Single-Molecule Orientations and Photophysics in Dyed Salt Crystals

Kristin L. Wustholz, Bart Kahr, and Philip J. Reid

Department of Chemistry, University of Washington, Box 351700, Seattle WA 98195

Introduction

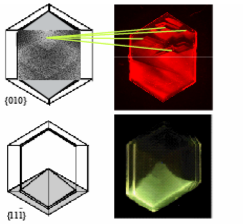
Electro-optic (EO) switches utilize the field-induced change in index of refraction of a non-linear optical (NLO) material to electrically modulate an optical field. Polymer-based materials with switching frequencies in excess of 100 GHz, and drive voltages less than 1 V have been demonstrated.[1] However, in order to attain the full potential of these devices, it is necessary to ascertain the molecular details that currently limit their overall efficiency. For NLO chromophores embedded within a polymer, bulk anisotropy is established by applying an external electric or "poling" field across the composite material. The importance of molecular alignment to the EO activity of a material is illustrated by the following relationship:

$$EO \propto \left| N\beta < \cos^3\theta > \right|$$

Understanding the factors that influence chromophore orientation has taken a backseat to the development of enhanced molecular properties (i.e. β). Yet, recent work suggests that poling is only partially effective in achieving molecular alignment[2] – making it quite clear that the poling procedure and ordering parameter are not well understood.

To experimentally test the efficacy of poling, and hence bulk EO device efficiency, it makes sense to begin with a system in which the chromophores are intrinsically aligned by the host. Here, a natural comparison presents itself in the study of the NLO properties of chromophore-polymer composites and dye-doped single crystals. Single crystals of potassium hydrogen phthalate (KAP) are easily grown from aqueous solution in the presence of several luminescent chromophores.[3] The focus of this work[4] is to interrogate the alignment and photophysics of single molecules of Violamine R (rhodamine analog), DCM (prototypical NLO chromophore), and DCDHF-2V (highly-fluorescent NLO chromophore)[5] in dye-doped crystal hosts using confocal microscopy.

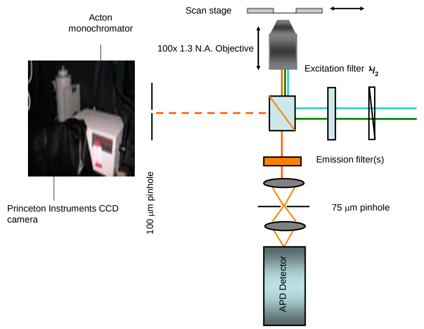
Experimental: Crystal Growth



Photographs of the polarized fluorescence from VR (top) and DCM (bottom) dyed KAP.

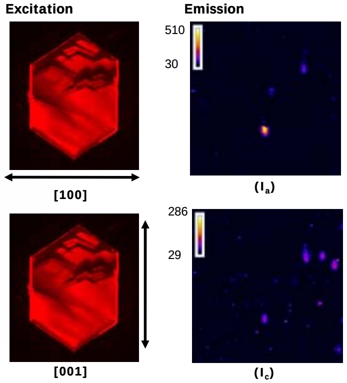
Fluorescent crystals of Violamine R (VR), 4-(dicyanomethylene)2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM), and DCDHF-2V doped KAP were grown by slow evaporation from supersaturated aqueous solutions containing 10^{-4} to 10^{-8} M dye, at 30°C in a temperature-controlled air chamber. Single-molecule concentrations were observed when grown from solutions containing ~1 x 10^{-8} M dye. The resultant single crystals were cleaved along [001], producing a thin slice (<1 mm) to be studied by confocal microscopy.

