Quest for Order in Chaos: Hidden Repulsive Level Statistics in Disordered Quantum Nanoaggregates

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ABSTRACT The local distribution of exciton levels in disordered cyanine-dye-based molecular nanoaggregates has been elucidated using fluorescence line narrowing spectroscopy. The observation of a Wigner–Dyson-type level spacing distribution provides direct evidence of the existence of level repulsion of strongly overlapping states in the molecular wires, which is important for the understanding of the level statistics, and therefore the functional properties, of a large variety of nanoconfined systems.

One of the current dreams in the field of molecular optics is the full understanding of nature’s way to harvest and use photonic energy, which ultimately could enable the development and design of highly efficient functional optical devices using molecular arrangements as building blocks. One of the crucial elements of such photonic assemblies are the “wires” which transport the energy between the different functional units of the devices. Natural systems often utilize structures of coupled aggregated pigments to transport energy in the form of excitonic excitations.†-‡ Such structures can also be mimicked in synthetic systems, greatly assisting studies aiming to understand their fundamental properties. An important class of synthetic species, on which we focus here, is found in the so-called one-dimensional (1D) J-aggregates based on, for instance, pseudoisocyanine, porphyrin, and benzimidazole carbocyanine dyes.‡-§

Synthetic as well as natural systems usually exhibit a substantial degree of disorder, arising from the environment and from vibrations and disorder within the systems themselves. In general the presence of disorder in gapped systems leads to the formation of highly localized states inside of the optical, electronic, or magnetic energy gap of the unperturbed system, that is, to a tail of the density of states (DOSs) inside of the gap generally referred to as the Lifshits tail.‡-‡ There are many systems in which optical properties are governed by exciton-like excitations highly susceptible to disorder, leading to localization and level repulsion phenomena. These include conjugated oligomer aggregates,†-‡ and polymers,§ molecular J-aggregates,‡-§ semiconductor quantum wells and quantum dots,¶ gold nanoparticles,¶ semiconductor quantum wires,‡¶ as well as photosynthetic light-harvesting complexes and proteins (see refs 6 and 7 for a recent overview). In all of these systems, excitons are confined at least in one dimension at a nanometer scale.

The physical and transport properties of most of the above-mentioned systems are predominantly determined by the states residing in the vicinity of the energy gap, that is, the gap excitation itself and the Lifshits tail below it, even at finite temperatures.¶,§ The localization of the exciton states within the Lifshits tail gives rise to a local (hidden) statistics of the levels, which deviate substantially from the overall statistics.¶,¶ The level statistics of such a system is known as Wigner–Dyson statistics (see the excellent textbook by Metha for an overview).

Level repulsion phenomena in nanoconfined materials have recently drawn considerable attention, in particular, concerning localized Wannier excitons in disordered quantum wells,¶-¶ wires,¶-¶ and disordered graphene quantum dots as well as concerning vibronic states in polyatomic molecules.¶,¶ Time-resolved resonant Rayleigh scattering and near-field spectroscopy have been used to study them. In ref 36, an alternative method has been proposed to analyze the level statistics of low-temperature time-resolved selectively excited excitation fluorescence spectroscopy, widely known as fluorescence line narrowing (FLN) spectroscopy. Under a narrow (compared to the J-bandwidth) excitation within the J-band, the fluorescence spectrum

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Figure 1. Low-temperature steady-state absorption (solid line) and fluorescence (dotted line) spectra of the J-aggregate of PIC-Cl in the neighborhood of the J-band. The fluorescence spectrum was measured after off-resonance excitation far in the blue tail at a temperature of $T = 4$ K. The inset show the absorption spectrum in a wider spectral range.

consists of a sharp intensive peak at the excitation energy and, growing in time, a red-shifted feature, resulting from the exciton band relaxation. It is this feature that contains information about the level statistics of the spatially overlapped states.

Here, we apply a variant of this method to reveal the repulsive statistics of levels residing in the Lifshits tail of J-aggregates of pseudoisocyanine (PIC) with a chloride counterion (PIC-Cl). In contrast to the earlier proposal to use time-dependent FLN, we here show that also steady-state FLN, which is much simpler in realization, can be utilized to extract the desired information. We extract the conditional probability distribution of the repelled states from the experimental data and show that this distribution is Wigner–Dyson-like, indicating zero probability for zero energy spacing, which is a fingerprint of the level repulsion.

