

Optical Limiting in Organic Molecular Nano/Microcrystals: Nonlinear Optical Effects Dependent on Size Distribution

A. Patra,[†] N. Venkatram,[‡] D. Narayana Rao,[‡] and T. P. Radhakrishnan^{*,†}

School of Chemistry and School of Physics, University of Hyderabad, Hyderabad 500 046, India

Received: April 29, 2008; Revised Manuscript Received: August 13, 2008

Several recent investigations have revealed interesting size-dependent linear optical responses in molecular nanocrystals. However, little is known about similar effects in the nonlinear optical behavior of such nanomaterials. The current study addresses optical limiting characteristics and nonlinear absorption/scattering effects in nano/microcrystals of a strongly zwitterionic diaminodicyanoquinodimethane molecule fabricated in the colloidal state through a reprecipitation–digestion protocol. Optical limiting response observed for 800 nm femtosecond laser pulses is found to be appreciable and dependent on the size distribution of the molecular crystals in the colloid. Z-scan studies reveal that the ultrashort pulses lead to multiphoton absorption with saturation effects, both becoming more pronounced with smaller particle sizes. The nano/microcrystals in the colloidal state exhibit strong nonlinear scattering; when thermal effects are excluded, these responses are found to be largely independent of the distribution of particle sizes.

Introduction

The unique optical and nonlinear optical properties of nanocrystals arise due to the characteristic dependence of electronic structure and dynamics on the size, shape, and organization of the nanocrystals. Nonlinear optical effects such as optical limiting have been extensively investigated in metal and semiconductor nanoparticles.¹ Strongly size-dependent responses have been demonstrated in nanoparticles of metals such as gold, silver, and copper² as well as semiconductors like cadmium sulfide, cadmium selenide, and lead sulfide.³ Another important class of efficient optical limiters is that based on carbon black and carbon nanomaterials such as fullerenes and nanotubes;⁴ size-dependent effects have been observed with multiwalled carbon nanotubes.⁵ Even though a large number of organic molecules including phthalocyanines, porphyrins, stilbenes, and perylenes have been shown to exhibit efficient optical limiting in the form of solutions and thin films,⁶ there is little known about optical limiting in colloids based on organic molecular nano/microcrystals and potential size-dependent responses in such systems. In view of the flexibility and tailorability of organic molecular structures and the feasibility of preparing their nano/microcrystals through facile reprecipitation protocols, demonstration of potential size-dependent optical limiting effects in these systems would be interesting from both fundamental and application perspectives. If strong multiphoton absorption⁷ can be realized in these systems, they would be interesting candidates for applications such as non-invasive, high-resolution bioimaging.⁸

Size-dependent optical absorption and emission in molecular nanocrystals has been investigated extensively in recent years.^{9–12} The observed effects have generally been attributed to the increase of average cohesive strength with size of the crystals.¹⁰ We demonstrated the evolution of optical properties of molecular crystals of a family of strongly zwitterionic diaminodicyano-

quinodimethane molecules over a wide range of crystal sizes spanning the nano- to the microregime.^{11,12} The spectroscopic observations were interpreted using a model of hierarchical emergence of intermolecular interactions with increasing crystal size. In view of the large hyperpolarizabilities that they possess, the present investigations have focused on the nonlinear optical responses of nano/microcrystals of one of these molecules, 7,7-bis(4-chloroanilino)-8,8-dicyanoquinodimethane (BCADQ, Figure 1a); semiempirical quantum chemical calculations indicate second hyperpolarizabilities, $\gamma \approx 100 \times 10^{-36}$ (static) and 500×10^{-36} esu (at 800 nm excitation) for this molecule.^{13,14} Investigation of the optical limiting capability revealed appreciable and size-dependent responses. Open aperture Z-scan measurements indicated nonlinear absorption dependent on the size distribution in the samples, and closed aperture measurements demonstrated nonlinear scattering which is nearly independent of particle size when thermal effects are excluded. These studies provide insight into the origin of the optical limiting responses of these molecular nanomaterials.

Experimental Section

BCADQ was synthesized following the procedure we described earlier.¹¹ Crystals with sizes varying from about 50 nm to 1 μm could be fabricated by the reprecipitation procedure involving rapid addition of solutions in DMSO (100 μL) into 20 mL of ultrapure water (Millipore MilliQ, resistivity = 18 M Ω cm) followed by digestion for 1 h at different temperatures. BCADQ colloids are very stable over extended periods of time, showing no signs of precipitation. In the present study, we used colloids digested at three different temperatures: 30, 60, and 90 °C; they are designated, respectively, as BCADQ30, BCADQ60, and BCADQ90. The size and morphology of the colloidal crystals were examined using HITACHI S-4300SE/N FESEM using a beam voltage of 20 kV. Microcrystals collected on a 100 nm pore polycarbonate membrane (Millipore, VCTP) by filtration of the colloidal solution and coated with a thin layer of sputtered gold were used for the FESEM studies. Extinction spectra of these colloids were recorded on a Cary 100 Bio UV–visible spectrophotometer; samples with an identical molar

* To whom correspondence should be addressed. Phone: 91-40-2313-4827. Fax: 91-40-2004-5893. E-mail: tpssc@uohyd.ernet.in.

