23. Once the fullerenes were deposited in the Sudbury structure (Onaping Formation), they were protected from oxidation and irradiation by a surrounding sulfide-silicate matrix, which allowed them to survive to the present (*1*).
24. This calculation uses an average cosmic-ray–induced crustal production [T. E. Cerling and H. Craig, *Annu. Rev. Earth Planet. Sci.* **22**, 273 (1994)] of ^{3}He determined for silicates (rate of 100 atoms per gram per year) at the latitude and altitude of Sudbury. The efficiency of the recoil of cosmic-ray ^{3}He from the silicate matrix into the C_{60} structure is not possible to evaluate.
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33. Carbon soot formation in these stars is expected to be initiated through the formation of polyenes [acetylene-like C chains without H, such as C_2, C_3, and C_4 (*30*)]. The lack of H minimizes saturation of dangling C bonds, allowing pentagons to be incorporated into the aromatic structure. The introduction of pentagons induces warping and curling of the aromatic planes, which would lead to closure and fullerene formation. It was the laboratory experiments used to probe these questions (laser ablation of graphite in an inert environment) that resulted in the initial discovery of fullerenes (C_{60} and C_{70}) and the proposal that this unique form of C may be involved in the C nucleation process (*30–32*).
34. Recent calculated equilibrium constants for the incorporation of noble gas atoms inside the C_{60} molecule (two different models were used to calculate the potential between the noble gas atom and each C atom) indicate that the potentials agree for encapsulation of He and Ne but disagree strongly for encapsulation of Kr and Xe. If this is the case, then the C_{60} molecule may preferentially incorporate the lighter noble gases over the heavier noble gases (H. A. Jiménez-Vásquez and R. J. Cross, *J. Chem. Phys.*, in press).

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Orientation-On-Demand Thin Films: Curing of Liquid Crystalline Networks in ac Electric Fields

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Electric fields have been used in the processing of thin film, liquid crystal thermosets to produce cured network structures selectively oriented either parallel or perpendicular to a film substrate. Orientation, which depends on both the liquid crystal nature of the thermosets and their dielectric anisotropy, is selected by varying the frequency of the alternating electric field and is locked into a robust network structure by a cross-linking reaction that takes place concurrent with orientation. Structural changes and orientation during the curing reaction were measured in real time with synchrotron x-ray diffraction. Diffraction studies show that, before curing in a modest electric field of 1 volt per micrometer, reorientation can be induced by changing, for example, from a high-frequency (>1000 hertz) to a low-frequency (<50 hertz) electric field, which causes a 90-degree flip in the molecular orientation.

The ability to control organization at the molecular level is revolutionizing the design of materials and leading to new structures, which range from self-assembled monolayers (*1*) to mesoporous inorganics (*2*). The molecular assemblies used in the formation of these complex compositions are usually built from aliphatic compounds with long alkyl segments that produce spontaneous organization similar to surfactants. Layer-by-layer assembly, which makes use of ionic and hydrogen-bond formation between alternate layers of polymers, has also been used to form stable, lamellar structures useful for applications such as light-emitting diodes (*3*). Liquid crystals (LCs), however, have similar self-assembly characteristics for forming complex phases and provide additional features, such as their remarkable ability to respond to applied fields.

When aligned with external fields, LCs can be used in a wide range of applications, including optical filters, displays, and data storage. By locking-in the anisotropic properties of LCs (*4*, *5*) through the formation of covalently bonded networks, controlled-order materials can be created. The development of LC thermosets (small-molecule LC precursors that can link up to form such networks) has been motivated by their potential use in structural applications where the need for more versatile polymeric materials with tunable strength and stiffness and well-controlled mechanical anisotropy exists (*6*).

Our goal in this study was to create a molecular system in which one could not only align the components in external fields to form anisotropic networks but also selectively control and lock-in the direction of alignment by network formation. Such materials have physical and chemical properties that are very different along each orientation, and one can conceive of using photochemistry, for example, to form films with order and orientation set in specified regions. By establishing orientation in a controlled fashion, one can vary the properties of such a film on demand before cross-linking with a single chemical precursor to form materials with tunable transport, optical, and mechanical properties. Orientation, which occurs in seconds in the uncross-linked thermoset under modest electric fields of E = 1 V/μm, is retained at temperatures more than 100°C above the glass transition because of the presence of the network.

