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ABSTRACT
Photo-luminescence (P-L) intermittency (or blinking) in semiconductor nanocrystals (NCs), a phenomenon ubiquitous to single-emitters, is generally considered to be temporally random intensity fluctuations between “bright” (“On”) and “dark” (“Off”) states. However, individual quantum-dots (QDs) rarely exhibit such telegraphic signals, and yet, a vast majority of single-NC blinking data are analyzed using a single fixed threshold which generates binary trajectories. Furthermore, while blinking dynamics can vary dramatically over NCs in the ensemble, the extent of diversity in the exponents ($m_{On/Off}$) of single-particle On-Off-time distributions ($P(t_{On/Off})$), often used to validate mechanistic models of blinking, remains unclear due to a lack of statistically relevant data sets. Here, we subclassify an ensemble of QDs based on the emissivity of each emitter and subsequently compare the (sub)ensembles’ behaviors. To achieve this, we analyzed a large number (>1000) of blinking trajectories for a model system, Mn$^{+2}$ doped ZnCdS QDs, which exhibits diverse blinking dynamics. An intensity histogram dependent thresholding method allowed us to construct distributions of relevant blinking parameters (such as $m_{On/Off}$).

Interestingly, we find that single QD $P(t_{On/Off})$s follow either truncated power law or power law, and their relative proportion varies over subpopulations. Our results reveal a remarkable variation in $m_{On/Off}$ amongst as well as within subensembles, which implies multiple blinking mechanisms being operational amongst various QDs. We further show that the $m_{On/Off}$ obtained via cumulative single-particle $P(t_{On/Off})$ is distinct from the weighted mean value of all single-particle $m_{On/Off}$, evidence for the lack of ergodicity. Thus, investigation and analyses of a large number of QDs, albeit for a limited time span of a few decades, are crucial to characterize the spatial heterogeneity in possible blinking mechanisms.

Published under license by AIP Publishing. https://doi.org/10.1063/1.5095870

I. INTRODUCTION
Fluorescence intermittency (or blinking) is a photo-induced phenomenon exhibited by single emitters, such as single molecules and semiconductor nanocrystals (NCs). Photo-luminescence (P-L) blinking involves discrete switches in emission intensity between a bright (“On”) and a dark (“Off”) intensity state at a seemingly random time scale. There has been considerable effort to understand this phenomenon, as intermittent emission restricts the usage of NCs as single photon sources or in optoelectronic devices such as lasers, apart from complicating interpretation of superlocalized single-particle tracking data to probe biomolecular dynamics. To understand the origin, several models have been proposed; blinking of quantum dots (QDs) has been attributed to charging-discharging (Auger ionization-recombination, AIR), long lived traps (surface defects) with fluctuating energy barriers, as well as time-varying activation/deactivation of multiple recombination centers (MRCs) associated with traps within a QD, amongst other propositions. Recently, it has even been suggested that blinking can originate from a combination of aforesaid processes within a single QD. While the mechanisms of NC intermittency are...
still being debated, there is an underlying presumption that the intermittency of all the emitters in an ensemble owes to similar physical processes. However, there have been no attempts to validate whether the origin of intermittency is the same for the vast majority of emitters or if there is a diversity of blinking processes amongst QDs in the ensemble. Such questions can potentially be addressed if a very large number of single-emitters are investigated which would allow for the analyses of distributions of experimentally obtained blinking parameters.

Typically, each intensity-time trajectory of a single QD is analyzed as a quasitelegraphic signal between two states (“On” or “Off”) considering a single fixed threshold (FT), which is kept invariant for all QDs investigated. The resulting binary trajectories are subsequently used to extract blinking parameters, such as exponents \( m_{\text{On/Off}} \) of On-/Off-time-duration distributions \( P(t_{\text{On/Off}}) \). It is reported that single-NC \( P(t_{\text{On/Off}}) \) follows either power law (PL) or truncated power law (TPL) with varied truncation times \( (\tau_r) \), depending on the nature of the NC system. It is therefore important to develop alternate methods which do not involve a FT for all QDs and simultaneously include the effect of “gray” states in the construction of On-/Off-time duration distributions.

Barring a few models of blinking such as transient activation of MRCs, the ionization-neutralization based models predict certain ranges or mean values of On-/Off-exponents. Thus, experimentally extracted \( m_{\text{On/Off}} \) has often been used to infer the alternate possible mechanism(s) of intermittency. For instance, “\( m_{\text{On/Off}} \)” values around 1.5 or slightly higher are thought to be a consequence of MRCs, the ionization-neutralization based models predict certain first-time events \( P(t_{\text{On/Off}}) \), which may not yield dependable single-particle \( P(t_{\text{On/Off}}) \) or \( m_{\text{On/Off}} \).

It is therefore important to note that QD blinking trajectories often exhibit intermediate intensity “gray” states, leading to a quasicontinuous distribution of intensities. Under these situations, two-state analysis of blinking traces using FT often eludes “gray” states, which may not yield dependable single-particle \( P(t_{\text{On/Off}}) \) or \( m_{\text{On/Off}} \). Alternatively, “diffusion-controlled electron transfer (DCET)” predicts that initial exponent values range from 0.5 to 1.5. However, a wide range of experimental \( m_{\text{On/Off}} \) (0.5–2.5) have been reported for various NC systems,

which may not necessarily be correlated with existing models. Unlike molecules, individual emitters in the ensemble of NCs with very similar composition/morphology are inherently distinct with different numbers of atoms, surface ligand density, as well as population, nature, and spatial distribution of defects, all of which can affect blinking characteristics and/or mechanisms. Therefore, depending on the particular QD being probed, the origin of intermittency can vary, which may be reflected in the diversity of single-particle \( m_{\text{On/Off}} \) values.