[†] School of Chemistry.

[‡] School of Physics.

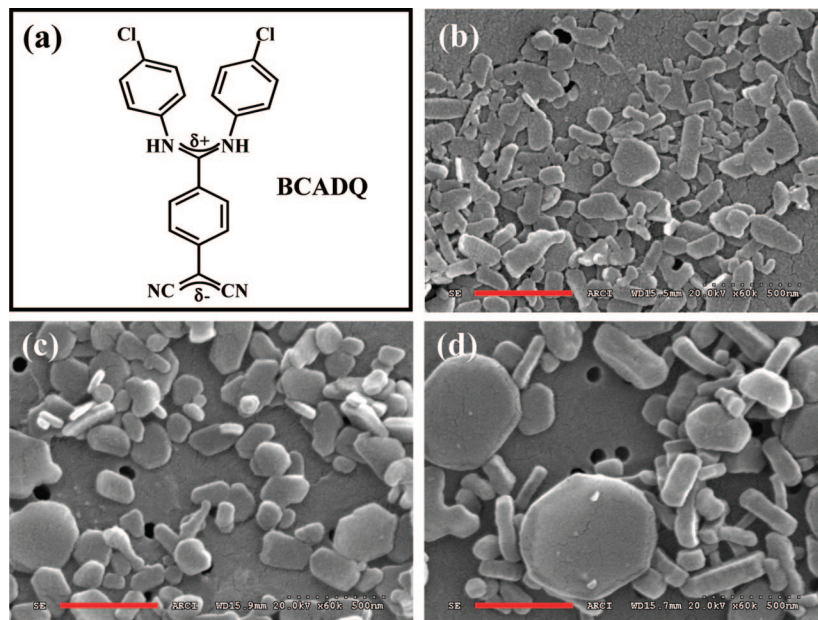


Figure 1. (a) Molecular structure of BCADQ and FESEM images of BCADQ crystals fabricated by digestion at different temperatures: (b) BCADQ30, (c) BCADQ60, and (d) BCADQ90 (scale bar = 500 nm).

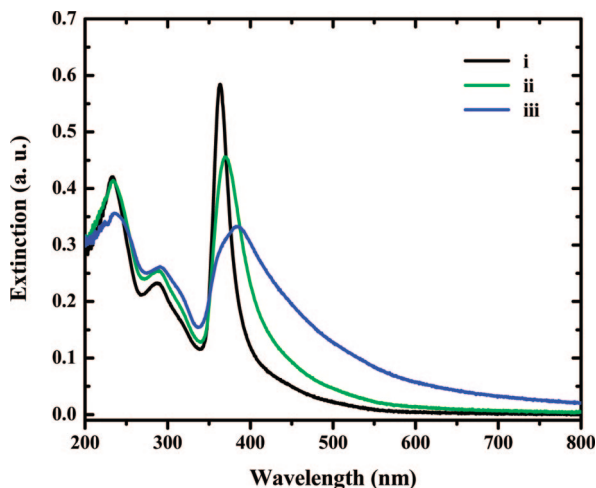


Figure 2. Extinction spectra (see text for details) of the colloids: (i) BCADQ30, (ii) BCADQ60, and (iii) BCADQ90.

content of BCADQ (1.67×10^{-5} M) were used in all experiments.

Nonlinear optical studies were carried out using a Ti:Sapphire laser (800 nm, ~ 110 fs, 1 kHz) as the excitation source; lower pulse frequencies were generated using a mechanical chopper. Optical limiting studies were carried out with $f/30$ geometry using a 12 cm focal length lens and a beam diameter of ~ 0.4 cm. Open and closed aperture Z-scan measurements were carried out by moving the sample across the focus of the laser beam using a computer-controlled translation stage;¹⁴ the scans were repeated several times to ensure reproducibility of the data. The laser beam was focused using a 12 cm focal length lens; the beam waist was $\sim 27.6 \mu\text{m}$ at focus, leading to a peak intensity in the range $0.38\text{--}1.55 \text{ TW/cm}^2$, i.e., fluences in the range $0.04\text{--}0.17 \text{ J/cm}^2$. The input intensity could be varied using calibrated neutral density filters. Closed aperture experiments used an aperture of diameter 0.1 cm after the sample and were carried out at lower intensities where colloids do not show any appreciable nonlinear absorption. The transmitted output was collected using a calibrated fast photodiode (FND 100) and processed using a data acquisition system consisting of a lock-

in amplifier, ADC, and computer. All experiments were carried out using samples with an identical molar content of BCADQ (5.0×10^{-5} M).

