Supplementary Material (ESI) for *Nanoscale*

Supporting Online Materials

Dendrimer Adjusted Nanocrystals of DAST: Organic Crystal with Enhanced Nonlinear Optical Properties

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Supporting Materials

Preparation of DAST NCs

The CSiO-G5 [1] and DAST [2] were synthesized by following the reported procedures. The DAST NCs were prepared through the reprecipitation method: A micro-volume (50 μL) of a DAST methanol solution (4 mM) was injected rapidly into 10 mL of diethyl ether. The mixture was stirred vigorously for 30 seconds to allow complete solvent mixing, and then the mixture was ripened at room temperature. This leads to a DAST concentration of 2×10^{-5} M. A yellow precipitation formed immediately after the injection, contrasting to a red solution of DAST in methanol. CSiO-G5 was used to improve the reprecipitation method and to form a stable dispersion of DAST NCs. The preparation of NCs with dendrimer was carried out by injecting the organic solution into the solution of CSiO-G5 in diethyl ether. A yellow precipitation formed much more rapidly than that prepared without CSiO-G5.

Measurements

SEM images of DAST NCs are acquired on scanning electron microscopy (SEM, Hitachi S-4300 FEGd). The SEM samples of the DAST NCs were prepared by dropping the suspension of the DAST NCs with variable evolving time onto a slide glass and allowed to evaporate the solvent at room temperature. Then the samples were covered with aurums by a vacuum coat. The UV-Vis absorption and fluorescence emission spectra are recorded using a Shimadzu UV-2500 spectrophotometer and a Hitachi FL-4500 spectrophotometer, respectively. The fluorescence quantum yield is using fluorescein in 0.1 N aqueous NaOH solution ($\Phi = 0.9$) as a reference standard. Both of the DAST NCs and DAST solution are excited at 480 nm. Time resolved fluorescence measurements are carried out using a single photon fluorescence spectrometer F900 from Edinburgh Instruments Co., UK. The decay data was collected at 545 nm with an excitation wavelength λ_{ex} of 475 nm at room temperature. Time resolved fluorescence of DAST methanol solution was measured using a streak scope camera (Hamamatsu, C4334) with the excitation of femtosecond laser pulse at the wavelength of 400 nm. The time resolution of the system was limited by the time resolution of the streak camera of about 10ps. The lifetime of the DAST NCs is 3.95 ns, which is very close to 4.41 ns for the longer lifetime of the DAST NCs without CSiO-G5, and much longer than 88 ps for DAST solution (Figure S3). The two-photon excited fluorescence (TPEF) spectra is recorded on a SD2000 spectrometer (Ocean Optics). A mode-locked Ti-sapphire laser (Tsunami, Spectra-Physics) was employed as the excitation source, of which the oscillating wavelength, pulse width and repetition rate are 923 nm, 80 fs and 82 MHz, respectively.

Calculation of two-photon absorption (TPA) cross section[3]:

$$\delta_x = \delta_r\left(\frac{C_r}{C_x}\right)\left(\frac{n_r}{n_x}\right)\left(\frac{F_x}{F_r}\right)\left(\frac{\phi_r}{\phi_x}\right)$$

TPA cross section can be defined as follows:

$$\frac{\eta_x}{\eta_r} = (\frac{C_r}{C_x})(\frac{n_r}{n_x})(\frac{F_x}{F_r})$$

C and *n* are the concentration and refractive index of the sample solution, respectively, *F* is the TPEF integral intensity and *Φ* is the quantum yield, δ is TPA cross section and η stands for the two photon action cross section. The subscript r means reference, x means sample.

Calculation of radiative rate and nonradiative rate[4]:

$K_r = \Phi_f/\tau$, $K_{nr} = \tau^{-1} - K_r$

K_r is the radiative rate constant and K_{nr} is the total nonradiative rate constant, τ is the lifetime, Φ_f is the quantum yield.

The K_{nr}/K_r is around 23 times and 166 times for DAST NCs and molecules, respectively. It indicates that the nonradiative emission is prevented in DAST NCs. It directly demonstrates that the enhancement of the fluorescence quantum yield in DAST NCs.

