

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/228931963>

# Probing Multiexcitonic Emission in Single CdSe – Oligo (phenylenevinylene) Composite Nanostructures

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY C · AUGUST 2009

Impact Factor: 4.77 · DOI: 10.1021/jp9051787

---

CITATIONS

4

---

READS

20

6 AUTHORS, INCLUDING:



Michael D Barnes

University of Massachusetts Amherst

146 PUBLICATIONS 2,318 CITATIONS

SEE PROFILE

## Probing Multiexcitonic Emission in Single CdSe–Oligo(phenylenevinylene) Composite Nanostructures

Michael Y. Odoi,<sup>†</sup> Kevin T. Early,<sup>†</sup> Ravisubhash Tangirala,<sup>‡</sup> Pallikkara K. Sudeep,<sup>‡</sup> Todd Emrick,<sup>‡</sup> and Michael D. Barnes<sup>\*,†</sup>

*George R. Richason Jr. Chemistry Research Laboratory, Department of Chemistry, and Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003*

*Received: June 2, 2009; Revised Manuscript Received: June 30, 2009*

Fluorescence intensity fluctuations from individual CdSe quantum dots coordinated with oligo(phenylenevinylene) ligands (CdSe–OPV) have been previously observed to be qualitatively different from conventional capped CdSe quantum dots. In particular, the high degree of blinking suppression observed in these (inherently multichromophoric) systems was suggestive of multichromophoric emission. In this paper we describe results of second-order fluorescence intensity correlation function  $g^{(2)}(\tau)$  measurements from individual CdSe–OPV nanostructures to definitively assess the multiexcitonic character of the emission from these species. Our results point to a weak multiexcitonic character ( $g^{(2)}(0) \approx 0.2$ ) under 405 nm excitation where both the organic ligand and quantum dot absorb. Using 514.5 nm excitation, where the ligand absorption is negligible, the quantum dot emission is completely antibunched ( $g^{(2)}(0) \approx 0.05$ ), similar to that of ZnS-capped CdSe control samples. These results provide new insights into the mechanism of intensity *flickering* and electronic interactions in composite quantum dot/conjugated organic composite systems.

### Introduction

Thin film blends of quantum dots and conjugated polymers have attracted a great deal of interest in the context of light harvesting photovoltaic and optoelectronic devices.<sup>1–10</sup> Electronic interaction between the quantum dot and the conjugated organic component facilitate charge transport, enhance energy transfer, and improve fluorescence quantum yield. However, the problem of phase segregation results in the formation of separate domains of the quantum dots and the organic component and leads to overall weak electronic interaction between the two in thin film devices. Recently, work in our laboratory has focused on the photophysics of a CdSe quantum dot/conjugated organic composite system, where the conjugated organic ligand, oligo(phenylenevinylene) (OPV), is coordinated directly to the surface of the quantum dot, referred to hereafter as CdSe–OPV.<sup>11,12</sup> This architecture allows intimate contact between the quantum dot and the organic ligands and provides for tunable ligand length and quantum dot size, enabling detailed study of ligand–dot electronic interaction at the single-molecule level.

Our previous work on this system has shown a number of interesting photophysical behaviors including suppressed blinking, spectral stability, “gray level” intensity flickering and polarization dependent emission,<sup>12–16</sup> features which are linked to OPV ligand coverage on the quantum dot surface.<sup>16</sup> We proposed that observed blinking suppression and reduced fluorescence lifetime, with a weak correlation to intensity (count rate) from time-tagged time-resolved measurements,<sup>13–15</sup> could be explained in the context of the diffusive coordinate model

proposed by Frantsuzov and Marcus,<sup>17</sup> which connects blinking in quantum dots to Auger assisted hole trapping rates due to fluctuations in the  $1S_e-1P_e$  electron energy difference in the quantum dot. A common feature in reports of quantum dot blinking suppression makes use of electron donating species,<sup>18,19</sup> which can influence the electron  $1S_e-1P_e$  energy separation via Stark interaction. This, in turn, suppresses Auger-assisted hole trapping and hence the nonradiative decay rates. In the diffusive coordinate model applied to our system,<sup>13</sup> such slow fluctuations of the quantum dot electron energy separation are confined to regions of energy space where nonradiative and radiative decay rates are in competition, resulting in a “gray level” (nonbinary) intensity flickering and a significantly reduced fluorescence lifetime consistent with experimental observation.<sup>13,15,20</sup> Recent polarization anisotropy studies also showed that excitations formed within the OPV ligands result in a linear-polarized transition dipole moment in both absorption and emission.<sup>12,21</sup>

