

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/40820897>

# Collective Fluorescence Blinking in Linear J-Aggregates Assisted by Long-Distance Exciton Migration

ARTICLE *in* NANO LETTERS · FEBRUARY 2010

Impact Factor: 13.59 · DOI: 10.1021/nl9036559 · Source: PubMed

CITATIONS

63

READS

40

6 AUTHORS, INCLUDING:



**Hongzhen Lin**

Chinese Academy of Sciences

47 PUBLICATIONS 676 CITATIONS

SEE PROFILE



**Rafael Camacho**

University of Leuven

14 PUBLICATIONS 156 CITATIONS

SEE PROFILE



**Yuxi Tian**

Nanjing University

38 PUBLICATIONS 587 CITATIONS

SEE PROFILE



**Ivan G Scheblykin**

Lund University

80 PUBLICATIONS 1,494 CITATIONS

SEE PROFILE

# Collective Fluorescence Blinking in Linear J-Aggregates Assisted by Long-Distance Exciton Migration

Hongzhen Lin,<sup>†</sup> Rafael Camacho,<sup>†</sup> Yuxi Tian,<sup>†</sup> Theo E. Kaiser,<sup>‡</sup> Frank Würthner,<sup>‡</sup> and Ivan G. Scheblykin<sup>\*,†</sup>

<sup>†</sup>Chemical Physics, Lund University, Box 124, 22100, Lund, Sweden, and <sup>‡</sup>Universität Würzburg, Institut für Organische Chemie and Röntgen Research Center for Complex Material Systems, Am Hubland, 97074 Würzburg, Germany

**ABSTRACT** Fluorescence blinking corresponding to collective quenching of up to 100 dye monomers is reported for individual J-aggregates of a perylene bisimide (PBI) dye. This implies an exciton diffusion length up to 70 nm in these one-dimensional assemblies. The number of quenched monomers was directly measured by comparing the fluorescence brightness of the J-aggregates with that of noncoupled PBI molecules. This brightness analysis technique is useful for unraveling photophysical parameters of any individual fluorescent nanosystem.

**KEYWORDS** Single molecule spectroscopy, fluorescence quantum yield, fluorescence brightness, energy migration, J-aggregate

In the late 1980s, the great idea of combination of fluorescence microscopy and optical spectroscopy gave birth to single molecule spectroscopy (SMS)—a method to study fluorescence light coming from a single molecule (or other nano-object).<sup>1,2</sup> SMS allows studying underlying dynamics that are unobservable in experiments on bulk materials due to *ensemble averaging*. A well-known example is fluorescence “blinking”—strong fluctuations of fluorescence intensity of a single molecule or single nanoparticle under continuous excitation, which is usually explained by the molecule (or nanoparticle) from time to time temporarily residing in a long-lived nonfluorescent “dark” state. Note that such a phenomenon was observed not only for single quantum systems like dye molecules and small quantum dots but also for multichromophore ensembles such as conjugated polymers,<sup>3</sup> polymer aggregates,<sup>4</sup> and natural light-harvesting complexes.<sup>5</sup> Observation of fluorescence intensity blinking in multichromophoric systems (called also “collective blinking effect”) was related to energy exchange between chromophores.<sup>6–9</sup>

The general idea is that once a photogenerated quencher exists in an ensemble of chromophores, it can quench any singlet exciton created therein. Even if an exciton is not formed in the vicinity of the quencher, it will reach the quencher due to efficient energy migration among the chromophores. It has been demonstrated that the quencher responsible for blinking at time scale of seconds in conjugated polymers is a hole polaron.<sup>4,10–12</sup> The size of the ensemble, i.e., the number of chromophores that can be collectively quenched, depends on

the excitation migration distance and the quenching radius. Because of this dependence, the blinking effect has become a tool for monitoring energy transfer in individual macromolecules and nanoaggregates.

It is important to realize that the collective quenching process has a direct relation to operation of light-driven molecular devices like, e.g., solar cells.<sup>13</sup> Indeed, in order to use light energy effectively, all photoexcitations created at a large antenna should be harvested at a reaction center (quencher) to produce electron–hole pairs or to run a desired chemical reaction. This is exactly the same effect, which reveals itself as collective blinking in single molecule experiments.

The conclusion of collective reversible quenching of many chromophores in conjugated polymers was drawn by assuming that all the chromophores were active in harvesting light and creating excitons. However, this assumption should not have been taken for granted because the primary photoexcitations in conjugated polymers at certain condition are mainly nonemissive.<sup>14,15</sup> Our very recent work<sup>16</sup> has shown that, contrary to the common belief, isolated long chains of poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene (MEH-PPV) in polymer host matrices inherently and permanently possess most of their chromophores in dark states, which are unobservable at all by fluorescence techniques. Therefore, the fluorescence blinking of single MEH-PPV molecules can hardly be called “collective”. This strongly motivated us to find multichromophoric systems in which collective blinking of tens of chromophores can indeed take place.

Just by looking at the relative fluorescence intensities, one cannot tell how many chromophores are quenched without knowing how many chromophores are indeed contributing to fluorescence before the quenching happens. Therefore,

\* To whom correspondence should be addressed, Ivan.Scheblykin@chemphys.lu.se.

Received for review: 11/1/2009

Published on Web: 00/00/0000



measuring the absolute number of collectively quenched chromophores becomes an important task, which, to the best of our knowledge, has never been accomplished.

