

Caged structural water molecules emit tunable brighter colors by topological excitation

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Experimental Section

Chemicals

All chemical reagents were directly used without any isolation or purification. LTA zeolite (Na-LTA, Si/Al=1~2) and Y-type zeolite (Si/Al=2~3) were ordered from Nankai University Catalyst Co., Ltd.. AgNO₃ Polyacrylic acid (PAA) were ordered from Sigma-Aldrich. NaOH, HNO₃ and all the other organic solvents were purchased from Sinopharm Chemicals Beijing Co. Beijing, China. Ultrapure water with a resistivity of 18.2 MΩ·cm was used throughout all experiments.

Synthesis

Synthesis of Ag loaded zeolite (Ag-LTA)

The silver loaded zeolite Ag-LTA(Na) was prepared by suspending 1 gram of the zeolite material (Na-LTA, Si/Al = 1~2) in 500 mL of a silver nitrate aqueous solution, the suspension was then agitated for 2 hours in the dark. The powder was recovered by filtration using a Büchner filter and washed several times with milliQ water. Then the sample was calcined overnight at 450 °C (5 °C min⁻¹) following 2 steps of 15 minutes each at 100 and 150 °C to prevent any damage in the zeolite structure during the calcination process. After heat treatment the sample was cooled under ambient conditions, allowing the sample to reach a fully hydrated state, and stored in the dark for further analysis.

Synthesis of PAA-Ag NCs:

The synthesis of luminescent PAA-Ag NCs refers to literature reports.¹ Typically, The PAA (0.4 M, 20 mL) were dissolved in an aqueous solution of 0.5 g sodium hydroxide, then the mixture was added into the freshly prepared aqueous solutions of AgNO₃ (0.1 M, 20 mL) under gentle stirring (600 rpm) at room temperature. NaOH or 0.1 M HNO₃ adjusted the pH. After 10 min, the solution was transferred into fluorescence cuvettes, followed by the UV irradiation (photoreduction) at $\lambda=365$ nm (Shanghai Jihui Scientific Analyze Instrument Co., China, ZF-20D, 24W) at various time intervals. The silver nanoclusters have good stability at low temperature and were stored at 4 °C.

Characterization

Absorption (or extinction) spectra were collected with a two-beam UV-Vis spectrometer (PERSEE TU-1901, China). DRIFTS measurement: Catalyst samples were packed into a Harrick Praying Mantis high temperature reaction chamber (ZnSe windows) mounted inside of a Thermo Scientific Praying Mantis diffuse reflectance adapter, set inside of a Thermo Scientific Nicolet iS10 FT-IR spectrometer. N₂ were flowed to the reaction chamber using Teledyne mass flow controllers. Thermogravimetric analysis (TGA) was conducted on a NETZSCH STA449F3 analyzer under air atmosphere (flow rate of 50 mL·min⁻¹). The X-ray diffraction (XRD) patterns were required using a Rigaku

Ultima Discover X-Ray Diffractometer at a wavelength of Cu K α (1.5405 Å). The SEM images were taken using Hitachi S-4800 microscope. HR-TEM images of NCs were collected with a JEOL JEM 2010 microscope operating at 200 kV. Fluorescence was measured by using a FluorMax-4 fluorimeter (Horiba, Japan). Fluorescence lifetime was measured with a homebuilt time-correlated single photon counting (TCSPC) system with a time resolution of sub-100 ps. Phosphorescence lifetime was excited with a μ F2 lamp and measured with FLS 980 spectrofluorimeter (Edinburgh Instruments). The transient absorption (TA) measurements were conducted in a femtosecond transient absorption spectrometer (Helios Fire, Ultrafast System) with pump probe beams generated with a Ti:sapphire laser system (Astrella, 800 nm, 100 fs, 7 mJ/pulse, and 1 kHz repetition rate, Coherent Inc.). A fraction of the fundamental beam was focused into the sapphire to generate a white light continuum probe beam from 420 to 800 nm. Another fraction of the fundamental beam was used to produce pump beams via an optical parametric amplifier (OPerA Solo, Coherent Inc.), and the power was adjusted to \sim 0.3 mW by a neutral-density filter wheel. All experiments were carried out at room temperature. 2 mm cuvettes were used for all spectroscopy measurements.