Stability of the samples through the experiments was ascertained by recording the extinction spectra before and after the experiments;¹⁴ the intensities above which the samples show signs of degradation, the damage thresholds, are noted at the relevant points below. Since we observed that the DMSO–water system is capable of showing its own nonlinear optical response with the high intensity femtosecond pulses, control experiments were carried out on the solvent medium obtained by filtration of the colloids through nanoporous membranes (Millipore, mixed cellulose esters, average pore size = 50 nm). This filtration was found to effectively eliminate the BCADQ nano/microcrystals (irrespective of the digestion temperature) as demonstrated by complete disappearance of the optical absorption. It may be noted that rather than a DMSO–water mixture with the same composition as that used in the preparation of the colloids, the filtrate obtained as described is the right reference medium as some of the DMSO is likely to be incorporated with the BCADQ crystals during colloid fabrication. Identical nonlinear optical responses were observed independent of which of the colloids digested at different temperatures was filtered. It is significant to note further that experiments carried out using a frequency-doubled Nd:YAG laser (532 nm, 6 ns, 10 Hz) showed no nonlinear response from the solvent medium but appreciable responses from the BCADQ colloids.¹⁴

Results and Discussion

FESEM images of BCADQ crystals in the different colloids are shown in Figure 1b–d; the larger crystals in BCADQ60 and BCADQ90 possess well-defined rectangular/hexagonal morphology, whereas BCADQ30 crystals are comprised of relatively smaller ones as well as a few exhibiting a fused appearance, perhaps owing to their softer nature and effective compression during the filtration process. The different microscopy investigations^{11,14} show that the BCADQ crystals are in the form of plates typically 30–100 nm thick; the diagonals of

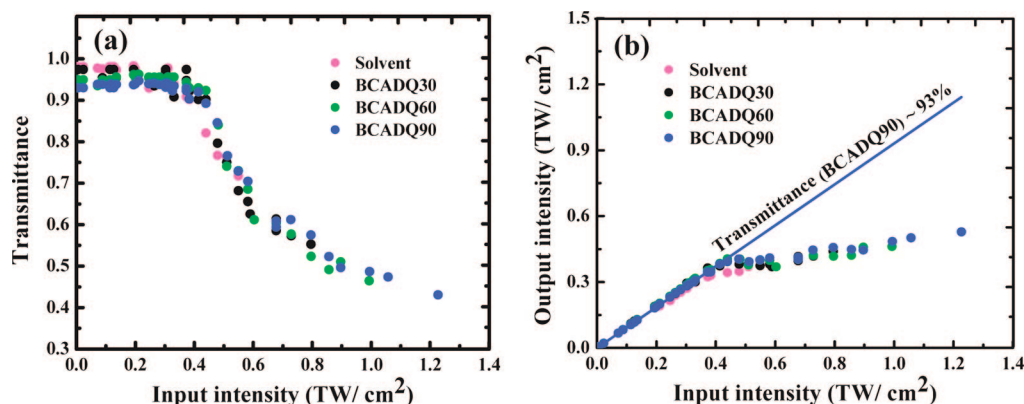


Figure 3. Plots of (a) transmittance versus input intensity and (b) output versus input intensity of BCADQ colloids digested at different temperatures and the reference solvent for femtosecond laser pulses.

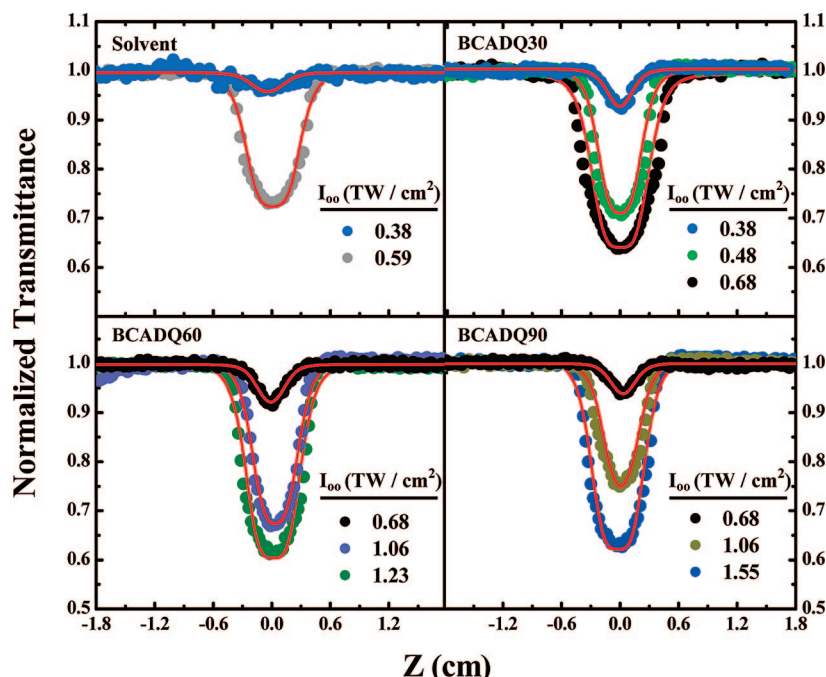


Figure 4. Open aperture Z-scan traces for the reference solvent and BCADQ colloids at different input intensities. Red solid lines indicate the fitting of the data to eq 1 taking into account 4-photon absorption and saturation effects (see text for details).