Studies carried out previously in our laboratories on LC cyclic siloxanes in an E field showed frequency-addressable switching, that is, frequency-dependent orientation selection either parallel or perpendicular to an applied ac electric field (*7*). Our experience with the processing of these low–molecular weight mesomorphic compounds suggested that we could orient LC

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thermosets in a similar fashion provided that they had the correct dipolar structures (8). To introduce the prerequisite perpendicular dipole into a mesogen, we used a phenyl benzoate structure (Fig. 1A) (9). The ester functions designed into the mesogenic cores of our thermosetting molecules provide the dipolar "handle" needed for selectively switching the molecules in an ac electric field. This response can be tuned to convenient frequency and temperature ranges by molecular design.

For this reason, the two compounds reported in this paper were constructed with simple architectures (Fig. 1, B and C), each containing two ester functions but slightly different interior groups in order to adjust curing behavior and *E*-field response. The dicyanate (DCN) contains a central phenylene ring, whereas the CHDCN molecule is built from a more flexible cyclohexyl structure. Methyl groups on the aromatic rings of both DCN and CHDCN significantly lower the melting and network-forming (or curing) temperatures of these compounds (~150°C) while permitting the reduced reaction rates and low viscosities needed for orientation (*10*). The target LC thermosetting monomers were designed with a switching crossover frequency (the frequency at which orientation flips) in the range of 1 to 10,000 Hz. This design produced materials with excellent *E*-field response for dual frequency alignment and provided enough time for orientation before network formation was completed (*11*). The reactive group used for network formation was the cyanate function. Heating such compounds leads to cyclotrimerization of the cyanate groups to form a compact, six-membered triazine ring as the cross-link site. This cross-link function neither interferes with *E*-field alignment nor disrupts mesophase formation. For example, a glassy nematic phase is formed after several hours for compound DCN and within minutes for compound CHDCN. Despite their molecular similarity, there are significant differences in the mesophase behavior of these two thermosets.

To evaluate the effectiveness of these structures for formation of orientation-on-demand thin films, we studied the curing process of these thermosets in an ac field in real time using synchrotron x-ray diffraction (XRD). The experimental apparatus used in our real-time study permitted simultaneous heating, *E*-field alignment, and observation in the x-ray beam (*12*). The high-flux beam provided by this technique enables us not only to monitor the curing process and degree of alignment of the molecular director, but to adjust the *E*-field conditions as needed to achieve a given orientation, because the time needed to acquire an XRD pattern can be on the order of milliseconds. Thermoset films 100 μm thick were cured between temperature-controlled electrodes using *E* fields with amplitudes of ~1 V/μm. Such an oriented film has a thickness equivalent to ~50,000 molecular layers, representing a monumental effort if produced with layer-by-layer techniques.

The stiffer thermoset monomer, DCN, had better processing properties for creating selectively oriented thin films, because both changes in and refinement of orientation are possible during curing as a result of the longer, adjustable curing time (*13*) (Fig. 2). The DCN molecule is isotropic immediately after melting, and only upon curing does it become liquid crystalline (*4*), which leads to an induction period because the *E* field has no affect on the isotropic melt. As cross-linking occurs, viscosity builds up and the orientation time (initially seconds) becomes longer until the orientation is permanently locked in. At this time, the applied field can no longer cause reorientation. The more flexible CHDCN immediately melts into a nematic phase, which has shorter curing times (~3 min) even at lower curing temperatures, and reorientation is soon prevented by network formation. Curing rates are rapid enough that orientation cannot be switched by a change of frequency after cure onset, but for CHDCN, a combination of frequency and orientation was chosen before curing. With this method, orientation of the nematic director perpendicular to the film plane can be achieved at low frequencies (10 Hz), and parallel orientation of the thermoset in the film plane at high frequencies (10,000 Hz) can still be produced (Fig. 3A). No switching is possible shortly after the CHDCN thermoset is aligned.