In prior literature, the value of \( m_{\text{On/Off}} \) has been extracted from experimental data in a variety of ways. Most often, the average \( m_{\text{On/Off}} \) value \( \langle m_{\text{On/Off}} \rangle \) has been obtained from several to tens of single-QD \( P(t_{\text{On/Off}}) \). In contrast, the exponents from a single-QD \( P(t_{\text{On/Off}}) \) over very long time periods (5-6 decades) have been compared with model predictions. Furthermore, the ensemble-averaged \( m_{\text{On/Off}} \) has often been extracted from a single cumulative distribution obtained via combination of few tens of limited-time (3-4 decades) single-particle \( P(t_{\text{On/Off}}) \). It is relevant to note that both the latter methods rely on the inherent assumption that the ergodicity hypothesis remains valid for blinking, i.e., the ensemble average of exponents and the exponent obtained from time-ensemble averaged \( P(t_{\text{On/Off}}) \) are invariant. However, ergodic behavior may not hold if multiple blinking mechanisms are operational within a single QD \( (t) \), i.e., if there is an intrinsic temporal dependency, or there are distinct subensembles of emitters which undergo intermittency via contrasting mechanisms. Thus, to understand the heterogeneity in blinking parameters as well as ergodicity, it is crucial to analyze the blinking characteristics of a large number of QDs.

Although the intermittency of any two QDs in an ensemble is never identical even when data are acquired under identical conditions, there are often prominent differences in blinking characteristics of individual emitters. For instance, the blinking dynamics of Mn\(^{2+}\) doped ZnCdS QDs with very similar morphology, immobilized in a polymer film, exhibit diverse intermittency patterns in terms of their emissive propensity. Figure 1a shows representative traces from three such individual QDs, being either mostly, moderately, or rarely emissive throughout data acquisition. Several other NC systems, including CdSe-ZnSe alloy core-shell QDs of similar size [Fig. 1b], also exhibit such contrasting blinking characteristics in terms of time-averaged intensity distributions, albeit the fraction of different subpopulations may vary. Interestingly however, whether the nature of intermittency has any correlation with blinking parameters (such as \( m_{\text{On/Off}} \)), it still remains obscure due to the lack of statistically relevant distributions.

FIG. 1. Diverse blinking characteristics of two NC systems: (a) Mn\(^{2+}\) doped ZnCdS QDs (NC-A) and (b) CdSe-ZnSe alloy core-shell QDs (NC-B), measured under identical conditions (see Sec. II). The middle-left panels are TEM images of NCs depicting uniform size distributions, and lower-left panels are fluorescence images of spatially segregated NCs. The intermittency behaviors and corresponding time-averaged intensity distributions of the three representative NCs for each system (A1–A3; B1–B3) depict different subpopulations having distinct blinking patterns (color coded), such as being “Dominantly emissive” (green), “Moderately emissive” (purple), and “Mostly nonemissive” (blue), as well as frequent occurrence of intermediate “gray” states. Such a diverse intermittency pattern of a few QDs in the ensemble is shown in Movie M1. Multimedia view: https://doi.org/10.1063/1.5095870.1
Here, we have subclassified a large number of QDs in the ensemble based on their individual intensity distributions (emissivity) and subsequently evaluated the distributions of blinking parameters. We have chosen Mn$^{12}$ doped ZnCdS and CdSe-ZnSe alloy core-shell QDs as model systems as both these NCs exhibit diverse blinking propensity in terms of their emissivity; however, we report the results of one of these systems, namely the doped ZnCdS QDs. To address blinking dynamics with “On,” “Off,” and “gray” intensity levels, we have developed an intensity histogram dependent thresholding (IHDT) method, where multiple thresholding explicitly considers the presence of “gray” states, and the threshold values are based on the intensity distribution of each emitter. For subensemble analysis, we classified the QDs in three broad categories based on the emissivity [% On-time, $\tau_{on}(\%)$] for each QD, namely, “Mostly On,” “Intermediate,” and “Mostly Off.” To understand how blinking parameters vary over each subensemble, we have performed statistical analysis considering more than 1000 single emitters, which is an order of magnitude higher than that done in most prior reports. This allowed us to compare the mean behaviors as well as the variability of blinking parameters of various subensembles with that of the entire population.

II. EXPERIMENTAL METHODS

A. Sample preparation and data acquisition

Mn$^{12}$ doped ZnCdS QDs (NC-A) were synthesized and characterized by Hazarika, as done in Ref. 51, and these samples were provided by Prof. D. D. Sarma. CdSe-ZnSe alloy core-shell NCs (NC-B) were prepared following the previously reported literature. To immobilize the QDs in a polymethyl methacrylate (PMMA) thin film (200 nm), one drop of a ~2 nM solution was spin cast at 2000 rpm on freshly cleaned silica coverslips. For details, see the supplementary material as well as Refs. 51 and 58. The NC-A and NC-B samples were excited by a 457 nm (argon ion) cw laser excitation (at 0.5 kW cm$^{-2}$ A and NC-B samples were excited by a 457 nm (argon ion) cw laser excitation (at 0.5 kW cm$^{-2}$). All data were collected at 295 K. Although offolding ($\tau_{off}$) based on the time-averaged intensity distributions for each QD in a movie were simulated before further analyses, the details of which are provided in Sec. III. For the construction of On-/Off-time distributions $\{P(t_{on/off})\}$, we chose only those simulated blinking traces which possess at least five distinct “On” or “Off” time durations ($t_{on/off}$), following a least square method with a statistical weightage scheme following Kuno et al.’ Power law $[PL: P(t) = A \cdot t^{-m}]$ and truncated power law $[TPL: P(t) = A \cdot t^{-m} \cdot \exp(-(t/\tau_c))]$ type $P(t_{on/off})$ are then segregated according to the magnitude of truncation time $\tau_c$: an emitter with higher $\tau_c$ value than 10 s has been observed to follow PL nature as a best fit in the least square method. Exponent values ($m_{on/off}$) of $P(t_{on/off})$ from the single QDs which follow either PL or TPL have been extracted for further analysis. All analyses were performed in MATLAB R2018a. Further details of data analysis procedures are provided in the supplementary material.