Here, we probe the multiexcitonic character of isolated CdSe–OPV nanostructures using photon-pair correlation spectroscopy to address the question of charge and energy transfer between the OPV ligands and the quantum dots. To do this, we used a standard Hanbury Brown–Twiss,<sup>22–25</sup> two-detector configuration with two different excitation wavelengths (405 and 514 nm) corresponding to OPV + CdSe absorption and CdSe absorption, respectively. This measurement provides us with key information about exciton recombination rates (the radiative lifetime) and the number of independent emitters that is not directly accessible in conventional time-correlated single-photon counting measurements.

Fluorescence intensity correlation techniques have been a major tool for characterizing the quantum nature of single fluorescent molecules or nanostructures such as quantum

\* Corresponding author. E-mail: mdbarnes@chem.umass.edu.

<sup>†</sup> Department of Chemistry.

<sup>‡</sup> Department of Polymer Science and Engineering.

dots,<sup>26–33</sup> single polymer chain<sup>34–42</sup> sodium atoms,<sup>43</sup> and color centers in diamond.<sup>44</sup> In particular, it has proven useful in the investigation of multichromophoric systems such as conjugated polymers.<sup>34–42</sup> For a two-level quantum emitter the second-order intensity correlation function  $g^{(2)}(\tau)$  vanishes for  $\tau = 0$ , where  $\tau$  is the time difference between two consecutive photon detection events. In the limit of saturated absorption, the spontaneous radiation is rate limiting in the absorption/emission cycle. For a molecular system with  $N$ -independent emitters,  $g^{(2)}(\tau)$  can be modeled approximately as

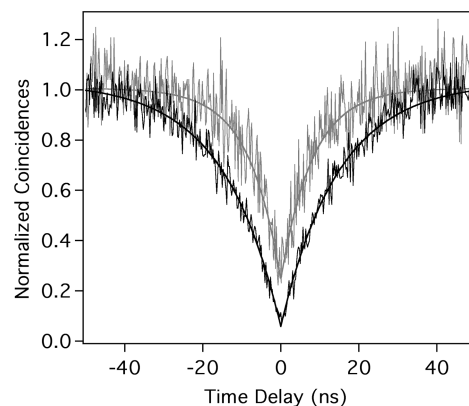
$$g^{(2)}(\tau) \cong 1 - \frac{1}{N} \exp[-|\tau|(W_p + \Gamma_n)] \quad (1)$$

where  $W_p$  is the pump rate and  $\Gamma_n$  is the electron–hole pair recombination rate ( $1/\Gamma_n$  is the pure radiative lifetime). The second-order intensity correlation function was obtained experimentally by constructing histograms of time intervals ( $\tau$ ) between successively emitted photons from a single CdSe–OPV at two different excitation wavelengths where either both the quantum dot and the OPV absorb (405 nm) or only the dot absorbs (514 nm). Since two photons are required to generate the correlation function, the risetime in  $g^{(2)}(\tau)$  provides a direct measure of the radiative decay rate (in the saturation limit). Another piece of important information contained in the correlation measurement is the number of independent emitters extracted from  $g^{(2)}(0)$ , a well-known technique used to report excitonic energy transfer within a single polymer chain to localized emissive sites.<sup>34,35,38–41</sup>

