

Single-molecule confocal microscopy studies of chromophore-polymer composite materials

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Introduction

One strategy for increasing the efficiency of electro-optic devices based on chromophore-polymer composite materials is to improve chromophore ordering. In these materials, ordering is induced through the interaction of the chromophore dipole moment with an external electric field, applied at temperatures near the T_g of the polymer host, a process referred to as "poling". In this study, single-molecule rotational dynamics of three chromophores are monitored through the time-evolution of the fluorescence anisotropy, the effect of an applied electric field on molecular rotational dynamics was also explored.^{1,2} This work demonstrates the utility of polarization-sensitive single-molecule microscopy in elucidating the details of molecular reorientation during the poling process.

Experimental

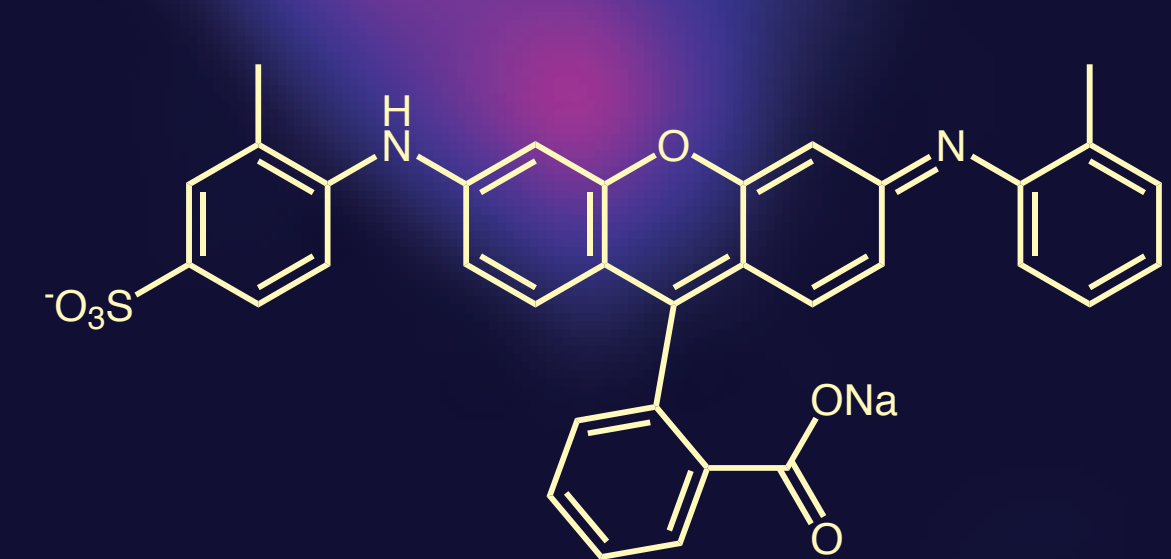
Aluminum electrodes were fabricated on cover slips with a $\sim 10\text{-}\mu\text{m}$ gap. Three chromophores were investigated in this study: Rhodamine B (RhB, upper right), Violamine R (VR, above left), and 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylaminostyryl)-4H-pyran (DCM, middle).

A solution of 10^{-9} M chromophore in 15 wt% poly(methyl acrylate) (PMA, below) was prepared, 100- μL aliquots of the sample solution were spun coat onto the substrate.

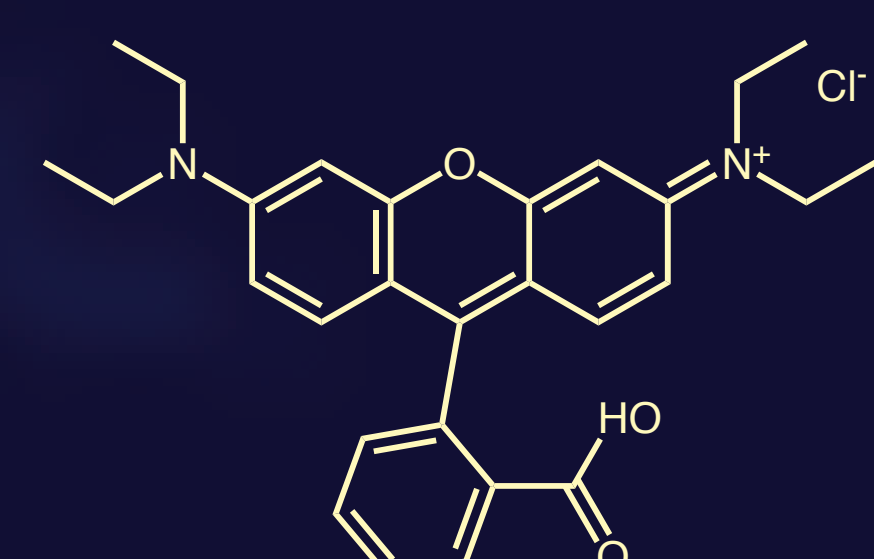
The samples were interrogated using an inverted confocal fluorescence microscope.

Orientation information was obtained by monitoring the fluorescent intensity along both polarization components from a single molecule's fluorescence as a function of time.

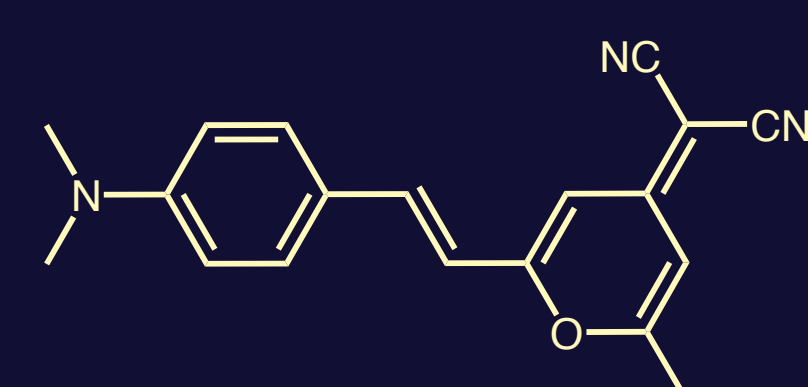
False-color $5 \times 5 \mu\text{m}$ images of 10^{-9} M RhB in 15 wt% PMA employing $0.1\text{-}\mu\text{m}$ steps are presented. The images correspond to fluorescence polarized parallel to the applied electric field (left), and perpendicular (right). A scan representing the total fluorescence intensity recorded is shown below.



