Revised

Supporting Information for

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

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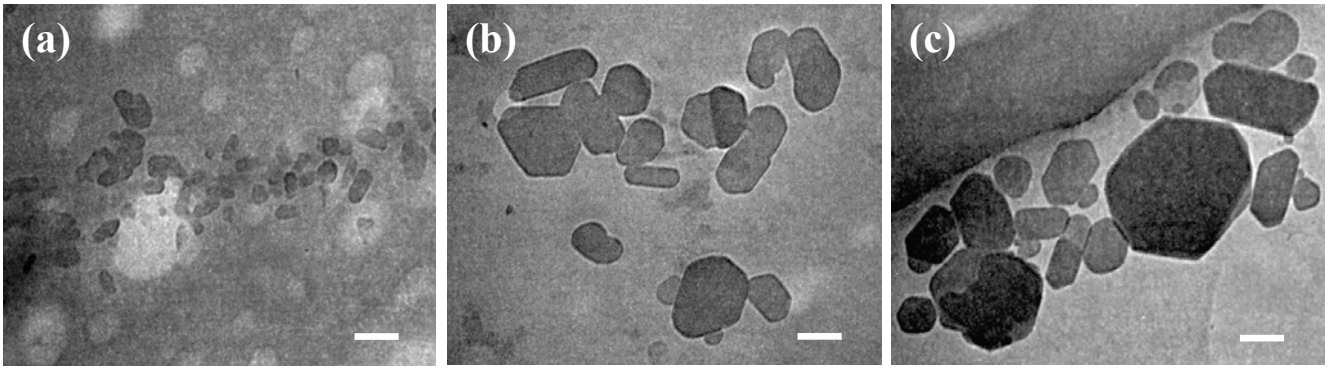
Contents

Microscopy

Transmission electron microscopy :

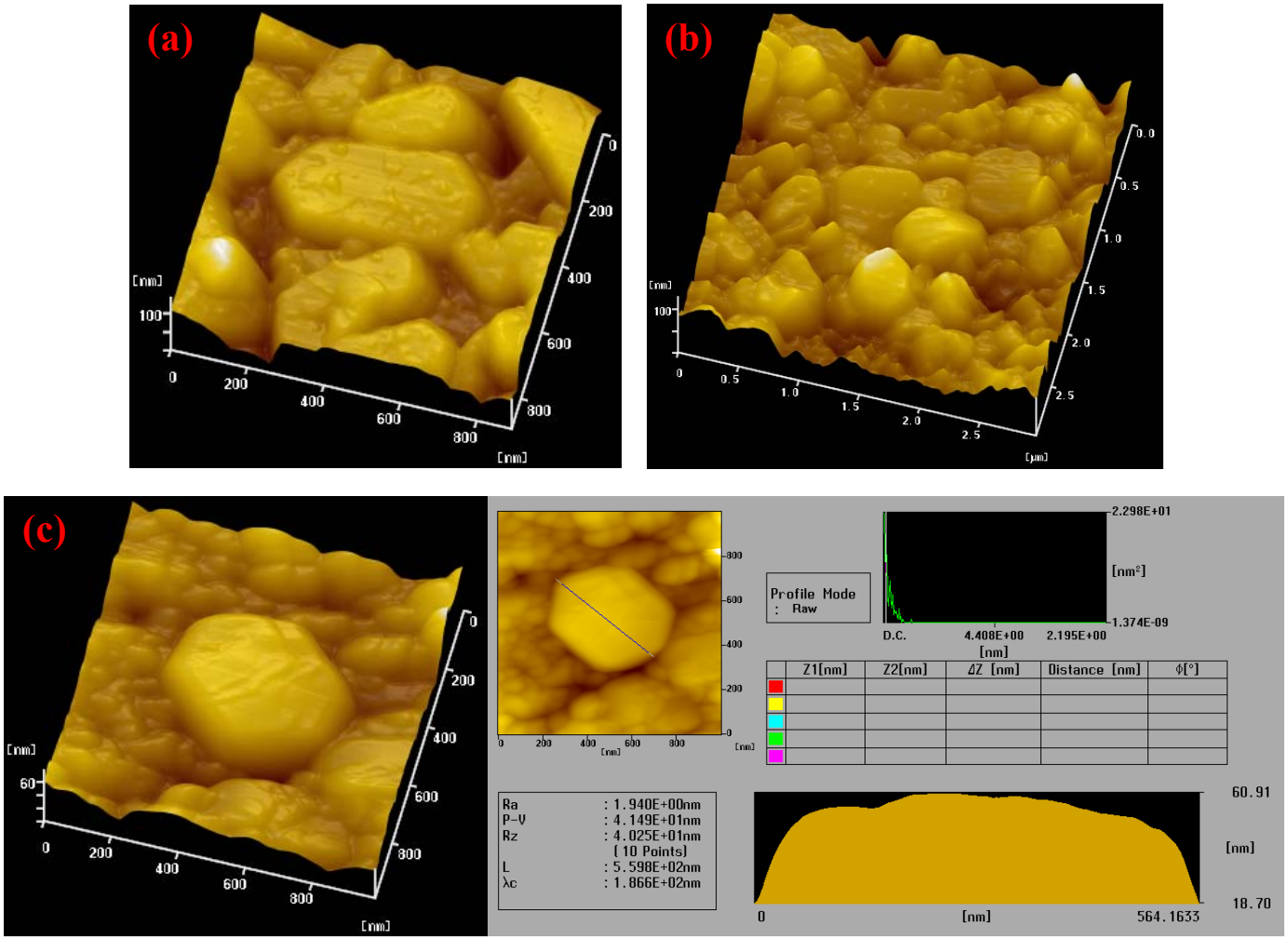
The samples for TEM were prepared by placing a drop of the colloidal solution on a polymer (polyvinyl formvar) - coated copper grid and drying at room temperature; size and morphology of the colloidal crystals were examined using TECNAI G^2 FEI F12 transmission electron microscope at an accelerating voltage of 120 kV.