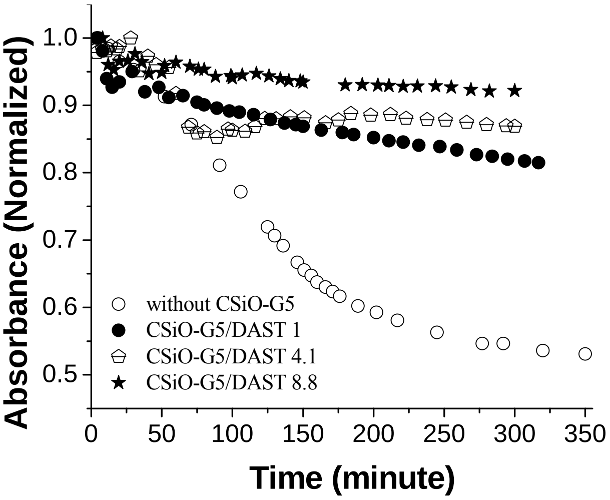


Fig. S1. The UV/Vis absorbance intensity at 475 nm of NCs prepared without and with CSiO-G5 under different CSiO-G5/DAST ratios (CSiO-G5/DAST=0, 1, 4.1, 8.8) during the evolution time. DAST NCs (2×10^{-5} M in molecule).

The variation of the absorbance change indicates that the kinetic process is slowed down with the assistance of the CSiO-G5.

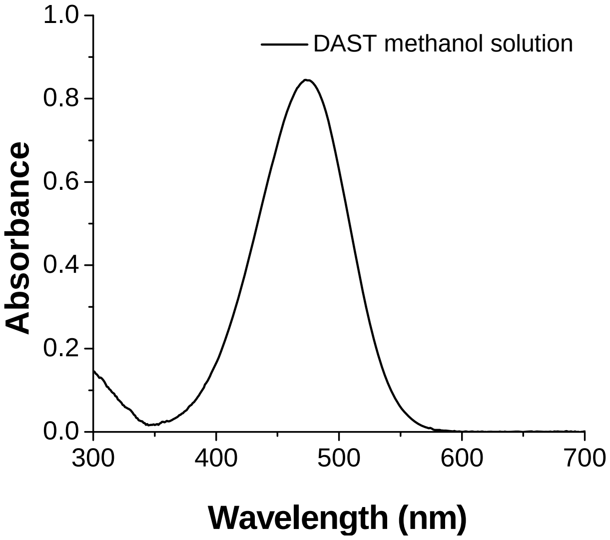
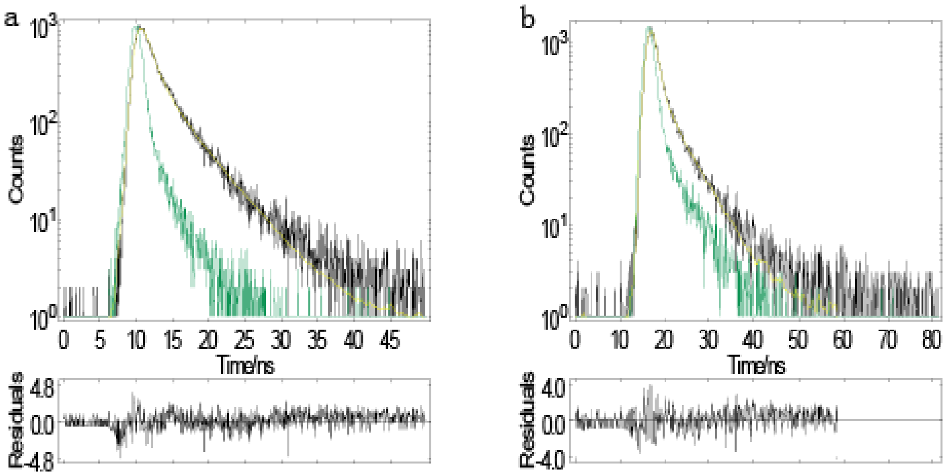


Fig. S2. UV-Vis absorbance spectra of DAST methanol solution (2×10^{-5} M).



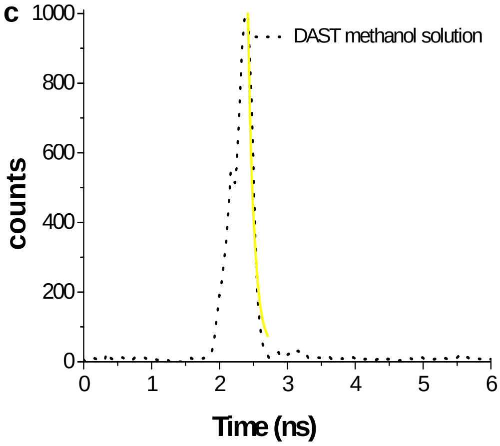


Fig. S3. The fluorescence lifetime of DAST NCs prepared without CSiO-G5 (a), with CSiO-G5 (b) and DAST solution in methanol (c) at the concentration of 2×10^{-5} M.

References:

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