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Supporting information

Tailoring the energy gap to promote long wavelength emission of nitrogen-doped sulfur quantum dots via dual functional ethylenediamine

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2.1 Chemicals and Reagents

Sulfur powders were provided by Tianjin Fuchen. Ethylenediamine (EDA) was from Beijing Chemical Works. Ethanol (EtOH) (99%), NaOH and HCl were purchased from Tianjin Guangfu Technology Development Co., Ltd., Dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF) and acetone were all obtained from Sigma-Aldrich (Shanghai, China). Distilled water used with an electrical resistance of 18.2 $M\Omega \cdot cm^{-1}$. All the chemicals were used without further purification.

2.2 Synthesis of N-SQDs

First, 40 mg of sublimated sulfur powder was added to 10 mL ethylenediamine (EDA) and sonicated for 5 min to form a dark brown solution. Subsequently, the dark brown solution was reacted at 180 °C for 15 h in poly tetrafluoroethylene (Teflon)-lined autoclave (25 mL). Finally, the solution was filtered to remove unreacted material via 0.22 μm microporous filtering film, then excess reaction solvent EDA was removed by rotary evaporation to yield N-SQDs-15 and stored at 4 °C. Fixing the reaction time as 5 h, 10 h, and 20 h give a final product of N-SQDs-5, N-SQDs-10 and N-SQDs-20, respectively.

2.3 Instruments and Characterizations

The morphology of the prepared N-SQDs was investigated by transmission electron microscopy (FEI, USA). X-ray photoelectron spectroscopy (XPS) spectra were conducted on ESCALab220I-XL. Fourier transform infrared spectroscopy (FT-IR) measurements were carried out on a PerkinElmer Frontier IR/FIR, US. The optical properties were performed with a fluorescence spectrophotometer (F-7000, Hitachi,

Japan) to record fluorescence spectra and a UV-2600 spectrophotometer (Shimadzu, Japan) to monitor UV-vis absorption spectra. The absolute QY of SQDs was estimated by using fluorescence spectrometer FLS-980 (Edinburgh, England).

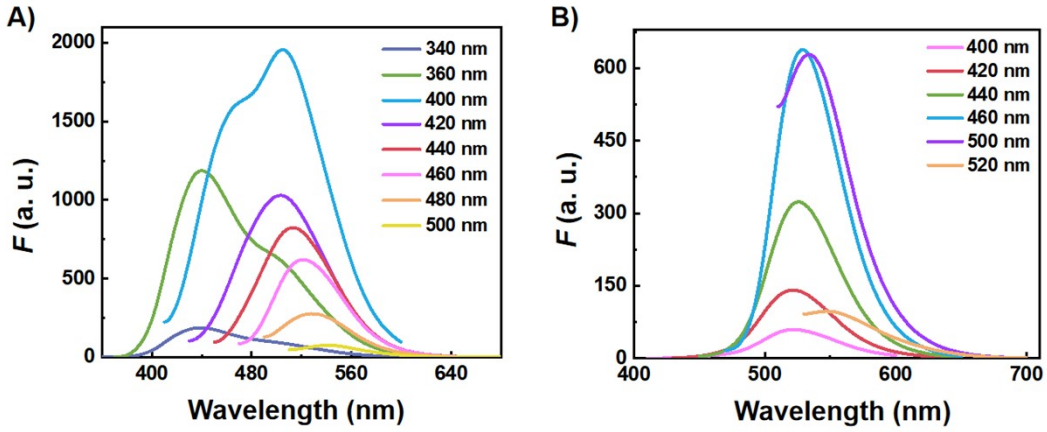

Figure S1. PL spectra of N-SQDs obtained from the reaction using different amount of sulfur powders. (A) 20 mg sulfur powders; (B) 60 mg sulfur powders. Other condition: 10 mL EDA, temperature: 180 ^{o}C.

