Supporting Information

DAST optical damage tolerance enhancement and robust lasing via supramolecular strategy

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1. Materials and experimental details

(1) Materials

4-N, N-dimethylamino-4'-N'-methyl-stilbazolium tosylate (DAST) crystals powder was purchased from Daiichi Pure Chem. Co. Ltd which has merged into Sekisui Medical Co. Ltd. β-cyclodextrin (β-CD) and surfactant cetyltrimethylammonium bromide (CTAB) were purchased from Sigma-Aldrich and used without further purification. Methanol (99.9%, Super Dry, with molecular sieves, water ≤ 30 ppm) purchased from J&K Scientific. Distilled water was purchased from Watsons. Octadecyltrichlorosilane (OTS) was purchased from Tokyo Chemical industry.

(2) Preparation of DAST@β-CD CMCs, MPs

DAST@β-CD CMCs preparation. The DAST@β-CD CMCs were prepared by a one-drop self-assembly method. First, 0.01 g DAST powder and 0.19 g β-CD are dissolved in 10 mL of distilled water and stirred homogeneously. Glass substrates are treated with OTS, followed by a deep UV irradiation treatment to remove the OTS using a deep UV ozone cleaner (Novascan PSDUV) with primary output wavelengths of 254 nm (90%) and 185 nm (10%) for 1 h. The hydrophilic glass substrate is then placed on a hot plate and heated to 80 °C, one drop (~50 µL) of the DAST@β-CD water solution is dropped onto the substrate and heated continuously for 30 minutes to obtain the CMCs.

DAST@β-CD MPs and NWs preparation. The DAST@β-CD NWs and MPs were fabricated via an additional cultivation process. In this case, the DAST : β-CD weight ratio is 0.01:0.038 g, per 10 mL of water. A hydrophilic substrate is placed on a hot plate and heated to 150 °C. Then, one drop (~50 µL) of the DAST@β-CD water solution is dropped onto the heated substrate. As the water solvent spread and evaporation, the DAST@β-CD micro-crystals are rapidly deposited on the substrate. Next, the samples are placed in a petri dish and sealed with approximately 300 µL of methanol solvent for the cultivation process. After three days of cultivation at room temperature, the DAST@β-CD MPs and NWs can be obtained.

(3) Preparation of DAST MPs/NWs

The DAST microcrystals used in this study were grown by a substrate-supported rapid evaporation crystallization method combined with a culturing process under saturated methanol vapor pressure environment. First, glass substrates are treated with OTS, followed by a deep UV irradiation treatment to remove the OTS using a deep UV ozone cleaner (Novascan PSDUV) with primary output wavelengths of 254 nm (90%) and 185 nm (10%) for 1 h. The glass substrate is then placed on a hot plate and heated to ca. 145 °C, then one drop (~50 µL) of 4 mM DAST methanol solution was dropped.
onto the glass substrate subsequently. As the methanol rapidly evaporated, the DAST nano/micro-crystals deposited on the substrate immediately. Next, the substrate with nano/micro-crystals was placed in a petri dish and sealed with approximately 300 µL of methanol solvent for the cultivation process. After three days of cultivation at room temperature, the DAST microcrystals can be obtained.


(4) Characterization
The microscopy images of DAST@β-CD CMCs and MPs were studied by fluorescence microscope (Zeiss Scope.A1) equipped with CCD (RETIGA R6), the crystal structure of DAST@β-CD MPs was investigated by high resolution transmissions electron microscope (HRTEM, JEOL TEM-2100F/EDS) and by scanning electron microscopy (SEM, Hitachi S4800). The structure of the MPs was examined using XRD (Bruker AXS D8 Advance diffractometer with a Cu Kα source). The fluorescence and absorption properties were investigated by a spectrometer with resolution of 0.226 nm (Idea optics PG2000pro, 544–800 nm, 25 mm slit). The 1HNMR spectra were measured on a Bruker AVANCE 400 MHz spectrometer using tetramethylysiane (TMS, δ=0 ppm) as an internal standard and D₂O as solvent (4.76 ppm). The absolute quantum yields were measured by using the Hamamastu Absolute Quantum Yield Spectrometer C11347. The fluorescence decay measurements were
performed by an Edinburgh FLS-900 instrument.

Figure S 1. The XRD of DAST powder, DAST@β-CD NWs, β-CD and DAST@β-CD CMCs.

