

Polymer Glass Transitions Switch Electron Transfer in Individual Molecules

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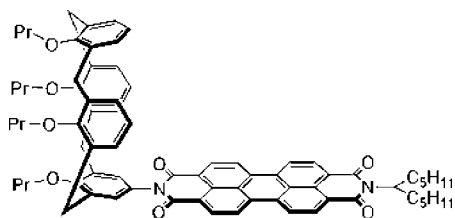
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Thin polymer films are widely used in industry for coatings, lubricants, and adhesive materials and also in high-tech semiconductor lithography and production of devices based on organic materials, such as light-emitting diodes,¹ field-effect transistors,² and a variety of sensors.³ Knowledge of the fundamental properties of polymers, in particular the glass transition temperature (T_g), is very important for proper design of the final products. Above T_g , the material behaves like a supercooled liquid. Lowering the temperature causes rigidification of the polymer matrix.⁴ A number of experimental and theoretical studies describe a spatial heterogeneity at the glass transition.⁵ Single-molecule spectroscopy (SMS) is an excellent tool for studying such heterogeneities at the molecular level.⁶ Probing individual molecules avoids obscuring the distributions of physical properties by the averaging that takes place in ensemble measurements and ensures minimal contact or perturbation of the system under study. This method allows the description of the dynamics of individual molecular probes embedded in polymers and gives information about the environment of each molecule. SMS is commonly used to follow orientation changes of fluorescing molecules,⁷ decay time variations,⁸ blinking behavior,⁹ or/and spectral shape changes.¹⁰

Here we used a perylene bisimide chromophore substituted with a calix[4]arene unit (**oc**, Chart 1)¹¹ as a novel molecular probe of polymer properties. We will compare its behavior with that of *N,N'*-bis(2,5-di-*tert*-butylphenyl)perylene-3,4:9,10-bis(dicarboximide) (**oref**), a well-known fluorophore that has attracted considerable attention because of its high fluorescence quantum yield ($\Phi_f = 0.99$ in toluene, $\tau_f = 4.0$ ns), which forms the basis for its applications in various fields.^{1b,12}

Chart 1. Molecular Structure of **oc**



The spectral properties of **oc** (Figure 1) are practically identical to those of **oref**, with three distinct absorption maxima and an emission spectrum that is the mirror image of the absorption spectrum with a small Stokes shift ($\lambda_{em} - \lambda_{abs}$) of 250 cm^{-1} .

The fluorescence of **oc** in toluene was reported to be strongly quenched by electron transfer from the electron-rich calix[4]arene

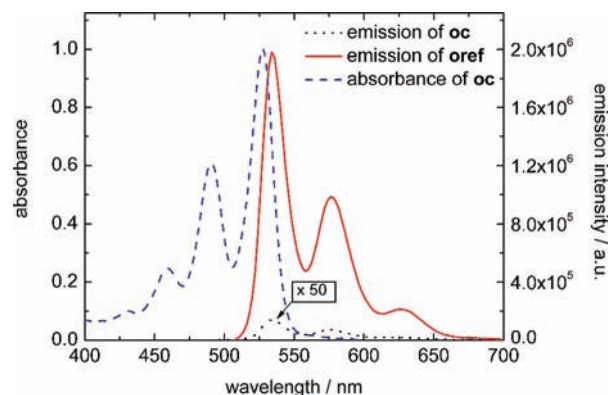


Figure 1. Normalized absorption spectrum of **oc** and steady-state fluorescence spectra of **oc** and **oref** in toluene.

part to the electron-poor perylene core of the molecule ($\Phi_f \leq 0.02$, $\tau_f = 25$ ps).¹¹

Electron transfer usually requires a structural reorganization of the medium to support the drastically changed electrical charge distribution. The driving force for typical photoinduced electron transfer (PET) processes has been shown to be smaller by ~ 0.8 eV in the solid state than in a polar solvent.¹³ In the present work, we exploited the strong dependence of the PET process on medium reorganization to switch the fluorescence of **oc** on and off in response to temperature changes around the glass transition of a polymer. Because of the high brightness and photostability of the perylene bisimide chromophore, the effect of the glass transition can be observed at the level of individual molecules.

We performed variable-temperature fluorescence intensity measurements on a drop-cast film¹⁴ of poly(methyl acrylate) (**pma**, $T_g = 13$ °C, $M_w = 32\,000$ g/mol) containing **oc**. Decreasing the temperature caused a significant rise in the emission intensity, which was ~ 15 times stronger at $1-2$ °C than above T_g of **pma** (Figure 2).

The reversible fluorescence emission switching of **oc** upon passing through the glass transition could be repeated many times. No changes in emission intensity were observed over the same temperature range for **oc** in polystyrene (**ps**, $T_g = 94$ °C) or **oref** in **ps** or **pma**. The decay times of **oref** in **pma** and **ps** in drop-cast films at 25 °C were 3.5 and 3.7 ns, respectively, which are close to the τ_f value in toluene.