In fact, many applications of SMS require knowing how many chromophores contribute to the fluorescence light that appears as single diffraction limited spot at the image. Approaches to measure this based on total number of emitted photons<sup>17</sup> and photon correlation analysis<sup>18</sup> have been proposed.

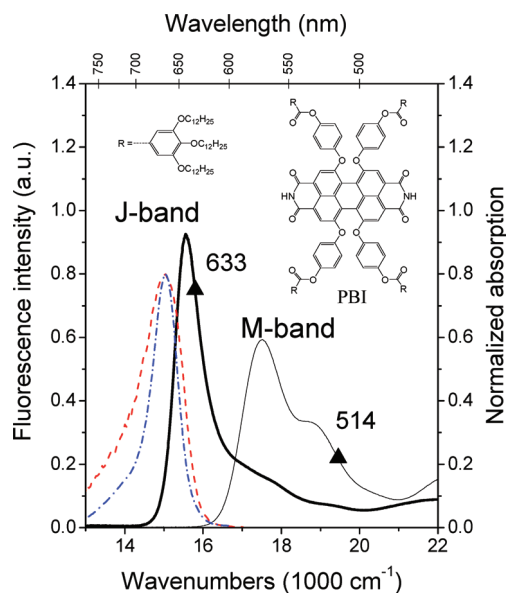
Since their discovery in 1930s,<sup>19,20</sup> molecular J-aggregates have attracted substantial attention due to their unique optical properties and their application in photography as sensitizers. These systems can be regarded as low-dimensional self-assembled structures of excitonically coupled organic dye molecules. Excited states in J-aggregates are Frenkel excitons delocalized over a certain number of dye molecules depending on disorder and temperature.<sup>21–25</sup>

The intermolecular resonance interaction responsible for exciton delocalization facilitates energy migration within the aggregate. Such a system consisting of coherently coupled chromophores could work as extremely efficient light-harvesting antenna. The SMS approach has been shown to be useful to study structure of the exciton bands at low temperature by monitoring excitation spectra of individual aggregates.<sup>26</sup>

Formation of classical J-aggregates usually occurs in polar solvents such as water and often requires the presence of a high concentration of salts, making them inconvenient for applications. Recently, some of us have introduced a new class of highly fluorescent J-aggregates that are formed in apolar organic solvents by hydrogen bonding and  $\pi$ - $\pi$  stacking interactions of perylene bisimide (PBI) dyes.<sup>27,28</sup> These J-aggregates are sufficiently robust for orientation by shearing forces and transfer to substrate surfaces by spin-casting. Atomic force microscopy studies<sup>27,28</sup> showed J-aggregates as separated one-dimensional threadlike structures without tendency to bundle formation. Individual J-aggregates of this new type are the focus of this study.

The PBI dye (Figure 1) was synthesized according to a previously reported method.<sup>27</sup> Spectrophotometric grade solvents methylcyclohexane (MCH) and dichloromethane (DCM) were purchased from Sigma-Aldrich and distilled prior to use.

Samples for fluorescence microscopy were prepared by spin-casting of  $10^{-7}$ – $10^{-8}$  M solutions of PBI in MCH on microscope coverslips (Menzel-Glaser, used as received). Well-separated diffraction-limited fluorescent spots having characteristic fluorescence spectra were assigned to individual J-aggregates. Different J-aggregates in the spin-coated sample were found possessing almost identical emission spectra. Figure 1 shows the typical emission spectrum of a single J-aggregate. It is slightly broader than the emission spectrum of the J-aggregates in MCH solution,<sup>27</sup> implying that the aggregates on the surface possess more disordered structure than those in the solution. Note that J-aggregates in such diluted solutions are thermodynamically unstable and that dissociation to monomers occurs within 1–2 h at



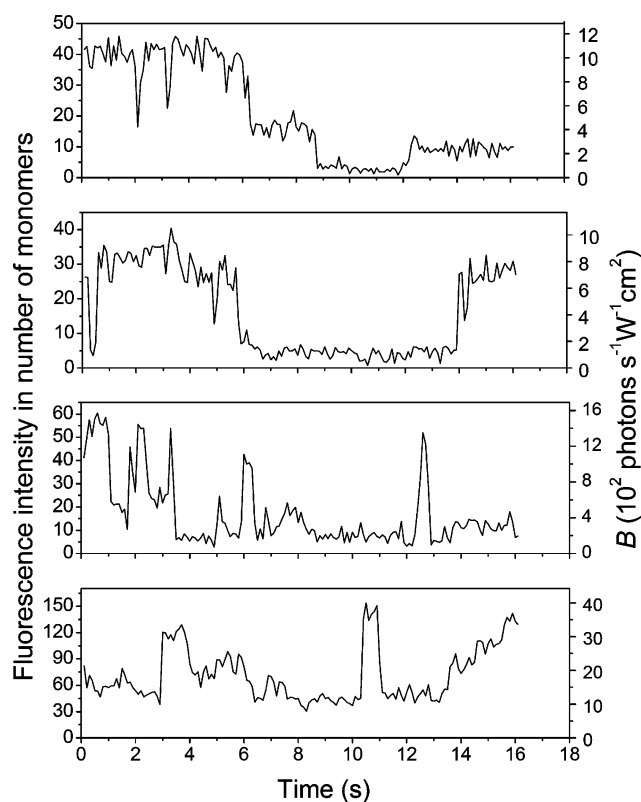
**FIGURE 1.** Chemical structure of PBI (inset), absorption spectra  $A(\nu)$  of PBI monomer solution in DCM (thin solid line) and J-aggregates in MCH (bold solid line), emission spectrum of the J-aggregates in MCH solution (dash-dot line), and typical emission spectrum of an individual J-aggregate on glass surface (dash line). The areas under the absorption spectra were normalized to 1 (see eq 8). Relative absorption cross sections at the corresponding excitation wavelengths (514 nm for free monomers, and 633 nm for J-aggregates) are indicated by triangles.

