

Nitrogen and sulphur co-doped carbon quantum dots and their optical power limiting properties

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1. General Information

Materials and Instruments

All solvents and reagents were purchased from Energy Chemical, and used as is unless otherwise stated. The synthetic routes for precursor **1** and CQDs are illustrated in Scheme S1. The synthesis of precursor **1** has been reported previously. The synthetic procedures and characterization data for precursor **1** and CQDs provided below.

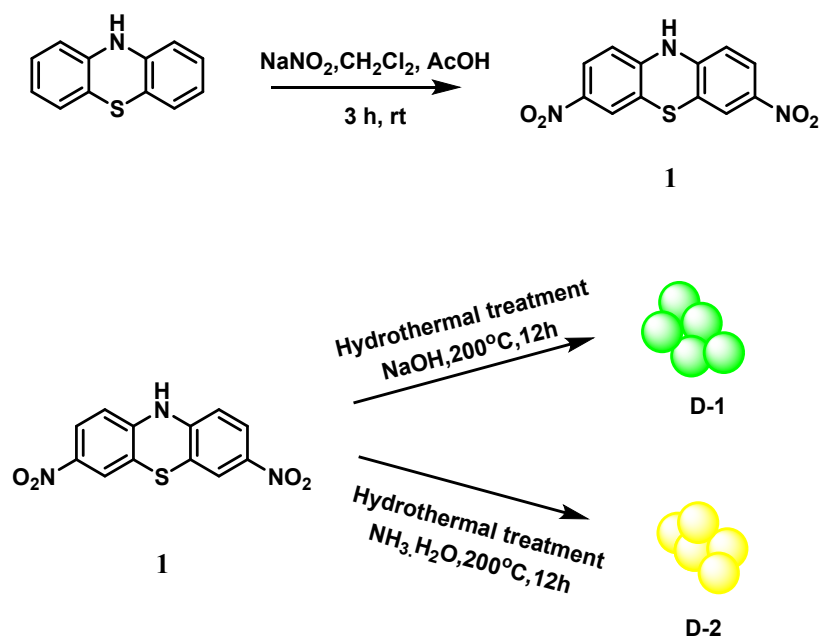
A Tecnai F20 transmission electron microscope (TEM) was used to investigate the morphologies of CQDs. Atomic force microscopic (AFM) image was taken with MultiMode 3D. FT-IR spectra image was obtained from Nicolet 6700

spectrophotometer. Powder X-ray diffraction (XRD) patterns of the samples were collected on a Bruker D8 Advance powder diffractometer. DSC experiments were recorded on a NETZSCH DSC 204 instrument at a scanning rate of $c10 \text{ K min}^{-1}$. X-ray photoelectron spectroscopy (XPS) analysis was carried out on ESCALAB 250.

Photophysical and nonlinear optical measurements

The spectroscopic grade solvents were used for the photophysical experiments. Optical absorption spectra were obtained by using a TU-1900 UV-vis spectrophotometer in different solvents. Photoluminescence spectra were carried out on a Hitachi F-4600 fluorescence spectrophotometer. The photostability experiments are carried out under 100W UV light, the intensities at 486 nm for **D-1** and at 535 nm for **D-2** are monitored every five or ten minutes. The NLO and OPL performances of the samples were investigated by Z-scan using a Nd:YAG laser (EKSPLA, PL2143B) and 532 nm pulses of 4 ns, operating at 10 Hz repetition rate. The Ti:sapphire regenerative amplifier (1000 nm, 35 fs, 1 kHz) excitation source was also employed. The focal length of the lens is 5 cm. beam size is 90 μm . To facilitate comparison, all sample concentrations in dry DMF were adjusted to the same 70% linear transmittance at 532 nm in NLO and OPL experiments. All samples were measured in 1 mm quartz cells.

2. Synthesis of precursor 1 and CQDs.



Scheme S1 Synthetic procedures of precursor **1** and CQDs

Synthesis of precursor **1**

Phenothiazine (100 mmol, 20 g) were dissolved in CH_2Cl_2 (100 mL) and CH_3COOH (40 mL), The mixture was stirred at R.T. Then Sodium nitrite (300 mmol, 20 g) was added and stirred for another 1 h. The reaction mixture was quenched with water and extracted in dichloromethane. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel eluted with mixed solvent of petroleum ether–dichloromethane (2 : 1) to afford a purple solid in a yield of 82%. ^1H NMR(400 MHz; $\text{DMSO}-d_6$): 6.69 (d, $J = 4\text{Hz}$, 2H), 7.70 (s, 2H), 7.82 (d, $J = 4\text{Hz}$, 2H). HRMS (ESI) m/z calc. for $\text{C}_{12}\text{H}_8\text{N}_3\text{O}_4\text{S}^+$ ($\text{M}+\text{H}$) $^+$: 290.0230, found: 290.0245. Elemental analysis calculated for $\text{C}_{12}\text{H}_8\text{N}_3\text{O}_4\text{S}$: C, 49.83; H, 2.44; N, 14.53; Found: C, 49.95; H, 2.51; N, 14.61.

