

## ***Universal emission intermittency in quantum dots, nanorods, and nanowires***

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Virtually all known fluorophores, including semiconductor nanoparticles, nanorods and nanowires exhibit unexplainable episodes of intermittent emission blinking. A most remarkable feature of the fluorescence intermittency is a universal power law distribution of on- and off-times. For nanoparticles the resulting power law extends over an extraordinarily wide dynamic range: nine orders of magnitude in probability density and five to six orders of magnitude in time. The exponents hover about the ubiquitous value of  $-3/2$ . Dark states routinely last for tens of seconds, which are practically forever on quantum mechanical time scales. Despite such infinite states of darkness, the dots miraculously recover and start emitting again. Although the underlying mechanism responsible for this phenomenon remains an enduring mystery and many questions remain, we argue that substantial theoretical progress has been made.

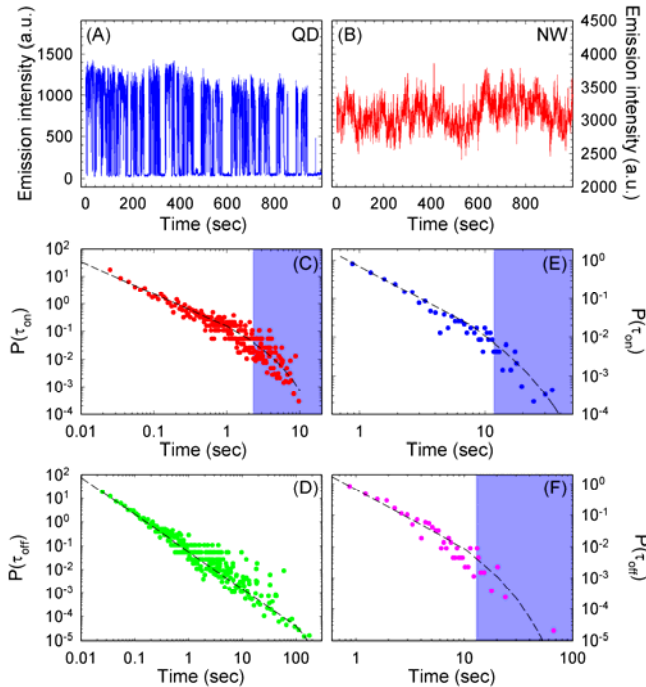
### ***Introduction***

Very few problems of early quantum mechanics remain unsolved today. Fluorescence intermittency is one exception. At the dawn of modern quantum mechanics, Niels Bohr predicted “quantum jumps” of electrons between discrete energy levels of atoms and molecules. Such jumps were observed directly only during the 1980s with the advent of single ion traps [1]. An ongoing series of experiments brought spectacular progress to single molecule imaging [2], raising more questions than answers about these emission “jumps”.

Basically all known fluorophores studied to date exhibit fluorescence intermittency. They include single molecules[3-7], individual fluorescent proteins[8], polymer segments[9], semiconductor nanoparticles[10-23], nanorods[24] and even nanowires (NWs).[25,26] Such jumps, where the fluorophore literally stops emitting light under continuous excitation, are very different from those predicted by Bohr. Rather than occurring on the micro- to millisecond timescales, they last seconds and even minutes. These experimentally observed off-times are vastly longer than any timescale one would retrieve from a standard quantum mechanical model: The “dark” states live practically forever. After these very long periods of darkness, the fluorophore eventually emerges into an emitting state. The new emissive state would be impossible if off periods were simply photobleaching events.

Even more intriguing are the statistics of the intermittency. Whereas Bohr would have postulated exponential distributions of “on”-times and “off”-times, universal power law on-time and off-time probability densities are actually observed [11]. For colloidal quantum dots (QDs), this power law extends over an extraordinarily wide range that spans nine orders of magnitude in probability density and five to six orders of magnitude

in time. This is remarkable for many reasons. First, the experimentally observed distribution refuses to yield a time scale. Second, universality on a lesser scale has revolutionized our understanding about phase transitions [27]. Finally, such statistics arise from the behavior of *single* fluorophores, not an ensemble. Given that single organic molecules also blink and exhibit near-identical power law blinking kinetics [3-7], it is tempting to speculate that such striking similarity is not an accident. We therefore ask whether there exist unrecognized points of commonality between seemingly disparate entities such as molecules and semiconductor nanostructures. While the underlying mechanism for answering such questions remains a mystery, we argue in this perspective that many, if not all, key experiments have already been conducted and that substantial theoretical progress has been made.