TABLE 1: Nonlinear Optical Characteristics of the BCADQ Nano/Microcrystals Obtained by Analysis of the Open Aperture^a and Closed Aperture^b Z-Scan Using Femtosecond Laser Pulses

colloid	open aperture Z-scan ^c		n_2^{eff} (from closed aperture Z-scan) (cm²/W)	
	I_{sat} (TW/cm²)	δ (cm⁵/TW³)	$\nu = 1$ kHz	$\nu = 10$ Hz
BCADQ30	0.55	5.800	8.263×10^{-16}	1.957×10^{-16}
BCADQ60	0.78	0.529	6.121×10^{-16}	1.930×10^{-16}
BCADQ90	1.01	0.343	4.288×10^{-16}	1.954×10^{-16}

^a I_{sat} = saturation intensity; δ = effective 4-photon absorption coefficient. ^b n_2^{eff} = effective nonlinear refractive index; ν = laser pulse frequency. ^c $I_{00} = 0.68$ TW/cm².

the flat faces are in the range 0.05–0.25, 0.15–0.60, and 0.20–1.00 μm in BCADQ30, BCADQ60, and BCADQ90, respectively. With increasing digestion temperature, larger crystals are formed and hence the size distribution becomes broader; we will refer to this combined effect as size/distribution enhancement.

Extinction spectra of BCADQ colloids (Figure 2) reveal strong size dependence as reported in our earlier study;¹¹ the

term extinction signifies that absorption as well as scattering effects are contained in the spectra.¹⁵ The spectra become broader from BCADQ30 to BCADQ90. Fluorescence excitation spectra which have close correspondence to these extinction spectra¹⁴ prove that the broadening is not simply an effect of increased scattering due to larger crystals formed in the colloid but a consequence of the emergence of new electronic states at lower energies. The possibility of the spectra broadening due to the wider size distribution in the colloids digested at higher temperatures can be ruled out on the basis of our observation that microcrystalline samples containing only large crystals with sizes in the range 40–70 μm selected through sieving show spectra nearly identical to that of BCADQ90.¹⁴ Our earlier spectroscopic studies, crystallographic examination of supramolecular interactions, and computational investigations led to a model for the hierarchical emergence of new electronic states with increasing crystal size.¹¹ As the size increases, the ratio of surface to bulk molecules decreases, resulting in an increase in the average crystal cohesive energy.¹⁰ In crystals such as BCADQ where intermolecular interactions with varying strengths are

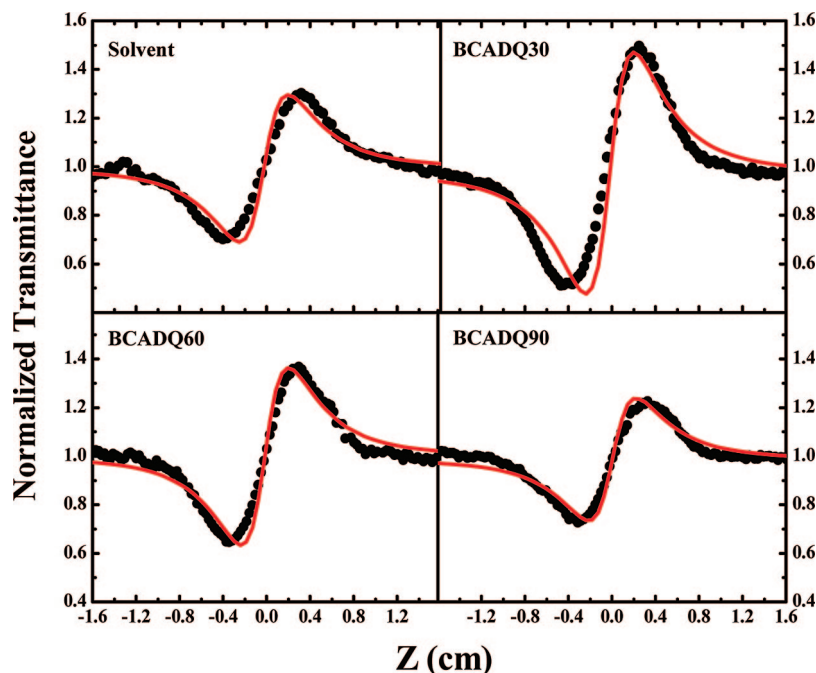


Figure 5. Closed aperture Z-scan traces of reference solvent and BCADQ colloids recorded at an input intensity of 0.38 TW/cm^2 with a pulse frequency of 1 kHz. Red solid lines indicate fitting of the data to eq. 3.