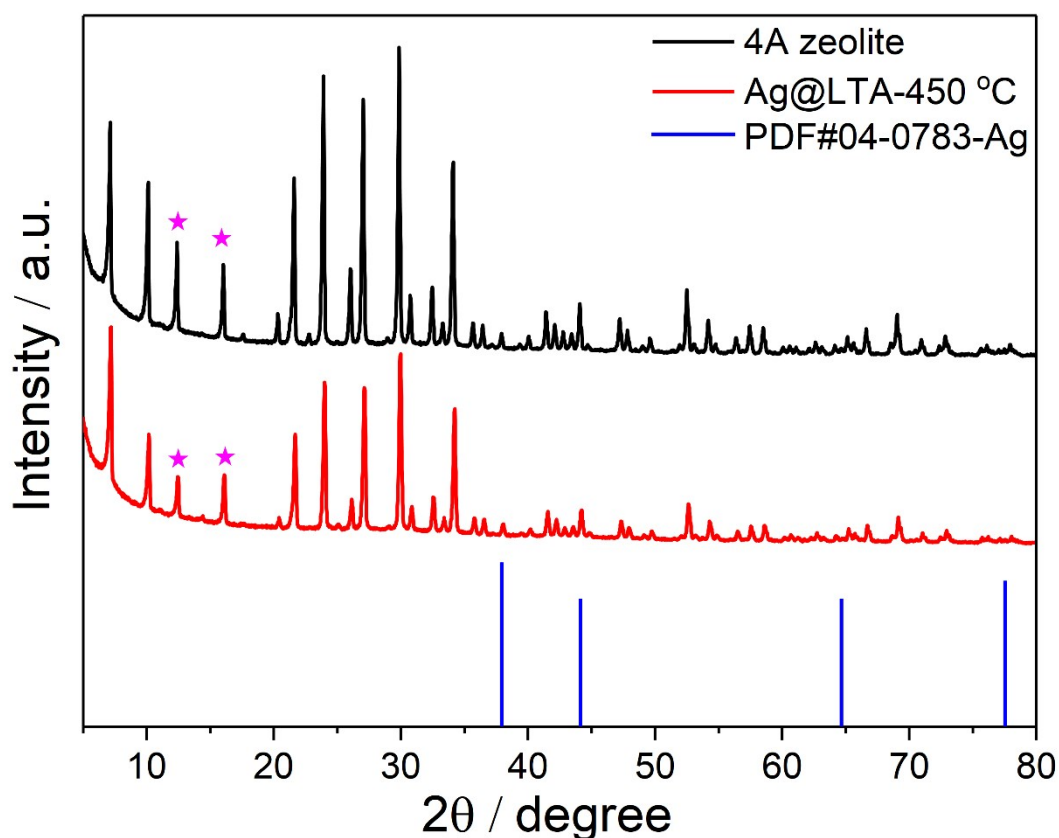


Figure S1. XRD patterns of 4A zeolite and Ag@LTA-450 °C.