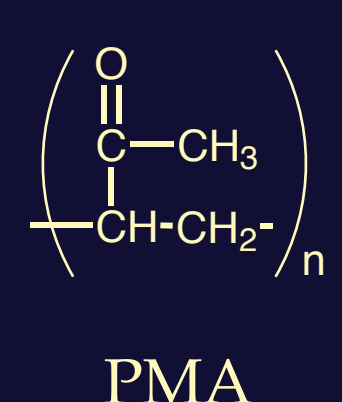
VR



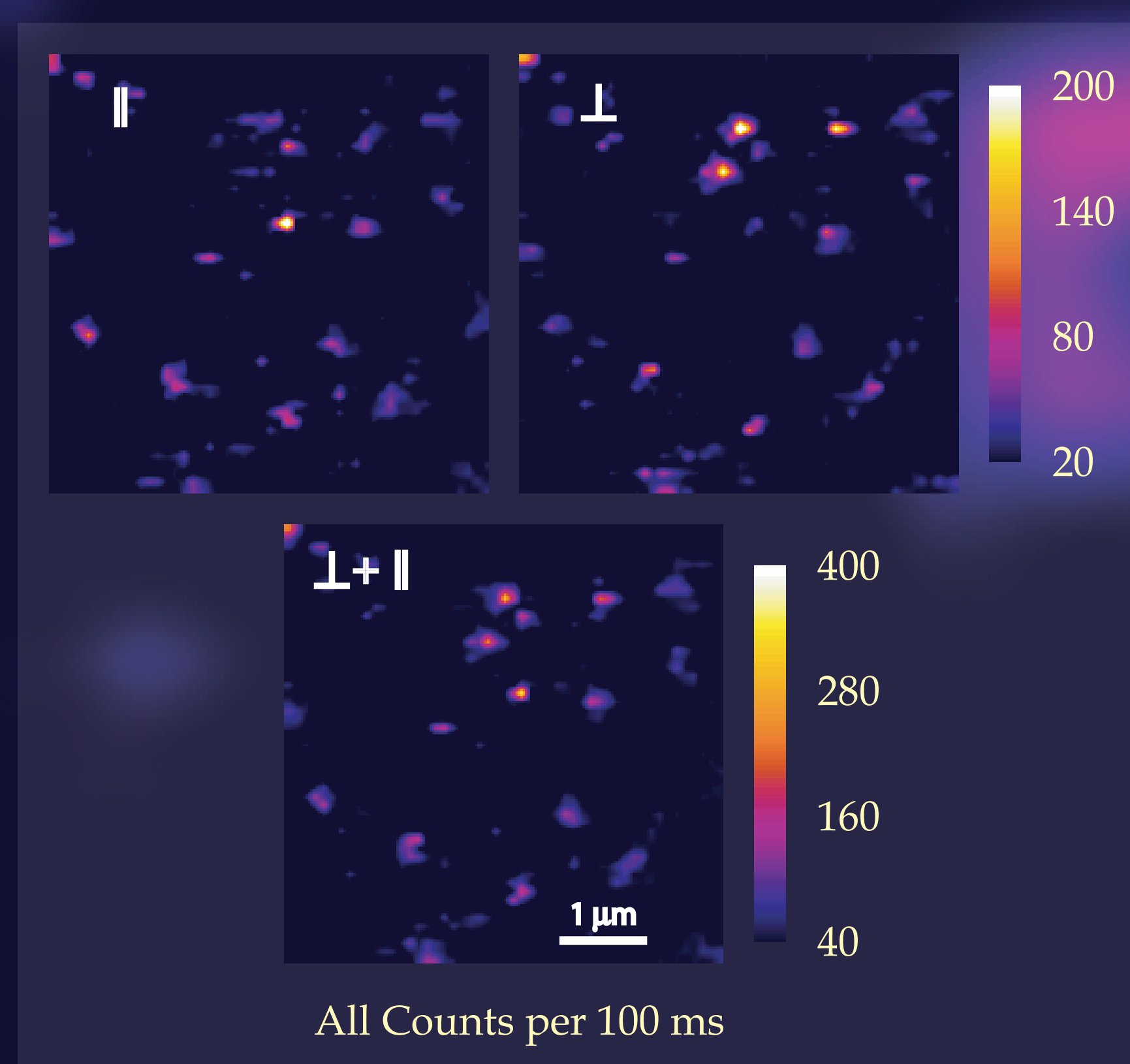