room temperature. Therefore, the time period between the dilution of the thermodynamically stable stock solution ( $6 \times 10^{-5}$  M) and spin-casting could be used to adjust the length and concentration of the aggregates in the resulting samples.

For comparison, single-molecule samples containing isolated noncoupled PBI molecules were also prepared by spin-casting dilute solutions ( $\sim 10^{-10}$  M) of the dye in DCM on clean quartz coverslips. Owing to the high polarity and polarizability of this solvent,  $\pi$ - $\pi$  stacking and hydrogen-bonding interactions are strongly reduced and no J-aggregates are formed even at higher concentrations.<sup>29</sup>

The above samples were investigated with a home-built wide-field fluorescence microscopy setup based on an Olympus IX-71 inverted microscope and a CCD camera with on-chip multiplication gain (Photometrics, Cascade 512B). A sample placed in a nitrogen chamber was excited by a circularly polarized continuous wave (CW) laser light at 514 nm (for monomers) or 633 nm (for J-aggregates) through an oil-immersion objective lens (Olympus UPlanFLN 60 $\times$ , N.A. = 1.25). The excitation beam was defocused to give an excitation spot of  $\sim 30$   $\mu$ m in diameter in the sample plane. The typical excitation power density used in this study was  $\sim 50$  W/cm<sup>2</sup>, which was low enough to exclude singlet–singlet exciton annihilation.

Strong fluorescence intensity fluctuations (blinking) were observed in the studied single J-aggregates at excitation power density  $I = 50$  W/cm<sup>2</sup> (Figure 2, time resolution 100 ms). As far as we know, a fluorescence blinking effect has



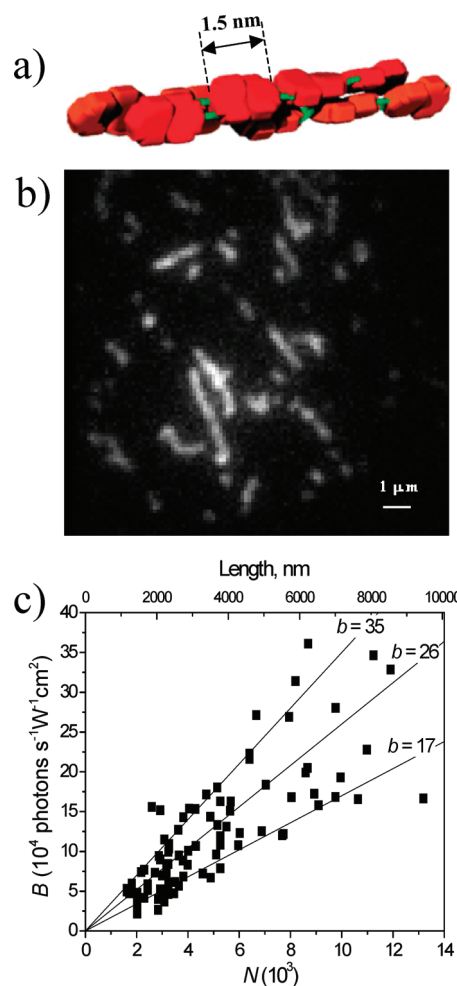
**FIGURE 2.** Fluorescence intensity trajectories (time resolution 100 ms) for several individual J-aggregates under CW excitation at 633 nm. Fluorescence intensity is shown in numbers of dye monomers contributing to the fluorescence (see the text for details) and in brightness coefficient  $B$ , i.e., photon counts per second at  $1 \text{ W/cm}^2$  of excitation power density.

never been reported for J-aggregates before. The fluorescence blinking observed in this study was caused by photo-generated quenchers with lifetimes longer than 100 ms (our time resolution) and could be suppressed by decreasing the excitation power (see an example in the Supporting Information). The most probable origin of such long-lived quenchers with lifetimes up to several seconds lies in photoinduced charge-transfer processes of the aggregates. A detailed quenching mechanism is under investigation and beyond the scope of this study.

Fluorescence blinking is a result of temporal fluctuation of the fluorescence quantum yield  $\Phi = \Phi(t)$ . Because the quenchers which cause the blinking are photogenerated,  $\Phi$  is also parametrically dependent on the excitation power density  $I \text{ (W/cm}^2\text{)}$ . In order to see how many monomers were collectively quenched in each blinking event, the fluorescence intensity of a J-aggregate should be “translated” into the number of monomers contributing to the fluorescence  $N(t)$ , which can be defined as

$$N(t) = N_{\text{total}} - N_{\text{quenched}} = N_{\text{total}} \frac{\Phi(t, I)}{\Phi_a^0} \quad (1)$$

where  $N_{\text{total}}$  is the total number of monomers in the aggregate and  $\Phi_a^0$  is the fluorescence quantum yield in the