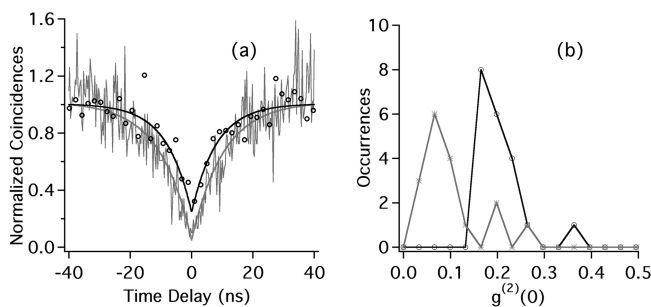
## Experiment

Single CdSe–OPV nanostructures, synthesized in the Emrick group according to previously reported procedures,<sup>11,12</sup> were obtained by drop casting from an ultra dilute ( $\approx 10^{-11}$  M) sample of CdSe–OPV in THF onto a plasma-cleaned coverslip and allowed to air-dry under ambient conditions. The excitation sources were a continuous wave (cw) 405 nm diode laser (Crystalaser), and the 514 nm line of an Ar<sup>+</sup> ion laser (Spectra Physics), focused through a 1.4 NA oil immersion objective in a total-internal-reflection geometry onto the sample plane on a Nikon Eclipse TE 2000-U inverted microscope. The average CdSe–OPV nanostructure size was inferred from fluorescence-correlated atomic force microscopy measurement<sup>14,15</sup> to be  $\approx 13$  nm with a CdSe quantum dot core diameter of 4.5 nm. The fluorescence from single CdSe–OPV nanostructures was collected through the same objective and sent through appropriate filters to ensure that we collect fluorescence from both the OPV and the quantum dot channels, and to remove scattered excitation light.

Time intervals for photon-pair coincidences were obtained from individual CdSe–OPV nanostructures by collimating the fluorescence through the side port of the microscope and focusing onto the photocathode of two orthogonally aligned single-photon counting avalanche photodiode (APD) detectors (Perkin-Elmer SCPM AQR-14), using a 50/50 nonpolarizing beam splitter. Both APDs were registered with a confocal image point to detect photons from only one and the same molecule at any time. Relative arrival times between consecutive photon were recorded in a start stop fashion with a PC based time-to-digital converter (TimeHarp 200, Picoquant GmbH) with a timing resolution of 34 ps. The contribution from background counts (source and dark noise) to the coincidence histogram was kept to a minimum by employing low excitation power



**Figure 1.** Intensity correlation function from a single ZnS-capped CdSe dot (black) (obtained commercially from Evident Technologies) and a single, CdSe–OPV nanostructure (gray) under 405 nm cw excitation. The total accumulation time was 20 min and binned at 340 ps. The smooth solid curves are single exponential fits from eq 1.  $g^{(2)}(0)$  for ZnS–CdSe and CdSe–OPV are 0.05 and 0.25, respectively.



**Figure 2.** (a) Coincidence histogram from single CdSe–OPV nanostructure under 405 nm (open black circles with black fit) and 514 nm (gray with a smooth gray fit) under cw excitation with  $g^{(2)}(0) = 0.3$  and 0.05, respectively. (b) Distribution of  $g^{(2)}(0)$  black (405 nm) and gray (514 nm) from individual CdSe–OPV nanostructures. The average  $g^{(2)}(0)$  values are 0.22 at 405 nm and 0.05 at 514 nm excitation.

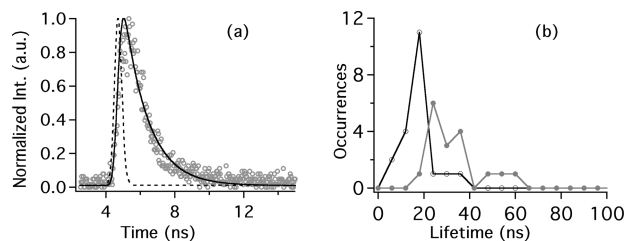
(150  $\mu$ W) to reduce source noise. We used a 50 ns time delay in the stop channel to access both positive and negative times and thus the full correlation function about zero time delay.

## Results and Discussion

Figure 1 shows a representative photon pair correlation measurement of a single CdSe–OPV (gray) and a single ZnS-capped CdSe dots (Evident Technologies) (black) under 405 nm cw excitation. The data were acquired within 20 min and binned into 340 ps time intervals. We observe significant change in modulation depth of  $\approx 95\%$  ( $g^{(2)}(0) = 0.05$ ) for ZnS-capped CdSe dots consistent with published work,<sup>29,30</sup> and  $\approx 75\%$  ( $g^{(2)}(0) = 0.25$ ) for CdSe–OPV.

Figure 1 illustrates two important features of the data: (i) though there are about 15–20 OPV ligands on the CdSe quantum dot surface, the single CdSe–OPV nanostructure acts to a very good approximation as a single quantum system. Modeling with eq 1 suggests a weak multiexcitonic character with  $\approx 1.3$  emissive sites; (ii) the risetime of 18 ns is consistent with coincidence measurement on ZnS-capped CdSe dots reported in the literature, thus inferring a similar radiative decay rate.<sup>29,30</sup> We investigated the effect of tuning the excitation wavelength from 405 to 514 nm, on the rise time and modulation depth. Parts a and b of Figure 2 show coincidence histograms and  $g^{(2)}(0)$  distribution for single CdSe–OPV under 405 nm (black curves) and 514 nm (gray curves).