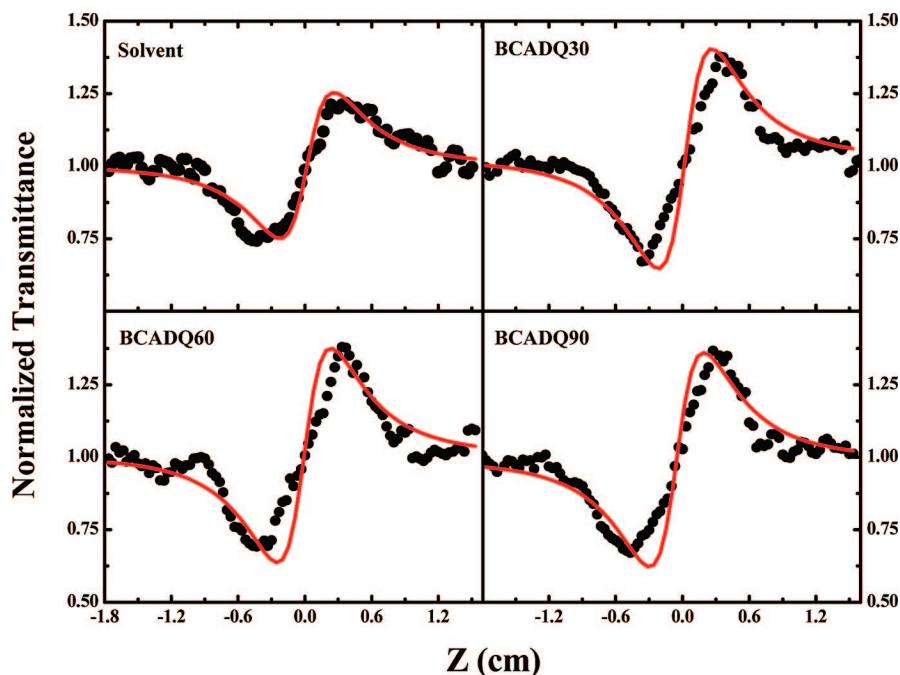


Figure 6. Closed aperture Z-scan traces of reference solvent and BCADQ colloids recorded at an input intensity of 1.23 TW/cm^2 with a pulse frequency of 10 Hz. Red solid lines indicate fitting of the data to eq. 3.

possible due to a range of interactions such as H bonds and dipole–dipole, smaller and hence softer crystals exhibit signatures of only the stronger interactions, whereas with increasing size the crystal manifests additionally the presence of weaker interactions and hence additional accessible electronic states. Thus, the larger crystals present in the colloids digested at higher temperatures give rise to the broadened spectra with additional low-energy peaks. We show below that the electronic spectra of BCADQ colloids and the model developed earlier and described above provide useful insight into some of the nonlinear optical characteristics investigated now.

Data obtained from the optical limiting experiments on the reference solvent as well as the three colloids are provided in Figure 3. It is observed that the transmission in the linear regime is quite high for all systems but shows a minor but steady decrease with particle size/distribution enhancement, clearly suggesting increasing extinction at 800 nm. The linear transmission for BCADQ90 is $\sim 93\%$. The reference solvent shows a mild tendency toward optical limiting; however, it suffers damage at a relatively low input laser intensity of $0.55\text{--}0.60 \text{ TW/cm}^2$, as revealed by noisy and irreproducible response beyond this point; therefore, no significant optical limiting can be elicited. We believe that the nonlinear response of the

reference solvent is likely to be due to some form of network structure established in the DMSO–water system and that the damage may be related to the breakdown of such a network. In the case of the colloids, the optical limiting sets in at slightly higher input intensities and there is a clear trend observed in terms of the damage thresholds. The colloids with larger crystals are able to sustain higher laser intensities than those with smaller crystals. This aspect of practical significance possibly arises due to the enhancement of the average cohesive energy and hence robustness with particle size.¹⁰ The output clamp threshold, limiting threshold, $I_{1/2}$ (the input intensity at which the transmittance reduces to one-half of the linear transmittance), and dynamic range (the ratio of the damage and limiting thresholds)¹⁶ for BCADQ90 are, respectively, 0.48 TW/cm², 1.06 TW/cm², and ~ 1.3 , indicating appreciable optical limiting capability of these colloids. In order to obtain some insight into the origin of the optical limiting effects observed in these colloids, we carried out detailed open and closed aperture Z-scan measurements described below.

Open aperture Z-scan experiments can provide information on nonlinear responses arising at high laser intensities due to a variety of effects including multiphoton, saturable, and reverse saturable absorptions. The data recorded for the reference solvent and colloids at different input laser intensities are provided in Figure 4. The reference solvent shows nonlinear absorption at relatively lower intensities but as seen earlier manifests signs of damage at intensities higher than ~ 0.6 TW/cm². The lowest input intensities where appreciable nonlinear absorption sets in increase progressively in the colloids from BCADQ30 to BCADQ90. It is also seen that the highest intensities that can be sustained before damage is observed also increase in parallel. The enhancement of damage thresholds is consistent with those observed in the optical limiting experiments. The decreasing efficiency of nonlinear absorption with increasing size/distribution of the BCADQ crystals can be quantified through an analysis of the Z-scan data. We explored the possibility of fitting the data to different models; simple 2-photon and 3-photon absorption models provide very poor fitting. Further, the relatively low curvature near focus, especially at high input laser intensities, suggests the presence of saturation effects. It is interesting to note that this is consistent with the trends in the optical limiting curves (Figure 3), which indicate slight enhancements in the output intensities over the limiting value at high input intensities close to the damage threshold. The open aperture curves for the BCADQ colloids as well as the reference solvent can be satisfactorily fitted by a model involving a combination of 4-photon absorption and saturation effects. An effective 4-photon absorption can occur in several ways, for example, as (a) direct 4-photon absorption or (b) cascade effects through 2-photon absorption followed by vibrational relaxation and further 2-photon absorption or (c) 3-photon process followed by excited-state absorption.¹⁷ The theoretical expression for 4-photon absorption with saturation effects, that can be adapted from related equations developed in ref 18 shows that transmission, $T(z)$ at sample position z is given by eq 1