**Figure 1.** Emission trajectory from a single (A) QD and (B) NW. Corresponding QD log-log plot of the (C) on-time and (D) off-time probability density. Analogous log-log plot of the NW (E) on-time and (F) off-time probability density.

A log-log plot demonstrates this, showing linear behavior for both on- and off-time distributions over many decades in probability density and time (QD: Figure 1 c,d; NW: Figure 1 e,f). Even more impressive is the fact that the same power law kinetics appears in vastly different systems such as molecules.

Let us now summarize several of the facts learned from the first decade of observing QD blinking. Any self-consistent and comprehensive theory of fluorescence intermittency must account for the following:

**(a) The existence of power laws from a threshold analysis:** Blinking occurs over a wide range of timescales ( $\mu\text{s}$  to minutes). The shortest and longest times are currently both set by experimental limitations. Distributions  $P(\tau_{\text{on}})$ , and  $P(\tau_{\text{off}})$  can be fit to power laws of

### **Key features of blinking**

Figure 1 shows representative examples of blinking in QDs and NWs. An emission “trajectory” from both systems is provided, plotting emission intensity as a function of time. In both cases the intensity fluctuates. When a threshold is used to distinguish on- from off-states, second-to-minute long off-times are apparent.

In principle, plotting both on-time and off-time probability densities on a semi-logarithmic plot enables one to extract characteristic rates for turning the fluorophore on or off. However, QDs, molecules and even NWs exhibit power law (i.e. scale-free) kinetics, indicating that the rate must be distributed over many

the form  $t^{-m_{on/off}}$  where  $m_{on/off}$  ranges from 1.2 to 2.0 [28,29]. More recently, truncation times (“cutoffs”) were discovered in on-time distributions [12]. Such cutoffs occur on the second timescale and may represent a competing physical process which interrupts power law blinking. A corresponding off-time cutoff in QDs has not been reported, although it is speculated to occur on a week timescale [17]. Figures 1 e,f show examples of such cutoffs in recent NW blinking data.

**(b) The existence of power law power spectral densities:** Pelton and Guyot-Sionnest[13a] have demonstrated that the power spectrum of the ensemble QD emission exhibits a power law of the form  $p(f) \sim f^{-\alpha}$  ( $\alpha \sim 1$ ). This was also confirmed in the case of single QDs. Furthermore, a kink in the power spectral density was observed more recently with slopes reverting from  $\approx 1.0$  at low frequencies to  $\approx 2.0$  above 100 Hz [13b].

**(c) The light-driven nature of the blinking process:** Intermittency is light-induced, as indicated by experiments revealing statistical “aging” of emission trajectories [30]. The ensemble emission intensity decays under continuous excitation and recovers in the dark [17].

**(d) A general lack of temperature dependence:** No significant temperature dependence of the power law kinetics has been observed so far. Specifically, on/off power law slopes are generally temperature independent between 10 K and 400 K [11,12]. This has led some to speculate tunneling or another temperature independent physical processes at play.

**(e) A connection to spectral diffusion:** Neuhauser and Bawendi have suggested that blinking is connected to another ubiquitous single molecule phenomenon: spectral diffusion[18]. Large shifts in the spectrum coincided with equally rare jumps of intensity. This suggests a direct correlation between spectral diffusion and emission intermittency through the redistribution of charges on or nearby the QD surface.

**(f) A continuous distribution of emission intensities and excitation lifetimes:** Typical fluorescence intensity trajectories from single QDs do not mimic random telegraph noise[1]. Unique “on” and “off” levels are not seen, but instead a wide range of intensities exist. Schegel and Mews [15] have since found that such intensity fluctuations are correlated with changes in the QD emission lifetime. Additional studies [14, 16] have confirmed this and have, in turn, shown through simultaneous emission quantum yield measurements that fluctuations in the non-radiative recovery rate are connected to these intensity variations.