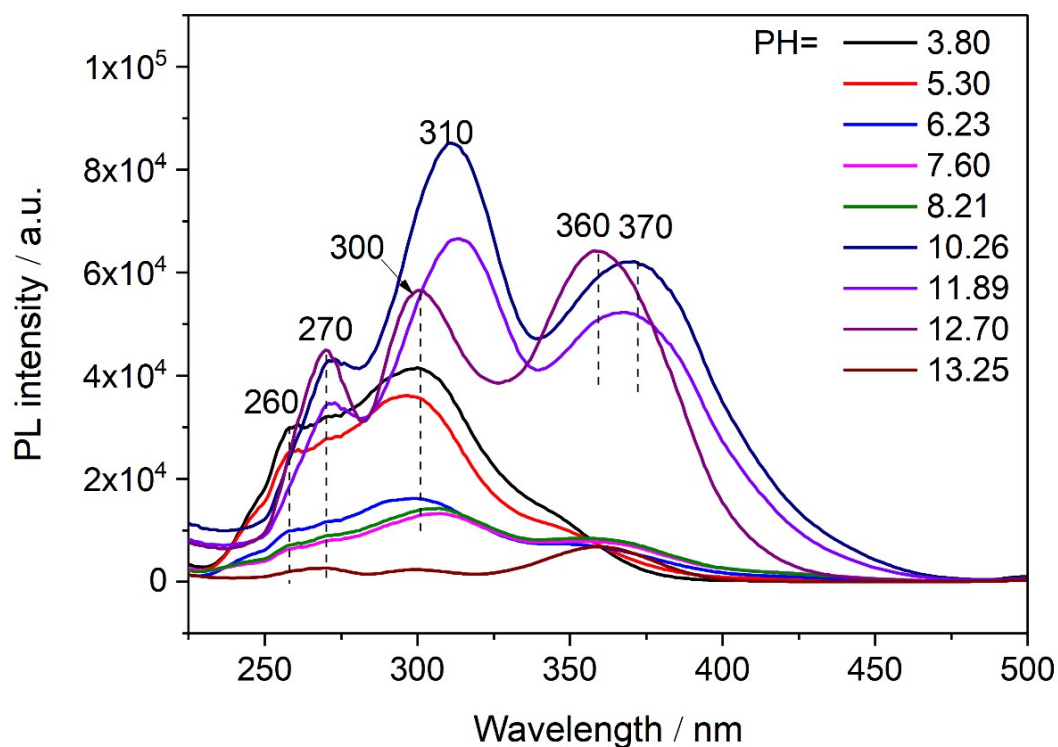


Figure S2. Excitation spectra of Ag@LTA-450 °C solution at different pH condition.

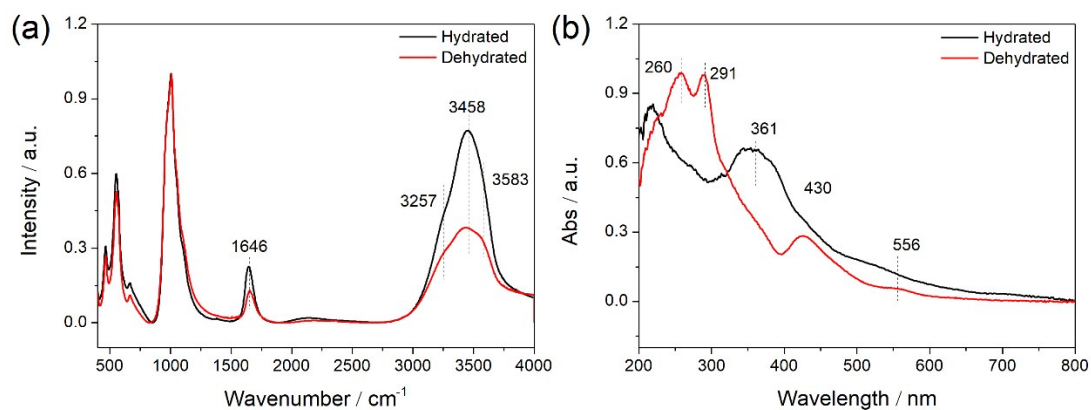


Figure S3. FTIR spectra (a) and UV-Vis absorption spectra (b) of hydrated Ag@LTA-450 °C under hydrated and dehydrated state.

Table S1. XPS peak parameters for the O (Fig. 1g) and Ag (Fig. 1h) states of Ag@LTA-450 °C.

Atom	Item	binding energy	content
O _{1s}	Ag ⁺ -OH ⁻	530.6 eV	16.4%

	Ag ⁺ -H ₂ O	531.7 eV	17.8%
	Si-O-Si	532.8 eV	65.8%
Ag _{3d}	Ag ⁺	368.3 eV	56.5%
	Ag ⁰	370.1 eV	43.5%

Table S2. Lifetime parameters of Ag@LTA-450 °C in water and DMSO solution. The steady state optical characterizations are presented in Figure 2, b and e.