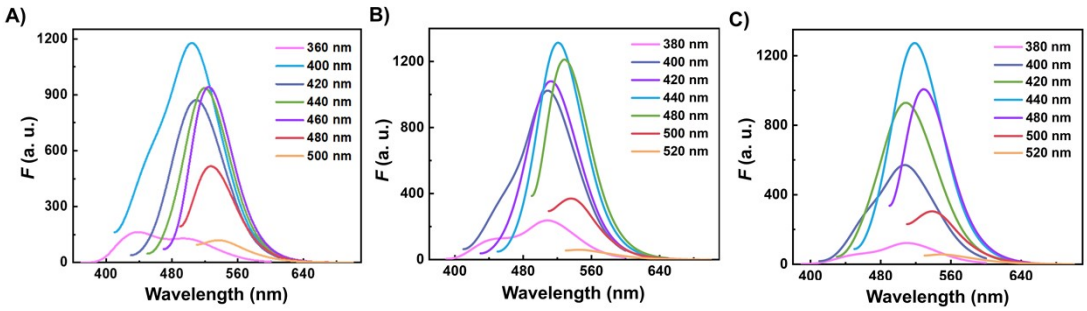

Figure S2. PL spectra of N-SQDs obtained from the reaction different reaction time. (A) 5 h; (B) 10 h; (C) 20 h. Other conditions: 40 mg sulfur powders and 10 mL EDA, temperature: 180 ^{o}C.