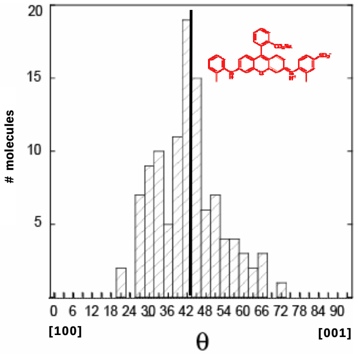
Experimental: Single Molecule Confocal Microscopy

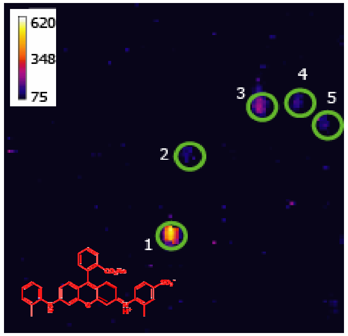


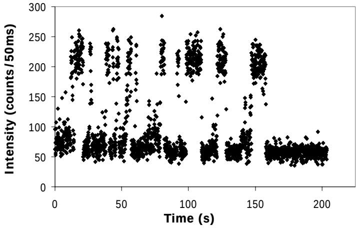
Single-molecule experiments were performed using an inverted microscope (Nikon). Dyed crystals were mounted on a closed loop x-y piezo scanning stage (Queensgate), and excited with low power (<10 μW) illumination from a 532-nm (Spectra Physics, Millennia) or 488-nm (Novalux, Protera) laser that was filtered (Chroma) and focused to a diffraction-limited spot with a 100× oil-immersion objective (Nikon, 1.3 NA). The excitation polarization was adjusted using a half-wave plate (CVI Laser). Emission from the sample was spectrally filtered using the appropriate dichroic mirror and emission filters (Chroma) and spatially filtered with a confocal pinhole (Thor Labs, 50 or 75-μm). Total emission intensity was detected using a single-photon counting avalanche photodiode (PerkinElmer). Single-molecule fluorescence spectra were collected using a monochromator (Acton) and liquid N_2-cooled CCD camera (Princeton Instruments) assembly.[6] Data collection was systematized with Labview (National Instruments).

Confocal Microscopy of Single Violamine R Molecules in KAP Host



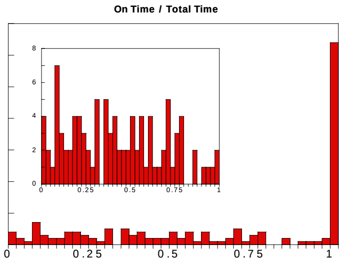


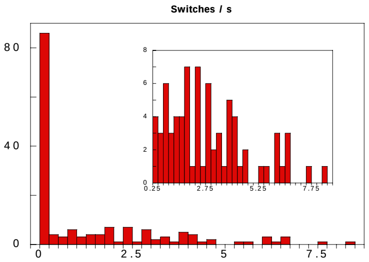




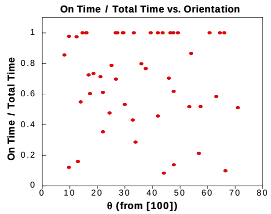
Single-molecule confocal microscopy of Violamine R dyed KAP. (Left) 10x10 μm false-color images of the fluorescence intensity from a 1 x 10^{-8} M VR dyed KAP single crystal grown at 30 °C. (Top right) Orientational histogram of 141 VR molecules, solid line represents the ensemble averaged orientation. (Bottom right) Representative time trace of single-molecule VR blinking dynamics.

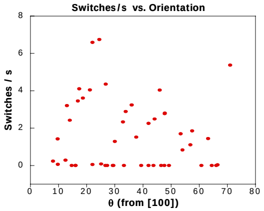
Photophysics of Violamine R in KAP





Photophysics of single molecules of Violamine R in KAP quantified in terms of "on time/total time" (left) and "switches/s" (right). Of the 161 sampled molecules, 64 molecules (39.8%) exhibit persistent emission and are characterized as being "on". The inset histograms include the remaining 97 molecules, and in both cases, reveal a wide distribution of photophysical behavior.