From the x-ray patterns of the DCN and CHDCN networks after curing (Fig. 3, B and C), orientation parameters were calculated (*14*). The orientation of DCN is superior to that of the more flexible and faster curing CHDCN: The calculated orientation parameter of 0.6 for cured DCN is comparable to that typically obtained for oriented nematic phases, whereas that for

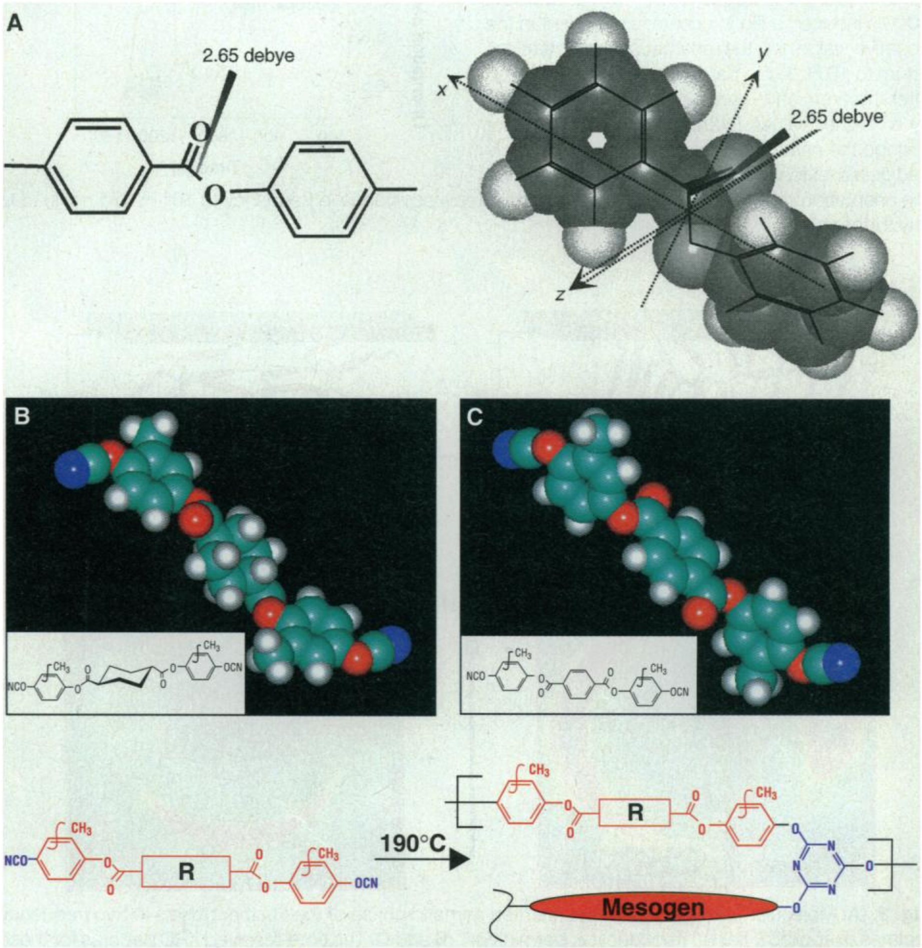

Fig. 1. (**A**) Molecular modeling calculations of the dielectric dipole of the ester unit present in our thermoset system, made with the Hyperchem computational package. Estimated dipole is 2.65 debye, lying largely parallel to the C=O bond (out of plane). (**B** and **C**) Space filling models of (B) the flexible dicyanate monomer CHDCN (melting temperature T_m = 155°C) and (C) the stiffer monomer DCN (T_m = 160°C) in a minimized conformation. Only one isomer of the three possible is shown. A general scheme for curing mesogenic dicyanates is shown below each model. Curing above 190°C leads to network formation in which triazine rings (blue) serve as cross-link sites between mesogens (red). (**Insets**) Chemical formulas of the monomers.

CHDCN is relatively low at 0.35 but still shows the presence of an oriented nematic phase (*15*). Once orientation is achieved, network formation locks in this arrangement and holds it at temperatures well above the glass transition of the networks. Such films have a high degree of mechanical and optical anisotropy and have very low degrees of thermal expansion and high modulus in the direction of orientation (*4*).

Orientation-on-demand is possible despite the continuously changing chemical and mesomorphic nature of the curing system. The reorientation rate of the molecular director and hence the final alignment of the network is dependent on viscosity, the strength of the dipole, the elastic constants, and the *E* field. This fact enables us to establish orientation in the uncured LC thermoset even in the fast-curing CHDCN. At the same time, the crossover frequency (typically 1000 Hz) does change with time as a result of the curing chemistry. Molecular design enables us to minimize the shift of the crossover frequency and to maintain our selective control of the orientation.