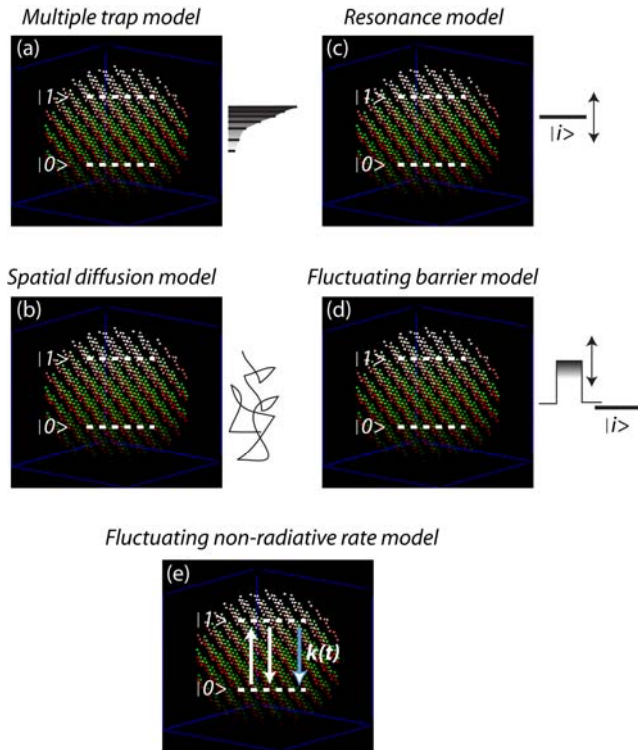
**(g) A sensitivity to electric fields:** Cichos and co-workers have found that off-time slopes depend upon the dielectric permittivity of the immediate QD surroundings [28]. Larger slopes are seen for cases where the dielectric permittivity of the surrounding is small. Conversely, smaller slopes are seen when the dielectric permittivity of the environment is large. Recently, Barbara and co-workers have also demonstrated that the emission from single QDs is modulated by externally applied electric fields [23]. The sign of the

modulation varies slowly in time suggesting that blinking is connected to changes in local electric fields stemming from charges on the QD surface.

### Theoretical models

From the above list of key experimental findings, constraints on any comprehensive theoretical model, even if phenomenological, appear formidable. Most current models for blinking can broadly be categorized into one of two groups: a) those that focus solely on analyzing power law statistics [36-37] and b) those that postulate a physical mechanism for intermittency [30,31,33-35]. We focus here on the latter models and provide representative cartoons in Figure 2.

The first QD blinking model was developed by Efros and Rosen[31]. This is an extremely successful model, and despite a few shortcomings, still lies at the heart of conventional wisdom for explaining fluorescence intermittency. Within this model, QDs are thought to undergo Auger ionization events under photoexcitation: Electrons are ejected from the dot to surrounding acceptor-like states. This leaves behind a positively charged QD. Subsequent electron-hole pairs then experience rapid Auger-like nonradiative relaxation to the ground state, quenching any emission and thereby rendering the particle dark. This process continues until the QD is neutralized [32a,32b].



**Figure 2.** Cartoon diagrams of various theoretical blinking models

distributions (a) are naturally obtained. Furthermore, this model readily explains the dependence of off-time power law slopes with the dielectric properties of the environment [28]. Finally, the lack of temperature dependence (d) can be explained through a tunneling process.

The Efros/Rosen model provided the first intuitive picture for blinking, and became a major step towards understanding fluorescence intermittency. However, a key problem remains: In sharp contrast with the experimental findings, it predicts characteristic on/off rates and corresponding exponential on-time/off-time distributions. To circumvent these limitations, a series of modifications have since been proposed. They include:

1. **Multiple trap model:** (Figure 2a) Verbek and Orrit[33] assume the existence of multiple electron traps near the QD. Due to a static distribution of trapping and de-trapping rates, which vary with distance, power law off-time

2. **Spatial diffusion model: (Figure 2b)** Margolin and Barkai[30] suggested that any ejected electron performs a 3D diffusion in space about the QD prior to its return. While the model predicts naturally a  $t^{-3/2}$  distribution of off-times according to random walk theory, deviations (cf. **(a)**) from the -1.5 exponent would require the introduction of anomalous diffusion processes. Furthermore, a finite probability exists for the carrier to never return to the QD, leading to permanently dark dots in the limit of long observation times. As before, the spatial diffusion models implies a strong temperature dependence, not in agreement with **(d)**.