RhB



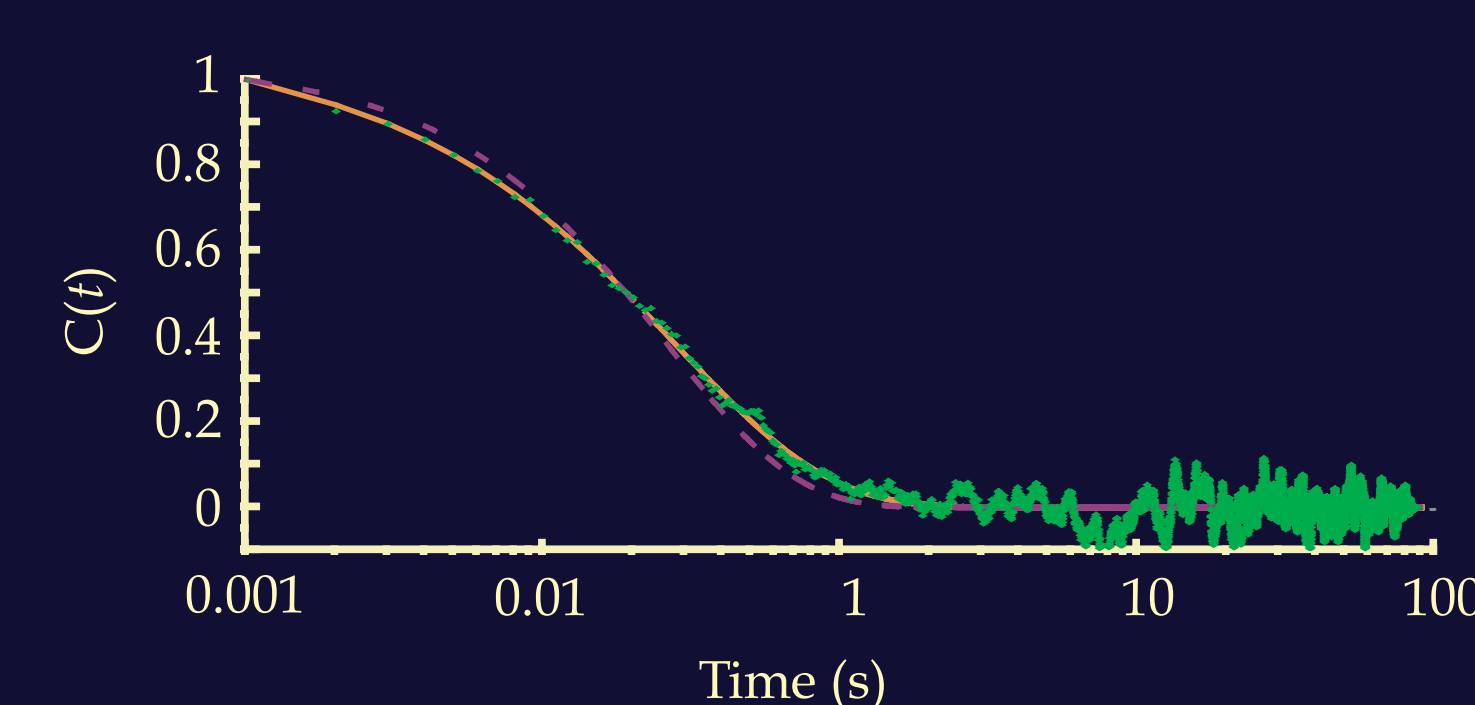
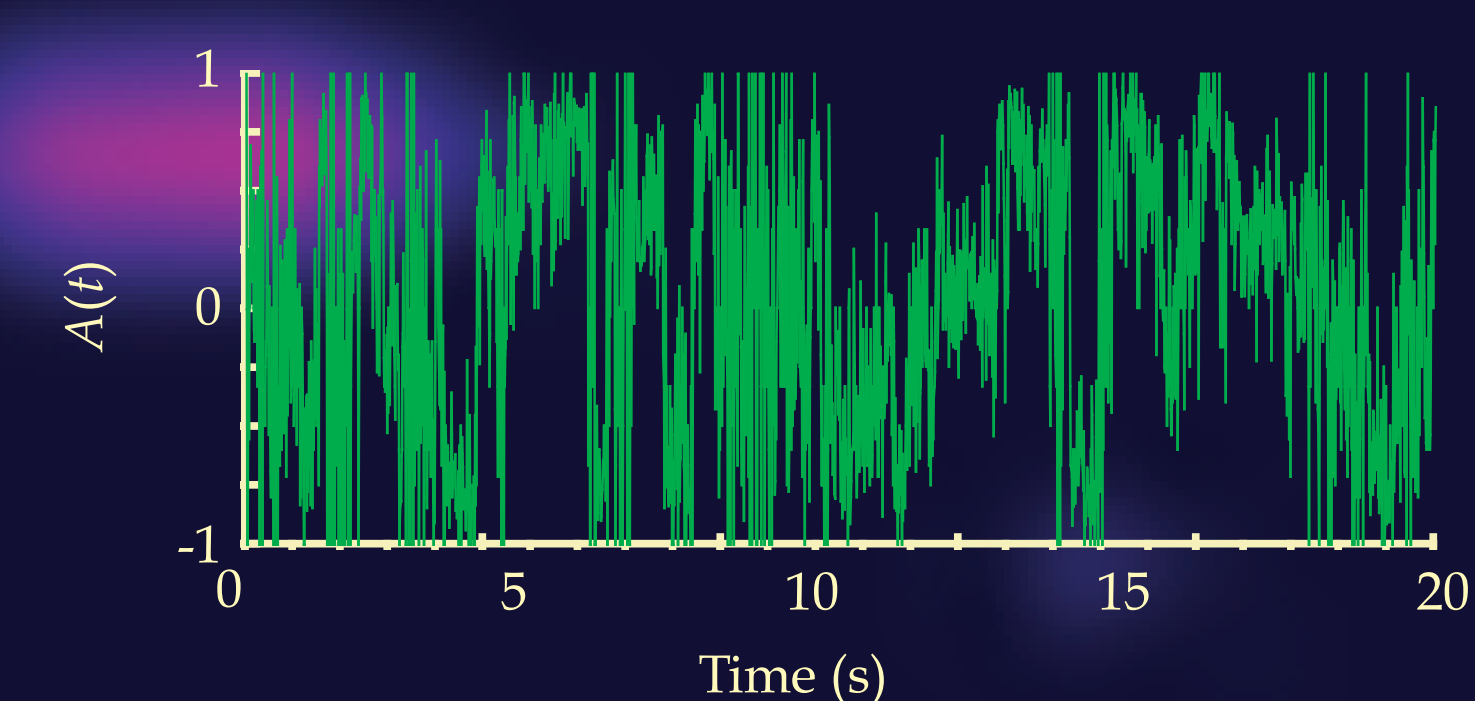