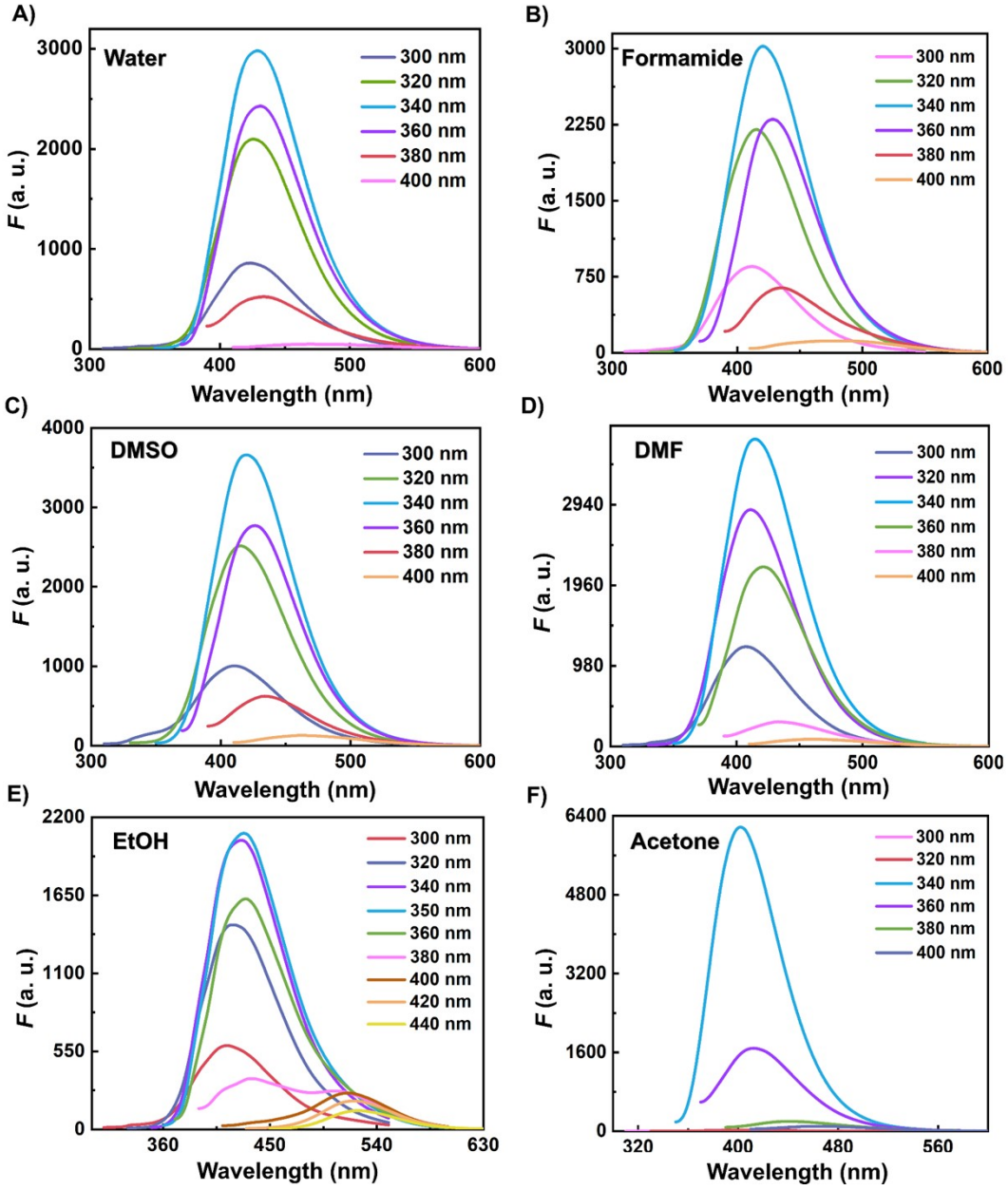

Figure S3. PL spectra of N-SQDs-15 under different excitations (0.4mg/ml) in various solvents (A)-(F).

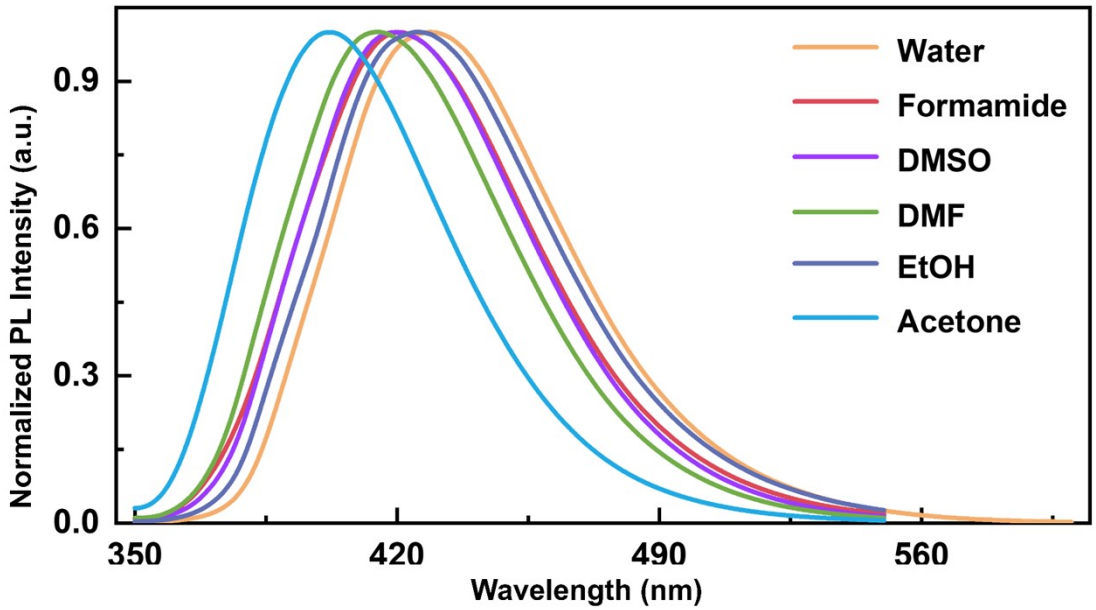

Figure S4. Normalized PL spectra of N-SQDs-15 in various solvents under excitation of 340 nm.

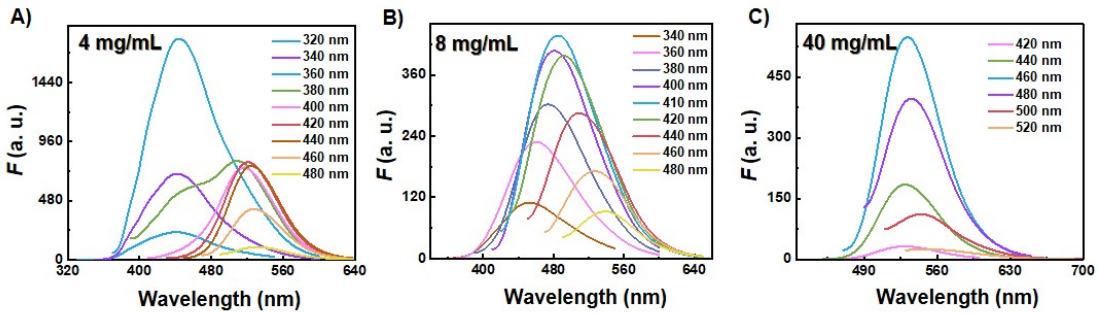

Figure S5. PL spectra of various concentrations of N-SQDs-15 with under different excitation.

