Supporting Information

Super-long salicylideneaniline semiconductor nanobelts by magnetic nanoparticle assisted self-assembly process for luminescence thermochromism

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S1 Experimental section.

1.1 Reagents. 4-aminobenzoic acid and salicylaldehyde were procured from Chemical Reagent Company. Ferrocene (Fe(C₅H₅)₂, ≥98%), hydrogen peroxide (H₂O₂, 30%), and acetone (C₃H₆O) (≥99%) were of analytic grade from the Shanghai Chemical Factory, China. All of the reagents and solvents were of analytical reagent grade and used as received.

1.2 Preparation of 4-(2-hydroxybenzylideneamino)-benzoic acid (HBA). 4-(2-hydroxybenzylideneamino)-benzoic acid (HBA) were prepared according to a reported process with some modifications.¹ Briefly, 5.42 g (0.0396 mol) of 4-aminobenzoic acid was dissolved in 120 mL of ethanol, and 4.83 g (0.0396 mol) of salicylaldehyde in 80 mL of ethanol was added rapidly under magnetically stirring. After several minutes, the final yellow product started to precipitate. The mixture was totally stirred 2 h at room temperature, and the precipitated solid was isolated by filtration through a glass frit. The product was washed with ethanol and dried in a vacuum oven at 313 K. The yellow 4-(2-hydroxybenzylideneamino) benzoic acid (HBA) was obtained. In order to identify the structures of HBA, the ¹H NMR
spectra were recorded in DMSO-d6. The $^1$H NMR results confirmed the existence of five kinds of H in the molecular structure of the product (Figure S1). $^1$H NMR (DMSO): $\delta$/ppm: 12.70 (br s, 1H), 9.00 (s, 1H), 8.01 (d, 2H), 7.70 (d, 1H), 7.48 (d, 2H), 7.43 (d, 1H), 7.00 (t, 2H). Furthermore, HBA could also be revealed by FTIR (Figure S2). It could be seen that a series of characteristic bands 1679 cm$^{-1}$ (C=O aryl acid band), 1600 cm$^{-1}$ (C=C aromatic valence), 1569 cm$^{-1}$ (C=C aromatic valence), 1287 cm$^{-1}$ (C-O band), 860 cm$^{-1}$ (aromatic 1, 4-disubstitution), 751 cm$^{-1}$ (aromatic 1, 2-disubstitution) in the spectra of HBA, which coincided with those reported in the literature for the HBA. Actually, the results were essentially the same as previous reported.$^{2,3}$

1.3 Synthesis of magnetite nanoparticle. In a typical synthesis, ferrocene (0.30 g) was dissolved in acetone (30 mL). After intense sonication for 30 min, 1.50 mL of hydrogen peroxide was slowly added into the above mixture solution, which was then vigorously stirred for 30 min with magnetic stirring. After that, the precursor solution was transferred to the Teflon-lined stainless autoclave with a total volume of 50.0 mL, and then heated to and maintained at 240 °C. After 72 h, the autoclave was cooled naturally to room temperature. After intense sonication for 15 min, the products from the Teflon-lined stainless autoclave were magnetized for 10 min by a magnet with 0.20 T, and the supernatant was discarded under a magnetic field. The precipitates were then washed with acetone three times to remove excess ferrocene. Finally, the black products were dried at room temperature in a vacuum oven.$^4$
Figure S1. $^1$H NMR spectrum of 4-(2-hydroxybenzylideneamino)-benzoic acid (HBA).

Figure S2. FTIR spectra of 4-(2-hydroxybenzylideneamino)-benzoic acid (mHBA).
Figure S3. XRD patterns of magnetite-carbon nanoparticles (MCNP) and standard pattern of iron oxide (JCPDS 88-0315).

Figure S4. Experimental absorption and fluorescence emission spectra of 4-(2-hydroxybenzylideneamino)-benzoic acid mHBA at room temperature (295 K).
S2 Crystal data and structure refinement parameters of HBA.

Table S1  Crystal data of 4-(2-hydroxybenzylideneamino)-benzoic acid (HBA).

| Property               | Value               |
|------------------------|---------------------|
| chemical formula       | C_{14}H_{11}NO_{3}  |
| formula weight         | 241.24              |
| temp/K                 | 293(2)              |
| wavelength/Å            | 1.54186             |
| cryst syst             | monoclinic          |
| space group            | P21/c               |
| a/Å                    | 5.8687(3)           |
| b/Å                    | 4.7866(2)           |
| c/Å                    | 41.133(2)           |
| β/deg                  | 92.208(3)           |
| vol/Å³                 | 1589.5(3)           |
| Z                      | 4                   |

Figure S5. Molecular packing diagram of enol HBA according to crystal data from Table S1.
S3 The theoretical data of HBA using DFT method.