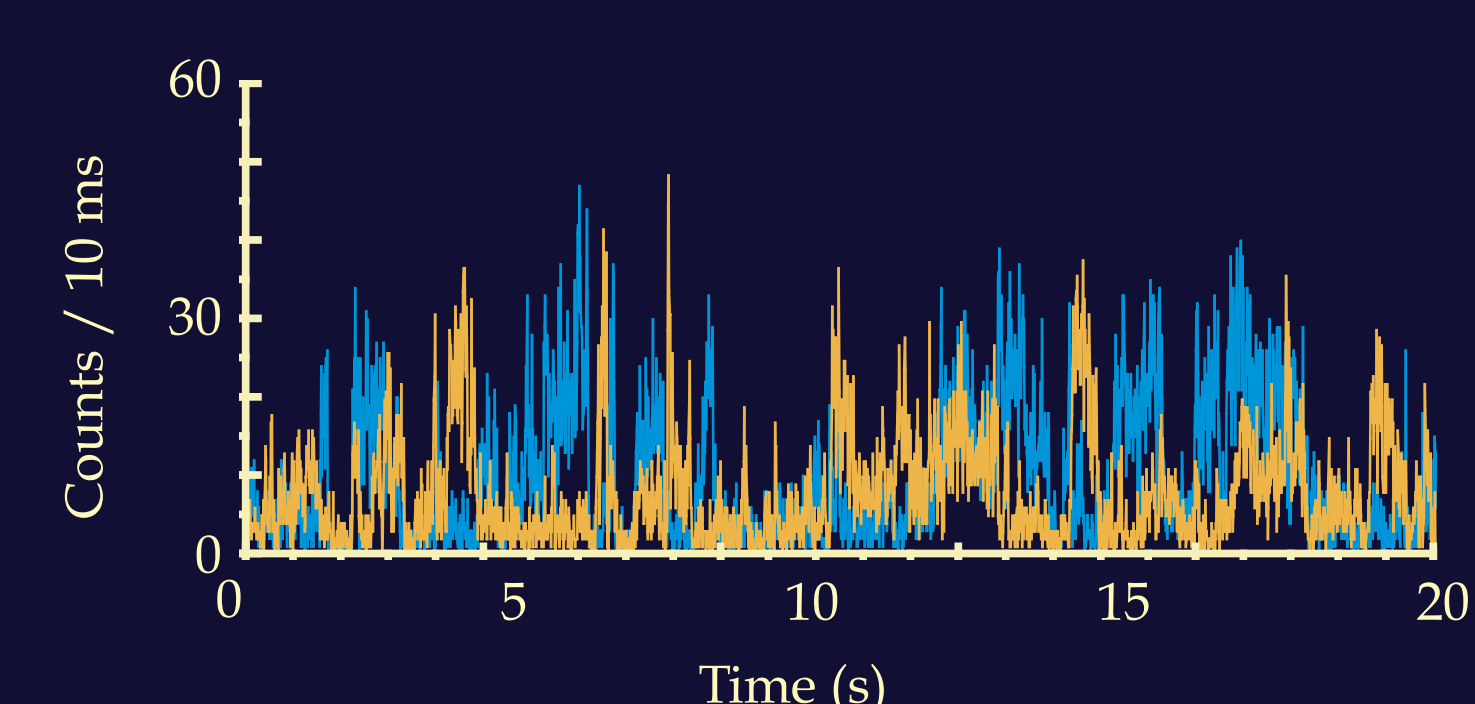
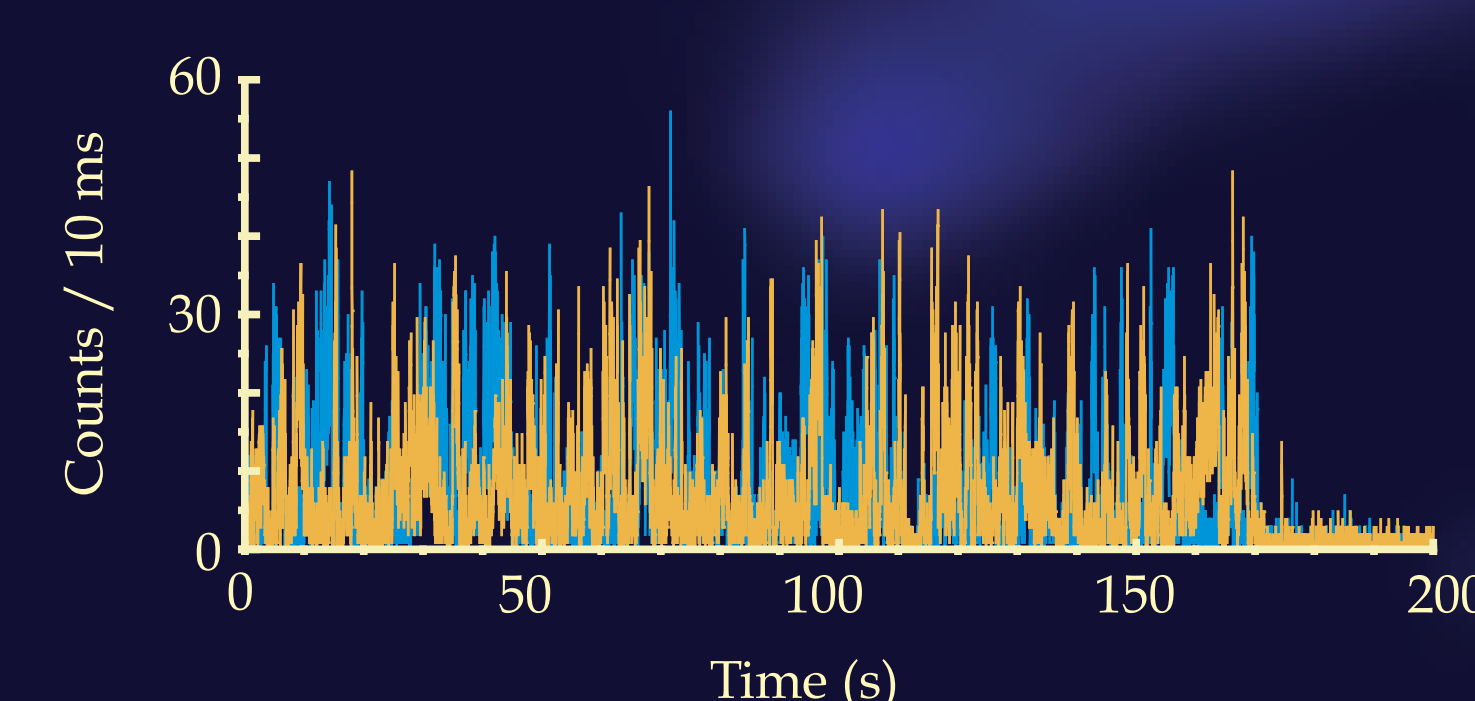
DCM