TEM images of BCADQ crystals fabricated by digestion at 30, 60 and 90°C respectively: (a) BCADQ30, (b) BCADQ60, (c) BCADQ90 (scale bar = 300 nm).

Atomic force microscopy :

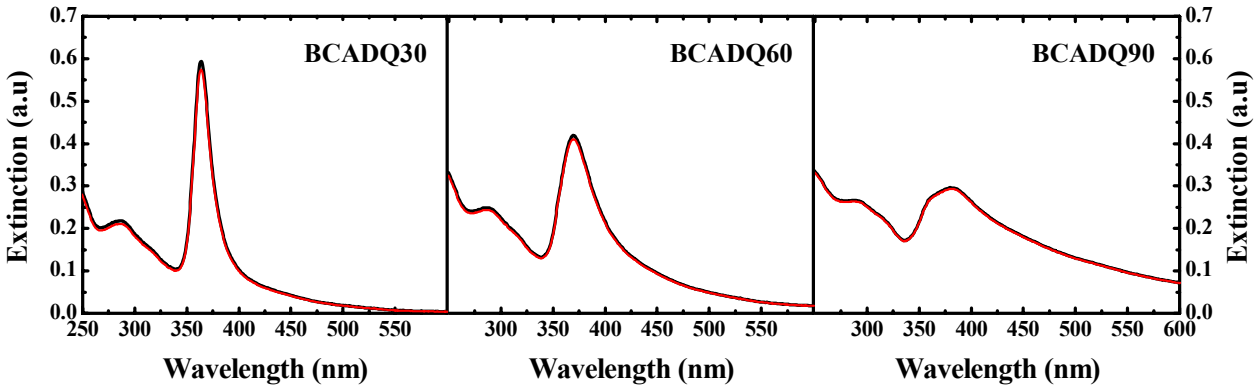
Samples for the AFM investigation were collected on a 50 nm pore mixed cellulose esters membrane (Millipore, VSWP) through filtration of the colloidal solution; microscopy was done using SEIKO Model SPA 400 atomic force microscope in the dynamic force (non-contact) mode using a tip having a force constant of 12 N/m.