Properly constructed materials offer the prospect of forming structures with controlled orientation. Molecular orientation-on-demand either perpendicular or parallel to a film plane may be readily produced by this method of thin film construction. We anticipate that such materials and processing methods that make use of orientation-dependent mechanical or transport properties will be used in applications ranging from advanced adhesives to barrier materials. Although the reported films are simple oriented nematic structures, a smectic network would provide, in addition, a repeated layer arrangement consisting of alternate planes of cross-links and mesogens. Control of more than the molecular director is therefore possible and may lead in the future to single-molecular materials with spatially tunable optical, electrical, or dielectric behavior.

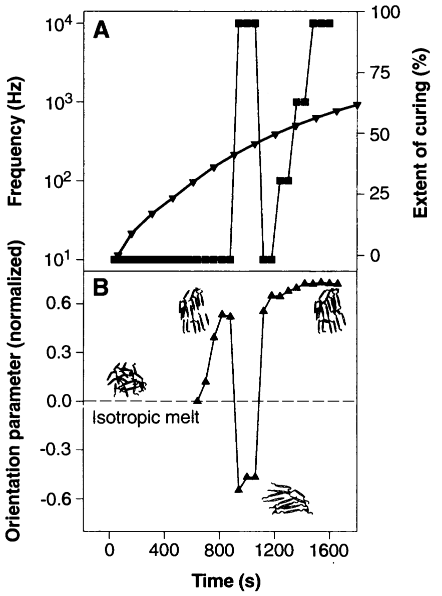

Fig. 2. Time-resolved experiment with thermoset DCN held isothermally at 190°C in a 1-V/μm electric field. (**A**) (■) Applied frequency for the curing thermoset as a function of time and (▼) its extent of curing as measured by Fourier transform infrared spectroscopy. (**B**) Orientation parameter calculated from the azimuthal scan. For an ideally oriented sample, the normalized orientation parameter is 1; for an isotropic material, it is 0; and for perpendicular alignment, it is −0.5. For better comparison, perpendicular alignment has been calculated with a reference direction 90° to the applied field, and the absolute value has been used. After an induction period of about 500 s, the now LC material oriented with the applied *E* field, and the orientation parameter increased with time. A change in frequency to 10^4 Hz at about 1000 s induced a flip in orientation, evident in the negative value for the orientation parameter. A return to 10 Hz led to parallel alignment. However, after this time, an increase of the applied frequency to higher values (starting at 1200 s) did not change the nematic director because the sample had gelled (extent of cure greater than ~50%) and the orientation of the sample was locked in. The stepwise change in frequency to 10^4 Hz did not lead to any further change in orientation.