III. INTENSITY HISTOGRAM DEPENDENT THRESHOLDING (IHDT)

It is known that the choice of a single threshold can lead to artifacts in simulated binary trajectories. In some reports, the average noise has been used to set a single FT; for instance, the mean of 2–3 times the standard deviation of background counts or the threshold is chosen as the highest background count over the entire duration of the experiment. An alternate approach is to choose the FT value from the minimum of the time-averaged (bimodal) intensity distributions via fitting two Gaussians for the “On” and “Off” states. Regardless of the particular method used to generate the threshold, the majority of reported data use a single FT for all the QDs to generate binary trajectories for further analyses. However, such a procedure may not be ideally suited for every trajectory in the ensemble, especially when the blinking dynamics are heterogeneous, and the occurrence of “gray” levels is common (see Fig. 1). For example, we find that for blinking, switching frequency (SF) as well as the $P(t_{on/off})$ changes systematically with the choice of FT (vide infra), owing primarily to miscounting of blinking events (Figs. S1 and S2 of the supplementary material). Therefore, we have developed a method that yields flexible (single or multiple) threshold(s) based on the time-averaged intensity distributions for each QD blinking trajectory, the salient features of which are as described below.

In the IHDT approach, we first fit the time-averaged intensity distribution of the entire blinking trajectory using two Gaussian functions. Based on the mean positions of the peaks and the standard deviation of the Gaussians, two values of the threshold are chosen (see Fig. S3 and methods, supplementary material). The threshold at a lower intensity [$I_{th}(On)$] value has been considered as the “On” threshold when the change in PL intensity between successive frames ($I_t - I_{t-1}$) is positive, while the “Off” threshold is set
at a higher intensity [$I_{th}(Off)$] when $I_{t} - I_{t-1}$ is negative (Fig. 2, and Fig. S3, supplementary material). However, under certain circumstances, such as very dominant “Mostly On” or “Mostly Off” type blinking trajectories, the algorithm (Fig. S4, supplementary material) allows two thresholds to converge into one single threshold. In the case of multiple (two) thresholds, any intensity fluctuation in the region between $I_{th}(On)$ and $I_{th}(Off)$ with a duration of more than two consecutive frames (>100 ms) is considered as the “gray” or third intensity state (with a value set at 0.5) apart from the “On” and “Off” states (with values of 1 and 0, respectively). It is important to note that the program also allows us to exclude these “gray” (third) intensity states to perform two-state blinking analysis, rather than considering an “On”-“gray”-“Off” (three state) scenario. Such detection followed by the removal of the “gray” state without compromising on the blinking events is exemplified in Fig. 2(b) for one NC. Here, the difference between FT (black dotted line) and IHDT (solid red line) simulated trajectories can be readily identified in the temporally blown up section of duration ~16 s. In all subsequent analyses for traces using multiple thresholds generated by IHDT, $\tau_{ON}$s for the individual emitters were calculated after the elimination of the “gray” intensity level. More details on the algorithm of the IHDT are provided in the supplementary material (see Figs. S3–S5). The comparison of several blinking parameters obtained using IHDT and FT methods is discussed in Sec. IV A.

IV. RESULTS AND DISCUSSION

We first compare the results from a FT analysis with that for the IHDT and subsequently discuss the results from subensemble statistical analysis. We find that for Mn$^{+2}$ doped ZnCdS QDs [Fig. 1(a), NC-A], the emissivity, $\tau_{ON}$, over 166.5 s varies between 2.58% and 79%. Therefore, we divided 1040 QDs into three rudimentary subensembles based on an equal range of $\tau_{ON}$ [see Fig S6, supplementary material]. These three broad subensembles are “Rarely emissive” or “Mostly Off” [$\tau_{ON} < 28\%$], “Moderately emissive” or “Intermediate” [28% < $\tau_{ON} < 53.5\%$], and “Mostly emissive” or “Mostly On” [$\tau_{ON} > 53.5\%$], which are designated as categories I, II, and III, respectively.

A. Comparison of IHDT and FT analysis for (sub)ensemble blinking behaviors

Figure 3 shows the nature of the $P(t_{ON/Off})$ and corresponding exponent values ($m_{ON/Off}$) of three representative single QD traces from the above-mentioned blinking categories, constructed using a FT @ 0.25 [(a)–(c)] and the IHDT [(d)–(f)] method. First, our results from both the FT and IHDT models reveal that $P(t_{ON/Off})$ of individual QDs can exhibit either PL or TPL nature (over three decades), which contradicts the notion that QDs of the same material composition and size follow very similar blinking statistics. Furthermore, we find that depending on the particular QD being investigated, often there are considerable deviations in exponent values ($m_{ON/Off}$) and truncation times ($\tau_t$), and these differences are pronounced for certain categories (subensembles) (vide infra). Our observations indicate that analysis of blinking statistics of individual QDs in the ensemble is likely to produce ambiguous values of blinking parameters, which in turn can lead to difficulty in their interpretation.