The  $g^{(2)}(0)$  obtained with 405 nm excitation (open black circles with a solid black fit) in Figure 2a shows a modulation



**Figure 3.** (a) Representative decay curve (gray open circles) of a single CdSe–OPV with a lifetime of 1.5 ns. The solid black curve is a single exponential fit to the data with the dashed black curve being the instrument response. (b) Distribution of rise times under 405 nm (black) and 514 nm (gray) excitation constructed from 20 and 17 different single CdSe–OPV nanostructures, respectively. The average rise times are 19 ns for 405 nm and 34 ns for 514 nm.

depth of about 70% ( $g^{(2)}(0) = 0.3$ ) compared to about 95% ( $g^{(2)}(0) = 0.05$ ) with 514 nm excitation (gray with a smooth gray fit). This difference in modulation depth is observed in several of the CdSe–OPV nanostructures studied in this measurement.

We extracted a higher number of independent emitters,  $1.3 \pm 0.1$  with 405 nm (black curve) compared to  $1.1 \pm 0.1$  under 514 nm (gray curve), shown in Figure 2b. This indicates a significant probability of multiexciton radiative recombination in single CdSe–OPV nanostructures. This multiexcitonic behavior (more than one emissive site or  $g^{(2)}(0) > 0.1$ ) was evident in the nanostructures studied under 405 nm excitation where the OPV ligands have a strong absorption.<sup>21</sup> We identify two possibilities that could lead to incomplete photon antibunching: (i) multiexciton formation in the quantum dot core and (ii) simultaneous emission from both the quantum dot and the ligands. We rule out the first option on the basis of our experimental conditions; the excitation flux was kept in the regime with a low probability of multiple excitation formation in the dot. The results from 405 nm excitation present compelling evidence that emission from the ligands also contributes to the coincidence histogram that leads to incomplete antibunching in the correlation function. However, the number of independent emitters estimated at  $g^{(2)}(0)$  from a fit to eq 1 showed an average of 1.3 emitters per nanostructure; it is therefore reasonable to conclude that most of the excited states generated in the ligands decay nonradiatively through charge/energy transfer to the dot with a small fraction radiatively relaxing and hence contributing to the coincidence histogram.

Time-correlated single-photon counting measurement on a single CdSe–OPV shows a relatively short fluorescence lifetime of about 1.5 ns shown in Figure 3a, an order of magnitude shorter than ZnS-capped CdSe dots (25 ns). Figure 3b compares the distribution of the radiative lifetimes of single CdSe–OPV under the two excitation wavelengths. These histograms were constructed from 20 and 17 different individual CdSe–OPV nanostructures under 405 and 514 nm excitation, respectively.

The risetime distributions obtained from 514 nm ( $34 \pm 12$  ns) and 405 nm excitation ( $19 \pm 6$  ns) are consistent with other published work on ZnS-capped CdSe dots.<sup>30,31,45,46</sup> We find strong evidence in the data from Figure 3b that the radiative decay rate in CdSe–OPV is not affected by the presence of the ligands and supports the explanation that the observed changes in the photophysics (blinking suppression and reduced lifetime) of CdSe–OPV is a result of changes in the nonradiative decay rates in the quantum dot component of the nanostructure. This is consistent with our explanation based on the diffusive coordinate model<sup>17</sup> that exciton dissociation in the ligands followed by charge transport to the quantum dot surface induces

low amplitude fluctuations in the electron  $1S_e$ – $1P_e$  energy separation and hence Auger-assisted hole trapping rates, giving rise to a competition between radiative and nonradiative decay rates in the dot. This competition ensures that neither dark nor bright periods dominate and result in “gray level” intensity fluctuations and a drastic reduction in excited state lifetime in CdSe–OPV nanostructures.

In summary, we have used photon-pair correlation measurement to show that single CdSe–OPV nanostructures exhibit nonclassical photon emission, with wavelength dependent modulation depth as evidence that fluorescence from photoexcited ligands also contributes to the coincidence histogram. We find that the average radiative lifetime of  $\approx 19$  ns is consistent with ZnS-capped CdSe quantum dots and shows that the radiative decay rate of the dot in CdSe–OPV remains unchanged. We deduce that the previously observed fluorescence lifetime (1.5 ns) in CdSe–OPV is attributed to nonradiative decay rates influenced by surface charges provided by exciton dissociation in photoexcited OPV ligands. These results provide additional support to the mechanistic picture of electron donating species near the dot surface inducing fluctuations in nonradiative decay rates that underline the “gray level” intensity flickering,<sup>13,20</sup> spectral stability,<sup>16</sup> reduced lifetime,<sup>15</sup> and polarized emission<sup>21</sup> in the fluorescence intensity trajectories of CdSe–OPV nanostructures.