3. **Spectral diffusion model: (Figure 2c)** Shimizu and Bawendi [12] hypothesized a resonant tunneling mechanism where the diffusion of the environment's acceptor energy level causes power law distributed on-to-off and off-to-on kinetics. Tang and Marcus[34] later developed this by assuming spectral diffusion of both QD and acceptor state energies. A key prediction is a change in the slopes of both on-time and off-time power-laws from 3/2 at long times to 1/2 at short times. Interestingly, this has recently been corroborated by power spectral density experiments conducted by Pelton [13]. Open questions remain though, and further investigation is necessary into the role of electronic interactions with dielectric media and phonons inside QD. While these effects have the tendency to widen the transition region, and possibly shorten the range of the power-law dependence, the experimental confirmation by Pelton strongly supports this class of model.

4. **Fluctuating barrier model: (Figure 2d)** Kuno and Nesbitt[11] have alternatively suggested a model where emission intermittency involves fluctuations in the height or width of a tunneling barrier between an electron within the QD and an external trap state. Furthermore, during the tunneling process, the local environment was postulated to change such that between each off-to-on or on-to-off transition the tunneling barrier would differ.

Each of these proposals was successful in bringing the Efros-Rosen theory in line with many, but not all experimental constraints. In particular, a key problem shared by all models is the general difficulty in explaining a continuous distribution of relaxation times [14]. Alternative models [23,35], which don't invoke long-lived ( $> 1$  s) electron traps, have been suggested to account for the distribution of relaxation times.

5. **Fluctuating non-radiative rate models: (Figure 2e)** Frantsuzov and Marcus[35] have suggested that the QD intermittency is a result of the fluctuations of the non-radiative recombination rate. Recombinations occur through the Auger-assisted excitation of deep surface states and consequent relaxation to the ground state. The trapping rate is then governed by the spectral diffusion of a second excited QD state (1Pe), which modulates the eventual non-radiative recovery of the system. The mechanism naturally explains a continuous distribution of relaxation times. However, it leaves unanswered several model constraints **(a)**: it gives slope 3/2 for both on and off distributions regardless of the threshold level, although a modified version of the same model was suggested recently by Barnes[22] to explain suppression of blinking after

ligand exchange. A similar model was developed by Barbara[23] to explain the apparent external electric field modulation of QD emission intensities.

### ***Discussion and conclusion***

Single QDs, NWs and molecules all demonstrate universal emission intermittency over large timescales. Furthermore, a threshold analysis reveals truncated power-law distributions for both on-time and off-time probability densities. Explaining these two observations has been the cornerstone of much work in the field for the last 10 years. As we have shown above, the available theoretical frameworks have been quite successful in explaining a surprisingly large subset of the experimental constraints. They include, but are not limited to **(a)-(h)**. However, no theory exists at this time, which consistently accounts for all the observables.

### **References**

- [1] *Possibility of Direct Observation of Quantum Jumps*, R. J. Cook, H. J. Kimble, Phys. Rev. Lett. 54, 1023, (1985).
- [2] *Illuminating single molecules in condensed matter*, W. E. Moerner, M. Orrit, Science 283, 1670, (1999).
- [3] *Dispersive kinetics from single molecules oriented in single crystals of potassium acid phthalate*, K. L. Wustholz, E. D. Bott, C. M. Isborn, X. Li, B. Kahr, P. J. Reid, J. Phys. Chem. C, 111, 9146, (2007).
- [4] *Characterizing the fluorescence intermittency of photobleaching kinetics of dye molecules immobilized on a glass surface*, E. K. L. Yeow, S. M. Melnikov, T. D. M. Bell, F. C. De Schryver, J. Hofkens, J. Phys. Chem. A, 110, 1726, (2006).
- [5] (a) *Power-law-distributed dark states are the main pathway for photobleaching of single organic molecules*, J. P. Hoogenboom, E. M. H. P. van Dijk, J. Hernando, N. F. van Hulst, M. F. Garcia-Parajo, Phys. Rev. Lett., 95, 097401, (2005); (b) *Accurate and unbiased estimation of power-law exponents from single-emitter blinking data*, J. P. Hoogenboom, W. K. der Otter, H. L. Offerhaus, J. Chem. Phys., 125, 204713, (2006); (c) *Power-law blinking in the fluorescence of single organic molecules*, J. P. Hoogenboom, j. Hernando, E. M. H. P. van Dijk, N. F. van Hulst, M. F. Garcia-Parajo, ChemPhysChem, 8, 823, (2007). (d) J. Hoogenboom, Workshop on “Fluorescence intermittency in molecules, quantum dots and quantum wires” Notre Dame, IN April 1-3, 2007.
- [6] (a) *Blinking of single molecules in various environments*, J. Schuster, F. Cichos, C. von Borczyskowski, Opt. Spect., 98, 778, (2005); (b) *Influence of self-trapped states on the fluorescence intermittency of single molecules*, J. Schuster, F. Cichos, C. von Borczyskowski, Appl. Phys. Lett., 87, 051915, (2005).