**FIGURE 3.** (a) The double string structure of the PBI J-aggregates. The dye molecule has a length of approximately 1.5 nm; however, due to double string geometry, every dye molecule adds only 0.75 nm to the J-aggregate length.<sup>27</sup> (b) A typical fluorescence image of a sample containing isolated long J-aggregates with length  $>1 \mu\text{m}$ . (c) Scatter plot of fluorescence brightness coefficient ( $B_{\text{long}}$ ) as a function of number of monomers ( $N_{\text{long}}$ ) for 92 individual long J-aggregates, where  $N_{\text{long}}$  was estimated according to the aggregate length measured from the fluorescence images. Fluorescence brightness per monomer ( $b = B_{\text{long}}/N_{\text{long}}$ ) was calculated to be  $26 \pm 9 \text{ photons s}^{-1} \text{ W}^{-1} \text{ cm}^2$ .

absence of quenchers, which can be approached by using very low excitation power density ( $I \rightarrow 0$ ).

$N_{\text{total}}$  in a J-aggregate can be calculated from its length. According to the arrangement of monomers in the 1D aggregate (Figure 3a),<sup>27,28</sup> every monomer adds 0.75 nm to the aggregate length. It was impossible to measure the lengths of those blinking aggregates directly from the fluorescence images because they were obviously shorter than the optical resolution of the microscope. However, using more concentrated solutions for spin-casting, we were able to prepare much longer aggregates with lengths ( $>1 \mu\text{m}$ ) directly measurable from the fluorescence images (Figure 3b). The numbers of monomers in such long aggregates could then be estimated. Note that these long aggregates did not show any blinking because they were such large en-



sembles that independent fluorescence intensity fluctuations of their different parts were averaged out in the overall fluorescence signal. Below we will show how fluorescence of such long aggregates can be used as a reference to determine  $N(t)$  for blinking aggregates.

In general, the detected fluorescence emission rate  $F(t)$  (counts/s) of any fluorescent object is dependent on efficiency of the light detection system ( $\eta$ ), fluorescence quantum yield  $\Phi(t, I)$ , absorption cross-section  $\sigma$  at the excitation frequency  $\nu$ , and excitation power density  $I^{30}$

$$F(t) = \eta \frac{\sigma \Phi(t, I) I}{h\nu} \quad (2)$$

It is convenient to use excitation power density independent *fluorescence brightness coefficient*,  $B$ , which can be experimentally measured or calculated

$$B(t) = \frac{F(t)}{I} = \eta \frac{\sigma \Phi(t, I)}{h\nu} \quad (3)$$

For a J-aggregate  $\sigma$  is directly proportional to  $N_{\text{total}}$ . Let us compare the fluctuating brightness  $B(t)$  of a small aggregate containing  $N_{\text{total}}$  monomers with the ensemble-averaged brightness  $B_{\text{long}}$  of a micrometer-size long aggregate containing  $N_{\text{total}}^{\text{long}}$  monomers

$$\frac{B(t, I)}{B_{\text{long}}(I_{\text{long}})} = \frac{\sigma \Phi(t, I)}{\sigma_{\text{long}} \Phi_{\text{long}}(I_{\text{long}})} = \frac{N_{\text{total}} \Phi(t, I)}{N_{\text{total}}^{\text{long}} \Phi_{\text{long}}(I_{\text{long}})} \quad (4)$$

where  $I$  and  $I_{\text{long}}$  are excitation power densities used to excite the small and the large reference aggregate, respectively. Using eq 4 and the definition of  $N(t)$  given in eq 1 we get

$$N(t) = \frac{B(t, I)}{B_{\text{long}}(I_{\text{long}})/N_{\text{total}}^{\text{long}}} \frac{\Phi_{\text{long}}(I_{\text{long}})}{\Phi_a^0} \quad (5)$$

When  $I_{\text{long}} \rightarrow 0$ ,  $\Phi_{\text{long}}(I_{\text{long}}) \rightarrow \Phi_a^0$  giving

$$N(t) = \frac{B(t, I)}{B_{\text{long}}/N_{\text{total}}^{\text{long}}} = \frac{B(t, I)}{b} \quad (6)$$

where  $b = B_{\text{long}}/N_{\text{total}}^{\text{long}}$ , fluorescence brightness per monomer unit measured at low excitation power density conditions.

Excitation power density of 0.5 W/cm<sup>2</sup> (100 times less than the one used to observe blinking) was found to be low enough that the effect of photogenerated quenchers on the fluorescence quantum yield was negligible,<sup>31</sup> allowing us to measure the coefficient  $b$  (eq 6).

Contour lengths of 92 long aggregates were measured directly from the corresponding images, and their fluorescence brightness coefficients were extracted. There indeed exists a linear relationship  $B_{\text{long}} \approx b N_{\text{total}}^{\text{long}}$ , where  $b = 26 \pm 9$  photons s<sup>-1</sup> W<sup>-1</sup> cm<sup>2</sup> (Figure 3c). The distribution of  $b$  is broadened due to the inhomogeneous environment around the single J-aggregates (see discussion below) and the experimental error in the determination of  $N_{\text{total}}^{\text{long}}$  (see Supporting Information).

Note that so far we have not considered a possibility that some of the monomers could be permanently quenched

(e.g., oxidized) so that not all the monomers were contributing to the fluorescence even at low excitation power density. In order to make sure that the effect of such “inherently dark monomers” is negligible, we will apply below yet another approach solely based on fluorescence intensity comparison with a reference molecule.