Figure 1 shows the absorption $A$ and fluorescence $F$ spectra of J-aggregates of PIC-Cl, the latter measured after excitation using 400 nm light. Both spectra exhibit an intense peak arising from the dominant exciton transitions (the J-band) and a much less intense and broad shoulder located on the red side of the J-band. We relate this red feature to aggregates in the vicinity of the substrate as the relative intensity of this shoulder decreases upon increasing thickness of the aggregated film. For completeness, we note that the overall absorption spectrum of our samples (see inset in Figure 1) is found to be in good agreement with earlier results.

Before turning to the main experimental results, we briefly sketch some of the theoretical background relevant for the present study; more details on the model and the energy level structure of the disordered J-aggregates have been discussed in ref 24. A typical realization of the calculated low-energy level structure and wave functions for a one-dimensional aggregate is depicted in Figure 2. This calculation on a chain of 300 chromophores used a Gaussian disorder distribution of the chromophore energies with a standard deviation of $\sigma = 0.1 J$ (disorder degree from now on), $J$ being the transfer interaction between chromophores (for more details, see ref 24 and the Supporting Information).

Figure 2. A typical realization of the exciton wave functions $\Phi_{\nu}$ ($\nu = 1, \ldots, 14$) in the neighborhood of the bare exciton band edge $E_0 J = -2.404$. The Lifshits tail of the DOS $(E < E_0)$ is shaded. The origin of the energy is chosen at $E_0 = 0$, and the baseline of each wave function represents its energy in units of $J$. Wave functions are in arbitrary units. $N^*$ denotes the typical localization size of the tail states. Filled red curves are s-like states which overlap weakly. Some of them appear even slightly above the bare band edge. Filled blue curves are p-like states which overlap well with their s-like partner state lying below. Higher gray-shaded states are band states. They are delocalized to a larger extent as compared to the tail states.

Without disorder, wave functions are fully delocalized, and the lowest state is located at $-2.404 J$. The presence of disorder leads to localization of the wave functions within so-called segments and to the appearance of highly localized states within the band gap, that is, in the Lifshits tail (gray-shaded area in Figure 2). These are the states of our primary interest since they determine the optical properties and transport in the J-aggregates. They originate from localization in well-like fluctuations of the site potential on the molecules. The optically dominant states resemble s-like wave functions which have no nodes within their localization segments. The s-like states lying deep in the Lifshits tail usually appear as singlets and are localized by the so-called optimal fluctuations of the site energy. Close to the band edge, however, the s-like states often have partners localized within the same localization segment. The latter look like p-states, having one node within their localization segment. Manifolds like these form the local (hidden) structure of the tail of the DOSs. Since these states are localized on the same segment, one may expect level repulsion to occur for them, as is indeed observed. In contrast, states from distant (nonoverlapping) manifolds can be arbitrarily close in energy.

Optical experiments probe the states with a finite transition dipole moment. For the s-like states, the transition dipole moment scales proportionally to $(N^*)^{1/2}$, where $N^*$ is the typical localization length of the states. This enhancement of the dipole moment is known as superradiant enhancement. Typically, the p-like states have a transition dipole moment which is several times smaller than the s-like states. Nevertheless, since the p-states are not perfectly antisymmetric, they do have a finite transition dipole moment, and these states can be optically excited too. Therefore, optical experiments can be used to probe the level statistics by studying the relaxation between p- and s-like levels.

To experimentally study the level statistics in the neighborhood of the exciton band edge, we performed steady-state
resonance fluorescence measurements using a narrow excitation line to excite states within the J-band. Figure 3 shows a number of such spectra recorded at low temperature using different excitation energies. The spectra show a strong peak at the excitation wavelength, together with a broad red-shifted emission band separated from the main peak by a pronounced dip. The red-shifted emission originates from relaxation of the initially excited exciton states into states of the Lifshits tail of the DOSs. The position of the maximum of this band remains almost unchanged while J-aggregates are excited on the blue side of the J-band. For the red-side excitation, the peak position moves to the red, the line shape changes considerably, and the dip washes out. This is a consequence of the changes in the relaxation pathways since red-side excitation predominantly excites s-like states.

The dip close to the excitation energy in the blue-side excited spectra distribution shows that energy relaxation into states close to the excitation energy is substantially suppressed, hinting to the occurrence of level repulsion. The sheer existence of the dip, however, is not enough to conclude on the level statistics. The problem is that the relaxation process from the initially excited states to the lower-lying levels is phonon-assisted, and hence, the line shape is determined by the product of the level spacing distribution function and the phonon spectral density. Since the phonon spectral density vanishes for zero energy, one expects the spectral intensity to vanish at the excitation energy, even without level repulsion. Moreover, one also should bear in mind that together with the fluorescence of the relaxed excitons, two more processes contribute to the red feature and affect its line shape, the phonon sideband fluorescence and surface-mediated fluorescence in our thin samples. All three contributions to the red-shifted feature are spectrally superposed and must be separated in order to extract the signal in which we are interested. We note, however, that if the observed red-shifted feature would solely originate from the phonon sideband, its line shape and position would be virtually independent of the excitation wavelength, clearly in contradiction to the experimental observations.

