Supporting Information

A novel nanoscale organic-inorganic hybrid system with significantly enhanced AIE in aqueous media

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Experimental Section

1 Materials

Gallium chloride (99.999 %) was purchased from Alfa Aesar Chemicals. Sodium Oleate, tetrahydrofuran (THF) were purchased from Sinopharm Chemical Reagent Co. Ltd. 2,4-Dihydroxybenzaldehyde, methyl 6-bromohexanoate, potassium fluoride, 2hydroxybenzaldehyde and hydrazine monohydrate were all perchased from Sigma-Aldrich.

2 Synthesis of GaOOH nanocubes

The GaOOH nanocubes were prepared by a hydrothermal method. 2 mmol sodium oleate (NaOA) was dissolved in 14 mL deionized water with magnetically stirring at room temperature for 10 min. Then 1.5 mL gallium chloride solution (0.2M) was titrated into the NaOA solution and stirred for another 10 min. The mixtures were transferred to a 20 mL Teflon-lined hydrothermal autoclave and heated at 180°C for 15 h. The products were centrifuged out and washed with deionized water 3 times. These products can be colloidally dispersed in water for further characterization.



Scheme S1 The synthetic routes for compound CM-SAA and CA-SAA.

3 Procedure for CA-SAA synthesis

Compound 1: 2,4-Dihydroxybenzaldehyde (0.8 g, 5.74mmol), methyl 6-bromohexanoate (1 g, 4.78mmol), and dried potassium fluoride (0.28 g, 5.74mmol) were dissolved in dry acetonitrile (100 mL) and heated under reflux for 18 h. After cooling to room temperature, the solution was extract with EtOAc (250 mL) and washed with water (200 mL x 3). The organic layer was dried over anhydrous Na₂SO₄ and the solvent removed in vacuo. The crude product was further purified using column chromatograph (DCM/ petroleum ether, 60/30) to give white solid product (0.49 g, 1.86mmol, yield: 39%).¹H NMR (400 MHz, CDCl₃) δ 11.47 (s, 1H), 9.71 (s, 1H), 7.41 (d, J = 8.7 Hz, 1H), 6.52 (dd, J = 8.7, 2.3 Hz, 1H), 6.40 (d, J = 2.3 Hz, 1H), 4.01 (t, J = 6.4 Hz, 2H), 3.67 (s, 3H), 2.35 (t, J = 7.4 Hz, 2H), 1.86-1.77 (m, 2H), 1.74-1.69 (m, 2H), 1.55-1.45 (m, 2H).

Compound CM-SAA: Compound 1 (0.35g, 1.31 mmol) , 2-hydroxybenzaldehyde (0.16 g,1.31 mmol) and hydrazine monohydrate (0.063mL, 1.31mmol)were dissolved in alcohol (50 mL), which was refluxed for 2 h at 80°C. After cooling to room temperature, then the solution was extract with DCM(250 mL) and washed with water (200 mL x 3). The organic layer was collected and dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude product was further purified using column chromatograph (DCM/petroleum ether, 90/20) to give orange solid (0.25g, 0.650mmol,yield: 50%). ¹H NMR (400 MHz, CDCl₃) δ 11.67 (s, 1H), 11.46 (s, 1H), 8.66 (s, 1H), 8.63 (s, 1H), 7.39-7.32 (m, 2H), 7.24-7.22 (m, 1H), 7.03-7.01 (m,1H), 6.98-6.96 (m, 1H), 6.53-6.50 (m, 2H), 4.00 (t, J = 6.4 Hz, 2H), 3.68 (s, 3H), 2.36 (t, J = 7.5 Hz, 2H), 1.86-1.78 (m, 2H), 1.73-1.68 (m, 2H), 1.54-1.45 (m, 2H).



13C NMR spectrum for CM-SAA molecules.

Compound CA-SAA: To a solution of lithium hydrate (40 mg, 96.25 µmol) in H₂O (7 mL), solution of compound CM-SAA (37 mg, 96.25 µmol) was added in THF (7 mL) and the resulting solution stirred at 40 °C for 6 h.After cooling to room temperature,the solution was extract with DCM (200 mL) and washed with water (200 mLx3). The organic layer was collected and dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude product was further purified using column chromatograph (DCM/CH₃COOC₂H₅, 80/20) to give pale yellow solid (29 mg, 78.29 µmol, yield: 82%).¹H NMR (400 MHz, DMSO) δ 12.00 (br, 1H), 11.46 (br, 1H), 11.16 (br, 1H), 8.92 (d, J = 12.9 Hz, 2H), 7.66 (d, J = 7.4 Hz, 1H), 7.55 (d, J = 8.6 Hz, 1H), 7.38 (t, J = 7.4 Hz, 1H), 6.96 (t, J = 7.6 Hz, 2H), 6.56 (d, J = 8.6 Hz, 1H), 6.51 (s, 1H), 4.01 (t, J = 6.2 Hz, 2H), 2.23 (t, J = 7.2 Hz, 2H), 1.72-1.70 (m, 2H), 1.56-1.54 (m, 2H), 1.43-1.41 (m, 2H).



13C NMR spectrum for CA-SAA molecules.

4 Procedure for CA-SAAs/GaOOH nanohybrids preparation

The obtained GaOOH NCs were dispersed in deionized water to form a 25 µg/mL colloidal suspension (without specification, all nanohybrids in the text were obtained from the GaOOH suspension with the same concentration). Different amounts of CA-SAAs were transferred into 5 mL colloidal suspension of GaOOH NCs. After ultrasonic treatment for 5 min, they could be suspended and grafted onto colloidal GaOOH NCs due to the abundant hydroxyl on GaOOH surfaces and formed colloidal CA-SAAs/GaOOH core-shell nanohybrids. By adding more CA-SAAs into the suspension with sonication, larger-size core-shell CA-SAAs/GaOOH nanohybrids were formed by CA-SAAs aggregation on GaOOH NCs.