From eq 3, one obtains

$$\sigma \Phi = \sigma_{\text{ref}} \Phi_{\text{ref}} \frac{B_{\text{ref}}}{B} \frac{\nu}{\nu_{\text{ref}}} \quad (7)$$

Therefore, the product  $\sigma \times \Phi$  for an unknown system can be determined by comparing its fluorescence brightness coefficient  $B$  with that ( $B_{\text{ref}}$ ) of a reference system with known absorption cross section  $\sigma_{\text{ref}}$  and fluorescence quantum yield  $\Phi_{\text{ref}}$ . The same idea has been used to determine fluorescence quantum yield of individual carbon nanotubes.<sup>32</sup> A good reference molecule should be highly fluorescent and stable. Single molecules of perylene bisimides have been proved to fit these requirements very well.<sup>33–35</sup> Here we simply used the noncoupled molecules of PBI (Figure 1) spin-cast from DCM solutions as a reference.

By taking into account the difference between absorption spectra of noncoupled monomer dye molecules and the same number of molecules coupled in a J-aggregate, one can derive (see Supporting Information) the following equation for the number of monomers  $N$  taking part in fluorescence of a J-aggregate

$$N = \frac{B_a A_m(\nu_m) \Phi_m \nu_a}{B_m A_a(\nu_a) \Phi_a^0 \nu_m} \quad (8)$$

where  $B_m$  and  $B_a$  are fluorescence brightness coefficients of the noncoupled monomer and the individual aggregate, respectively,  $\Phi_m$  and  $\Phi_a^0$  are fluorescence quantum yields of monomers and J-aggregates in the absence of quenchers, and  $A_m(\nu_m)$  and  $A_a(\nu_a)$  are normalized absorption spectra of the monomers and J-aggregates ( $\int A_a(\nu) d\nu = \int A_m(\nu) d\nu = 1$ ).

In order to see how the two techniques of measuring  $N$  agree with each other, we can calculate fluorescence brightness per monomer unit ( $b$ )

$$b = \frac{B_a}{N} = B_m \frac{A_a(\nu_a) \Phi_a^0 \nu_m}{A_m(\nu_m) \Phi_m \nu_a} \quad (9)$$

Spectra  $A_m(\nu_m)$  and  $A_a(\nu_a)$  for the PBI dye are shown in Figure 1. Fluorescence quantum yields of the dye and J-aggregates in the absence of quenchers were taken as 1.<sup>27</sup> Fluorescence intensity for several hundreds of individual PBI molecules were measured at low excitation power density (to reduce fluorescence blinking and other photoinduced quenching effects) giving  $B_m = 11$  photons s<sup>-1</sup> W<sup>-1</sup> cm<sup>2</sup> on average.<sup>36</sup> By substituting all the values to eq 9, we get  $b = 31$  photons s<sup>-1</sup> W<sup>-1</sup> cm<sup>2</sup>, which agrees well with the value obtained by the first method ( $26 \pm 9$  photons s<sup>-1</sup> W<sup>-1</sup> cm<sup>2</sup>). It means that both techniques give similar values for the number

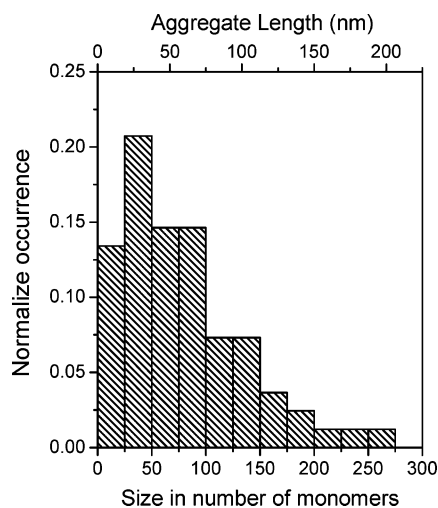


FIGURE 4. Size distribution for the studied J-aggregates of PBI dye. The size is estimated according to eq 6 where  $b = 26 \text{ photons s}^{-1} \text{ W}^{-1} \text{ cm}^2$  and presented in aggregate length (in nm) and number of dye monomers per aggregate.

of fluorescing monomers in individual J-aggregates within the limits of experimental errors. Therefore, contribution of inherently dark monomers is not important for our analysis.

Now eq 6 can be used to recalculate fluorescence intensity from photon count rate to  $N(t)$ . For convenience, the average value of  $b$ , i.e.,  $26 \text{ photons s}^{-1} \text{ W}^{-1} \text{ cm}^2$  was adopted for the calculation. Due to the relatively large error of the  $b$  value, an error is also introduced to the estimated  $N(t)$  (e.g., if  $N = 100$  when using  $b = 26$ , one gets  $N = 153$  by using  $b = 17$  and  $N = 74$  by using  $b = 35$ ) and other derived parameters such as aggregate sizes, jump amplitudes, and exciton diffusion lengths.