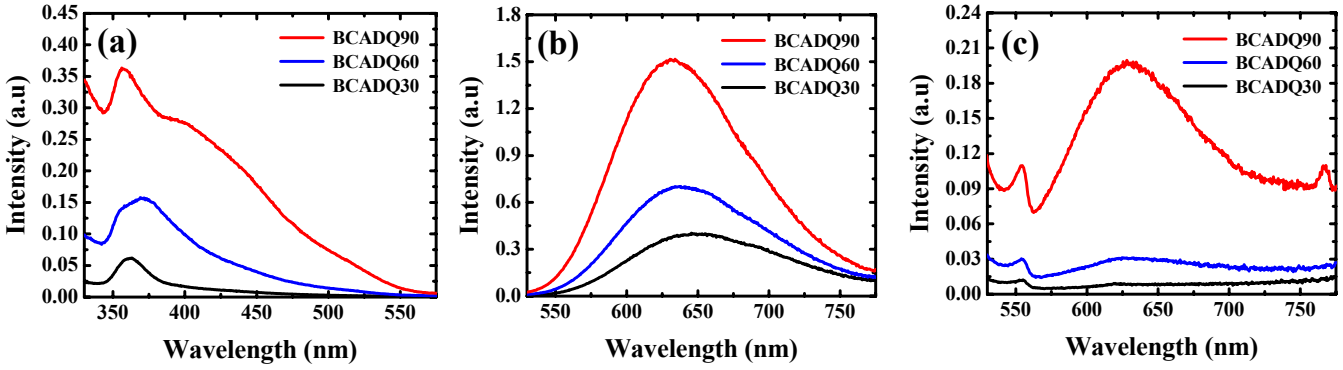
AFM image of BCADQ crystals: (a) colloid aged for 24 h at ~ 30°C, (b) colloid digested at 60°C for 1 h and (c) dimension of a single crystal digested at 60°C for 1 h revealed through line profile analysis

Spectroscopy

Electronic extinction spectra were recorded on a Shimadzu model UV-3100 UV-visible spectrometer. Steady state fluorescence excitation and emission spectra were recorded on a Jobin Yvon Horiba spectrofluorimeter (Model Fluoromax- 3 or Model Fluoromax- 4). Colloid samples for the studies involving the same 'concentration' were prepared by mixing 1 ml of the digested colloid with 2 ml of reference solvent (100 µl DMSO in 20 ml of water) so that the effective concentration of BCADQ was 1.67 x 10^{-5} M.

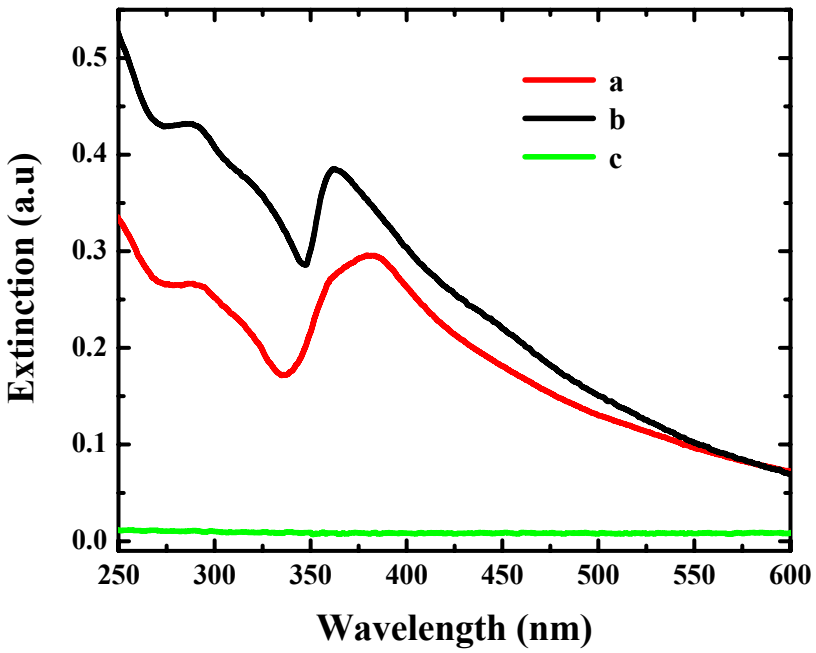


Electronic extinction spectra of BCADQ colloids before (black solid line) and after experiment (red solid line) clearly demonstrate the stability of the colloids through the experiment as no noticeable change is observed in the spectra



(a) Fluorescence excitation spectra (λ_{em} = 640 nm), (b) Fluorescence emission spectra (λ_{exc} = 365 nm) and (c) Fluorescence emission spectra (λ_{exc} = 510 nm) of BCADQ colloids digested at different temperatures with the same 'concentration'

The spectra above clearly show that as the particle size increases, new absorption at longer wavelengths (such as 510 nm) which leads to emission (at 640 nm) does appear.