With this in mind, we initially analyzed a statistically relevant number (>1000) of Mn$^{+2}$ doped ZnCdS single QDs’ blinking trajectories and compared their rudimentary blinking behaviors, such as the percent $\tau_{ON}$ and switching (“On” $\rightarrow$ “Off” or “Off” $\rightarrow$ “On”) frequency (SF) of the ensemble, using FT and IHDT. The ensemble distributions obtained for $\tau_{ON}$ and SF evaluated using these two methods are shown in Fig. 4. We find that the distributions of both the parameters vary significantly with the chosen threshold values (0.25, 0.4, and 0.55) for the FT analyses, and specifically, the mean as well as modal values progressively increase for SF with deceasing FT (as shown in Fig. 4). Furthermore, the IHDT method yields even higher average values for both the SF and $\tau_{ON}$ distributions in comparison with FT analyses. Clearly, IHDT is able to identify a
FIG. 3. Comparison of $P(t_{\text{on}})$ (circles) and $P(t_{\text{off}})$ (squares) obtained using conventional FT (@ 0.25) [(a)–(c)] and the IHDT [(d)–(f)] methods, for three single QDs belonging to the subensemble categories “Mostly Off” [(a) and (d)], “Intermediate” [(b) and (e)], and “Mostly On” [(c) and (f)]. The experimental data (symbols) extracted using FT and IHDT follow power law (PL) or truncated power law (TPL) as exemplified by the fits (solid lines).

larger number of switching events for individual QDs; FT analyses are unable to identify these events because of exclusion of relatively low amplitude and short-duration events (flickering) at both higher and lower intensities with respect to the chosen single threshold. It should be noted that excursions between On-/Off- and “gray” states were ignored in IHDT, which implies that the evaluated number of switching events represents the lower bound for the $SF$. This exemplifies one advantage of using IHDT.
TABLE I. (Sub)ensemble $\langle \tau_{ON}(\% \rangle$ and SF for IHDT and FT.

| (Sub)ensemble | $\langle \tau_{ON}(\% \rangle$ | $\Delta \langle \tau_{ON}(\% \rangle_{IHDT}^a$ | $\langle SF \rangle$ IHDT | $\Delta \langle SF \rangle_{IHDT}^a$ |
|---------------|------------------|-----------------|------------------|-------------------|
|               | IHDT (%)         | FT @ 0.25       | FT @ 0.40        | FT @ 0.55         | FT @ 0.25       | FT @ 0.40        | FT @ 0.55         |
| I             | 19.41            | +25.3           | +113             | +277              | 2.79            | +24.7           | +80.3             | +182              |
| II            | 39.15            | -6.75           | +3               | +18.8             | 3.76            | +14.8           | +16.6             | +18.7             |
| III           | 61.34            | -7.87           | +0.75            | +13.5             | 3.43            | +36.1           | +21.7             | +5.9              |
| I + II + III  | 34.40            | +35.3           | +126             | +313              | 3.33            | +33.2           | +81.3             | +175              |

$^a$Percent change in IHDT with respect to FT.

over FT analysis to capture the number of blinking events (“On” to “Off” or vice versa) closer to the actual value.

To decipher the origin of the observed deviations, we compared these blinking parameters of subpopulations with the ensemble. Out of 1040 QDs investigated, 412 (39.62%) were “Mostly Off” (category I), whereas 484 (46.54%) and 144 (13.84%) were “Intermediate” (category II) and “Mostly On” (category III), respectively. The results obtained from IHDT and FT on the mean $\langle \tau_{ON}(\% \rangle$) and average switching frequency ($\langle SF \rangle$) for the categorywise subensembles are shown in Table I (also see Fig. S6, supplementary material). While $\langle \tau_{ON}(\% \rangle$ increases for IHDT as compared to the FT analysis for the entire ensemble, this behavior is not necessarily true for all the subpopulations, such as for categories II and III. For instance, $\langle \tau_{ON}(\% \rangle$ evaluated using IHDT decreases with respect to that for the FT analysis. This is because a lower threshold (at 0.25) in FT analysis often considers a “gray” state as an “On” state, which frequently appears in category II and III type emitters, and thus increases the value of $\langle \tau_{ON}(\% \rangle$. However, IHDT considers “gray” states as neither “On” nor “Off” states, thereby resulting in a lower value of $\langle \tau_{ON}(\% \rangle$ for these subensembles. In contrast, the choice of moderately high value of FTs (0.4) is close to the mean of the normalized intensity distribution and falls within the regime of “gray” states. As a consequence, FT distributes “gray” states as either “On” or “Off” states, which statistically cancels out in evaluation of $\langle \tau_{ON}(\% \rangle$. In the same note, since IHDT does not assign “gray” states as “Off” states, a higher value of FT (0.55) results in lower $\langle \tau_{ON}(\% \rangle$ for both category II and III QDs.

