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Photon pair correlation spectroscopy of single tetrahedraloligophenylenevinylene molecules at room temperature

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Abstract

We have examined the photon statistics of single tetrahedral based oligophenylenevinylene (TOPV) molecules using photon pair correlation spectroscopy (PPCS). The second-order correlation function $g^{(2)}(\tau)$ can be obtained from PPCS and the value of $g^{(2)}(\tau)$ at small τ can be used to quantify the number of chromophores involved in emission. Comparison of $g^{(2)}(\tau)$ obtained from OPV 'arms' versus TOPV revealed limited interchromophore coupling in TOPV. Unlike previous studies on interchromophore coupling in organic semiconductors, TOPV molecules are able to sustain simultaneous emission from multiple arms.

1. Introduction

The potential for organic semiconductors as the active layer in devices such as organic light emitting diodes (OLEDs) has garnered significant research interest over the past several years. One promising materials platform is to produce low molecular weight oligophenylenevinylene (OPV) molecules whose structural and photophysical properties can be strictly controlled [1,2]. Although films cast from OPVs have high quantum yields, they exhibit significant crystallinity which gives rise to strong interchromophore interactions such as aggregate emission, and excimer formation [3]. These interactions tend to have a detrimental impact on device performance. To preclude chain packing in films, a tetrahedral based oligophenylenevinylene (TOPV) molecule was synthesized which contains four OPV 'arms' bound to a tetrahedral carbon core (Fig. 1). TOPV has been successfully used as the active layer in OLED devices [4,5] where its unique geometry directs the formation of amorphous films directly from solution.

In addition to their application in devices, the configuration of these TOPVs raises interesting fundamental questions about the nature of interchromophore coupling and how this is manifest in its photophysics. Specifically, can the excited state of this supermolecule be characterized as the product of four independent chromophores as opposed to a superposition of the excited states of four chromophores. Correspondingly, can a single tetrahedral molecule contain more than one excited chromophore and emit two or more photons simultaneously?

A previous study from our group [6] of the photoluminescence from single TOPV molecules has shown evidence of interchromophore coupling in the form of a well defined polarization anisotropy and intensity fluctuations indicative of collective behavior. In order to probe the extent of any interchromophore coupling in an isolated molecule a more definitive experiment is required.

The observation of photon antibunching has been used to unambiguously prove the inherent quantum mechanical nature of atomic systems [7,8], organic dyes [9,10], and semiconductor quantum dots [11,12]. Photon antibunching arises from the fact that the joint probability for the detection of photons at time, t, and $t+\tau$ vanishes as τ goes to zero due to the finite time required to absorb and then emit a photon. For a stream of photons, this can be measured as the photon pair coincidence distribution $C(\tau)$ where time intervals, τ, between photons are measured versus their occurrence.

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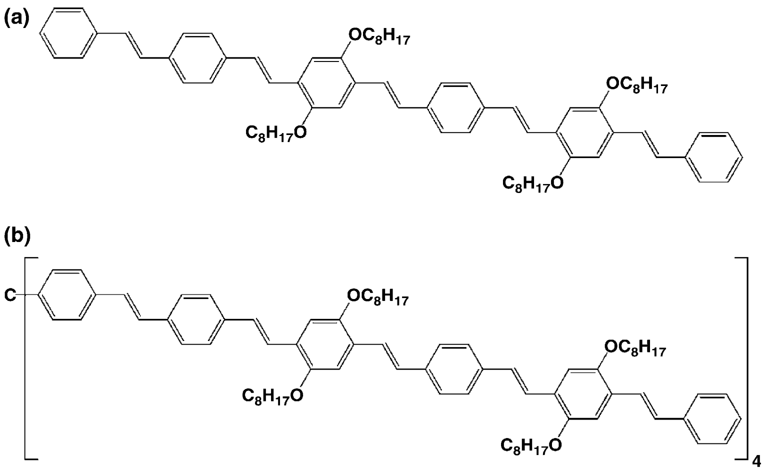

Fig. 1. Structures of OPV (6R-4OC_8H_{17}) (a) and TOPV (T-6R-4OC_8H_{17}) (b).