Item	α_1	α_2	α_2	τ_1	τ_2	τ_3	χ^2	Average lifetime
In water	33.4%	40.8%	25.8%	0.4ns	1.9ns	4.2ns	1.10	3.0ns
In DMSO	78.0%	22.0%	---	155.6 μ s	350.7 μ s	---	0.99	231.1 μ s

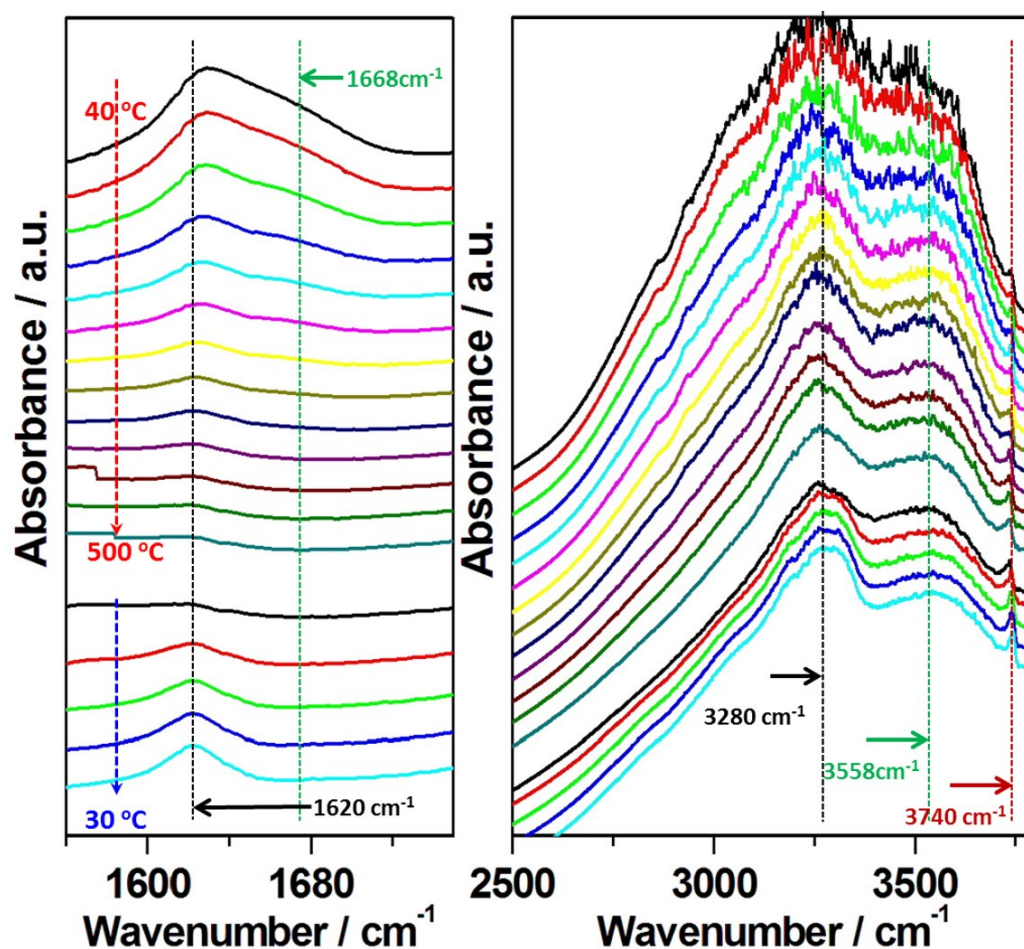


Figure S4. In situ DRIFTS of NH₄⁺@LTA-500 °C during a programmed heating and cooling process.

Table S3. Lifetime parameters of NH_4^+ -Y-type zeolite at room temperature (RT) and liquid nitrogen temperature (LNT). The steady state optical characterizations are presented in Figure 3e.