B. Statistical behavior of single-particle $P(t_{ON/Off})$

FIG. 5. The best fits to individual $P(t_{ON})$ (a) and $P(t_{OFF})$ (b) for more than 1000 single Mn$^{2+}$ doped ZnCdS QDs measured under identical conditions, obtained using the IHDT method. For both “On” and “Off” time, darker and lighter hues represent PL and TPL fits, respectively. The scatter plot of On-time (c) and Off-time (d) exponents ($\langle m_{ON} \rangle$ and $\langle m_{OFF} \rangle$) obtained from individual $P(t_{ON})$ and $P(t_{OFF})$ as a function of $\langle \tau_{ON}(\% \rangle$ for each QD. Circles represent the mean values, while the lengths of horizontal/vertical lines denote twice the value of the standard deviation ($\sigma$). Here, $\tau_{(ON/Off)}$ are the Pearson cross correlation coefficients.

As mentioned earlier in Fig. 3, depending on the particular QD being investigated, the single-particle $P(t_{ON/Off})$ follows either PL or TPL. The fits to experimental $P(t_{ON/Off})$ obtained using IHDT for more than 1000 individual Mn$^{2+}$ doped ZnCdS QDs are shown in Figs. 5(a) and 5(b). We observe that the majority (~75%) of single NC $P(t_{ON/Off})$ has TPL nature, and the relative proportion of QDs that exhibit TPL or PL behavior are not severely affected with the mode of analysis (IHDT or FT @ 0.25) (Fig. S7 and Table S1, supplementary material). It is relevant to mention that while $P(t_{ON})$ has been widely documented to be TPL while $P(t_{OFF})$ generally follows PL. In our results that show $P(m_{ON})$ exhibits truncation from PL for a considerable population of QDs. This is unlikely to be an artifact owing to finite trajectory lengths (of 166.5 s) as the $\tau_{C}$ values are typically much smaller (few seconds). Rather, relatively more occurrence of longer dwell times for Off-events leads to the truncation of PL, similar to that for On-times (in tune with prior reports). To understand how $P(t_{ON/Off})$ changes with the emissivity, we plotted all extracted $m_{ON/Off}$ against the corresponding $\tau_{ON}(\%)$ for each QD [Figs. 5(c) and 5(d)]. We find that the exponents are very widely distributed ($\tau_{ON} = 0.68$, $\tau_{OFF} = 0.38$) with mean values, $\langle m_{ON} \rangle = 1.11$ and $\langle m_{OFF} \rangle = 1.28$. We emphasize that such a wide distribution of exponents is not a consequence of (multiple) thresholds chosen by IHDT, as $P(m_{ON/Off})$ constructed for FT of 0.25, 0.4,
and 0.55 also exhibit a very similar, broad distribution of exponents (see Fig. S8, supplementary material). It is likely; however, there are blinking events faster than the data acquisition time scales (50 ms), as the absolute values of exponents are slightly higher for longer bin times (see Fig. S9, supplementary material). While the distribution of the power law exponents can be slightly biased due to binning, the spread in $P(m_{OnOff})$ as well as its dependency on the QD’s emissivity is not severely affected by the removal of fast intermittency events (50 ms) in $P(t_{OnOff})$. This indicates that the heterogeneous distribution of $m_{OnOff}$ [Figs. 5(c) and 5(d)] is not purely an artifact of binning. Intriguingly, we find that $m_{OnOff}$ for single NCs can be as low as ~0.1 for quite a few emitters and as high as ~4 (for On-time) and ~3 (for Off-time), which is significantly greater than previously reported values (~2.5). Furthermore, Figs. 5(c) and 5(d) depict either positive or negative correlation ($r_{On} = -0.41; r_{Off} = 0.43$) between single NC exponents ($m_{OnOff}$) and the corresponding $r_{On}$. This implies that, depending on whether they are mostly or rarely emissive, various subpopulations of QDs in the ensemble are likely to have contrasting $m_{OnOff}$. In effect, these statistical distributions of $m_{OnOff}$ demonstrate remarkable heterogeneity of blinking dynamics and suggest the possibility of diverse blinking mechanisms for various QDs.

To understand the origin(s) of the observed diversity of the extracted exponents, we segregated the QDs which exhibit PL and TPL nature for $P(t_{OnOff})$. The $m_{OnOff}$ values obtained from PL and TPL type single-particle $P(t_{OnOff})$ are shown in Figs. 6(a) and 6(b), where all the QDs investigated are arranged in the increasing order of $r_{On}$. (See Figs. S10(a) and S10(b) of the supplementary material for comparison with IHDY and FT). The frequency histograms of $m_{On}$ and $m_{Off}$ for PL and TPL nature of $P(t_{OnOff})$ are depicted in Figs. 6(c) and 6(d), where the corresponding mean values, $\langle m_{On} \rangle$ and $\langle m_{Off} \rangle$, are represented using vertical lines. We find that for the majority of QDs, $m_{OnOff}$ are close to or below 1.5 for TPL, while the corresponding values for PL are typically higher, as reflected in their mean values. Moreover, irrespective of PL or TPL nature of $P(t_{OnOff})$, $P(m_{Off})$ is more widely distributed compared to $P(m_{On})$, more so for turning into a dark state (“On” $\rightarrow$ “Off”). It is relevant to mention that for QDs which exhibit the TPL nature of $P(t_{OnOff})$, the (sub)ensemble average truncation times ($\tau_{c}$) (Table II) are nearly half for $P(t_{On})$ than that for $P(t_{Off})$ (~1.5 s). As the lifetimes ($\tau_{c}$) of the On-/Off- states have been related to the probability of trapping-detrappping processes, it is likely that the occurrence of trapping (“On” $\rightarrow$ “Off”) for “On” events is less frequent than the detrapping (“Off” $\rightarrow$ “On”) processes for the “Off” events.