$$T(z) = \left(1 + \frac{3\delta L_{\text{eff}} I(z)^3}{1 + (I(z)/I_{\text{sat}})^3} \right)^{-1/3} \quad (1)$$

where δ is the effective 4-photon absorption coefficient, L_{eff} is the interaction length (estimated using the transmittance in the linear regime and path length of the sample cell), I_{sat} is the

saturation intensity, and $I(z)$ is the input laser intensity at position z

$$I(z) = I_0 \left(\frac{z_0^2}{z_0^2 + z^2} \right) \quad (2)$$

where z_0 is the Rayleigh range and I_0 is the intensity at focus. Theoretical fitting of the data are also shown in Figure 4; in all cases, the correlation coefficient for the fitting is better than 0.9. The slight deviation of the theoretical fit from the experimental data in terms of the sides being slightly steeper indicates that it is not a pure 4-photon absorption. The effective 4-photon absorption possibly includes contributions from direct 4-photon absorption, multiple 2-photon absorption, and 3-photon absorption followed by excited-state absorption as noted above. The Rayleigh range required to fit the data was found to be 0.25–0.30 cm in all cases, conforming well to the value expected from the experimental set up. Even though minor variation is possible due to beam broadening resulting from scattering, the current observations suggest that such effects are not noticeably large as the beam diameter is of the order of several tens of micrometers and the crystal sizes are ~ 1 μm even in BCADQ90. The parameters, saturation intensity (I_{sat}), and effective 4-photon absorption coefficient (δ) of the different colloids, extracted through the fitting of the data at a common input intensity, are collected in Table 1; the reference solvent gets damaged at this intensity. It is seen that the 4-photon absorption decreases with increasing size/distribution of the BCADQ crystals, indicating clearly the significance of the smaller crystals. The increasing I_{sat} is consistent with the model noted earlier¹¹ of increasing number of excited states arising as the particle size increases that tends to reduce the saturation effects.

Closed aperture Z-scan measurements provide information on nonlinear scattering from the colloids; variation of the laser pulse frequency can be used to unravel the role of thermal effects in the responses. Data recorded for the reference solvent and colloids, using 1 kHz laser pulses, are collected in Figure 5; the transmittance divided by the corresponding values in the open aperture experiment are plotted in order to display the effects of nonlinear refraction alone. The curves indicate positive nonlinearity in all cases. BCADQ30 shows enhanced peak-to-peak intensity with respect to the reference solvent; however, the intensity decreases with increasing particle size/distribution, suggesting the impact of increasing thermal contribution possibly arising due to the high laser pulse frequency. We therefore carried out the closed aperture Z-scan experiment with 10 Hz pulses; the data are collected in Figure 6. In the absence of potential thermal effects, the responses from the different colloids are found to be very similar. These observations can be quantified by fitting the Z-scan traces to eq 3¹⁹

$$T(z) = 1 - \frac{4\Delta\phi_0(z/z_0)}{[1 + (z/z_0)^2][9 + (z/z_0)^2]} \quad (3)$$

where $\Delta\phi_0$ is the phase change. $\Delta\phi_0$ provides the effective nonlinear refractive index, n_2^{eff} , due to the molecular nanocrystals and the solvent medium. The values obtained at the two different pulse frequencies are provided in Table 1. The decreasing values of n_2^{eff} for BCADQ30 to BCADQ90 at 1 kHz arise due to the increasing thermal contributions (negative nonlinear refractive index) which can be explained by the small but definite decrease in the transmittance at 800 nm. The latter is clearly seen in the optical limiting curves in Figure 3. The n_2^{eff} of the colloids obtained at the lower laser pulse frequency are independent of

the crystal size/distribution; this is supported by independent measurements from degenerate four-wave mixing experiments.¹⁴

Conclusions

Colloids of a strongly zwitterionic molecule, fabricated by reprecipitation from DMSO solutions injected in water and digested at different temperatures to provide crystals with size distribution ranging from the nano- to the microregime, are investigated for their nonlinear optical responses in the femto-second time scale. Appreciable optical limiting responses are observed with colloids possessing larger particle sizes showing improved damage thresholds. Open aperture Z-scan studies reveal appreciable 4-photon absorption in the colloidal materials, the effect being enhanced in those containing primarily smaller particles; saturation effects are also observed, the saturation intensities increasing when larger particles are present. Positive nonlinear refraction in these colloids is largely insensitive to the particle size distribution. The current study demonstrates appreciable nonlinear optical responses in molecular nano/microcrystals with significant dependence on particle size and size distribution. It would be interesting to probe in detail the electronic structure basis for the observed nonlinear optical phenomena and develop new materials with improved and tunable attributes.

Acknowledgment. Financial support from the DST, New Delhi, is acknowledged. We thank Dr. G. Ravi Chandra and Mr. L. Venkatesh (International Advanced Research Centre for Powder Metallurgy and New Materials) for help with the FESEM studies. A.P. thanks the UGC, New Delhi, for a Senior Research Fellowship.