**Acknowledgment.** We acknowledge funding support for this work from the NSF-Sponsored Center for Hierarchical Manufacturing at UMass–Amherst (DMI-0531171), NSF-Sponsored MRSEC at UMass–Amherst, US-DOE Basic Energy Science (05ER15695), and NSF IGERT Program at UMass–Amherst (DGE-0504485).

## References and Notes

- Alivisatos, P. *Abstr. Pap. Am. Chem. Soc.* **2002**, 224, U56–U56.
- Anni, M.; Manna, L.; Cingolani, R.; Valerini, D.; Creti, A.; Lomascolo, M. *Appl. Phys. Lett.* **2004**, 85, 4169–4171.
- Clapp, A. R.; Medintz, I. L.; Fisher, B. R.; Anderson, G. P.; Mattoussi, H. *J. Am. Chem. Soc.* **2005**, 127, 1242–1250.
- Ebenstein, Y.; Mokari, T.; Banin, U. *Abstr. Pap. Am. Chem. Soc.* **2004**, 227, U340–U341.
- Ginger, D. S.; Greenham, N. C. *Synth. Met.* **1999**, 101, 425–428.
- Ginger, D. S.; Greenham, N. C. *Phys. Rev. B* **1999**, 59, 10622–10629.
- Greenham, N. C.; Peng, X. G.; Alivisatos, A. P. *Phys. Rev. B* **1996**, 54, 17628–17637.
- Greenham, N. C.; Peng, X. G.; Alivisatos, A. P. *Synth. Met.* **1997**, 84, 545–546.
- Soujon, D.; Becker, K.; Rogach, A. L.; Feldmann, J.; Weller, H.; Talapin, D. V.; Lupton, J. M. *J. Phys. Chem. C* **2007**, 111, 11511–11515.
- Willard, D. M.; Carillo, L. L.; Jung, J.; Van Orden, A. *Nano Lett.* **2001**, 1, 469–474.
- Skaff, H.; Sill, K.; Emrick, T. *J. Am. Chem. Soc.* **2004**, 126, 11322–11325.
- Sudeep, P. K.; Early, K. T.; McCarthy, K. D.; Odoi, M. Y.; Barnes, M. D.; Emrick, T. *J. Am. Chem. Soc.* **2008**, 130, 2384–2385.
- Early, K. T.; McCarthy, K. D.; Hammer, N. I.; Odoi, M. Y.; Tangirala, R.; Emrick, T.; Barnes, M. D. *Nanotechnology* **2007**, 18, 7.
- Hammer, N. I.; Early, K. T.; Sill, K.; Odoi, M. Y.; Emrick, T.; Barnes, M. D. *J. Phys. Chem. B* **2006**, 110, 14167–14171.
- Odoi, M. Y.; Hammer, N. I.; Early, K. T.; McCarthy, K. D.; Tangirala, R.; Emrick, T.; Barnes, M. D. *Nano Lett.* **2007**, 7, 2769–2773.
- Odoi, M. Y.; Hammer, N. I.; Sill, K.; Emrick, T.; Barnes, M. D. *J. Am. Chem. Soc.* **2006**, 128, 3506–3507.
- Frantsuzov, P. A.; Marcus, R. A. *Phys. Rev. B* **2005**, 72, 155321–1155321–10.