Sequential arrangement of all the QDs shown in Figs. 6(a) and 6(b) further allowed us to compare how PL/TPL nature and $m_{OnOff}$ vary amongst various subensembles (i.e., categories I, II, and III). The (sub)ensembles $\{m_{On}\}$ and $\{m_{Off}\}$ [horizontal lines, Figs. 6(a) and 6(b)] for each blinking category are shown in Table II. First, our analysis reveals that the proportions of QDs which exhibit the PL/TPL nature of $P(t_{OnOff})$ vary significantly among the three subensembles (Table II); the ratio of the population of QDs which exhibit TPL against PL is the highest (lowest) for $P(t_{On})$ for “Mostly On” (“Mostly Off”) QDs. In contrast, however, a reverse trend is observed for $P(t_{Off})$. Furthermore, irrespective of the PL or TPL nature of $P(t_{OnOff})$, the $\langle m_{On} \rangle$ and $\langle m_{Off} \rangle$ (Table II) depend on the (sub)ensemble categories; for instance, $m_{On}$ decreases along category $I \rightarrow III$ subpopulations, while $m_{Off}$ exhibit an opposing behavior [Figs. 6(a) and 6(b) and Table II]. Such a variation in $\{m_{On/Off}\}$ as well as alteration in the ratio to PL characteristic of $P(t_{OnOff})$ among the subensembles reflects diverse relative proportions of “long” to “short” On-/Off-event durations in the blinking trajectories of QDs in the ensemble. Thus, (blinking) categorywise fluctuations further contribute to the overall heterogeneity in $m_{OnOff}$. We emphasize that the deviation of categorywise ($\langle m_{On} \rangle$ and $\langle m_{Off} \rangle$) for QDs which exhibit either PL or TPL $P(t_{OnOff})$ can often be significant, and the $\langle m_{On} \rangle$ and $\langle m_{Off} \rangle$ obtained for the entire ensemble also...
do not represent the subensemble average behaviors. This provides evidence that the various subensemble categories likely originate from different blinking mechanisms.

Irrespective of the subensembles’ behaviors, it is tempting to speculate about the plausible blinking mechanisms that may be operational based on our experimental $m_{\text{On/Off}}$ distributions [Figs. 5(c) and 5(d)]. It is noted that discrimination of blinking mechanisms becomes ambiguous as multiple alternate models (related to ionization-neutralization of QDs) very often predict similar mean values of $m_{\text{On/Off}}$ with a significant overlap in the range 0.5 and 2.5 (Fig. S11, supplementary material). However, relying on the extracted exponents, and comparison with prior reports which have reported $m_{\text{On/Off}}$ (see Table SIII, supplementary material), we classified the proportion of QDs that might blink via certain proposed mechanisms. We estimate that ~20% of the QDs are likely to follow diffusion controlled electron transfer (DCET) ($0.5 < m_{\text{Off}} < 1$), while no more than a quarter undergoes Auger ionization-recombination (AIR) or DCET ($1.4 < m_{\text{Off}} < 1.6$ and $2 < m_{\text{Off}} < 2.5$). Furthermore, ~75% of the QDs have $m_{\text{On}}$ between 1 and 2, which can originate from other related processes, such as the involvement of long-lived trap states with fluctuating energy barriers. It is intriguing that a small proportion of the QDs exhibit $m_{\text{On}}$ beyond those predicted by existing models ($0.5 < m_{\text{Off}} < 2.5$), which suggests the plausibility of unexplored processes. Although we have assigned most emitters’ intermittency to various ionization-neutralization related processes, it should be mentioned that there is experimental evidence which suggests that charging-based models do not adequately explain all aspects of QDs’ intermittency.

### C. On the ergodicity in blinking process

Our results suggest the coexistence of multiple blinking processes being operational in the ensemble, at least for the QD systems investigated here. In this study, we have considered ergodicity as a uniform blinking mechanism present throughout the ensemble of QDs, which has been predicted in various reports via evaluation of $m_{\text{On/Off}}$ for $P(t_{\text{On/Off}})$ from a few tens of QDs. However, there is evidence for nonergodic behaviors in terms of diverse blinking processes, mostly based on the intermittency characteristics of a few NC or a small ensemble of QDs. Our observations on the diversity of single-QD $m_{\text{On/Off}}$ for more than 1000 emitters clearly suggest the possibility of various distinct On-Off-mechanisms in the ensemble, in tune with recent reports of simultaneous occurrence of two blinking mechanisms. Below, we provide arguments, based on the nature of $P(m_{\text{On/Off}})$ and analysis of various subensembles, on the lack of ergodicity for blinking processes.