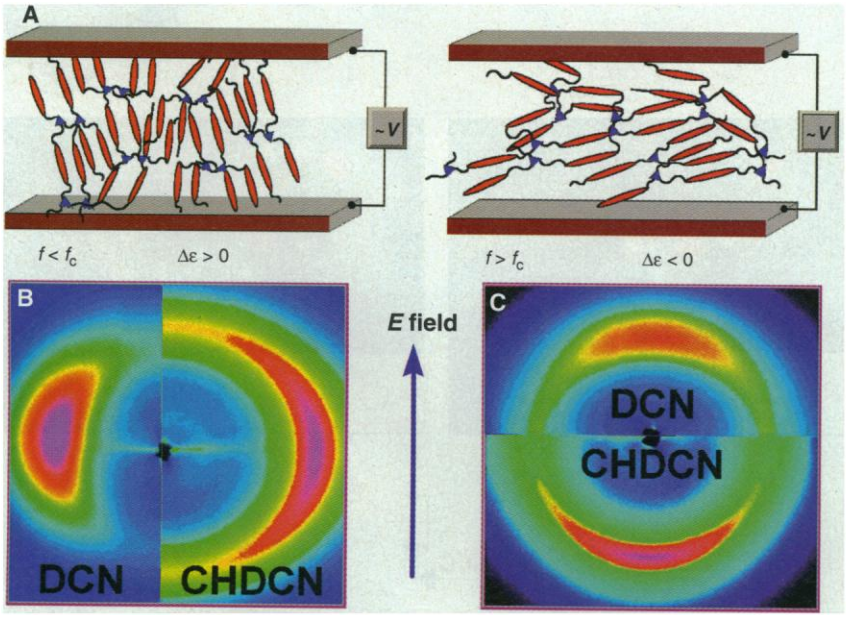

Fig. 3. (**A**) Molecular arrangement of the oriented nematic phase of the LC thermosets in two frequency regimes of applied *E* field (*f*, frequency; ε, permittivity). (**B** and **C**) The time-resolved XRD patterns for these thermosets aligned at (B) 10 Hz and (C) 10,000 Hz (1-V/μm *E* field at 190°C). The *d* spacing for average intermolecular distance is a typical value for CHDCN at 4.8 Å; however, the value of 5.2 Å for DCN is high compared to that expected for a nematic polymer. This observation is accompanied by an unusual radial width of the reflection for this thermoset. One explanation for the structural differences these molecules display despite their similar architectures is that the flexible cyclohexyl group in the mesogen of thermoset CHDCN can adjust, like a linear spacer, to steric incompatibilities caused by cross-linking. There is no way that the stiffer DCN can compensate the stress or strain caused by cross-link sites.

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8. The dielectric anisotropy of an aligned LC and its resulting coupling to an ac field are dependent on both frequency and temperature (*9*). The dielectric permittivity parallel to the molecular long axis ($\varepsilon_\parallel$) changes with frequency, whereas the perpendicular permittivity ($\varepsilon_\perp$) is almost constant, which leads to a crossover frequency at which the sign of the dielectric anisotropy $\Delta\varepsilon$ changes and molecular reorientation occurs. It is known from LC display technology that one can use this effect to introduce dual frequency addressability to a display and was used to control the molecular orientation before final cure in our system.
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10. The introduction of methyl groups leads to three isomers. Isomeric mixtures are known from LC displays to show better dual frequency switching behavior.
11. Compound DCN without these bulky lateral groups does not melt and decomposes without showing LC behavior. Cross-linking is therefore impossible. Both substituted compounds (DCN and CHDCN) can be synthesized in a two-step reaction involving inexpensive, commercially available materials.
12. We reoriented both DCN and CHDCN in an applied

E field by changing the frequency between low (10 Hz) and high (10,000 Hz) values while the material was curing. The direction of the nematic director could be rotated from homeotropic (perpendicular to film plane) to planar (parallel to film plane) alignment with respect to the electrode surface; that is, at low frequencies, we observed mesogens oriented parallel to the *E* field, but at high frequencies, the compound changed its director by 90°. Compared to known low–molecular weight compounds with similar structure, we expect the crossover frequency at 190°C to be on the order of 5000 Hz, but detailed dielectric measurements during curing have yet to be carried out to clarify this question.

13. At 190°C, DCN cures within 3 hours, and at 250°C, in 30 min, forming a densely cross-linked structure.
14. The calculations were carried out with the appropriate corrections for uniaxially oriented fibers after background correction. The *d* spacings from wide-angle XRD data were 5.2 Å for DCN and 4.8 Å for CHDCN.
15. In contrast, the radial width of the reflections, which can approximately describe the order of the nematic phase, shows a higher order for CHDCN than for DCN, where the wide-angle reflections are unusually broad along the radial direction. The radial width of a reflection offers information about the domain size of the nematic phase of a polymer. Although the orientation for CHDCN is weaker, its domain size is larger than that for DCN.

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Imaging and Time-Resolved Spectroscopy of Single Molecules at an Interface

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Far-field microscopy was used to noninvasively measure the room-temperature optical properties of single dye molecules located on a polymer-air interface. Shifts in the fluorescence spectrum, due to perturbation by the locally varying molecular environment, and the orientation of the transition dipole moment were correlated to variation in the excited-state lifetime. The lifetime dependence on spectral shift is argued to result from the frequency dependence of the spontaneous emission rate; the lifetime dependence on dipole orientation was found to be a consequence of the electromagnetic boundary conditions on the fluorescent radiation at the polymer-air interface.