Examples of abrupt fluorescence intensity changes involving quenching of tens of monomers in single events are presented in Figure 2. Figure 4 shows the distribution of maximal values of  $N(t)$  (which corresponds to  $N_{\text{total}}$ ) for individual J-aggregates probed in the given sample. The distribution is broad, ranging from 10 to 300 monomers with a peak around 30 monomers. The distribution of jump amplitudes was further extracted (Figure 5a). On average one jump with amplitude of more than  $\sim 50$  monomers happened every 10 s of CW excitation (integral of the distribution from 50 to 120 is equal to 0.8 (jumps/10 s)). Every 100 s a jump of more than 90 monomers could be observed. In some rare cases jumps of more than 100 monomers were detected. These results indicate that collective quenching of many monomers indeed occurred in single J-aggregates.

Figure 5b schematically shows how the jump amplitude (number of collectively quenched monomers) is dependent on the quenching radius and the exciton coherence length. The exciton coherence length is  $\sim 3$  monomers according to the emission bandwidth of the J-aggregates,<sup>28</sup> and a typical quenching radius (Förster distance) of 4 nm is assumed. Accordingly, direct quenching by a single quencher<sup>37</sup>

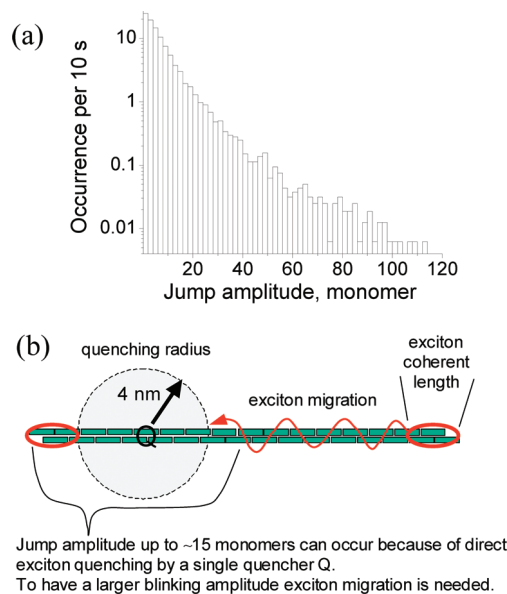


FIGURE 5. (a) Distribution of fluorescence intensity jump amplitudes in single J-aggregates of PBI, represented by the average occurrence per 10 s under excitation. The aggregate length distribution for this sample is shown at Figure 4. (b) Schematic illustration of the effect of quenching radius, exciton coherent length, and migration distance on the jump amplitude (number of collectively quenched monomers) in PBI J-aggregates.

can account only for jump amplitudes up to 15 monomers. To explain the much larger blinking amplitudes observed experimentally, one has to take into account an exciton migration over the 1D aggregate chain. For the experimentally observed collective quenching of 100 monomers, the migration distance should be as large as 75 nm. One of the possible reasons for the low probability of such large jumps is that among the probed aggregates those containing more than 100 monomers were substantially fewer than those containing, e.g., 20 monomers (Figure 4). Moreover, the J-aggregate structure is expected to possess large heterogeneity on the scale of tens of nanometers.<sup>38</sup>

This heterogeneity is also reflected by the distribution of the data points on the  $B$  vs  $N$  graph (Figure 3c). It may result in very different efficiency of energy transport in different aggregates, or even in the different parts of the same aggregate. Long-range energy transport can be indeed very efficient in some cases, e.g., in highly ordered J-aggregates. It is the single molecule spectroscopy approach that allowed us finding such self-assembling aggregates with one-dimensional exciton diffusion on the order of 70 nm, which is similar to that recently reported for crystallites of diindonoperylene molecules.<sup>39</sup>

We stress that the brightness analysis can be also a very useful tool for studying other fluorescent nanosystems. By comparison with a standard dye, the fluorescence quantum yield of a single nano-object of interest can be estimated (eq 5).<sup>16,32</sup> This is analogous to fluorescence quantum yield measurements using reference dye solution—a routine technique in ensemble spectroscopy. Despite of the low accuracy

of this approach, fluorescence quantum yield obtained from the brightness analysis is more reliable than that derived from fluorescence lifetime. The lifetime approach (quantum yield = fluorescence lifetime/radiative lifetime) fails when static quenching<sup>50</sup> is present in the system. Static quenching is easily introduced when one studies isolated fluorescent macromolecules or nanoparticles immobilized on surfaces or in solid matrices by fluorescence microscopy techniques. This is because photogenerated products (charge-transfer states, triplets, radicals) and the environment possess drastic effects on the formation and evolution of the excited states.

In summary, we have developed a method to measure the actual number of chromophores in single fluorescent nano-objects, which is especially useful for characterizing collective fluorescing blinking in multichromophoric systems. Fluorescence blinking observed in individual J-aggregates of perylene bisimide fluorophores could be related to one-dimensional excitation transport over distances up to 70 nm in these materials. This shows that such well-organized self-assembled aggregates can compete in energy transfer efficiency with the best crystalline organic materials developed for solar cell applications.

**Acknowledgment.** This work has been supported by the European Science Foundation within COST Action D35. I.S. thanks the Swedish Research Council, The Royal Physiographic Society in Lund, and the Knut & Alice Wallenberg Foundation. Y.T. thanks Crafoord Foundation and the Swedish Institute for postdoctoral scholarships. H.L. acknowledges Marie Curie IIF scholarship. F.W. thanks the Deutsche Forschungsgemeinschaft (DFG) for financial support within research training school 1221 "Control of electronic properties in aggregated  $\pi$ -conjugated molecules". I.G.S. appreciates support from Linnaeus Grant to Lund Laser Centre.