Wide-field microscopy imaging of individual **oc** molecules in spin-coated films (thickness ~ 100 nm) complements the ensemble measurements. Each of the bright spots in the images in Figure 3 corresponds to one fluorescing molecule. The fluorescence intensity varies from molecule to molecule as a result of factors such as orientation of the molecular transition dipole moment with respect

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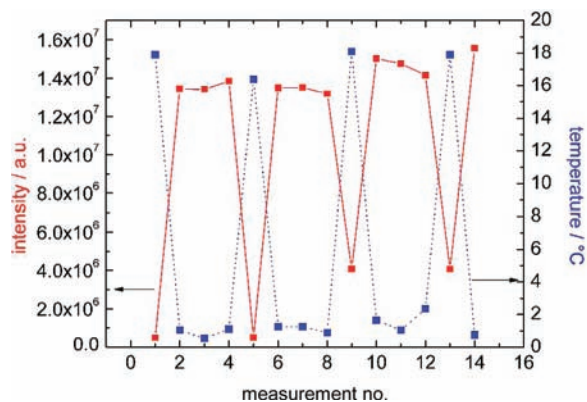


Figure 2. Changes in the integrated emission intensity of **oc** in a **pma** film caused by varying the temperature above and below T_g of the polymer (13 °C).

to the polarization of the excitation light¹⁵ or blinking behavior. No translational mobility in either polymer was observed. Defocused imaging,⁷ however, showed rotations of **oref** as well as of the molecules observed in the **oc** sample in **pma** above its T_g but not at lower temperatures or in **ps** [for details, see the Supporting Information (SI)]. In Figure 3b, only very few molecules are visible because of PET quenching occurring above T_g for **pma**.

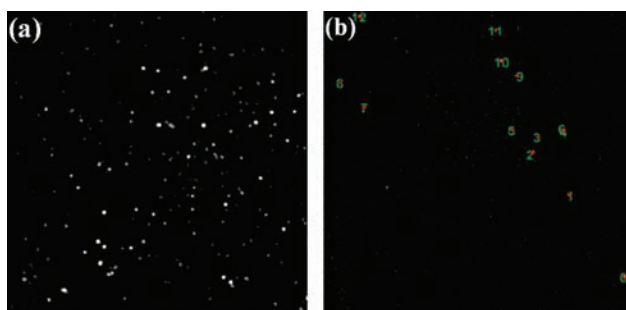


Figure 3. Wide-field images ($26 \mu\text{m} \times 26 \mu\text{m}$) of **oc** embedded in a **pma** film (a) below and (b) above T_g .

In order to evaluate the behavior of molecules in a smaller temperature window around the polymer T_g , we used poly(vinyl acetate) (**pvac**, $T_g = 28 \text{ °C}$, $M_w = 26\,000 \text{ g/mol}$). Figure 4 shows the result of counting single molecules on wide-field images taken over a range of temperatures. The lower and upper horizontal dotted lines show the number of background molecules and the total number of molecules expected to be on the measured area (error = ± 10 molecules), respectively. The total number of fluorescing molecules was calculated on the basis of the volume of the polymer on the measured area and the concentration of the spin-coating solution.

Average numbers (for five experiments) of fluorescing single molecules in **ps**, **pma**, and **pvac** films and their average decay times are collected in Table 1.

The data in Table 1 show that a small number of emitting molecules was found in case of the **pma** and **pvac** films doped with **oc** above T_g . A similar density of luminescent spots was found in a blank sample of **pma**, suggesting that these few molecules were actually due to an impurity. This was further confirmed by the spectra recorded for the emitting species in **pma** at ambient temperature, which were quite different from those of **oc** and **oref** (see the SI).

The switching that was observed at the ensemble level can also be monitored with the single-molecule-counting approach. The

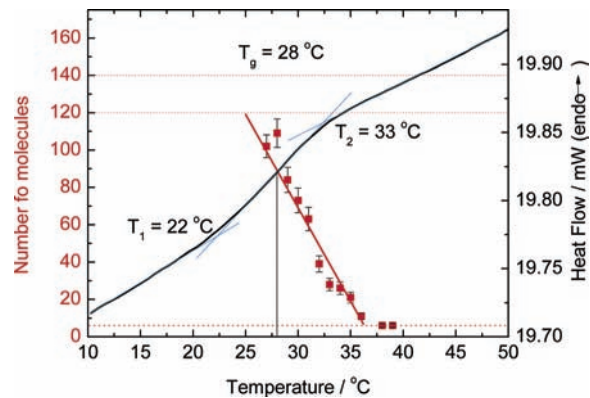


Figure 4. Number of fluorescing **oc** molecules detected in a $26 \mu\text{m} \times 26 \mu\text{m}$ area in a **pvac** matrix (left axis) as a function of temperature and part of the DSC curve (right axis) with the determined T_g of the polymer.