In the analysis of the observed spectra, we limit ourselves to those spectra measured using excitation on the blue side of the J-band since it is here that one expects the p-like states to contribute most strongly. In order to discriminate the true relaxation-mediated fluorescence (RMF) from the surface-mediated and the phonon sideband fluorescence, we use a simple subtraction method. For this, we consider the differential spectrum between two experimental spectra with close excitation wavelengths \( \lambda_2 \) and \( \lambda_1 \) defined by

\[
\Delta F(\lambda_1, \lambda_2, \lambda) = F(\lambda_2, \lambda) - \beta F(\lambda_1, \lambda - \lambda_2 + \lambda_1)
\]

where the second term on the right-hand side is the RMF spectrum shifted in wavelength to match its excitation peak position with that of the \( F(\lambda_2, \lambda) \) spectrum. In addition, this term is rescaled by a factor of \( \beta \) in order to cancel the red tail in the spectra; any feature that is not wavelength-dependent is suppressed in the difference spectrum eq 1, and the resulting difference spectrum represents just the RMF differential signal \( \Delta R(\lambda_1, \lambda_2, \lambda) \)

\[
\Delta R(\lambda_1, \lambda_2, \lambda) = R(\lambda_2, \lambda) - \beta R(\lambda_1, \lambda)
\]

Assuming that the only contribution to the RMF originates from processes which include only a single step of relaxation, which is justified by the low quantum efficiency of the RMF signal (around 0.1) when exciting on the blue side, the theoretical RMF line shape can be expressed as \( R(\lambda_0, \lambda) \approx S(\lambda - \lambda_0)P_{sp}(\lambda_0, \lambda - \lambda_0) \), where \( S(\lambda - \lambda_0) \) is the one-phonon spectral density, and \( P_{sp}(\lambda_0, \lambda - \lambda_0) \) is the conditional (sp) level spacing distribution (see Supporting Information). We can now relate two RMF spectra taken for different (close) excitation wavelength \( \lambda_2 \) and \( \lambda_1 \) as

\[
R(\lambda_2, \lambda) \approx \frac{S(\lambda - \lambda_2)}{S(\lambda - \lambda_1)} R(\lambda_1, \lambda)
\]

where we assumed that the energy spacing distribution function varies much slower than the phonon spectral density, the assumption which, as will be seen, is consistent with the final results. Substituting eq 3 into eq 2, we arrive at a relationship between the differential and ordinary RMF spectra

\[
\Delta R(\lambda_1, \lambda_2, \lambda) \approx g(\lambda) R(\lambda_2, \lambda)
\]

where

\[
g(\lambda) = \frac{1 - \beta}{\frac{S(\lambda - \lambda_1)}{S(\lambda - \lambda_2)}}
\]

that is, the line shape of the RMF spectrum can be extracted from the line shape of the differential RMF spectrum by dividing it by the known correction function \( g(\lambda) \), provided that the factor \( \beta \) is adjusted to cancel the long red tail.

The described approach has been applied to the spectra recorded using excitation in the blue part of the absorption spectrum (\( \lambda_1 = 568.5 \text{ nm} \) and \( \lambda_2 = 569 \text{ nm} \)). The results, assuming a Debye-like spectral density \( S(\lambda) \propto \lambda^{-\gamma} \), are shown in Figure 4. The extracted RMF spectrum, obtained by choosing \( \beta = 1.06 \), is plotted in the figure by the open circles. Clearly, the non-RMF contributions leading to the long red tail of the fluorescence spectrum are, as expected, nearly fully eliminated. The solid curve in Figure 4 represents the theoretical spectrum which has been calculated within the framework...
phonon scattering strength calculated for the Debye-like spectral density RMF transitions. Also shown is the theoretical RMF spectrum to eliminate the contribution of the long red tail resulting from non-RMF transitions. Also shown is the theoretical RMF spectrum calculated for the Debye spectral density $S(\lambda) = \lambda^{-3}$. 