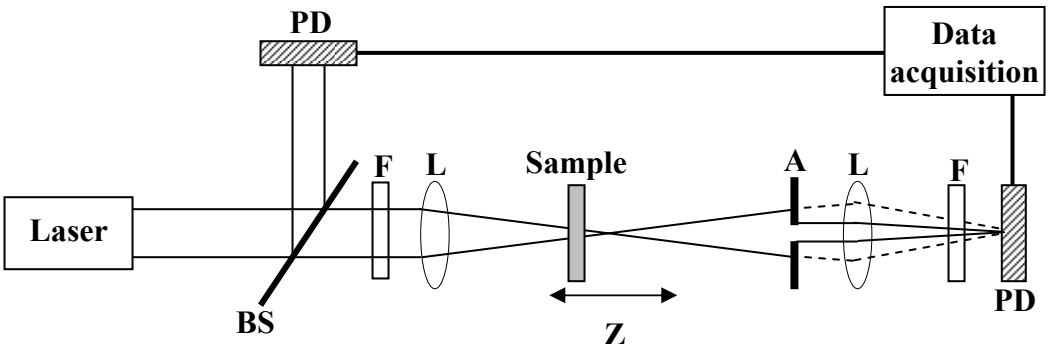


Extinction spectra of (a) BCADQ90 colloid, (b) microcrystalline sample of BCADQ solid with crystal sizes in the range of 40 – 70 µm and (c) filtrate obtained by filtration of a suspension of the microcrystalline sample in (b) through a G-2 sintered glass filter (lower cut-off limit = 40 µm).

Samples of BCADQ containing exclusively, crystals with sizes in the range 40 – 70 µm were prepared by sieving microcrystalline powders through standard sieves. The extinction spectrum of such samples (b) is found to be very similar to that of BCADQ90 (a). The size range of these crystals was confirmed further by filtering an aqueous suspension of these crystals through a sintered glass filter with porosity grade 2 (lower cut off limit = 40 µm) and recording the extinction spectrum of the filtrate (c) which does not show any extinction due to nano or microcrystals of BCADQ. We have also found that this filtrate does not show any fluorescence, confirming that no BCADQ is present in it either in solution or colloidal state. Similarity of spectra (a) and (b) proves that the broadened spectrum of BCADQ90 arises due to the larger crystals present in the colloids digested at higher temperatures and not due to the wide range of sizes of BCADQ (from nano to micro).

Nonlinear optical studies

Setup for the Z-scan and optical limiting studies; the aperture is removed for the open aperture Z-scan experiment.

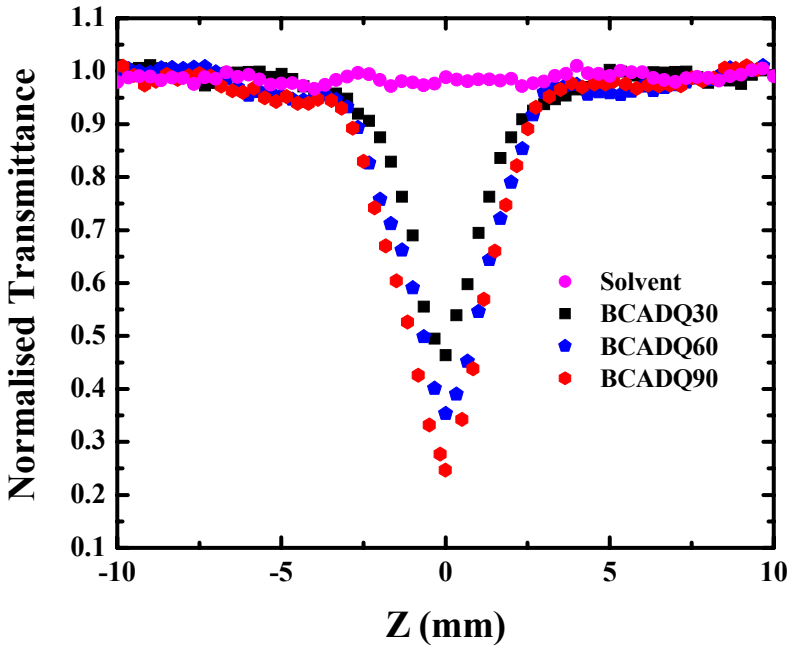


A = aperture, BS = beam splitter, F = ND filter, L = lens, PD = photodiode

Laser :
Ti:Sapphire laser (800 nm, ~110 fs, 1 kHz / 10 Hz) or
Nd:YAG laser, second harmonic (532 nm, 6 ns, 10 Hz)

Z scan studies in the nanosecond regime :

A frequency doubled Nd:YAG laser (532 nm, 6 ns, 10 Hz) was used as the excitation sources for the nonlinear optical studies in the nanosecond regime. Z-scan measurements were carried out by moving the sample across the focus of the laser beam using a computer-controlled translation stage. Nanosecond pulse laser was focused using a lens of 60 mm focal length; the beam waist was 13.5 μm at focus leading to peak intensity in the range 0.04 – 0.92 GW/cm^2 ie. fluences in the range 0.24 – 5.52 J/cm^2. The input intensity could be varied using calibrated neutral density filters. The transmitted output was collected using a calibrated fast photodiode (FND 100) and processed using a data acquisition system consisting of a boxcar averager, ADC and computer.