Table 1. Average Numbers of Fluorescing Single Molecules and Corresponding Decay Times (ns) Found in a 100 nm Thick Polymer Film on an Area of $26 \mu\text{m} \times 26 \mu\text{m}$

compound	polymer	temperature (°C)	number of molecules [decay time (ns)]
oref	ps	15–18	267 [3.5]
		1–3	278
pma	pma	15–18	269 [4.0]
		1–3	281 [3.7]
oc	ps	15–18	246 [3.6]
		1–3	262
	pma	15–18	19 [3.3]
		1–3	257 [3.4]
	pvac	38	6 ^a [3.8]
		28	109 ^a [3.8]

^a The smaller average numbers of fluorescing molecules in the case of **pvac** are due to lower concentrations of **oc** in the spin-coating solution.

sequence shown in Figure 5 consists of images taken on the same area of the sample (**oc** in **pma**) as the temperature was changed. In each cycle at decreased temperature, the same molecules become fluorescent; the appearance or disappearance of individual molecules (i.e., close to the T_g of the polymer) gives information on the environmental state around the probe. The practical limitation at this point is the photobleaching of **oc**. Degradation of the compound, however, may be greatly decreased by conducting the measurements under nitrogen.

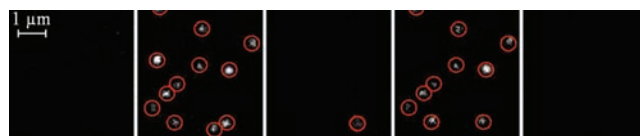


Figure 5. Sequence of wide-field images of **oc** embedded in a **pma** film recorded as the temperature was varied above and below T_g of the polymer.

To date, only a few papers have reported single-molecule studies of intramolecular electron transfer in polymers.¹⁶ Fluctuations in the efficiency of the electron transfer process, resulting in fluctuations of the fluorescence decay times, have been attributed to the polymer chain dynamics occurring on millisecond to second time scales at temperatures well below T_g .¹⁶ The fluorescence quenching of electron donor–acceptor compounds by intramolecular electron transfer is accompanied by internal structural reorganization and relaxation of the medium. The observation that fluorescence of **oc** is strongly quenched even in the nonpolar solvent methylcyclohexane,¹⁷ however, indicates that electron transfer in this case does

not require the stabilization by solvent dipoles. Indeed, using a solvatochromic fluorescent probe molecule that reflects nanosecond medium reorganization in the position of its emission band,¹⁸ we showed that in **pvac** at temperatures of up to 39 °C, no substantial relaxation of dipolar groups occurs on the time scale of the nanosecond lifetime of the excited state (see the SI). Thus, we attribute the switching-off of the fluorescence of **oc** to the availability of sufficient free volume for the molecule to reach the geometry needed for efficient excited-state electron transfer. The polymer dynamics that are responsible for the free volume change appear to be slow.^{4a} Adhikari et al.^{19a} and Wei and Vanden Bout^{19b} recently reported dynamics on the minute time scale in polymers near T_g studied using the rotation of probe molecules. The results in Figure 4 were obtained after equilibration for ~5 min at each temperature. When the temperature was rapidly changed, the numbers of fluorescing molecules changed much less.

Other molecules should be able to show behavior similar to that of **oc**. The requirement is that there should be a strong driving force for excited-state charge separation coupled with a large structural reorganization. Preliminary experiments indicate that another perylene orange derivative, *N*-(1-hexylheptyl)-*N'*-(4-methoxybenzyl)-3,4:9,10-perylenebis(dicarboximide),²⁰ indeed behaves similarly to **oc**.

We have reported the first single-molecule probe that uses an electron transfer quenching mechanism for sensing the changes that occur when a polymer is taken through its glass transition. Our approach requires a PET probe with a barrier to PET that is overcome only in media with sufficient free volume and not in the more rigid dense environment below T_g . Such behavior is found for **oc**, whose fluorescence is strongly quenched in soft media but very bright in solid matrices. The electron transfer can be reversibly switched on and off many times in a controlled fashion by switching the environment of the molecule between the supercooled-liquid and glassy states. Ensemble measurements as well as single-molecule counting showed that **oc** has potential as a sensing molecule for changes in microscopic properties of polymers. These may be caused by temperature changes, as in the present work, but could also result from material inhomogeneity, the presence of structure deliberately created on the submicrometer scale, or the application of strain. Single-molecule techniques have shown their value in materials science.^{6b} The present results further extend the repertoire of techniques with a potentially simple and high-contrast experiment.

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solvatochromic probe molecule (see the SI) and some of its fluorescence data.

Supporting Information Available: Experimental details concerning sample preparation, steady-state and time-resolved spectroscopy, and microscopy. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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