PMA



Data Analysis



- Time-evolution of single molecule fluorescence intensity is measured for each emission polarization, ($I_{||}(t)$ and $I_{\perp}(t)$).
- Fluctuations and anticorrelation of $I_{||}(t)$ and $I_{\perp}(t)$ are observed corresponding to molecular rotation until permanent loss of signal occurs due to photodestruction.

- The reduced dichroism, ($A(t)$), is calculated from the polarized emission as follows:

$$A(t) = \frac{I_{||}(t) - I_{\perp}(t)}{I_{||}(t) + I_{\perp}(t)}$$

- The rotational dynamics are characterized using the autocorrelation of the reduced dichroism ($C(t)$):

$$C(t) = \frac{\sum_{i=0}^{\infty} A(0)A(0+t)}{[A(0)]^2}$$

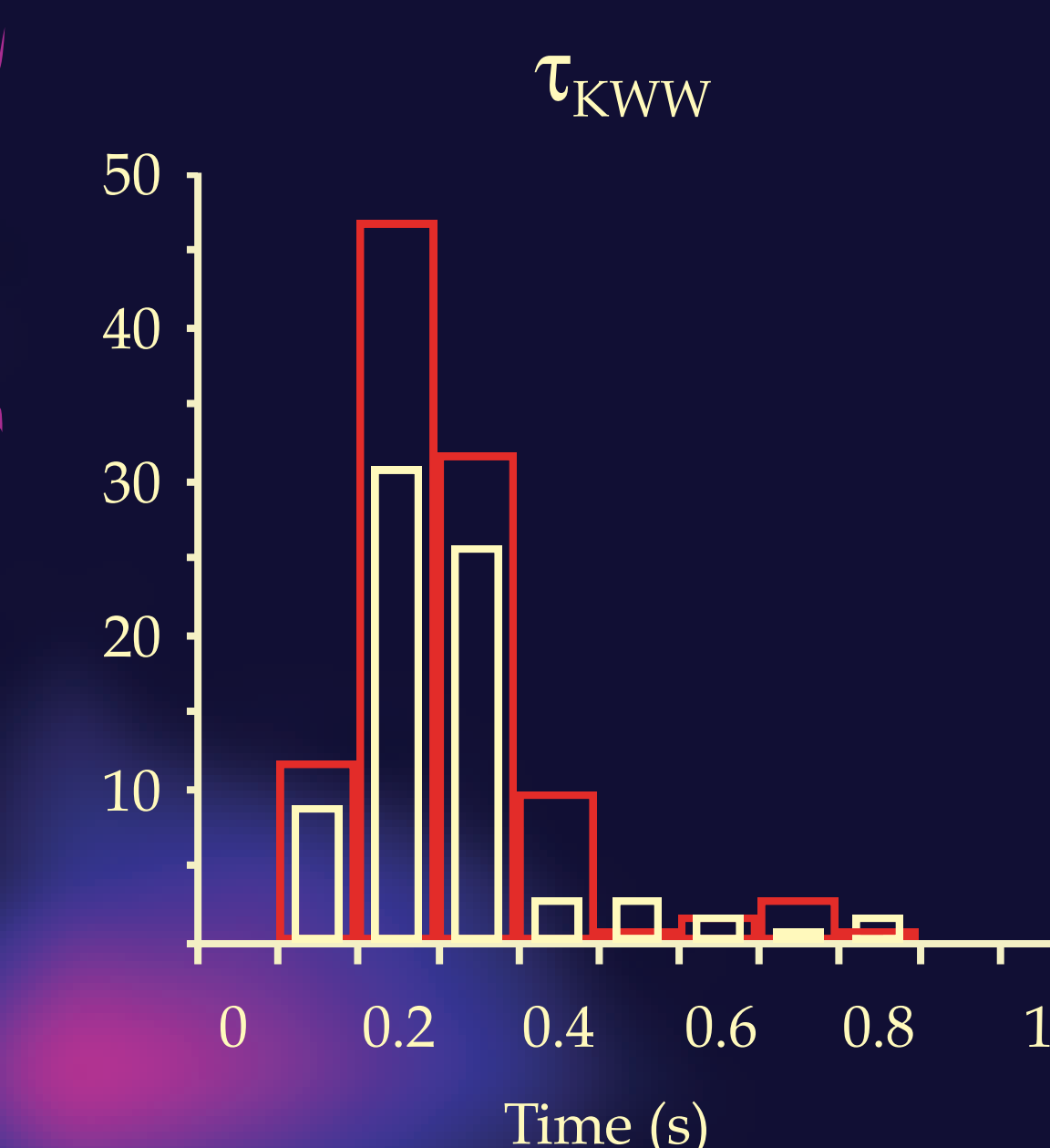
- The decay of $C(t)$ is not exponential as illustrated by the mismatch between the exponential fit (dashed purple line, $\tau = 0.14$ s) and the data (green squares).