Optical spectroscopy of single molecules can reveal the variation in molecular environments normally averaged over in ensemble measurements. A molecular emission spectrum and excited-state lifetime, perturbed by local fields and neighboring dipoles, can be a sensitive microscopic probe of chemical and biological processes, particularly if correlated to molecular location and orientation. High-resolution spectroscopy of single impurity molecules in bulk media has been obtained at cryogenic temperatures (*1–5*), and at room temperature, near-field microscopy has been used to study spatially resolved molecules at surfaces (*6–10*). However, the near-field method requires proximity of a molecule to a metallized near-field probe, which can perturb the molecular properties under study (*8–10*). Noninvasive far-field illumination of single molecules in liquids (*11*) and surfaces (*12*) has recently been reported, but far-field room-temperature spectroscopy has not been done. In the present study the location, orientation, fluorescence lifetime, and spectrum of single carbocyanine dye molecules at a polymer-air interface were measured by far-field microscopy. The method is not limited to molecules at a surface, allowing quantitative comparison with molecules in bulk media. On the basis of such a comparison, the dependence of the excited-state lifetime on spectral shifts and on dipole orientation was determined.

We obtained fluorescence images and spectral measurements of single molecules in an epi-illumination scanning microscope using a focused 532-nm laser beam for excitation (*13*). In the imaging we used raster-scanning of a sample across the focused laser spot; we performed spectroscopy by positioning and holding one molecule at a time under laser illumination. The samples consisted of randomly oriented carbocyanine dye molecules, $\mathrm{DiIC}_{12}(3)$ (*14*), in a polymethylmethacrylate (PMMA) film 20-nm thick on a quartz cover slip (*15*), prepared by spin-coating so that the areal density was one to five molecules per square micrometer. At this low coverage, molecules could be easily resolved spatially. Measurements were made at an excitation laser intensity of $\sim$500 W cm^{-2}, well below the saturation intensity of 10 kW cm^{-2} (*16*).

Fluorescence images were used to locate molecules immobilized in the PMMA film (Fig. 1). Next, polarized excitation with unpolarized-fluorescence detection was used to determine the component of the absorption transition dipole in the plane of the sample (the *x–y* plane in Fig. 1). For an absorption dipole oriented with polar and azimuthal angles of θ_a and ϕ_a, respectively, illuminated with laser light polarized in the *x–y* plane at an angle ϕ_L from the *x* axis, the detected fluorescence rate *R* is

$$R(\phi_L) = R_0 \sin^2\theta_a \cos^2(\phi_a - \phi_L) \qquad (1)$$

where R_0 is the detected fluorescence rate for a molecule aligned entirely along the polarization axis of the laser field (*17*). By rotating the laser polarization from $\phi_L = 0$ to $\phi_L = 90°$, we found that the azimuthal orientation of molecules a to d was along the *x* axis ($\phi_a = 0$), molecules e to i along the *y* axis, and molecules j and k at about $\phi_a = 45°$. The polar angle θ_a, and hence the *z* component of the absorption dipole, cannot be measured directly here because the *z* component of the laser field is too small (*18*). The polar orientation can be estimated from Eq. 1 if ϕ_a is measured and the maximum fluorescence rate R_0 is known or estimated. Molecular orientation, and in particular the emission dipole [which is not collinear with the absorption dipole for $\mathrm{DiIC}_{12}(3)$ (*19*)], can significantly affect the excited-state lifetime of a molecule near an interface.

Time-resolved spectroscopy (Fig. 2) was attempted on more than 200 molecules, of which about 30% survived irreversible photobleaching for a sufficient period to allow a measurement with good counting statistics. Molecules were characterized by their excited-state lifetime τ and their peak fluorescence wavelength λ_p, both of which varied from molecule to molecule. On the basis of 68 single-molecule measurements, a distribution of fluorescence lifetimes (Fig. 3A) and peak wavelengths (Fig. 3B) and the correlation of lifetime with peak wavelength (Fig. 3C) were determined. The mean values of τ and λ_p were 2.67 ns and 565 nm, respectively, in agreement with an ensemble measurement of $\tau = 2.7$ ns and $\lambda_p = 565$ nm shown in Fig. 2. However, the dispersion and correlation of these spectral properties, which we discuss below, could not be obtained from an ensemble measurement.

First, the peak fluorescence wavelength shifted by up to 30 nm, and the distribution had a width of 8 nm, or 30 meV, which is slightly larger than the thermal energy at room temperature. These spectral shifts, consistent with those observed with the use of near-field spectroscopy (*7*), are attributed to variation in the local PMMA environment. The PMMA polymer is polar and polarizable, whereas $\mathrm{DiIC}_{12}(3)$ has a large excited-state polarizibility. The perturbed molecular transition energies and hence the wavelength of the

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