**Supporting Information Available.** Additional details on dependence of blinking frequency on excitation powder density, distribution of  $b$ , and relationship between the brightness of single J-aggregates and that of noncoupled dye molecules. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## REFERENCES AND NOTES

- Moerner, W. E.; Kador, L. Optical-Detection and Spectroscopy of Single Molecules in A Solid. *Phys. Rev. Lett.* **1989**, 62 (21), 2535–2538.
- Orrit, M.; Bernard, J. Single Pentacene Molecules Detected by Fluorescence Excitation in A *p*-Terphenyl Crystal. *Phys. Rev. Lett.* **1990**, 65 (21), 2716–2719.
- Yu, J.; Hu, D. H.; Barbara, P. F. Unmasking electronic energy transfer of conjugated polymers by suppression of O<sub>2</sub> quenching. *Science* **2000**, 289 (5483), 1327–1330.
- Scheblykin, I.; Zorinants, G.; Hofkens, J.; De Feyter, S.; Van der Auweraer, M.; De Schryver, F. C. Photoluminescence intensity fluctuations and electric-field-induced photoluminescence quenching in individual nanoclusters of poly(phenylenevinylene). *ChemPhysChem* **2003**, 4 (3), 260–267.
- Bopp, M. A.; Sytnik, A.; Howard, T. D.; Cogdell, R. J.; Hochstrasser, R. M. The dynamics of structural deformations of immobilized single light-harvesting complexes. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, 96 (20), 11271–11276.
- De Schryver, F. C.; Vosch, T.; Cotlet, M.; Van der Auweraer, M.; Müllen, K.; Hofkens, J. Energy dissipation in multichromophoric single dendrimers. *Acc. Chem. Res.* **2005**, 38 (7), 514–522.
- Hofkens, J.; Maus, M.; Gensch, T.; Vosch, T.; Cotlet, M.; Kohn, F.; Herrmann, A.; Müllen, K.; De Schryver, F. Probing photophysical processes in individual multichromophoric dendrimers by single-molecule spectroscopy. *J. Am. Chem. Soc.* **2000**, 122 (38), 9278–9288.
- Van den Bout, D. A.; Yip, W. T.; Hu, D. H.; Fu, D. K.; Swager, T. M.; Barbara, P. F. Discrete intensity jumps and intramolecular electronic energy transfer in the spectroscopy of single conjugated polymer molecules. *Science* **1997**, 277 (5329), 1074–1077.
- Gesquiere, A. J.; Lee, Y. J.; Yu, J.; Barbara, P. F. Single molecule modulation spectroscopy of conjugated polymers. *J. Phys. Chem. B* **2005**, 109 (25), 12366–12371.
- Dyreklev, P.; Inganäs, O.; Paloheimo, J.; Stubb, H. Photoluminescence Quenching in A Polymer Thin-Film Field-Effect Luminescent. *J. Appl. Phys.* **1992**, 71 (6), 2816–2820.
- Hania, P. R.; Scheblykin, I. G. Electric field induced quenching of the fluorescence of a conjugated polymer probed at the single molecule level. *Chem. Phys. Lett.* **2005**, 414 (1–3), 127–131.
- Yu, J.; Song, N. W.; McNeill, J. D.; Barbara, P. F. Efficient exciton quenching by hole polarons in the conjugated polymer MEH-PPV. *Isr. J. Chem.* **2004**, 44 (1–3), 127–132.
- Gledhill, S. E.; Scott, B.; Gregg, B. A. Organic and nano-structured composite photovoltaics: An overview. *J. Mater. Res.* **2005**, 20 (12), 3167–3179.
- Rothberg, L. J.; Yan, M.; Papadimitrakopoulos, F.; Galvin, M. E.; Kwock, E. W.; Miller, T. M. Photophysics of phenylenevinylene polymers. *Synth. Met.* **1996**, 80 (1), 41–58.
- Wang, P.; Collison, C. J.; Rothberg, L. J. Origins of aggregation quenching in luminescent phenylenevinylene polymers. *J. Photochem. Photobiol., A* **2001**, 144 (1), 63–68.
- Lin, H.; Tian, Y.; Zapadka, K.; Persson, G.; Thomasson, D.; Mirzov, O.; Larsson, P. O.; Widengren, J.; Scheblykin, I. G. Fate of excitations in conjugated polymers: single molecule spectroscopy reveals non-emissive "dark" regions in MEH-PPV individual chains. *Nano Lett.* **2009**, 9 (12), 4456–4461.
- Cognet, L.; Tardin, C.; Negrier, M. L. M.; Breillat, C.; Coussens, F.; Choquet, D.; Lounis, B. Robust single-molecule approach for counting autofluorescent proteins. *J. Biomed. Opt.* **2008**, 13 (3).
- Weston, K. D.; Dyck, M.; Tinnefeld, P.; Müller, C.; Herten, D. P.; Sauer, M. Measuring the number of independent emitters in single-molecule fluorescence images and trajectories using coincident photons. *Anal. Chem.* **2002**, 74 (20), 5342–5349.
- Jelly, E. E. Spectral absorption and fluorescence of dyes in the molecular state. *Nature* **1936**, 138, 1009–1010.
- Scheibe, G. *Angew. Chem.* **1936**, 49, 567.
- Fidler, H.; Terpstra, J.; Wiersma, D. A. Dynamics of Frenkel Excitons in Disordered Molecular Aggregates. *J. Chem. Phys.* **1991**, 94 (10), 6895–6907.
- Knoester, J. Modeling the optical properties of excitons in linear and tubular J-aggregates. *Int. J. Photoenergy* **2006**, 1–10, Article ID 61364.
- Scheblykin, I. G.; Sliusarenko, O. Y.; Lepnev, L. S.; Vitukhnovsky, A. G.; Van der Auweraer, M. Excitons in molecular aggregates of 3,3'-bis-[3-sulfopropyl]-5,5'-dichloro-9 ethylthiacarbocyanine (THI-ATS): Temperature dependent properties. *J. Phys. Chem. B* **2001**, 105 (20), 4636–4646.
- Van der Auweraer, M.; Scheblykin, I. One-dimensional J-aggregates: Dependence of the properties of the exciton band on the model of the intermolecular coupling. *Chem. Phys.* **2002**, 275 (1–3), 285–306.
- Scheblykin, I. G.; Bataiev, M. M.; Van der Auweraer, M.; Vitukhnovsky, A. G. Dimensionality and temperature dependence of the radiative lifetime of J-aggregates with Davydov splitting of the exciton band. *Chem. Phys. Lett.* **2000**, 316 (1–2), 37–44.
- Lang, E.; Sorokin, A.; Drechsler, M.; Malyukin, Y. V.; Köhler, J. Optical spectroscopy on individual amphi-PIC J-aggregates. *Nano Lett.* **2005**, 5 (12), 2635–2640.
- Kaiser, T. E.; Wang, H.; Stepanenko, V.; Würthner, F. Supramolecular construction of fluorescent J-aggregates based on hydrogen-bonded perylene dyes. *Angew. Chem., Int. Ed.* **2007**, 46, 5541–5544.