- In contrast, $C(t)$ is well fit by a stretched exponential function (orange line) of the form:

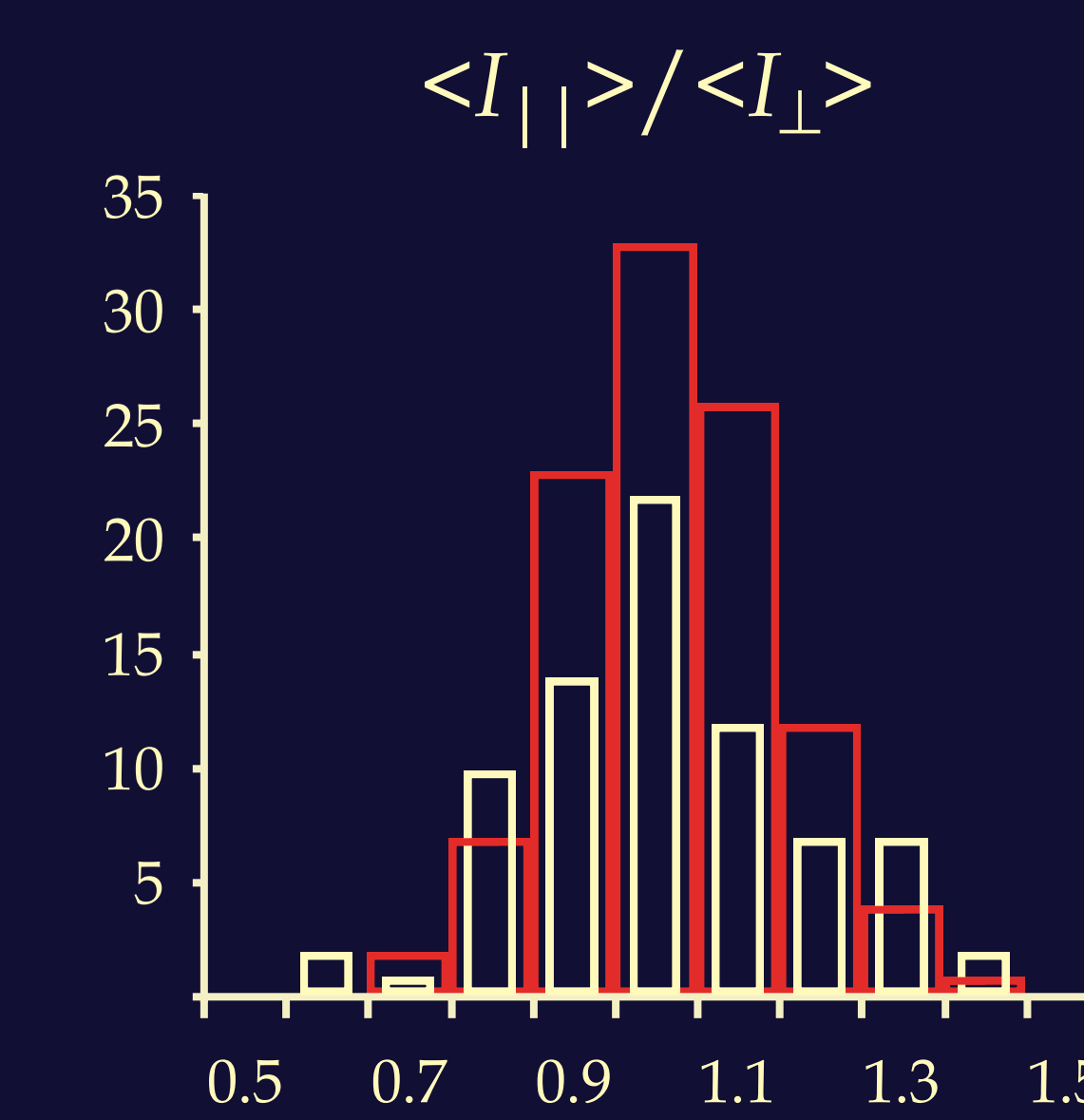
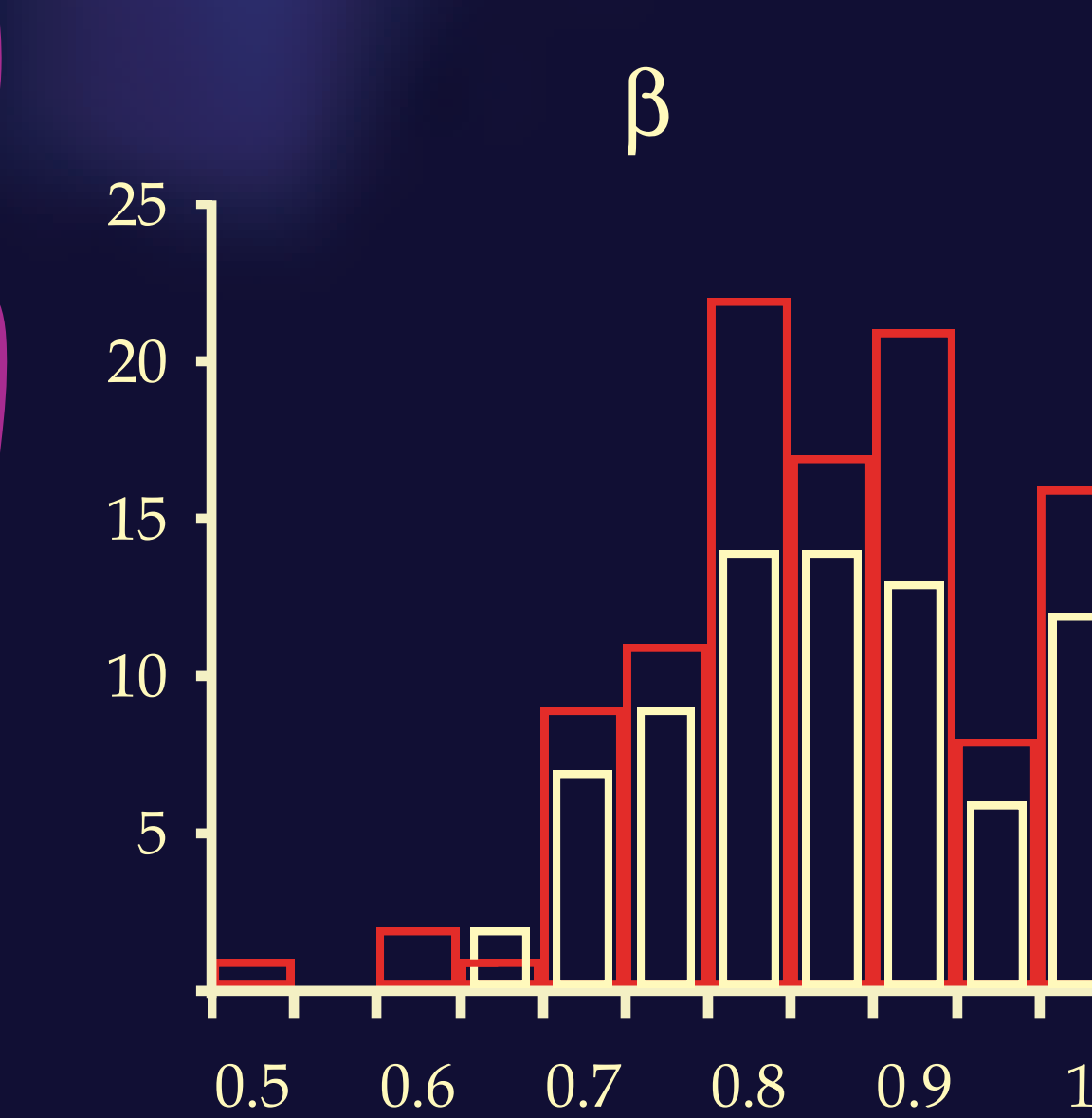
$$C(t) = \exp\left[-\left(t/\tau_{\text{KWW}}\right)^{\beta}\right]$$