- (18) Hohng, S.; Ha, T. *J. Am. Chem. Soc.* **2004**, *126*, 1324–1325.
- (19) Ray, K.; Badugu, R.; Lakowicz, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 8998–8999.
- (20) Hammer, N. I.; Early, K. T.; Sill, K.; Odoi, M. Y.; Emrick, T.; Barnes, M. D. *J. Phys. Chem. B* **2006**, *110*, 14167–14171.
- (21) Early, K. T.; McCarthy, K. D.; Odoi, M. Y.; Sudeep, P. K.; Emrick, T.; Barnes, M. D. *ACS Nano* **2009**, *3*, 453–461.
- (22) Brannen, E.; Ferguson, H. I. S. *Nature* **1956**, *178*, 481–482.
- (23) Brown, R. H.; Twiss, R. Q. *Nature* **1956**, *177*, 27–29.
- (24) Brown, R. H.; Twiss, R. Q. *Nature* **1956**, *178*, 1447–1448.
- (25) Purcell, E. M. *Nature* **1956**, *178*, 1448–1450.
- (26) Michler, P.; Imamoglu, A.; Kiraz, A.; Becher, C.; Mason, M. D.; Carson, P. J.; Strouse, G. F.; Buratto, S. K.; Schoenfeld, W. V.; Petroff, P. M. *Phys. Status Solidi B-Basic Res.* **2002**, *229*, 399–405.
- (27) Michler, P.; Imamoglu, A.; Mason, M. D.; Carson, P. J.; Strouse, G. F.; Buratto, S. K. *Nature* **2000**, *406*, 968–970.
- (28) Michler, P.; Imamoglu, A.; Mason, M. D.; Carson, P. J.; Strouse, G. F.; Buratto, S. K. *Proc. Int. Conf. Phys. Semiconductors, Pts I and II, 25th* **2001**, *87*, 1173–1174/1846.
- (29) Brokmann, X.; Coolen, L.; Dahan, M.; Hermier, J. P. *Phys. Rev. Lett.* **2004**, *93*, 107403–1107403–4.
- (30) Lounis, B.; Bechtel, H. A.; Gerion, D.; Alivisatos, P.; Moerner, W. E. *Chem. Phys. Lett.* **2000**, *329*, 399–404.
- (31) Messin, G.; Hermier, J. P.; Giacobino, E.; Desbiolles, P.; Dahan, M. *Opt. Lett.* **2001**, *26*, 1891–1893.
- (32) Mirin, R. P. *Appl. Phys. Lett.* **2004**, *84*, 1260–1262.
- (33) Zwiller, V.; Aichele, T.; Seifert, W.; Persson, J.; Benson, O. *Appl. Phys. Lett.* **2003**, *82*, 1509–1511.
- (34) Barbara, P. F.; Gesquiere, A. J.; Park, S. J.; Lee, Y. J. *Acc. Chem. Res.* **2005**, *38*, 602–610.
- (35) Barbara, P. F.; Hu, D. H.; Yu, J.; Song, N. W. *Abstr. Pap. Am. Chem. Soc.* **2001**, *221*, U261–U261.
- (36) Buratto, S. K.; Summers, M. A.; Robinson, M. R.; Kemper, P. R.; Bushnell, J.; Bazan, G. C.; Bowers, M. T. *Abstr. Pap. Am. Chem. Soc.* **2002**, *223*, C36–C36.
- (37) VandenBout, D. A.; Yip, W. T.; Hu, D. H.; Fu, D. K.; Swager, T. M.; Barbara, P. F. *Science* **1997**, *277*, 1074–1077.
- (38) Bussian, D. A.; Summers, M. A.; Liu, B.; Bazan, G. C.; Buratto, S. K. *Chem. Phys. Lett.* **2004**, *388*, 181–185.
- (39) Hollars, C. W.; Lane, S. M.; Huser, T. *Chem. Phys. Lett.* **2003**, *370*, 393–398.
- (40) Kumar, P.; Lee, T. H.; Mehta, A.; Sumpter, B. G.; Dickson, R. M.; Barnes, M. D. *J. Am. Chem. Soc.* **2004**, *126*, 3376–3377.
- (41) Lee, T. H.; Kumar, P.; Mehta, A.; Xu, K. W.; Dickson, R. M.; Barnes, M. D. *Appl. Phys. Lett.* **2004**, *85*, 100–102.
- (42) Zwiller, V.; Blom, H.; Jonsson, P.; Panev, N.; Jeppesen, S.; Tsegaye, T.; Goobar, E.; Pistol, M. E.; Samuelson, L.; Bjork, G. *Appl. Phys. Lett.* **2001**, *78*, 2476–2478.
- (43) Mandel, H. J. K. M. D. L. *Phys. Rev. Lett.* **1977**, *39*, 4.
- (44) Brouri, R.; Beveratos, A.; Poizat, J. P.; Grangier, P. *Opt. Lett.* **2000**, *25*, 1294–1296.
- (45) Brokmann, X.; Giacobino, E.; Dahan, M.; Hermier, J. P. *Appl. Phys. Lett.* **2004**, *85*, 712–714.
- (46) Zhang, K.; Chang, H.; Fu, A.; Alivisatos, A. P.; Yang, H. *Nano Lett.* **2006**, *6*, 843–847.

JP9051787