3. Characterization and photophysical properties of D1 and D2

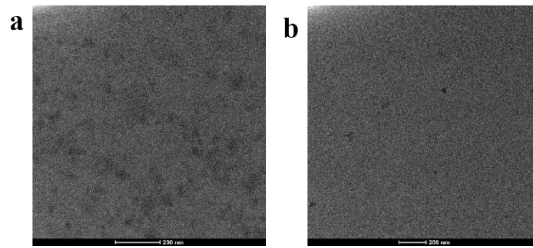


Fig. S1 TEM images of the obtained **D-1** and **D-2**

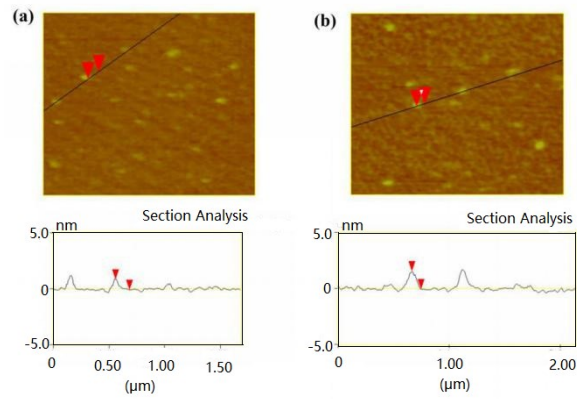


Fig. S2 AFM image of **D-1**(a) and **D-2**(b).