Open aperture Z-scan traces of reference solvent and BCADQ colloids recorded at an input intensity of 0.92 GW/cm^2

The open aperture Z-scan traces in above figure clearly demonstrate that solvent medium does not show any nonlinear response but BCADQ colloids exhibit size/distribution dependent nonlinear optical behavior with the nanosecond pulse laser. Nonlinear transmittance decreases with the increase of particle size; it is likely that this is primarily because of more scattering loss associated with the larger particles.

Degenerate four-wave mixing experiment

Degenerate four-wave mixing (DFWM) experiment was carried out with 800 nm, 110 fs laser pulses using the 'boxcar geometry'. Nonlinear refractive index of BCADQ colloids were calculated by comparing the sample signals with that of CCl_4.

Comparison of effective nonlinear coefficient (n_2^{eff}) of reference solvent and BCADQ nano/microcrystals from degenerate four-wave mixing experiments (ν = laser pulse frequency)

Samples	n_2^{eff} (cm^2/W)	
	ν = 1 kHz	ν = 10 Hz
Solvent	6.624×10^{-16}	6.362×10^{-16}
BCADQ30	6.838×10^{-16}	6.509×10^{-16}
BCADQ60	6.873×10^{-16}	6.542×10^{-16}
BCADQ90	6.916×10^{-16}	6.583×10^{-16}

Semiempirical AM1 Computations
Keywords and Geometry used

1SCF AM1 PECI=8 NUMCI SCFCRT=0.0000100000 ITRY=200 LEV-OK GEO-OK T=10D + NOINTER VESPA MULTIPOLE HYPERPOL=1.55

Atom Number	Atomic Symbol	Bond Length (Angstroms)	Bond Angle (degrees)	Twist Angle (degrees)	
1	C				
2	C	1.43878			1
3	C	1.35604	121.94298		2 1
4	C	1.44561	121.75550	0.61227	3 2 1
5	C	1.44558	116.16781	0.39561	4 3 2
6	C	1.35580	121.72848	-0.98555	5 4 3
7	C	1.41224	121.87814	178.6781	1 2 3
8	N	1.39389	119.98460	-155.93061	7 1 2
9	N	1.39359	120.15155	23.95870	7 1 2
10	C	1.41267	124.84286	-143.36757	9 7 1
11	C	1.41249	125.00082	-143.20701	8 7 1
12	C	1.40984	122.49521	28.95080	11 8 7
13	C	1.39146	120.31825	179.09226	12 11 8
14	C	1.39723	120.10221	-0.64084	13 12 11
15	C	1.39849	120.19816	0.00000	14 13 12
16	C	1.38978	120.06871	0.35486	15 14 13
17	C	1.40981	122.43937	29.30166	10 9 7
18	C	1.39138	120.32810	179.41643	17 10 9
19	C	1.39728	120.09090	-0.68598	18 17 10
20	C	1.39853	120.19706	-0.03728	19 18 17
21	C	1.38986	120.07701	0.36270	20 19 18
22	C	1.37382	121.95066	-179.52101	4 3 2
23	C	1.41794	121.95981	179.49624	22 4 3
24	C	1.41781	122.01744	-0.35133	22 4 3
25	N	1.16445	179.76206	-162.50890	23 22 4
26	N	1.16445	179.71671	169.82307	24 22 4
27	Cl	1.69705	119.93380	-179.85482	19 18 17
28	Cl	1.69710	119.92568	-179.84407	14 13 12
29	H	1.10208	119.51757	-177.41836	2 1 3
30	H	1.10167	120.53209	-178.78243	3 2 1
31	H	1.10170	117.73119	178.48088	5 4 3
32	H	1.10209	118.51766	177.99481	6 5 4
33	H	0.99934	115.30471	11.66384	8 7 1
34	H	0.99924	115.38173	11.52907	9 7 1
35	H	1.10123	120.66030	-0.81256	12 11 8
36	H	1.10148	119.61178	179.79582	13 12 11
37	H	1.10154	120.26694	-179.83383	15 14 13
38	H	1.10125	119.21014	179.86868	16 15 14
39	H	1.10122	120.66568	-0.52089	17 10 9
40	H	1.10146	119.59460	179.70241	18 17 10
41	H	1.10150	120.24006	-179.84958	20 19 18
42	H	1.10130	119.22243	180.03063	21 20 19