It is interesting that, apart from being considerably broad, both $P(m_{\text{On}})$ and $P(m_{\text{Off}})$ over the entire ensemble [Figs. 6I–6(d)] are not uniformly distributed (i.e., not symmetric) around their mean values. This skewness arises primarily due to contribution from two distinct nature (PL and TPL) of $P(t_{\text{On/Off}})$. It is important to note that $P(m_{\text{On/Off}})$ independently constructed from PL and TPL $P(t_{\text{On/Off}})$ [Figs. 6I–6(d)] are nearly symmetric. Our analysis shows that the skewness in the overall ensemble $P(m_{\text{On/Off}})$ originates from the difference in the PL and TPL distributions’ subpopulations. Thus, the larger extent of skewness for $m_{\text{On}}$ is a consequence of the significantly higher shift from $⟨m_{\text{On}}⟩$ (TPL) to $⟨m_{\text{On}}⟩$ (PL) values (1.25), compared to that for $m_{\text{Off}}$ (0.44). In addition, we find that the coefficient of variations (COVs) for the subensemble of QDs which exhibit TPL nature are quite large, much more so for $m_{\text{On}}$ (47%) as compared to $m_{\text{Off}}$ (28%). The high COV for $m_{\text{On}}$ for TPL behavior, which significantly contributes to the skewness of the entire $P(m_{\text{On}})$, indicating that the On-process (“On” → “Off”) is relatively more uniform than the Off-process (“On” → “Off”) among the QDs. This points out that the “On” and “Off” mechanisms may be different from each other, as suggested in a few earlier reports. To verify the extent of heterogeneity within the ensemble $m_{\text{On/Off}}$ values (i.e., blinking processes), we calculated the average of $m_{\text{On}}$ and $m_{\text{Off}}$ data points (for PL, TPL, and PL + TPL) above $⟨m_{\text{On/Off}}⟩$ (A) and below $⟨m_{\text{On/Off}}⟩$ (B) the overall mean for each of the distributions. This circumvents binning artifacts of the exponent histogram [Figs. 6I–6(d)] and is relevant for relatively small sample sizes. We observe that the deviation of $m_{\text{On/Off}}$ (A) and $m_{\text{On/Off}}$ (B) from the corresponding (sub)ensemble means is significantly different only for $P(m_{\text{On}})$ (TPL) and $P(m_{\text{On}} + TPL)$ (see Fig. S12, supplementary material). This provides evidence on the loss of ergodicity for the overall Off-mechanisms (“On” → “Off”).

### TABLE II. (Sub)ensemble blinking parameters from single-particle $P(t_{\text{On/Off}})$

| (Sub)ensemble category | Power law distribution | Truncated power law distribution |
|------------------------|------------------------|---------------------------------|
|                        | $QDs (%)$ | $⟨m_{\text{On}}⟩$ | $⟨m_{\text{Off}}⟩$ | $⟨t_{\text{C(On)}}⟩$ | $QDs (%)$ | $⟨m_{\text{On}}⟩$ | $⟨m_{\text{Off}}⟩$ | $⟨t_{\text{C(Off)}}⟩$ |
| $I$                    | 37        | 2.11          | 0.99          | 0.56                   | 17       | 1.40          | 1.08          | 1.39                   |
| $II$                   | 12        | 2.15          | 0.81          | 0.60                   | 23       | 1.66          | 1.21          | 1.20                   |
| $III$                  | 5         | 1.15          | 0.70          | 0.75                   | 36       | 1.86          | 1.47          | 1.58                   |
| $I + II + III$         | 21        | 2.09          | 0.85          | 0.61                   | 22       | 1.63          | 1.19          | 1.32                   |

$a$Weighted (entire ensemble) means of $⟨m_{\text{On}}⟩$ and $⟨m_{\text{Off}}⟩$ combining both TPL and PL are 1.11 ± 0.68 and 1.28 ± 0.38, respectively. (Sub)ensemble standard deviations of $m_{\text{On/Off}}$ are shown in Table SII.

$b$In seconds.
To substantiate this, it is imperative to compare the ensemble averaged \( \langle m_{\text{On/Off}} \rangle \) for all the QDs, with the time-averaged exponent \( \langle m_{\text{On/Off}} \rangle \) from individual blinking traces. It is important to note that extraction of reliable \( \langle m_{\text{On/Off}} \rangle \) requires the analysis of extremely long time (5–6 decades at least) blinking data. However, collection of such long time PL data on single QDs is particularly challenging due to material degradation with prolonged illumination (photobleaching) as well as practical limitations such as stage/focus drifts and data acquisition/storage capability. However, it is relatively easy to construct \( P(t_{\text{On/Off}}) \) using hundreds of traces from individual QDs each containing few thousand frames. Therefore, one practical approach has been to combine \( P(t_{\text{On/Off}}) \) acquired from many blinking trajectories of limited duration (~3 decades) and assume under the ergodicity hypothesis that the cumulative \( P(t_{\text{On/Off}}) \) would reflect the behavior of one single QD over an extremely long time.

Therefore, to test whether such analyses are applicable for QDs, we have constructed time-ensemble averaged (cumulative) On-/Off-time distribution \( \langle P(t_{\text{On/Off}}) \rangle \) using IHDT. Figure 7 shows the \( \langle P(t_{\text{On/Off}}) \rangle \) and the extracted exponents \( \langle m_{\text{On/Off}} \rangle \) for the entire ensemble, along with the three subcategory distributions. Interestingly, although individual QD may exhibit either PL or TPL nature for \( P(t_{\text{On/Off}}) \), we find that the \( \langle P(t_{\text{On/Off}}) \rangle \) for the (sub)ensemble always follow TPL. Such TPL nature of \( \langle P(t_{\text{On/Off}}) \rangle \) owes to the accumulation of long On-/Off-duration events from many emitters and TPL nature of \( P(t_{\text{On/Off}}) \) for a dominant fraction (~75%) of QDs. More importantly, the time-ensemble averaged exponents \( \langle m_{\text{On/Off}} \rangle \)\( \langle m_{\text{On/Off}} \rangle = 1.69, \langle m_{\text{On/Off}} \rangle = 1.89 \) of the entire population differ considerably from the respective ensemble (weighted) average (for PL + TPL) exponent values \( \langle m_{\text{On}} \rangle = 1.11 \pm 0.68 \) and \( \langle m_{\text{Off}} \rangle = 1.28 \pm 0.38 \), Fig. 5 and Table II). Furthermore, a significant deviation between the time-ensemble averaged and ensemble averaged values are found for the various subensemble categories (Fig. 7 and Table II). The mismatch between \( \langle m_{\text{On/Off}} \rangle \) and \( m_{\text{On/Off}} \) for ensemble and different blinking subcategories provides additional evidence for a loss of ergodicity in the blinking process of QDs.