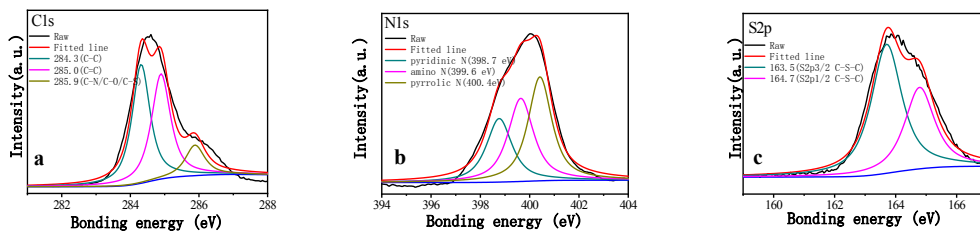


Fig. S3 The amplified (a) C1s, (b) N1s and (c) S_{2p} XPS spectra for **D-1**

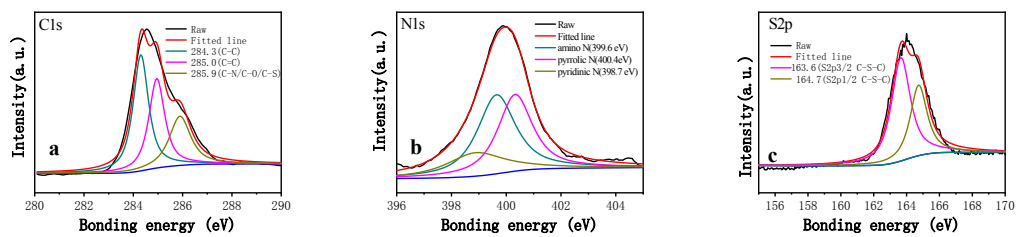


Fig. S4 The amplified (a) C1s, (b) N1s and (c) S_{2p} XPS spectra for **D-2**

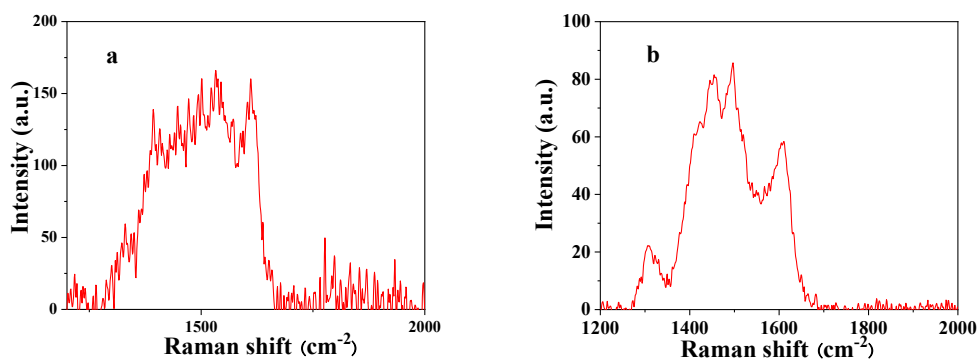


Fig. S5 Raman spectrum of D-1 and D-2

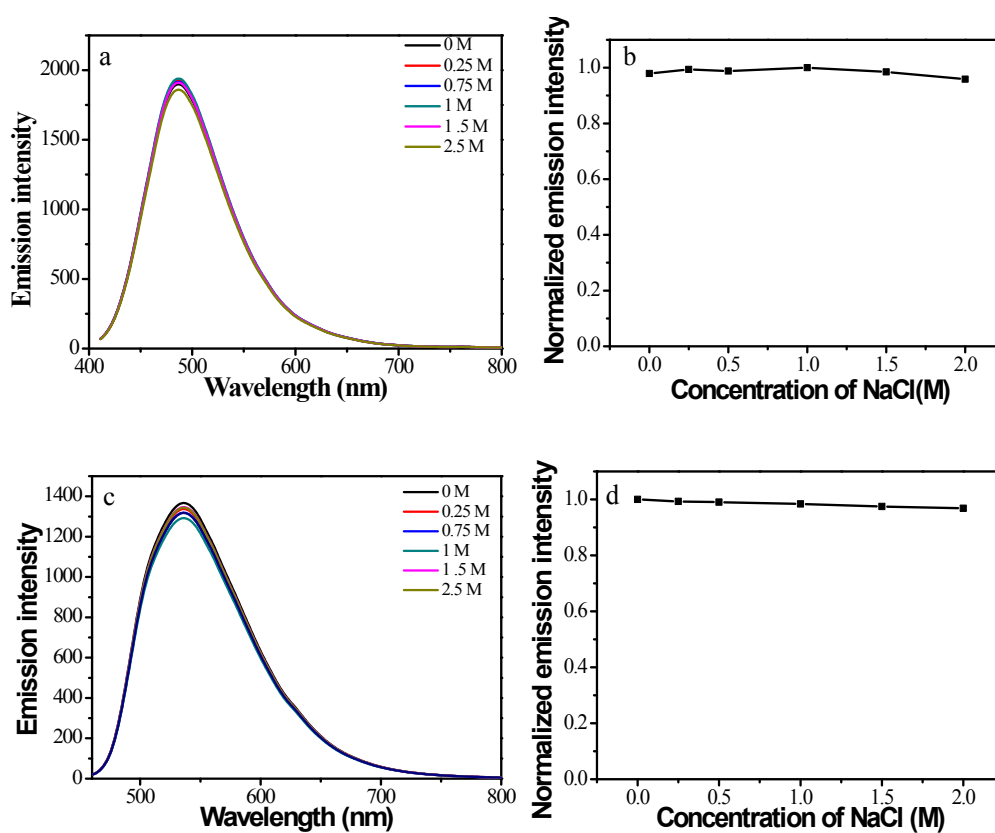


Fig. S6 Effect of ionic strength on the fluorescence intensity of D-1(a,b) and D-2(c,d), the fluorescence intensities are recorded at 486 nm and 535 nm for D-1 and D-2, respectively.

