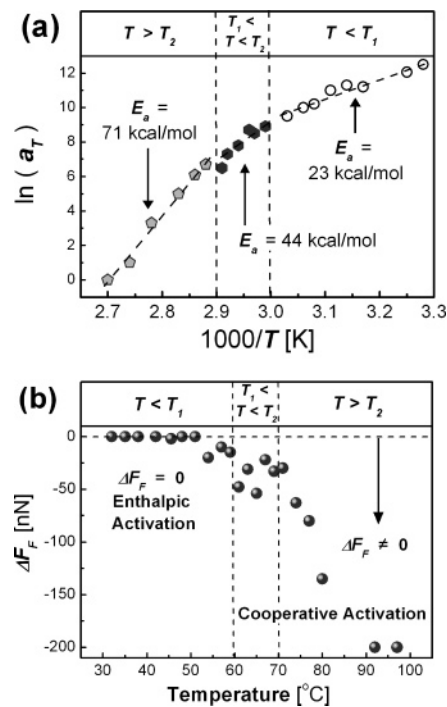


Figure 5. (a) a_T shift factor analysis of HDFD with apparent activation energies. (b) Vertical shift, ΔF_F , as a function of temperature for HDFD. Entropic (cooperative) contribution is noticeable above T_1 .



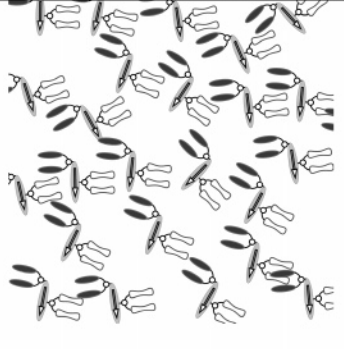
study, it was shown that the cooperation length $\xi(T)$ during the glass-forming process can be directly inferred from the resonance frequency and velocity, f_R and v_R , via

$$\xi(T) = \frac{[v_R(T)]_{\text{IFA}}}{[f_R(T)]_{\text{DS}}} \quad (3)$$

Thereby, f_R and v_R (see Figure 4a) originate from the corresponding DRS and IFA spectra, respectively. Thus, with the knowledge of v_R and E_a from the IFA analysis and $\xi(T)$ the enthalpic energy contribution ΔS^* can be deduced from eq 1 and eq 2. An analysis of Sills' data yields an entropic contribution of 70 ± 3 kcal/mol. Considering now that the cooperative (crank-shaft) backbone motion above the glass transition (i.e., the α -relaxation) requires on the order of 90 kcal/mol (temperature-averaged energy data from ref 17), an energy difference of ~ 20 kcal/mol is revealed. This energy difference corresponds to the isolated crank-shaft motion below the glass transition (i.e., the β -relaxation).^{22,23} In other words, if the enthalpic energy baseline of a specific relaxation is established, the entropic energy contribution, that is, the energy involved in the cooperative process can be determined.

Let us now turn to HDFD. Using eq 2 and the reasonable assumption that the correlation length $\xi(T)$ is within 0.1–20 nm, the $T\Delta S^*$ energy contribution is in the range of 26–30 kcal/mol above T_1 and 52–56 kcal/mol above T_2 . Further, the excess activation energies E_{ex} , obtained by subtracting the activation energy E_a below T_1 of 23 kcal/mol from the activation energies obtained above T_1 and T_2 , yield energy values that are again close to the calculated

Table 1. The Activation Energies and the Schematic of Molecular Dynamic Models of HDFD

Energy [kcal/mol]	Temperature range		
	$T < T_1$	$T_1 < T < T_2$	$T > T_2$
E_a^a	23	44	71
$E_{ex}=(E_a-23)$	-	21	48
$T\Delta S^*^b$	-	26-30	52-56
Molecular models			

^a IFA results. ^b Estimated from eq 2 and eq 3.

entropic energy contributions, as illustrated for polystyrene above. Thus, now we are ready to discuss the thermal dynamics in HDFD in terms of a dissociation model with its energies, as summarized and illustrated in Table 1.

On the basis of the information collected and knowledge of face-to-face phenyl/perfluorophenyl interactions, the dynamics and cooperativity in the HDFD system can be interpreted as follows. Below T_1 , the activation energy is associated with the dissociation of Ph-Ph^F pairs that take place randomly in isolated events, keeping however the average chain “length” aggregation constant. In the intermediate temperature range ($T_1 < T < T_2$), an increase in the density of dissociation sites leads to a cooperative phenomena, where molecules move in registry. Above but still close to T_2 , the assembly breaks down but the molecular building blocks still possess high cooperativity, typical of a polymer melt close to the glass transition.^{17,24,25}

Thus, while the dynamic enthalpy, that is, the dissociation of Ph-Ph^F pairs in HDFD, reflects a common relaxation mechanism for all three phases, the dynamic entropy exposes the phase variations in terms of cooperativity. With the introduced nanoscale thermomechanical methodology, it is now possible to study entropic phenomena of other molecular structures of self-assembled glass-forming NLO system with, for instance, more or less flexible dendrons or larger Ph and Ph^F moieties. Being able to deconvolute and quantify isolated processes from cooperative relaxation processes in condensed thin films, as shown in this letter, will prove to be very beneficial beyond electro-optics to many organic or even biological systems.

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