For a single quantum emitter, $C(\tau)$ drops to 0 as τ goes to 0. It has been shown that photon pair coincidence measurements can be used to determine the number of quantum emitters in a given collection volume [13–15]. For a number of emitters, N, the value of $C(0)$ scales as $[1 - 1/N]$. In this Letter, we report on photon pair coincidence distributions measured for both single OPV and TOPV molecules. The value of N obtained for a given distribution gives insight into the role that interchromophore interactions play in these multichromophoric systems.

2. Experimental

Single molecule samples were prepared by spin casting a 30 μL aliquot from a 0.1 nM toluene solution onto a clean glass slide yielding a mean separation between molecules of 1 μm. Fluorescence images from single molecules were collected using a home-built laser scanning confocal microscope (LSCM) described elsewhere [16]. An example of this image is presented in Fig. 2. All experiments were performed under strict anaerobic conditions.

Intensity fluctuations of single molecules were characterized by simultaneously measuring both the intensity trajectories and the photon pair arrival time distributions. Intensity trajectories were obtained by measuring the photocounts per 160 μs bin over hundreds of seconds. Photon pair arrival distributions were obtained with a setup analogous to the Hanbury–Brown–Twiss (HBT) apparatus which uses two APDs to overcome the 50 ns dead time of the individual APD. Signals from each of the two APDs were used as the start and stop channels of a time correlated single photon counting PC-Card (TCSPC, TimeHarp 200, Picoquant GmbH) with a 60 ns switchable cable delay on one channel to ensure that $\tau = 0$ was centered within the TAC window. During data collection, the TCSPC card was set at its highest temporal resolution of 37 ps and coincidence counts were stored in 100 ms segments. We determined our instrument response by measuring the coincidence distribution generated by elastically scattered 50 fs laser pulses from a glass slide. The resulting histograms were fit to gaussians with $\sigma^2 = 717 \pm 4$ ps. This corresponds to a mean APD time-jitter of ~470 ps.

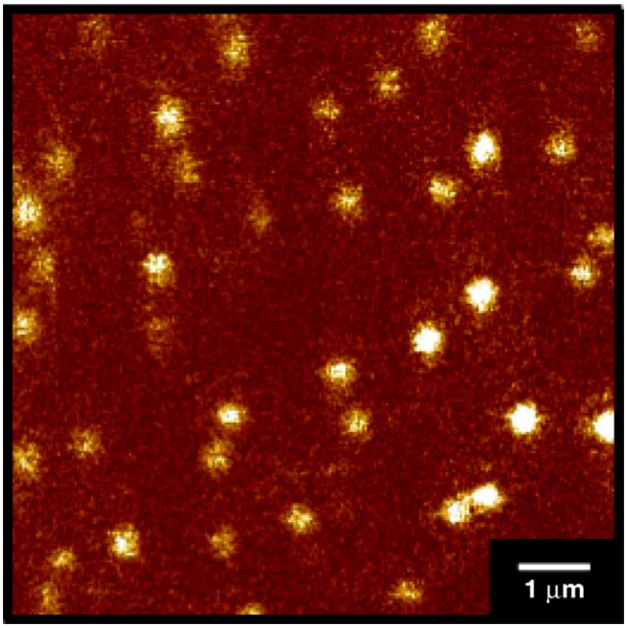

Fig. 2. 9×9 μm fluorescence image of TOPV molecules spatially isolated on a glass coverslip. The maximum depicted intensity is 12 kcps.