- [7] *Exponential and power-law kinetics in single-molecule fluorescence intermittency*, M. Haase, C. G. Hubner, E. Reuther, A. Herrmann, K. Mullen, Th. Basche, J. Phys. Chem. B, 108, 10445, (2004).
- [8] *On/off blinking and switching behavior of single green fluorescent protein molecules*, R. M. Dickson, A. B. Cubitt, R. Y. Tsien, W. E. Moerner, Nature 388, 355 (1997).
- [9] *Discrete Intensity Jumps and Intramolecular Electronic Energy Transfer in the Spectroscopy of Single Conjugated Polymer Molecules*, D. Vanden Bout, W. T. Yip, D. Hu, D. K. Fu, T. M. Swager, P. F. Barbara, Science 277, 1074 (1997).
- [10] *Fluorescence intermittency in single cadmium selenide nanocrystals*, M. Nirmal, B. O. Dabboussi, M. G. Bawendi, J. J. Macklin, J. K. Trautman, T. D. Harris, L. E. Brus, Nature, 383, 802, (1996).
- [11] (a) *Nonexponential 'blinking' kinetics of single CdSe quantum dots: A universal power law behavior*, M. Kuno, D. P. Fromm, H. F. Hamann, A. Gallagher, D. J. Nesbitt, J. Chem. Phys., 112, 3117, (2000); (b) *'On/Off' fluorescence intermittency of single semiconductor quantum dots*, M. Kuno, D. P. Fromm, H. F. Hamann, A. Gallagher, D. J. Nesbitt, J. Chem. Phys., 115, 1028, (2001).
- [12] *Blinking statistics in single semiconductor nanocrystal quantum dots*, K. T. Shimizu, R. G. Neuhauser, C. A. Leatherdale, S. A. Empedocles, W. K. Woo, M. G. Bawendi, Phys. Rev. B, 63, 205316, (2001).
- [13] (a) *Characterizing quantum-dot blinking using noise power spectra*, M. Pelton, D. G. Grier, P. Guyot-Sionnest, Appl. Phys. Lett., 85, 819, (2004); (b) *Evidence for a diffusion-controlled mechanism for fluorescence blinking of colloidal quantum dots*, M. Pelton, G. Smith, N. F. Scherer, R. A. Marcus, Proc. Natl. Acad. Sci. 104 14249, (2007).
- [14] *Continuous distribution of emission states from single CdSe/ZnS quantum dots*, K. Zhang, H. Chang, A. Fu, A. P. Alivisatos, H. Yang, Nano Lett., 6, 843, (2006).
- [15] *Fluorescence decay time of single semiconductor nanocrystals*, G. Schlegel, J. Bohnenberger, I. Potapova, A. Mews, Phys. Rev. Lett., 88, 137401, (2002).
- [16] *Emission intensity dependence and single exponential behavior in single colloidal quantum dot fluorescence lifetimes*, B. R. Fisher, H. J. Eisler, N. E. Stott, M. G. Bawendi, J. Phys. Chem. B 108, 143, (2004).
- [17] *Relationship between single quantum-dot intermittency and fluorescence intensity decays from collections of dots*, I. Chung, M. G. Bawendi, Phys. Rev. B, 70, 165304, (2004).