Supporting Information Available: Details of microscopy, spectroscopy, and nonlinear optical studies and computations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) (a) Joudrier, V.; Bourdon, P.; Hache, F.; Flytzanis, C. *Appl. Phys. B: Laser Opt.* **1998**, *67*, 627. (b) Sun, Y.; Riggs, J. E. *Int. Rev. Phys. Chem.* **1999**, *18*, 43. (c) Sun, Y.; Riggs, J. E.; Henbest, K. B.; Martin, R. B. *J. Nonlinear Opt. Phys. Mater.* **2000**, *9*, 481. (d) Zhang, H.; Zelmon, D. E.; Deng, L.; Liu, H.; Teo, B. K. *J. Am. Chem. Soc.* **2001**, *123*, 11300. (e) Sun, W.; Dai, Q.; Worden, J. G.; Huo, Q. *J. Phys. Chem. B* **2005**, *109*, 20854. (f) Venkatram, N.; Kumar, R. S. S.; Rao, D. N. *J. Appl. Phys.* **2006**, *100*, 074309. (g) Porel, S.; Venkatram, N.; Rao, D. N.; Radhakrishnan, T. P. *J. Appl. Phys.* **2007**, *102*, 033107. (h) Irimpan, L.; Nampoore, V. P. N.; Radhakrishnan, P.; Krishnan, B.; Deepthy, A. *J. Appl. Phys.* **2008**, *103*, 033105.
- (2) (a) François, L.; Mostafavi, M.; Belloni, J.; Delouis, J.; Delaire, J.; Fenevrou, P. *J. Phys. Chem. B* **2000**, *104*, 6133. (b) Qu, S.; Zhao, C.; Jiang, X.; Fang, G.; Gao, Y.; Zeng, H.; Song, Y.; Qiu, J.; Zhu, C.; Hirao, K. *Chem. Phys. Lett.* **2003**, *368*, 352. (c) Kiran, P. P.; Bhaktha, B. N. S.; Rao, D. N.; De, G. *J. Appl. Phys.* **2004**, *96*, 6717. (d) Gao, Y.; Chang, Q.; Ye, H.; Jiao, W.; Li, Y.; Wang, Y.; Song, Y.; Zhu, D. *Chem. Phys.* **2007**, *336*, 99.
- (3) (a) Jia, W.; Douglas, E. P.; Guo, F.; Sun, W. *Appl. Phys. Lett.* **2004**, *85*, 6326. (b) He, G. S.; Yong, K.; Zheng, Q.; Sahoo, Y.; Baev, A.;