The equation about a possible reaction mechanism for the synthesis of N-SQDs using EDA as solvent and nitrogen source are shown below.

$$NH_2CH_2NH_2 + S_8 \leftrightharpoons NH_2CH_2CH_2N + H_2 - S_7 - S^- \quad \textbf{(Eqn. 1)}$$

$$NH_2CH_2CH_2N + H_2 - S_7 - S^- + NH_2CH_2NH_2 \leftrightharpoons$$

$$N + CH_3CH_2NH_2 + NH_2CH_2CH_2NH - S_7 - S^- \quad \textbf{(Eqn. 2)}$$

$$NH_2CH_2CH_2NH - S_7 - S^- \leftrightharpoons NH_2CH_2CH_2NH - S_X - S\cdot + \cdot S - S_{5-X} - S^-$$

(Eqn. 3)

$$2RNH - S_X - S\cdot \leftrightharpoons RNH - S_X - S - S - S_X - NHR \quad \textbf{(Eqn. 4)}$$

$$RNH - S_X - S - S - S_X - NHR \xrightarrow{\textbf{Oxidation}} N - SQDs \quad \textbf{(Eqn. 5)}$$

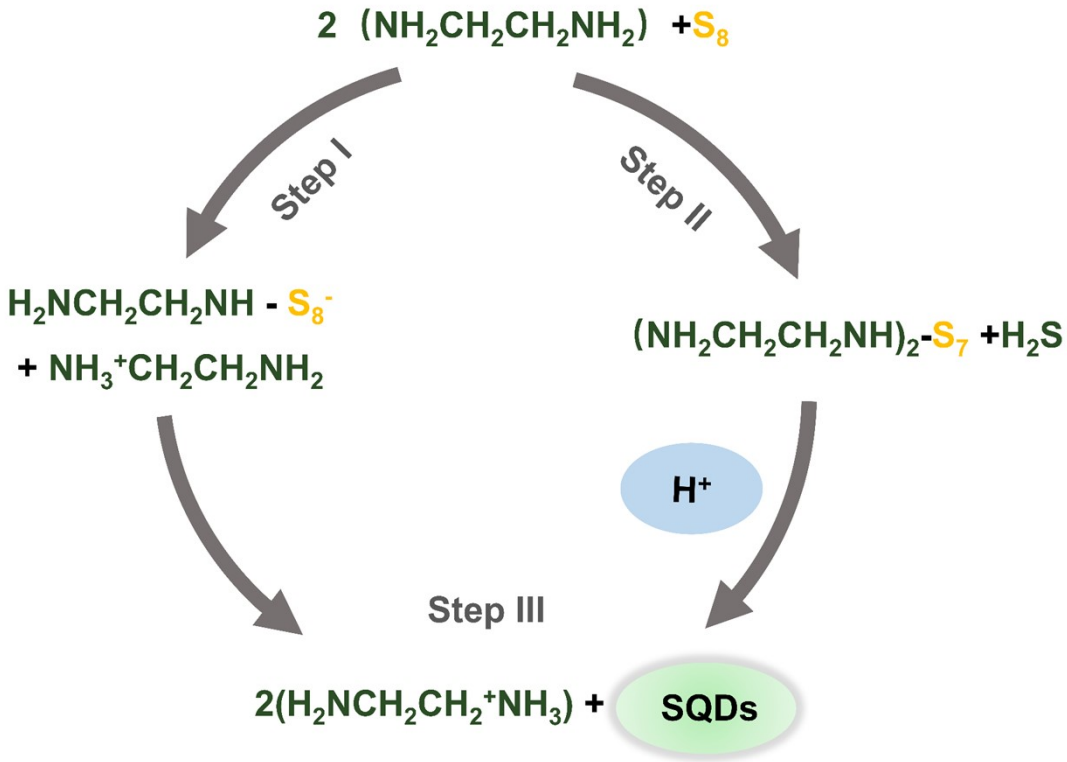

Figure S6. Other mechanism diagram of SQDs.