Item	α_1	α_2	τ_1	τ_2	χ^2	Average lifetime
In RT	97.4%	2.6%	1.58ns	5.29ns	1.10	3.0ns
In LNT	78.0%	22.0%	0.10s	0.94s	0.99	0.7s

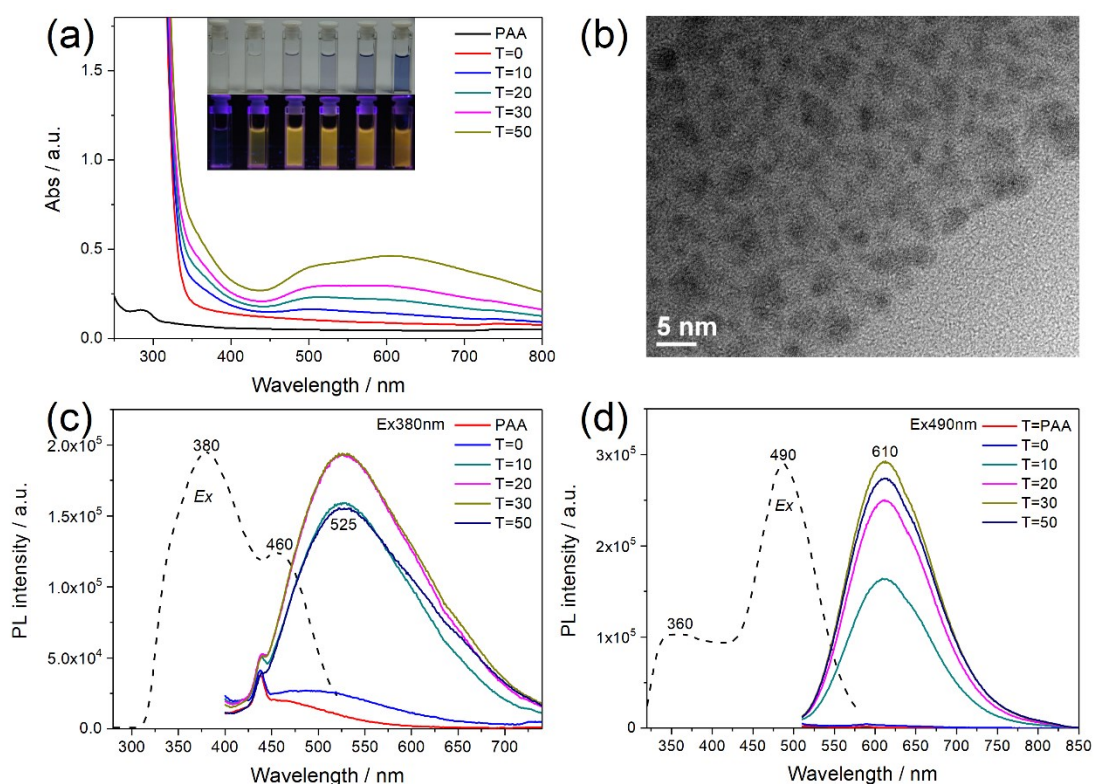


Figure S5. (a) UV-vis absorption of the freshly prepared PAA-Ag NCs at various radiation times. Corresponding PL spectra excited at 380 nm (c) and 490 nm (d). Inset images show the corresponding photographs of PAA-Ag NCs under room and UV light exposure at $\lambda = 365$ nm. (b) TEM image of freshly prepared PAA-Ag NC.

Table S4. Lifetime parameters of PAA-Ag NCs in water and DMSO solution. The steady state optical characterizations are presented in Figure 4, a and b.

Item	Em	α_1	α_2	α_3	τ_1	τ_2	τ_3	χ^2	Average lifetime
In water	610nm	5.2%	24.3%	70.5%	3.0ns	1.0 ns	0.1 ns	1.08	1.5ns
	460nm	1.1%	21.8%	77.2%	3.6ns	0.7 ns	0.2 ns	1.10	0.9ns
In DMSO	530nm	41.2%	58.8%	---	115.1 μ s	32.8 μ s	---	0.98	91.3 μ s