For the depicted fit, $\tau_{\text{KWW}} = 0.14$ s and $\beta = 0.78$.

Electric Field Dependence of Rotational Dynamics

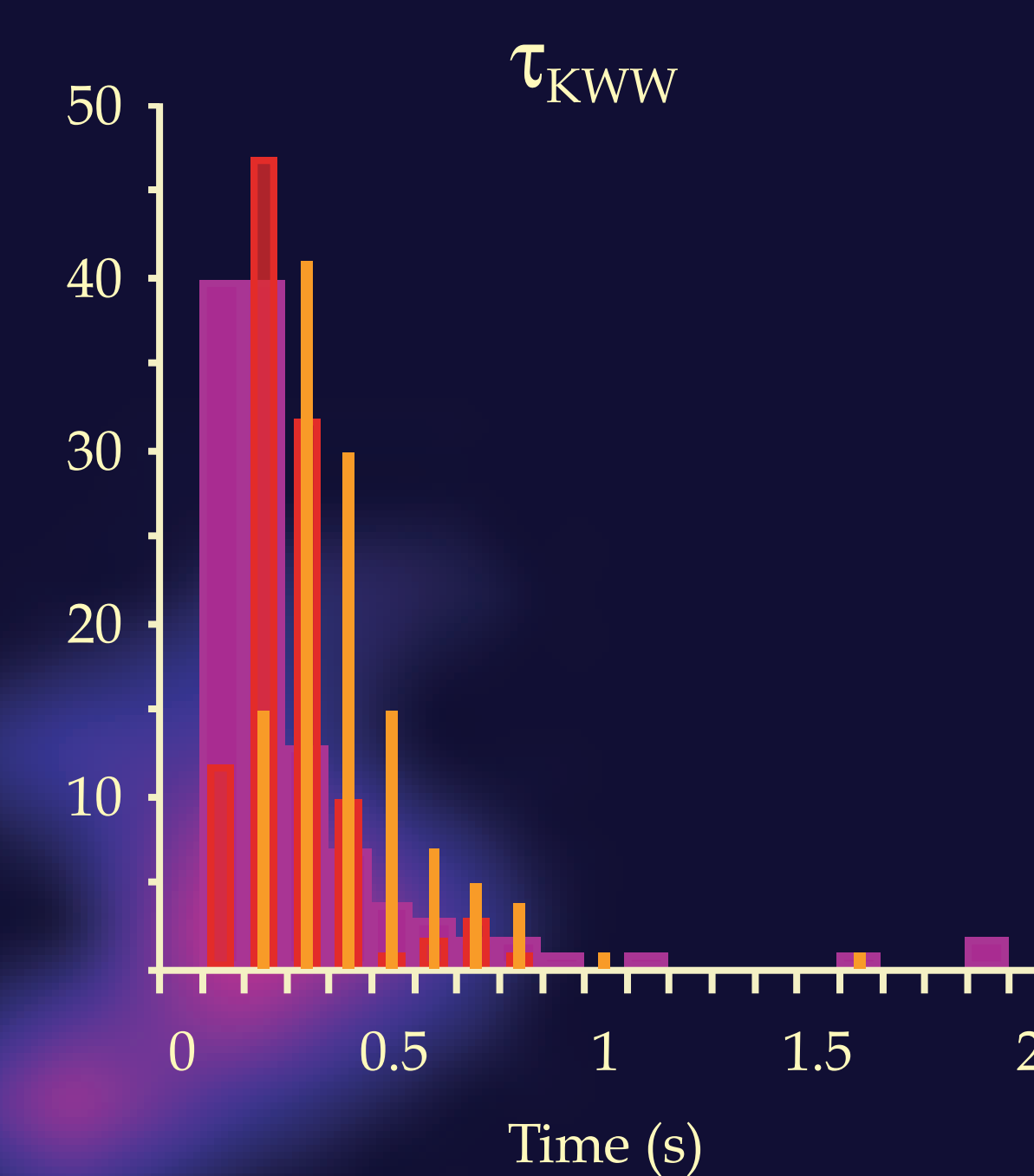
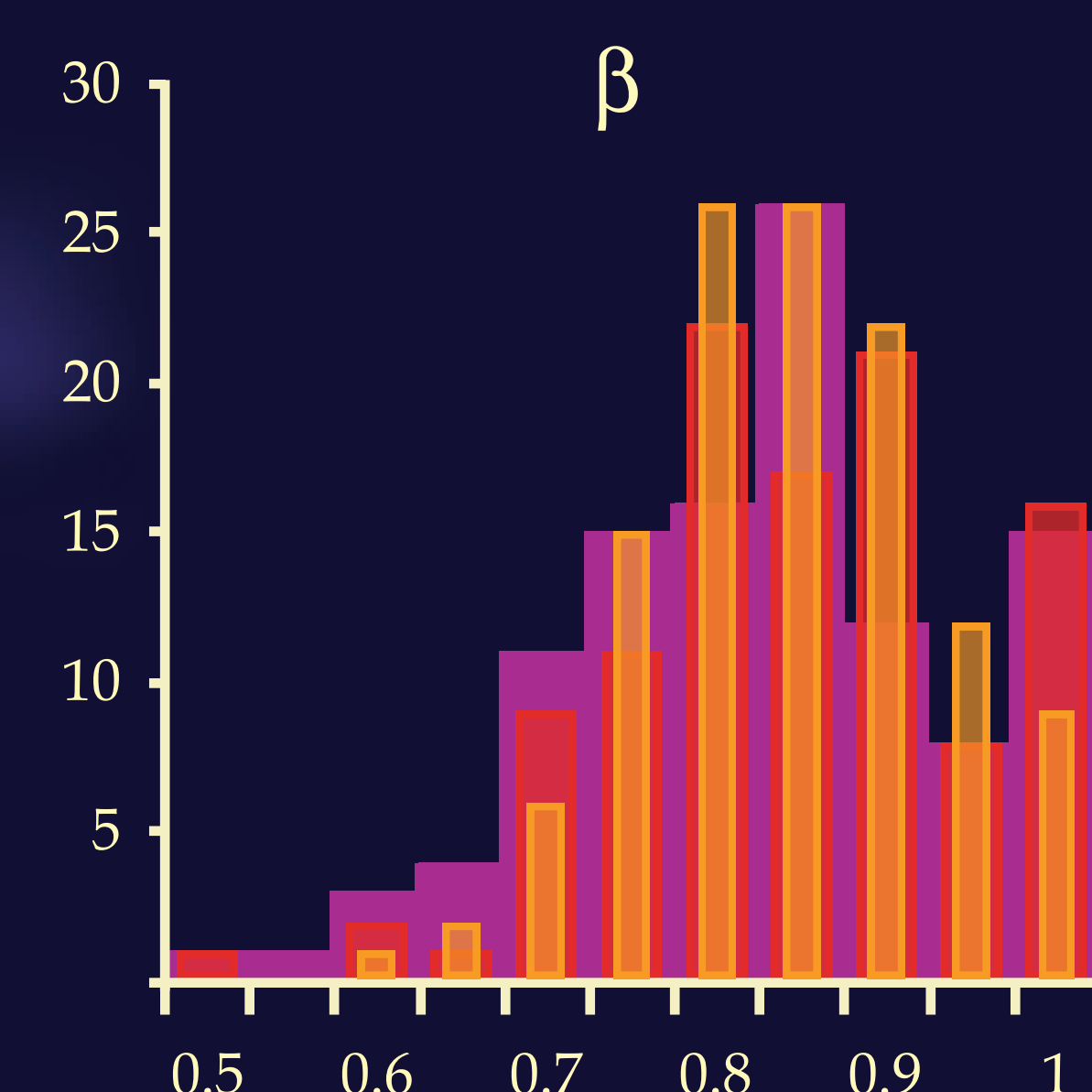