- Ryasnyanskiy, A. I.; Prasad, P. N. *Opt. Express* **2007**, *15*, 12818. (c) Zhang, Y. D.; Cao, B.; Zhang, H. G.; Zhu, J. *J. Solid State Phenom.* **2007**, *121–123*, 1367.
- (4) (a) Tutt, L. W.; Kost, A. *Nature* **1992**, *356*, 225. (b) Venturini, J.; Koudoumas, E.; Couris, S.; Janot, J. M.; Seta, P.; Mathis, C.; Leach, S. *J. Mater. Chem.* **2002**, *12*, 2071. (c) Neto, N. M. B.; Mendonça, C. R.; Misoguti, L.; Zilio, S. C. *Appl. Phys. B: Laser Opt.* **2004**, *78*, 1. (d) Wang, J.; Blau, W. J. *J. Phys. Chem. C* **2008**, *112*, 2298.
- (5) Jin, Z.; Huang, L.; Goh, S. H.; Xu, G.; Ji, W. *Chem. Phys. Lett.* **2002**, *352*, 328.
- (6) (a) Perry, J. W.; Mansour, K.; Lee, I.-Y. S.; Wu, X.-L.; Bedworth, P. V.; Chen, C.-T.; Ng, D.; Marder, S. R.; Miles, P.; Wada, T.; Tian, M.; Sasabe, H. *Science* **1996**, *273*, 1533. (b) Sanz, N.; Ibanez, A.; Morel, Y.; Baldeck, P. L. *Appl. Phys. Lett.* **2001**, *78*, 2569. (c) de la Torre, G.; Vázquez, P.; Agulló-López, F.; Torres, T. *Chem. Rev.* **2004**, *104*, 3723. (d) Collini, E.; Ferrante, C.; Bozio, R. *J. Phys. Chem. B* **2005**, *109*, 2. (e) Oliveira, S. L.; Corrêa, D. S.; Misoguti, L.; Constantino, C. J. L.; Aroca, R. F.; Zilio, S. C.; Mendonça, C. R. *Adv. Mater.* **2005**, *17*, 1890. (f) Belfield, K. D.; Bondar, M. V.; Hernandez, F. E.; Przhonska, O. V. *J. Phys. Chem. C* **2008**, *112*, 5618.
- (7) (a) Venkatram, N.; Sathyavathi, R.; Rao, D. N. *Opt. Express* **2007**, *15*, 12258. (b) Lin, T.; Zheng, Q.; Chen, C.; He, G. S.; Huang, W.; Ryasnyanskiy, A. I.; Prasad, P. N. *Chem. Commun.* **2008**, 389. (c) He, G. S.; Tan, L.; Zheng, Q.; Prasad, P. N. *Chem. Rev.* **2008**, *108*, 1245.
- (8) (a) Gura, T. *Science* **1997**, *276*, 1988. (b) Kim, S.; Pudavar, H. E.; Bono, A.; Prasad, P. N. *Adv. Mater.* **2007**, *19*, 3791.
- (9) (a) Kasai, H.; Oikawa, H.; Nakanishi, H. In *Organic Mesoscopic Chemistry*; Masuhara, H., de Schryver, F. C., Eds.; Blackwell Science: Oxford, 1999; p 145. (b) Fu, H.; Loo, B. H.; Xiao, D.; Xie, R.; Ji, X.; Yao, J.; Zhang, B.; Zhang, L. *Angew. Chem., Int. Ed.* **2002**, *41*, 962. (c) Wang, F.; Han, M.; Mya, K. Y.; Wang, Y.; Lai, Y. *J. Am. Chem. Soc.* **2005**, *127*, 10350. (d) Zhao, Y. S.; Xiao, D.; Yang, W.; Peng, A.; Yao, J. *Chem. Mater.* **2006**, *18*, 2302. (e) Grey, J. K.; Kim, D. Y.; Norris, B. C.; Miller, W. L.; Barbara, P. F. *J. Phys. Chem. B* **2006**, *110*, 25568. (f) Kang, L.; Wang, Z.; Cao, Z.; Ma, Y.; Fu, H.; Yao, J. *J. Am. Chem. Soc.* **2007**, *129*, 7305. (g) Heng, L.; Zhai, J.; Qin, A.; Zhang, Y.; Dong, Y.; Tang, B. Z.; Jiang, L. *ChemPhysChem* **2007**, *8*, 1513. (h) Wang, X.; Sandman, D. J.; Chen, S.; Gido, S. P. *Macromolecules* **2008**, *41*, 773.
- (10) (a) Kasai, H.; Kamatani, H.; Okada, S.; Oikawa, H.; Matsuda, H.; Nakanishi, H. *Jpn. J. Appl. Phys.* **1996**, *35*, L221. (b) Onodera, T.; Kasai, H.; Okada, S.; Oikawa, H.; Mizuno, K.; Fujitsuka, M.; Ito, O.; Nakanishi, H. *Opt. Mater.* **2002**, *21*, 595. (c) Xiao, D.; Xi, L.; Yang, W.; Fu, H.; Shuai, Z.; Fang, Y.; Yao, J. *J. Am. Chem. Soc.* **2003**, *125*, 6740. (d) Xiao, D.; Yang, W.; Yao, J.; Xi, L.; Yang, X.; Shuai, Z. *J. Am. Chem. Soc.* **2004**, *126*, 15439. (e) Asahi, T.; Matsune, H.; Yamashita, K.; Masuhara, H.; Kasai, H.; Nakanishi, H. *Pol. J. Chem.* **2008**, *82*, 687.
- (11) Patra, A.; Hebalkar, N.; Sreedhar, B.; Sarkar, M.; Samanta, A.; Radhakrishnan, T. P. *Small* **2006**, *2*, 650.
- (12) Patra, A.; Hebalkar, N.; Sreedhar, B.; Radhakrishnan, T. P. *J. Phys. Chem. C* **2007**, *111*, 16184.
- (13) (a) Materials Studio, Version 4.1.0.0; Accelrys Inc.: San Diego, CA, 2006. (b) Clark, T.; Alex, A.; Beck, B.; Burkhardt, F.; Chandrasekhar, J.; Gedeck, P.; Horn, A.; Hutter, M.; Martin, B.; Rauhut, G.; Sauer, W.; Schindler, T.; Steinke, T. VAMP, Version 8.1; Erlangen, 2003.
- (14) See Supporting Information.
- (15) (a) Bohren, C. F.; Huffman, D. R. *Absorption and Scattering of Light by Small Particles*; Wiley: New York, 1983; p 287. (b) Volkov, V. V.; Asahi, T.; Masuhara, H.; Masuhara, A.; Kasai, H.; Oikawa, H.; Nakanishi, H. *J. Phys. Chem. B* **2004**, *108*, 7674. (c) Lee, K.; El-Sayed, M. A. *J. Phys. Chem. B* **2005**, *109*, 20331. (d) Jain, P. K.; El-Sayed, I. H.; El-Sayed, M. A. *Nano Today* **2007**, *2*, 18.
- (16) Sutherland, R. L. *Handbook of Nonlinear Optics*; Marcel Dekker Inc.: New York, 1996; p 543.
- (17) Gu, B.; Ji, W. *Opt. Express* **2008**, *16*, 10208.
- (18) He, G. S.; Zheng, Q.; Baev, A.; Prasad, P. N. *J. Appl. Phys.* **2007**, *101*, 083108.
- (19) Sheik-Bahae, M.; Said, A. A.; Wei, T.; Hagan, D. J.; Stryland, E. W. V. *IEEE J. Quantum Electron.* **1990**, *26*, 760.

JP803724E