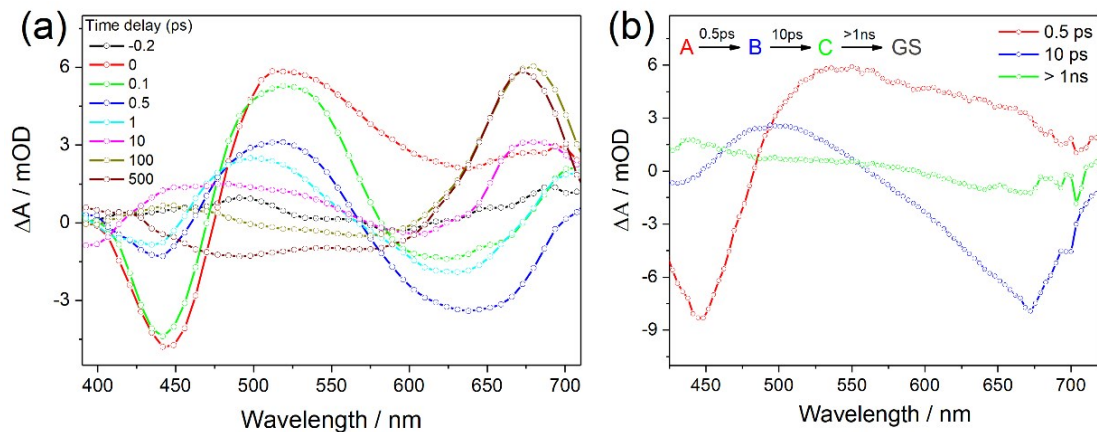


Figure S6. (a) Two-dimensional transient absorption spectra at selected time delays for PAA-Ag NCs in water solution. (b) Species-associated spectra obtained from global fitting on the TA data.

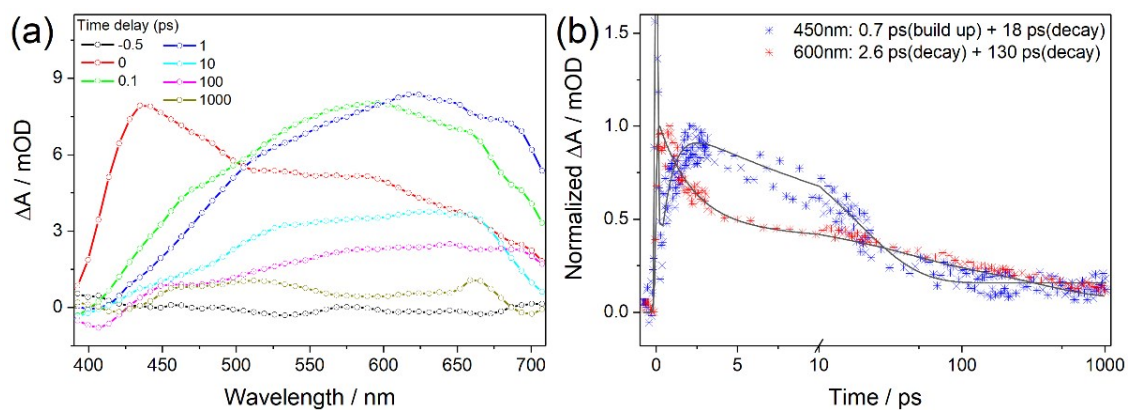


Figure S7. (a) Two-dimensional transient absorption spectra at selected time delays for PAA-Ag NCs in DMSO solution. (b) Selected decay traces and corresponding fitting, the fitting results are summarized in Table S4.

Table S5. Time constants of PAA-Ag NCs in water and DMSO solutions obtained using two components fitting. The fitting parameters was little different with global fitting results, since the global fitting need to take all wavelength-decay into consideration.

Item	probe	A ₁	τ_1 (ps)	A ₂	τ_2 (ps)	offset
In water	443nm	-0.008	0.6	0.001	350	0
	520nm	0.005	0.7	0.002	14.5	-0.0004
	590nm	-0.002	3.0	0.003	10.3	-0.0005
	680nm	-0.002	13.7	---	---	---
In DMSO	450nm	-0.003	0.7	0.0025	18	0.0004
	550nm	0.0043	3.1	0.0024	115.6	0.0008
	600nm	0.0051	2.6	0.0026	137.6	0.0009
	650nm	0.0048	2.6	0.0023	150.6	0.0012

Reference

- Chen, Y.; Yang, T.; Pan, H.; Yuan, Y.; Chen, L.; Liu, M.; Zhang, K.; Zhang, S.; Wu, P.; Xu, J., Photoemission mechanism of water-soluble silver nanoclusters: ligand-to-metal-metal charge transfer vs strong coupling between surface plasmon and emitters. *Journal of the American Chemical Society* **2014**, *136* (5), 1686-9.