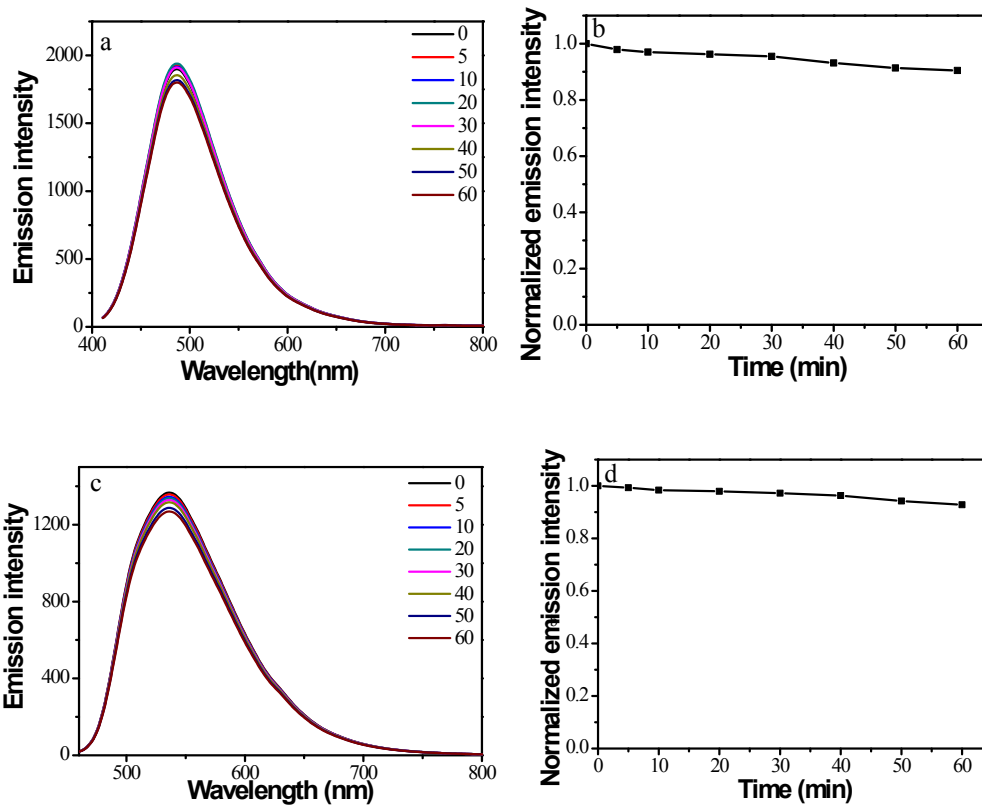


Fig. S7 Photostability of **D-1**(a,b) and **D-2**(c,d) under 100W UV light, the fluorescence intensities are recorded at 486 nm and 535 nm for **D-1** and **D-2**, respectively.

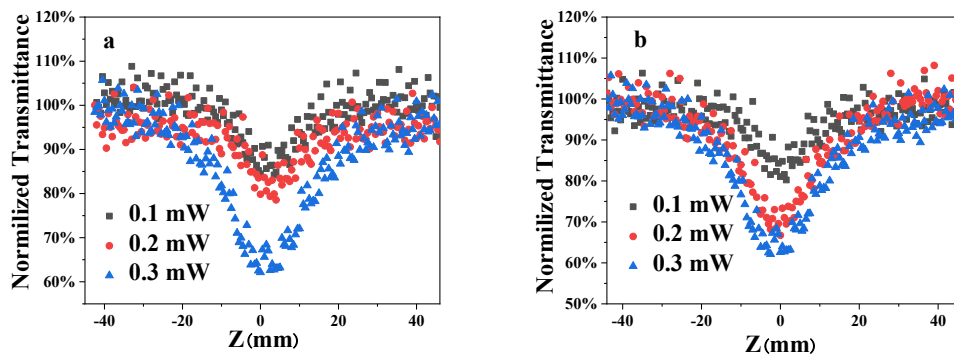


Fig. S8 Intensity dependent open-aperture Z-scan curves **D-1** (a) and **D-2** (b) with the same linear transmittance of 70% to 35 fs, 1000 nm optical pulses.

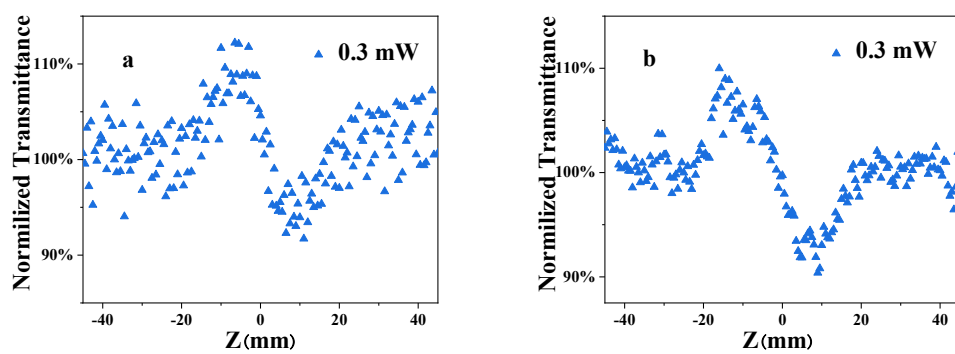


Fig. S9 Close-aperture Z-scan curves **D-1** (a) and **D-2** (b) with the same linear transmittance of 70% to 35 fs, 1000 nm optical pulses.