Figure S 2. $^1$H nuclear magnetic resonance ($^1$H NMR) of DAST, β-CD and DAST@β-CD inclusion complex.

We can see that after the inclusion, the chemical shifts of β-CD exterior protons, H$_1$, H$_2$, H$_4$, and H$_6$, move upfield by about 0.14, 0.15, 0.13, 0.06 ppm, respectively; whereas the interior protons, H$_3$ and H$_5$, also move to upfield by about 0.04, 0.09 ppm, respectively. For the protons...
of DAST, however, there are only very little chemical shifts can be observed. Based on these results, we deduced that the DAST molecule enters the β-CD with preferential insertion of the dimethylaminostyryl group and remains the positively charged pyridinium moiety and tosylate anion out of the β-CD barrel. Due to the electrostatic field of the ions, the β-CD exterior protons have larger shifts than the interior protons. On the other hand, the interaction between the β-CD and included DAST moiety is Van der Waals force, which is far weaker than the Colombian force, thus the shifts are almost neglectable.
Figure S 3. PL quantum yield measurement results of DAST MPs, DAST@β-CD MPs, and
DAST@β-CD CMCs.

In fluorescence quantum yield investigation, we used the Hamamastu Absolute Quantum Yield
Spectrometer (model: C11347, PL measurement wavelength range from 300 nm to 950 nm),
which performs absolute measurement by directly counting absorbed and emitted photons. A
quartz holder was used for the measurements and its effect was eliminated by the reference scan
before the execution of sample measurements.
The polarization dependence of the DAST@β-CD MPs was measured using a SHG microscope. A femtosecond (fs) laser with a wavelength of 1030 nm, repetition rate of 300 kHz, and pulse width of 800 fs was employed as the light source. A polarization beam splitter (PBS) was utilized to separate the incident light into two vertically linear polarized light beams. Half-wave plate (HWP) and quarter-wave plate (QWP) were used to continuously vary the polarization direction of the incident light for SHG study. The SHG signal from the crystal was collected by an objective, 50×, NA=0.75 (Zeiss, Epiplan) and detected using a spectrometer with 0.226 nm resolution (Idea optics PG2000 pro). A bandpass filter (PW-532LGP-Y25) was used to remove the excitation laser light. The polarization dependence of the incident laser was investigated by rotating the polarizer every 10° to change the polarization angle of the excitation laser. The SHG images were taken by the CCD camera (Retiga R6)
Figure S 5. The SHG spectrum of DAST@β-CD CMCs (red line) and DAST crystal powder (black line).

The pumping laser was a femtosecond (fs) laser with a center wavelength of 1030 nm, repetition rate of 40 MHz, and duration time of 50 fs. The SHG signals under an average pumping power of 1 W.
A 532 nm pumping source was generated by a picosecond (ps) pulse lase (wavelength 532 nm, repetition 100 Hz, and pulse duration 10 ps). A graduated neutral-density filter was used to control the pumping intensity. The position of the convex lens was altered to adjust the size of the laser spot (2 mm) onto the sample to ensure that the whole MP was excited under illumination. Emission spectra from the crystals were collected by a fiber spectrometer with a resolution of 0.226 nm (Idea optics PG2000pro). The lasing images were taken by a CCD camera (Retiga R6).
**Figure S 7.** PL spectrum of a DAST MP. The well-regulated small peaks on the spectrum are the Fabry-Pérot resonating signals of the MP.

**Figure S 8.** Ablation of DAST MPs under the laser irradiation for 10 minutes (99.52 nJ/cm²).
**Figure S 9.** Laser spectra under different irradiation fields (IF) and polarizer rotation angles (RA).

**Author Contribution**

Bin. Cai conceived the experiments. Tian Tian and Bin Cai conducted SEM, H$^1$ NMR, Fluorescence lifetime and absolute fluorescence quantum yields experiments. Tian Tian and Yunkun Wang conducted the PL and Abs observations. Tian Tian, Wenjing Zhang and Bing Wang conducted SAED and TEM. Tian Tian and Chuan Xu conducted the XRS EXPERIMENT. Tian Tian, Yunkun Wang, Gongjie Xu, and Guanjun You conducted the lasing experiment. Tian Tian, Yunkun Wang, Cheng Fan, Min Li and Shuai Yuan conducted SHG and TPEF experiment. Bin Cai, Tian Tian and Wenjing Zhang wrote the manuscript in collaboration with all of the other authors.