To validate the loss of ergodicity due to the existence of different inherent blinking mechanisms and their relation with the blinking propensity, we have performed the analysis of variance (ANOVA) for the categorywise \( m_{\text{On/Off}} \) values with that for the entire population. We find that the value of \( F \)-calculated \( [F_{\text{calc}} \langle m_{\text{On/Off}} \rangle = 81.54, F_{\text{calc}} \langle m_{\text{On}} \rangle = 103.25] \) is always greater than \( F \)-critical \( [F_{\text{cri}} \langle m_{\text{On}} \rangle = 3.0044, F_{\text{cri}} \langle m_{\text{Off}} \rangle = 3.0045] \). This corroborates the existence of three distinct subensembles of \( m_{\text{On/Off}} \) as well and implies a correlation between different blinking mechanisms and intensity distribution based subcategorization of QDs. Our inference that multiple blinking mechanisms are operational amongst various QDs is reminiscent of molecular diffusion through heterogeneous media, where, apart from normal Brownian diffusion, certain subpopulations exhibit anomalous diffusion/subdiffusion or correlated diffusion in passive systems (polymer films and gels)\(^{64,67}\) and both normal as well as diverse anomalous diffusion in active systems (cellular environments).\(^{65,69}\) The coexistence of various subensembles can lead to the loss of ergodicity,\(^{61,67}\) i.e., the time-ensemble average does not strictly correspond with the time-averaged values of certain parameters (within finite time scales of measurement), similar to the situation described here.

V. SUMMARY AND PERSPECTIVE

Using an intensity histogram based flexible thresholding method and emissivity based subensemble analysis of a large number (> 1000) of individual Mn\(^{12+}\) doped ZnCdS QDs, we show that the blinking dynamics of NCs can often be extremely diverse amongst individual species in the ensemble. Our results demonstrate that due to high NC-dependent variability, it is imperative to perform statistical analysis to estimate blinking parameters (such as \( m_{\text{On/Off}} \)) used to validate or contradict theoretical predictions. We further show that even a simple classification based on the single-particle emissivity \([\text{or } \tau_{\text{NC}}(\%)\]) allows us to distinguish statistical behaviors of subpopulations and the entire ensemble. Our results on Mn\(^{12+}\) doped ZnCdS reveal that blinking parameters such as \( SF \) and \( m_{\text{On/Off}} \) not only vary over different subpopulations, but even the nature of \( P(t_{\text{On/Off}}) \) in each subpopulation is not the same for every QD. Furthermore, \( m_{\text{On/Off}} \) for individual QDs can often be as low as 0.1 or as high as 3 or 4, considerably more diverse than the prior reported exponent values which lie typically between 1 and 2. This indicates the existence of alternate mechanisms for NC blinking than those proposed in the literature or may even point out to the limitation of the conventional intensity-based thresholding approach to explain mechanisms of QC intermittency. Thus, generalization of blinking mechanisms based on the characteristics of several or few tens of QDs is potentially misleading as several underlying processes can be responsible for intermittency of different NCs within the ensemble.
Owing to the limited number of blinking events or finite survival times of QDs, an alternate approach has been to combine the On-/Off-time duration distributions from individual intensity trajectories of several tens of QDs and subsequently extract $\langle m_{\text{On/Off}} \rangle$ from the cumulative distribution. Here, the underlying assumption is that the ergodic hypothesis holds for blinking in NCSs, even though there is some evidence to the contrary. Our results reveal that there is a significant difference between the exponent ($\langle m_{\text{On/Off}} \rangle$) of time-ensemble averaged On-/Off-time distribution $\langle P(t_{\text{On/Off}}) \rangle$ and the ensemble average of the exponents ($\langle m_{\text{On/Off}} \rangle$). Our analysis reveals that there is a loss of ergodicity in blinking amongst various QDs in the ensemble, owing primarily to the existence of different subpopulations of processes. Therefore, to infer mechanism(s), neither is it appropriate to analyze extremely long-time blinking trajectories from a handful of QDs, nor is it reliable to extract $\langle P(t_{\text{On/Off}}) \rangle$/$\langle m_{\text{On/Off}} \rangle$ from the cumulative combination of many finite-time blinking traces. Rather, the intermittency of a statistically relevant number of single QDs warrants independent investigation, as semiconductor NCSs of very similar composition and morphology are, in reality, distinct entities with their own blinking characteristics.

SUPPLEMENTARY MATERIAL

See supplementary material for details of experimental and analyses methods and supporting data (Figs. S1–S13 and Tables S1–SIII), along with a supplementary movie (Movie M1) “(Multimedia view).”

ACKNOWLEDGMENTS

A.M. thanks CSIR (India) for Ph.D. scholarships [Grant No. 09/087(0784)/2013-EMR-I], and C.P. acknowledges IIT Bombay for post-doctoral fellowship. A.C. acknowledges financial support [SERB Grant No. EMR/2017/004878] from the Department of Science and Technology (Government of India) to carry out this work. We thank D. D. Sarma and A. Hazarika for providing Mn-doped ZnCdS QD samples. We acknowledge MNRE (India) aided NCPRE for post-doctoral fellowship. A.C. acknowledges financial support [09/087(0784)/2013-EMR-I], and C.P. acknowledges IIT Bombay and Technology (Government of India) to carry out this work.

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