- (28) Kaiser, T. E.; Stepanenko, V.; Würthner, F. Fluorescent J-Aggregates of Core-Substituted Perylene Bisimides: Studies on Structure-Property Relationship, Nucleation-Elongation Mechanism, and Sergeants-and-Soldiers Principle. *J. Am. Chem. Soc.* **2009**, *131* (19), 6719–6732.
- (29) Würthner, F.; Thalacker, C.; Sautter, A.; Scharrtl, W.; Ibach, W.; Hollricher, O. Hierarchical self-organization of perylene bisimide-melamine assemblies to fluorescent mesoscopic superstructures. *Chem.—Eur. J.* **2000**, *6* (21), 3871–3886.
- (30) *Principles of fluorescence spectroscopy*, 3rd ed.; Lakowicz, J. R., Ed.; Springer: Berlin, 2006.
- (31) Decrease of excitation power density suppresses the photogeneration of long-lived quenchers. This effect appears as less frequent fluorescence blinking for individual short aggregates and increase of fluorescence brightness ( $B_{\text{long}}$ ) for long aggregates. To measure  $b$ , the excitation power density was decreased until  $B_{\text{long}}$  did not change anymore. It was found that the brightness of long aggregates increased about 2 times when excitation power density went down from 50 to 0.5 W/cm<sup>2</sup>. Note that quenchers with lifetime >100 ms (our time resolution), which caused the fluorescence blinking observed in short aggregates, can solely account for this ~2 times difference, suggesting that the effect of shorter lived quenchers (e.g., triplet states), if any, was minor at 50 W/cm<sup>2</sup>.
- (32) Carlson, L. J.; Maccagnano, S. E.; Zheng, M.; Silcox, J.; Krauss, T. D. Fluorescence efficiency of individual carbon nanotubes. *Nano Lett.* **2007**, *7* (12), 3698–3703.
- (33) Uji-i, H.; Melnikov, S. M.; Deres, A.; Bergamini, G.; De Schryver, F.; Herrmann, A.; Müllen, K.; Enderlein, J.; Hofkens, J. Visualizing spatial and temporal heterogeneity of single molecule rotational diffusion in a glassy polymer by defocused wide-field imaging. *Polymer* **2006**, *47* (7), 2511–2518.
- (34) Lang, E.; Würthner, F.; Köhler, J. Photophysical properties of a tetraphenoxy-substituted perylene bisimide derivative characterized by single-molecule spectroscopy. *ChemPhysChem* **2005**, *6* (5), 935–941.
- (35) Lang, E.; Hildner, R.; Engelke, H.; Osswald, P.; Würthner, F.; Köhler, J. Comparison of the photophysical parameters for three perylene bisimide derivatives by single-molecule spectroscopy. *ChemPhysChem* **2007**, *8* (10), 1487–1496.
- (36) Isolated single molecules of PBI showed a large diversity in fluorescence brightness coefficient because their properties are sensitive to inhomogeneity of the environment.
- (37) Mirzov, O.; Cichos, F.; von Borczyskowski, C.; Scheblykin, I. G. Direct exciton quenching in single molecules of MEH-PPV at 77 K. *Chem. Phys. Lett.* **2004**, *386* (4–6), 286–290.
- (38) Kaiser, T. E.; Scheblykin, I. G.; Thomsson, D.; Würthner, F. Temperature-dependent exciton dynamics in J-aggregates—when disorder plays a role. *J. Phys. Chem. B* **2009**, *113* (48), 15836–15842.
- (39) Kurrle, D.; Pflaum, J. Exciton diffusion length in the organic semiconductor diindenoperylene. *Appl. Phys. Lett.* **2008**, *92* (13), 133306.