Data from the OPV molecule was taken at a power density of 2 kW/cm^2 which yields an average count rate of approximately 2.8 kcps. At this intensity, over 500 arrival pairs were detected within a 40 ns window for a 100 s collection time. In order to obtain reliable statistics, pair count distributions from 100 OPV molecules were averaged together. The data was binned to 950 ps (see Fig. 4) in order to provide a good measure of the asymptotic value of $g^{(2)}(\tau)$. This binning, however, limits the number of points in the dip region and decreases the observed temporal resolution. In order to obtain a better measure of the position of the dip and the exponential rise, we also examined data with 470 ps bin (see Fig. 4 inset) which provides the requisite temporal resolution. This temporal resolution is sufficient to resolve antibunched photons from OPV and TOPV molecules given that fluorescence lifetimes obtained in dilute solution yield identical values of 870 ± 10 ps for both molecules. TOPV molecules were examined with a power density of 7 kW/cm^2 corresponding to maximum intensities of 12 kcps and 2000 arrival pairs over 100 s. A large number of possible conformations are possible for each TOPV molecule as dictated by the conformational distributions of the precursor, TOPV [17]. The fluorescence intensities achieved from these molecules are strongly influenced by the number of cis defects in each arm. The presence of cis defects in oligophenylenevinylene molecules drastically decreases the quantum efficiency. This is well illustrated by the large distribution of intensities found in Fig. 2. Data acquisition was purposefully skewed towards the most intense molecules which represent those with either all trans vinyl linkages or with a single cis defect. Photon pair arrival histograms were averaged from TOPV molecules that exhibited dramatic multilevel intensity fluctuations which we presume to be indicative of multiple photoactive arms.

3. Results and discussion

Inspection of the intensity trajectories in Fig. 3 for OPV and TOPV show marked differences. The OPV arm molecules show no observable intensity fluctuations outside the shot noise and have an average intensity of 3 kcps. In contrast, the intensity trajectory for TOPV shows dramatic intensity fluctuations on all time scales down to the bin time of the experiment (160 us). The fluctuations range from a peak intensity of 12 kcps down to the background of 1.5 kcps. Of particular interest are those fluctuations in the region between 75 and 100 s where the intensity drops from 12 to ~3 kcps in a single event. It is tempting to attribute this to a state where all four arms are emitting simultaneously and then three arms switch 'off'. Such an event suggests strong coupling between arms and raises the question of the number of chromophores actively involved in the emission process.

A quantitative measure of intensity fluctuations is the second-order correlation function:

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2}, \qquad (1)$$

where $I(t)$ is the intensity at time t and $I(t+\tau)$ is the intensity at time $t+\tau$. The photon pair coincidence distribution $C(\tau)$ is a good approximation of $g^{(2)}(\tau)$ when the range of inter-photon timings are on the order of the radiative lifetime. The photon pair coincidence distributions are presented as a histogram of interphoton times versus the number of detected occurrences as can be seen in Fig. 4. Here it should be noted that the observed coincidences are measured from 0 to 20 ns and thus the only phenomenon contributing significantly to fluctuations in this time range is that of cycling through the molecular excited state.

To characterize coincidence histograms obtained from single molecules, the second-order correlation function can be fit with the functional form:

$$g^{(2)}(\tau) = 1 - \frac{1}{N} e^{-|\tau(W_p+\Gamma)|}, \qquad (2)$$

where Γ is the rate of decay of the excited state, W_p is the effective pump rate, and N is the number of emitters in the collection volume. All measurements were made in a regime far from optical saturation and as such $\Gamma \gg W_p$. Thus, the rate constant of the exponential rise in the coincidence histograms is effectively equal to the rate of radiative decay ($\tau_{rad} \cong 1/\Gamma$).