- Histograms for DCM are shown for 108 molecules in the absence of the electric field (red) and 77 molecules in the presence of a $50 \text{ V}/\mu\text{m}$ electric field (yellow).
- $\langle \tau_{\text{KWW}} \rangle = 0.22 \pm 0.01$ s and 0.23 ± 0.02 s in the absence and presence of the electric field, respectively.
- $\langle \beta \rangle = 0.84 \pm 0.01$ and $\langle \beta \rangle = 0.85 \pm 0.01$ in the absence and presence of the electric field, respectively.
- The average value of $\langle I_{||} \rangle / \langle I_{\perp} \rangle$ is weakly dependent of the electric field ($\langle I_{||} \rangle / \langle I_{\perp} \rangle = 0.97 \pm 0.02$).



Molecular Dependence of Rotational Dynamics

- Histograms for τ_{KWW} and β are shown to the for 108 DCM molecules (red), 110 RhB molecules (orange), and 112 VR molecules (purple).
- The average value of β ($\langle \beta \rangle$) is 0.84 ± 0.01 , 0.82 ± 0.01 , and 0.81 ± 0.01 for DCM, RhB, and VR, respectively.
- $\langle \tau_{\text{KWW}} \rangle = 0.22 \pm 0.01$ s, 0.36 ± 0.02 s and 0.19 ± 0.02 s for DCM, RhB, and VR, respectively.



Conclusions

- Values of $\langle \beta \rangle$ remain relatively unchanged with respect to the chromophore or the presence of an electric field; illustrating that β is dominated by the polymer host.
- Rotational-correlation times for DCM in PMA are similar to the corresponding values observed for Rhodamine dyes the same polymer.
- The similarity of $\langle I_{||} \rangle / \langle I_{\perp} \rangle$ in the absence and presence of the electric field demonstrates that the molecular rotational dynamics of DCM are only slightly perturbed by a $50 \text{ V}/\mu\text{m}$ electric field.
- Given a $50 \text{ V}/\mu\text{m}$ poling field and 10 D dipole moment, $\mu E \approx 0.4kT$ is consistent with the observation that the poling field provides only a modest perturbation to the rotational dynamics of DCM.
- The results presented here suggest that understanding the interplay between changes in rotational dynamics accompanying a change in T relative to T_g of the polymer host and the strength of the applied field is critical to poling efficacy.

	n	$\langle \beta \rangle$	$\langle \tau_{\text{KWW}} \rangle$ (s)
VR	112	0.81 ± 0.01	0.19 ± 0.02
RhB	119	0.82 ± 0.01	0.36 ± 0.02
DCM	108	0.84 ± 0.01	0.22 ± 0.01
DCM in a $50 \text{ V}/\mu\text{m}$ field	77	0.85 ± 0.01	0.23 ± 0.02

(1) Wallace, P. M.; Sluss, D. R. B.; Dalton, L. R.; Robinson, B. H.; Reid, P. J. *J. Phys. Chem. B* 2005, 110, 75.
 (2) Sluss, D. R. B.; Wallace, P. M.; Truong, K.D.; Robinson, B. H.; Dalton, L. R.; Reid, P. J. *Proc. of SPIE* 2006, 6331, 63310K-1.