Figure 4. The conditional probability of the nearest-level spacing distribution $P_{\text{sp}}$ (diamonds) obtained by dividing the experimental curve (circles) by the Debye-like spectral density $S(\lambda) = \lambda^{-3}$ together with the calculated level spacing distribution $P_{\text{sp}}$ (dashed curve). The experimental RMF spectrum (circles) shows the data after applying the subtraction method (described in the text) to eliminate the contribution of the long red tail resulting from non-RMF transitions. Also shown is the theoretical RMF spectrum calculated for the Debye-like spectral density $S(\lambda) = \lambda^{-3}$ (solid curve) and the absorption spectrum (dotted curve).

Figure 5. Open circles represent the experimental red-shifted feature obtained after applying the subtraction approach (described in the text) to eliminate a contribution of the long red tail resulting from non-RMF transitions. The solid curve is the theoretical RMF spectrum calculated for the Debye spectral density $S(\lambda) = \lambda^{-3}$, while the dashed–dotted and dashed curves are the RMF spectra for $S(\lambda) = \lambda$ and $S(\lambda) = \lambda^{-2}$, respectively. The dotted curve denotes the absorption spectrum.

of an exciton relaxation model (see Supporting Information), also assuming the Debye spectral density $S(\lambda)$, exciton–phonon scattering strength $W_0 = 22.4 J$, and a Gaussian diagonal disorder of magnitude $\sigma = 0.2 J$. The latter fits the cryogenic PIC-Cl absorption spectrum.

It is interesting to note that only calculations using a Debye type of the spectral density (i.e., $S(\lambda) \approx \lambda^{-4}$ with $\alpha = 3$) lead to a satisfactory agreement with the experimental data. This is clearly demonstrated in Figure 5, which compares the various assumptions for $\alpha$. This apparent validity of the usage of the Debye model corroborates the results of ref 39, where this model has been successfully applied to explain the temperature dependence of the J-bandwidth and the radiative lifetime of J-aggregates of pseudoisocyanine.

Figure 4 shows the principal result of the present study, the conditional distribution of the nearest-level spacing, $P_{\text{sp}}(\lambda_c, \Delta \lambda)$ (diamonds), obtained after dividing the extracted RMF spectrum presented in Figure 4 (open circles) by the spectral density $S(\lambda) \approx \lambda^{-3}$. We see that $P_{\text{sp}}(\lambda_c, \Delta \lambda)$ tends to 0 upon $\Delta \lambda \to 0$. This is a clear signature of the repulsive statistics of the nearest-level spacing. If the distribution is a pure Wigner–Dyson one, then the probability should decrease linearly to 0 upon approaching zero level spacing. Though with the present data it remains difficult to determine whether this indeed holds, the result is strikingly close to a Wigner–Dyson distribution.

To conclude, we experimentally studied the statistics of the low-energy spectrum of disordered molecular nanoaggregates of pseudoisocyanine with the chloride counterion in the neighborhood of the exciton band edge. The fluorescence line narrowing technique, allowing one to probe the local energy level distribution, has been exploited for this goal. We found a clear signature of a Wigner–Dyson-like distribution for the nearest-level spacing, originating from the exciton states localized on the same segment of the aggregate and thus undergoing the quantum mechanical level repulsion. This is the first direct experimental proof of the existence of hidden structure of the exciton low-energy spectrum, the region which dominates the aggregate optical response and low-temperature transport.

Our finding has a wider applicability than that for the simple 1D Frenkel exciton system considered here. The reason is that the nature of the band edge states (mostly in the Lifshits tail) is shared by a large variety of systems, such as gold nanoparticles and quantum wells and quantum wires.

EXPERIMENTAL SECTION

The samples used in this study were obtained from stock solutions of $1 \times 10^{-3}$ M pseudoisocyanine chloride (PIC-Cl) (Hayoshibara) prepared by dissolving the dye in doubly distilled water and stirring at 80°C for 30 min. At this concentration, PIC-J-aggregates form while the solution cools down to room temperature. A droplet of warm solution was squeezed between two 0.12 mm thick glass microscope coverslips or between a copper plate and a microscope slip, first cooled to room temperature and then quenched to 77 K in liquid nitrogen. Subsequently, the sample was transported into a $^3$He continuous-flow cryostat (CF1204SEG, Oxford Instruments). All of the experiments on the aggregates were performed at cryogenic temperatures (4.5 K).

The continuous-wave fluorescence excitation measurements were performed by using an Xe arc lamp as an excitation source. The excitation spectrum was narrowed down to 0.1 nm by means of a double additive monochromator. The emission spectra were recorded by using a triple grating monochromator in the subtractive mode equipped with a liquid-nitrogen-cooled CCD detector (spectral resolution 0.05 nm).

SUPPORTING INFORMATION AVAILABLE Details of the theoretical treatment. This material is available free of charge via the Internet at http://pubs.acs.org.

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