A least squares algorithm was used to fit the coincidence histograms of OPV and TOPV to the symmetrized exponential given in Eq. (2). Examination of the coin-

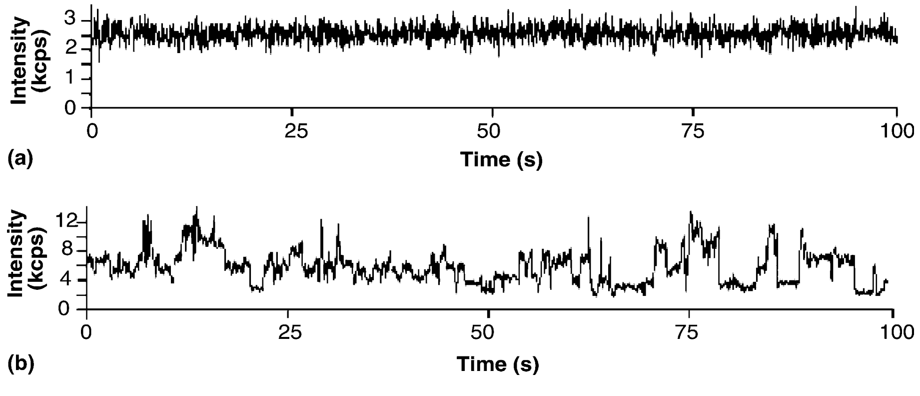

Fig. 3. Intensity trajectories with 80 ms bins for a single OPV molecule (a) and a single TOPV molecule (b).

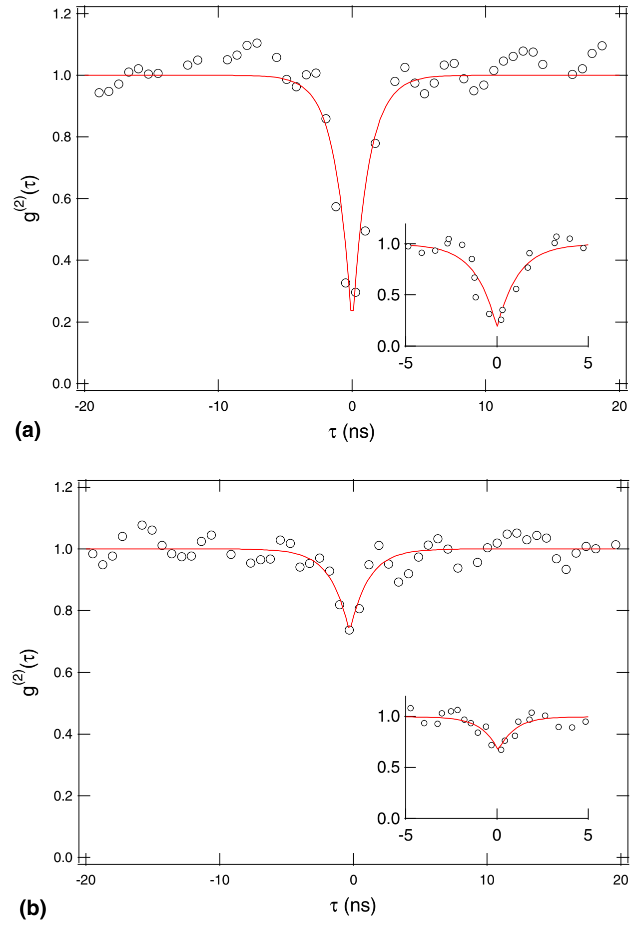

Fig. 4. Photon pair coincidence histograms for OPV (a) and TOPV (b). Histograms were produced by averaging coincidence data from 100 molecules (a) and 50 molecules (b). Insets: dip region with coincidence bins set at 470 ps.

cidence histogram obtained from OPV exhibits a drop of $g^{(2)}(0)$ well below 0.5. This is indicative of an antibunched, sub-Poissonian light field as would be expected from a single chromophore system. The fit yields a value of $N = 1.3$ and $\tau_{\mathrm{rad}} = 1.1$ ns. The deviation of N from 1 and Γ from 870 ps can be explained as a product of two factors. The first is the contribution of uncorrelated photons from a variety of sources including inelastically scattered laser light, background fluorescence, and photo-induced cross talk between the SPCMs. Secondly, the relative proximity of the instrument response to the radiative lifetime and the data bin size limits the sensitivity in the low count region near $\tau = 0$.