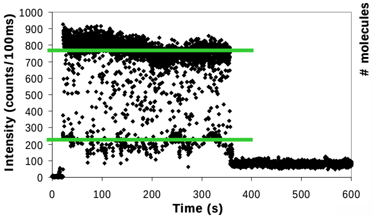


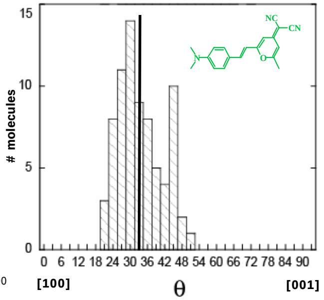


Scatter plots of photophysics with respect to orientation of single molecules of VR in KAP. The plots show the "on time/total time" (left) and "switches/s" (right) versus molecular orientation for 49 single molecules. These data suggest little correspondence between the orientation of VR molecules in the crystal and blinking dynamics.

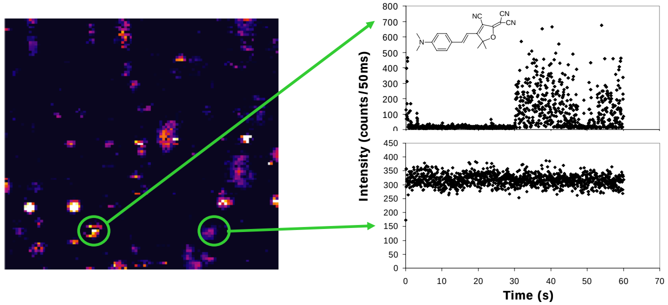
Confocal Microscopy of Single DCM Molecules in KAP Host

Single-molecule blinking dynamics and orientational distribution for DCM dyed KAP. The time trace (left) suggests the existence of two-state blinking, possible reflecting population of the twisted intramolecular charge transfer (TICT) excited state. Orientational distribution (right) for 75 DCM molecules





Confocal Microscopy of NLO Chromophore in KAP Host



(Left) 10x10 μm false-color image of the total fluorescence intensity from 1 x 10^{-8} M DCDHF-2V dyed KAP single crystal grown at 30 °C. The blinking dynamics of encircled molecules measured using 1.7 μW of 532-nm excitation are shown on the right.

Summary

- The average orientation of 108 single Violamine R molecules in KAP (42.3 ± 10.4°) is in good agreement with ensemble measurements (42°). However, single-molecule experiments show a broad distribution of orientations, ranging from 20.1° to 72.9° from [100]. The average orientation of 75 single DCM molecules in dyed KAP (31.9 ± 7.8°) is in good agreement with ensemble measurements (35°). Yet, single-molecule investigations reveal another surprisingly wide orientational distributions of included dyes, with values ranging from 20.8° to 50.7° from [100]. These observations are consistent with face-on adsorption of DCM to {11-1}. Furthermore, our preliminary data suggest that dual emission was observed when incorporated into the KAP host.

- The blinking dynamics of 161 single Violamine R molecules in KAP were quantified by using "on time/total time" and "switches/s". Of the sampled molecules, ~40% are "on", while the remaining molecules exhibit a variety of photophysical behaviors. These data suggest the presence of two subpopulations in the crystal: one where molecules exhibit persistent emission and another in which molecules exhibit a large distribution of blinking dynamics. From orientational and photophysical data obtained on 49 molecules of Violamine R in KAP, there appears to be little correlation between molecular orientation and blinking dynamics.

- A new system, DCDHF-2V dyed KAP was studied with confocal microscopy. Due to its large absorption cross-section, appreciable fluorescence quantum yield, and large hyperpolarizability, DCDHF-2V and its analogs show exceptional promise for further photophysical and orientational investigations.

References & Acknowledgements

[1] Dalton, L. R. Nonlinear Optical Polymeric Materials: From Chromophore Design to Commercial Applications. In *Advances in Polymer Science*; Springer Verlag: Berlin, 2002; Vol. 158.

[2] Robinson, B.H.; Dalton, L.R. *J. Phys. Chem. A.* **2000**, *2000*, 4785.

[3] Gurney, R.; Kahr, B. *Chem. Rev.* **2001**, *101*, 893.

[4] Wustholz, K.L.; Kahr, B.; Reid, P.J. *J. Phys. Chem. B* **2005**, *109*, 16357.

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[6] We would like to thank Stacy Oliphant (REU 2005 student) for her assistance with instrumental calibrations.