5 Quantum yields determination

Relative quantum yields of the samples were calculated using quinine bisulfate (QBS) as the reference substance on the basis of the following expression:

$$\Phi = \Phi_R \frac{I \times A_R \times n^2}{I_R \times A \times n_R^2}$$

where Φ is the quantum yield, I is the emission areas (wavelength scale), A is the absorbance at the excitation wavelength, and n is the refractive index of the sample. The subscript R denotes the reference QBS. A solution of QBS was prepared in 1 N H₂SO₄ as previously described. The quantum yield of QBS was determined to be 0.55.

6 Characterization and measurements

The crystallographic phase of GaOOH was determined by an X-Ray diffract meter (Rigaku D/Max 2200PC) with graphite monochromator and Cu K α radiation (λ = 0.1548 nm) at 40 kV and 20 mA . The XRD patterns were obtained over the scanning range of 10°-80° at room temperature with a scan rate of 10° min⁻¹. The morphology and size were characterized by a transmission electron microscopy (TEM, JEM-100CXII) with accelerating voltage of 80 kV and a field emission scanning electron microscopy (FE-SEM, ZEISS SUPRSTM55) with accelerating voltage of 5 kV. Size distributions of colloidal nanocubes and the CA-SAAs/GaOOH nanohybrids were performed using ZetaPALS Instruments (Brookhaven). The PL spectra were measured on a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies) with the excitation wavelength of 350 nm. The UV-Vis adsorption spectra were recorded on a Cary Series UV-Vis spectrophotometer (Agilent Technologies). Time-correlated single-photon counting (TCSPC) technique was used to measure the PL time dacay by FLS920 (Edinburge Instruments Ltd.) with EPL-375 Picosecond Plused Diode Laser (Edinburge Instruments Ltd.) at the wavelength of 377.8 nm with pulse duration of 72.5 ps.

7 GaOOH nanocubes characterization

As-synthesized GaOOH nanocubes can be colloidally dispersed in aqueous media. The electron microscopy images, the corresponding size distribution histogram and the XRD pattern of GaOOH nanocubes are shown in Fig. S1. Highly crystalline and monodisperse GaOOH nanocubes with homogeneous morphology and a narrow size distribution centered at ~73 nm were observed, as shown in Fig. S1 a, b and c. The selected area electron diffraction (SAED) pattern in the inset of Fig. S1a reveals the highly crystalline nature of the nanocube. The typical XRD pattern of GaOOH nanocubes is shown in Fig. S1d, all the diffraction peaks can be assigned to the orthorhombic α -GaOOH phase (JCPDS 06-0180). Sharp diffraction peaks with high intensity also reveals the high crystallinity nature of the product.



Fig. S1 Characterizations of GaOOH nanocubes (a) Low-magnification TEM image for GaOOH nanocubes with the corresponding selected area electron diffraction (SAED) pattern shown as the inset. (b) A typical SEM image for the monodispersed GaOOH nanocubes. (c) Size distribution histogram of GaOOH nanocubes. (d) XRD pattern of GaOOH nanocubes. The red lines are the standard pattern for α -GaOOH (JCPDS 06-0180).



Fig. S2 (a) IR spectra of CA-SAA molecules (red line), CA-SAAs/GaOOH nanohybrids (black line) and pure GaOOH nanocubes (green line). (b) Partial enlarged view of the IR spectra to compare the hydroxyl stretching band of pure CA-SAAs and the CA-SAAs/GaOOH nanohybrids.



Fig. S3 DLS size distributions of CA-SAAs/GaOOH nanohybrids with 0, 65, 125, 185 nM CA-SAA concentrations.



Fig. S4 DLS size distributions of (a) CA-SAAs/GaOOH nanohybrids (the sharp peak on the left) and CA-SAAs/GaOOH nanohybrid aggragations (the broad peak on the right) with 400 nM CA-SAAs. (b) DLS result for the aggregated CA-SAAs/GaOOH nanohybrids redispersed by adding 5 mL GaOOH NC suspension into the system under sonication.



Fig. S5 DLS diameters of the CA-SAAs/GaOOH nanohybrids prepared with different CA-SAA concentrations.



Fig. S6 Changes of the PL intensities upon different CA-SAA contents. Red line indicates increasing CA-SAA concentration and blue line indicates decreasing the CA-SAA concentration upon adding dispersed NCs.



Fig. S7 Absorption and emission spectra of 50 nM CA-SAA molecules in pure THF solvent.



Fig. S8 PL intensity for CA-SAA in pure THF (blue line) and NCs/H2O system (red line) as a function of CA-SAA molecule concentration.



Fig. S9 Compare the PL enol-type emissions of CA-SAAs in the NCs/H₂O system and 2% THF/H₂O system.



Fig. S10 DLS size distributions of CA-SAAs aggregations in the THF/H_2O mixtures with CA-SAA concentrations as 25, 65, 125, 180 nM.



Fig. S11 PL intensity in THF/H_2O (blue line) and NCs/H_2O (red line) systems as a function of varied pH values.



Fig. S12 PL emission spectra for CA-SAAs/GaOOH nanohybrids (a) and CA-SAA nanoaggregates (b) in THF/H₂O solution with different THF contents.

TOC

A novel aggregation-induced emission (AIE) system is obtained by grafting carboxyl group conjugated AIE molecules onto monodispersed colloidal GaOOH nanocubes.