- [18] *Correlation between Fluorescence Intermittency and Spectral Diffusion in Single Semiconductor Quantum Dots*, R. G. Neuhauser, K. T. Shimizu, W. K. Woo, S. A. Emedocles, M. G. Bawendi, Phys. Rev. Lett. 85, 3301, (2000).
- [19] D. J. Nesbitt, Workshop on “Fluorescence intermittency in molecules, quantum dots and quantum wires” Notre Dame, IN April 1-3, 2007.
- [20] *Memory in quantum-dot photoluminescence blinking*, F. D. Stefani, X. Zhong, W. Knoll, M. Han, M. Kreiter, New J. Phys., 7, 197, (2005).
- [21] *Near-complete suppression of quantum dot blinking in ambient conditions*, S. Hohng, T. Ha, J. Am. Chem. Soc., 126, 1324, (2004).
- [22] *Coverage-mediated suppression of blinking in solid state quantum dot conjugated organic composite nanostructures*, N. I. Hammer, K. T. Early, K. Sill, M. Y. Odoi, T. Emrick, M. D. Barnes, J. Phys. Chem. B, 110, 14167, (2006).
- [23] *Effect of electric field on the photoluminescence intensity of single CdSe nanocrystals*, S. J. Park, S. Link, W. L. Miller, A. Gesquiere, P. F. Barbara, Chem. Phys. 341, 169 (2007).
- [24] *Fluorescence blinking statistics from CdSe core and core-shell nanorods*, S. Wang, C. Querner, T. Emmons, M. Drndić, C. H. Crouch, J. Phys. Chem. B 110, 23221, (2006).
- [25] *Spatial and intensity modulation of nanowire emission induced by mobile charges*, V. V. Protasenko, S. Gordeyev, M. Kuno, J. Am. Chem. Soc. 129, 13160 (2007); *Disorder-induced optical heterogeneity in single CdSe nanowires*, Adv. Mater. 2005, 17, 2942.
- [26] *Synchronous photoluminescence intermittency (blinking) along whole semiconductor quantum wires*, J. J. Glennon, R. Tang, W. E. Buhro, R. A. Loomis, Nano Lett., 7, 3290 (2007).
- [27] *Static Phenomena near critical points – Theory and experiment*, L.P. Kadanoff, W. Gotze, D. Hamblen, R. Hecht, E.A.S. Lewis, V.V. Palciaus, M. Rayl, J. Swift, D. Aspnes, J. Kane, Rev. Mod. Phys. 39, 395 (1967).
- [28] *Power-law intermittency of single emitters*, F. Cichos, C. von Borczyskowski, M. Orrit, Curr. Op. Coll. Int. Scie. 12, 272 (2007).
- [29] *Optical properties of single semiconductor nanocrystals*, D. E. Gomez, M. Califano, P. Mulvaney, Phys. Chem. Chem. Phys. 8, 4989, (2006).
- [30] *Power law blinking quantum dots: Stochastic and physical models*, G. Margolin, V. Protasenko, M. Kuno, E. Barkai, Adv. Chem. Phys., 133, 327, (2006).

[31] *Random telegraph signal in the photoluminescence intensity of a single quantum dot*, Al. L. Efros, M. Rosen, Phys. Rev. Lett., 78, 1110, (1997).

[32a] *Charge, Polarizability, and Photoionization of Single Semiconductor Nanocrystals*, T. D. Krauss, L. E. Brus, Phys. Rev. Lett. 2000, 83, 4840 (1999).

[32b] An NSF-NIRT funded experimental effort to detect anti-correlation between fluorescence intermittency and charge fluctuation by using single-charge devices and near-field scanning optical microscope is currently being pursued at Notre Dame by B. Janko, K. Kuno, J. Merz and G. Snider.

[33] *Simple model for the power-law blinking of single semiconductor nanocrystals*, R. Verberk, A. M. van Oijen, M. Orrit, Phys. Rev. B, 66, 233202, (2002).

[34] *Diffusion-controlled electron transfer processes and power-law statistics of fluorescence intermittency of nanoparticles*, J. Tang, R. A. Marcus, Phys. Rev. Lett., 95, 107401, (2005).

[35] *Explanation of quantum dot blinking without the long-lived trap hypothesis*, P. Frantsuzov, R. A. Marcus, Phys. Rev. B., 72, 155321, (2005).

[36] *Nonegrodicity of blinking nanocrystals and other Levy-walk processes*, G. Margolin and E. Barkai, Phys. Rev. Lett. 94, 080601 (2005).

[37] *Fluorescence intermittency in blinking quantum dots: Renewal or slow modulation?*, S. Bianco, P. Grigolini, and P. Paradisi, J. Chem. Phys. 123, 174704 (2005).

[38] *1/f noise and other slow, nonexponential kinetics in condensed matter*, M. B. Weissman, Rev. Mod. Phys. 60, 537, (1988).

[39] *Suppressed blinking in single quantum dots (QDs) immobilized near silver island films (SIFs)*, Y. Fu, J. Zhang, J.R. Lakowicz, Chem. Phys. Lett. 447, 96 (2007).

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