In contrast, the coincidence histogram for TOPV in Fig. 4 shows a drastically reduced antibunching dip, ($g^{(2)}(0) = 0.672$) compared to the single arms. The fit to the data gives N to be 3.04 with $\tau_{\mathrm{rad}} = 810$ ps. The disparity in radiative lifetimes between OPV and TOPV is the result of timing uncertainty and variation in s/n between systems. An idealized model of TOPV with completely independent chromophores would be expected to have an antibunching dip with $N = 4$. In addition to the effects addressed previously, the deviation from $N = 4$ in our data is likely due to statistical contributions from molecules with 2, 3, and 4 emissive arms. Furthermore, inefficient fluorescence detection of chromophores with large components of transition dipole in the z direction undoubtedly artificially decreases the dip contrast.

It should be noted that the uncertainty in $g^{(2)}(\tau)$ for both OPV and TOPV near zero sets an upper and lower limit on N. For the OPV molecule the upper limit of $g^{(2)}(0)$ is 0.41 which is still indicative of only a single emitter. Conversely, the coincidence histogram for the TOPV molecule limits the range of N from 2.45 to 4.03. Thus, the data clearly demonstrates that the molecule averaged photon statistics of TOPV are a result of emission from more than two chromophores. Given that the regions of highest intensity dominate the coincidence histogram, TOPV molecules appear to have uncoupled emission.

The implication of simultaneous emission from multiple arms is striking considering how closely the chromophores are bound. This is in direct contrast to previously studied multichromophoric systems of conjugated polymers [14] and dendrimers [18] where antibunching signatures were observed in the photon pair arrival histogram. In these systems energy transport is highly efficient due to strong chromophore interactions. In the MEH-PPV studies of Hollars et al. [14], this coupling is facilitated by strong π-stacking between chromophore units which then provide rapid excitation transport to a few low energy sites on the polymer chain. Whereas the perylenimide dendrimers studied by Tinnefeld et al. [18], are presumed to have rapid exciton transport via Förster type incoherent dipole coupling which results in exciton–exciton annihilation and emission from only a single chromophore. Neither of these effects are observed for our molecules.

The geometry imposed by the tetrahedral core of the TOPV molecule excludes strong π-stacking between neighboring arms. However, there is considerable spectral overlap in the absorption and emission bands of the arms which could plausibly lead to energy transport via either a coulombic incoherent through-space coupling or exciton transport through the tetrahedral core. Given the ~2 Å interchromophore separation through the tetrahedral core, a Dexter-type electron exchange mechanism is unlikely due to limited electron density overlap. A coulombic through-space coupling such as the dipolar-type Förster coupling is perhaps more accessible. Using spectral data from TOPV, Förster theory predicts energy transfer on the order of tens of picoseconds over nearly all interchromophore angles. Previous ultrafast polarization anisotropy experiments on a similar tetrahedral OPV in solution showed a two component anisotropy decay which the authors attributed to contributions from both coherent and incoherent coupling [19]. However, this coupling does not appear to dramatically effect the emission statistics of isolated TOPV. Previous results [6] show a strong time-dependent polarization anisotropy which suggests significant motion of the OPV arms. Motion in the arms is postulated to be due in large part to motions about the 5 vinylene linkages and rotations about the tetrahedral carbon. Under this model, inter-arm contacts could vary from strict tetrahedral symmetry to conformations where arms are in contact. Accordingly, inter-chromophore interactions can range from weak coulombic coupling to highly delocalized excimer or aggregate states. We suggest that this dynamic coupling dictates the emission statistics of TOPV. Moreover, it this dynamic coupling that distinguishes the photophysics of TOPV from other highly coupled multichromophoric systems, such as those in [18].

4. Conclusions

In this report we have shown unambiguously that the emission of the TOPV molecule can be described as originating from multiple independently excited chromophores. This confirms the efficacy of producing multi-chromophore oligophenylenevinylene molecules as they have preferred geometries yet exhibit emission from multiple chromophores.

Acknowledgements

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