Table S2. Optimized geometries and molecular orbitals (HOMO and LUMO) of HBA (cis-enol, cis-keto and trans-keto) for both the ground and first excited states.

|     | Enol          | Cis-keto       | Trans-keto     |
|-----|---------------|----------------|----------------|
| Optimized Geometry | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) |
| LUMO Ground State $S_0$ | ![Image](image4.png) | ![Image](image5.png) | ![Image](image6.png) |
| HOMO Ground State $S_0$ | ![Image](image7.png) | ![Image](image8.png) | ![Image](image9.png) |
| LUMO Excited State $S_1$ | ![Image](image10.png) | ![Image](image11.png) | ![Image](image12.png) |
| LUMO Excited State $S_1$ | ![Image](image13.png) | ![Image](image14.png) | ![Image](image15.png) |
S4 Quantum yields of mHBA at different temperatures.

Quantum yield of HBA at room temperature is measured on a spectrofluorometer equipped with an integrating sphere. Quantum yield of HBA at the low temperatures is determined by comparison with that at room temperature \( (rt) \), using the following equation:

\[
\phi_x = \phi_{rt} \frac{\int f_x(\lambda) d\lambda}{\int f_{rt}(\lambda) d\lambda}
\]  

(1)

where \( \phi_x, \phi_{rt} \) is the fluorescence quantum yield at \( x \) K and \( rt \) respectively, and \( f_x(\lambda), f_{rt}(\lambda) \) is the fluorescence spectrum at \( x \) K and \( rt \), respectively. This equation is based on the following assumptions: (1) The sample is excited at the same wavelength and with the same intensity both at a low and the room temperature, and (2) the absorbance at the excited wavelength is the same at both of the temperatures. HBA shows temperature-dependant luminescence with a very high quantum yield (Table 1) over a wide temperature range (8 to 295 K). This intense thermosensitive emission over a wide range conquers the limitation that high temperatures induce a low signal/noise ratio, thus suggesting that mHBA is an excellent candidate for a reliable and absolute luminescent temperature sensor.

Table S3. Quantum yields of mHBA at different temperatures.

| T(K) | 8   | 25  | 40  | 55  | 70  | 85  | 100 | 115 | 140 | 165 | 190 | 215 | 240 | 265 | 295 |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| \( \phi \) | 0.87 | 0.71 | 0.95 | 0.96 | 0.94 | 0.87 | 0.86 | 0.80 | 0.65 | 0.53 | 0.39 | 0.30 | 0.21 | 0.16 | 0.11 |
Figure S6. Fluorescence intensity of mHBA (a) at 520 and 550 nm, mHBA-L (b) at 521, 551 and 585 nm as a function of temperature at 8-295 K.
The models of temperature-dependent fluorescence intensity of mHBA and mHBA-L.

**Figure S7.** Schematic diagram of the electronic energy states in mHBA; The electronic transition at different energy levels; The arrow shows the magnitude and direction of the dipole moment transition.

According to this model as show in Figure S7, the temperature dependent fluorescence intensity can be expressed as equation 1: ⁶

\[
I_T = I_0 \frac{\sum_{i=1}^{E_1} A_j \exp\left(-\frac{E_{1j}}{k_B T}\right)}{\sum_{j=1}^{E_1} C_j \exp\left(-\frac{E_{1j}}{k_B T}\right)}
\]  \hspace{1cm} (2)

Where, \( k_B \) is the Boltzmann constant; \( E_{1j} \) describes the energy difference between given excited states \( E_j \) and the lowest excited state \( E_1 \) for processes that increase the fluorescence intensity with increasing temperature; Assume the total number of the molecules of a given material is \( n \), and the number of molecules in the state \( E_j \) is \( n_j \), then where \( n_0 \) is the number of the molecules in the ground state \( E_0 \). \( K_{rj} \) and \( K_{nrj} \) are the radiative and non-radiative decay rates of excitons on \( E_j \) states, respectively, which are constant independent of temperature. \( K_{up} \) is the total pumping rate from ground state to all excited states; is the ratio of radiative decay rates of excitons in the \( E_j \) state to that in the \( E_1 \) state; is constant parameter related to the pump rate and
total decay rate of $E_j$ and $E_I$ excitons; is coefficient proportional to the total number of molecules and related to the pump rate and the total decay rate of the excitons in the lowest excited state $E_I$:

$$n_1 : n_2 : n_3 : \ldots : n_i = 1 : \ldots :$$  \hspace{1cm} (3)

and

$$I_1 : I_2 : I_3 : \ldots : I_i = 1 : \ldots :$$  \hspace{1cm} (4)

where $I_i$ represents the PL intensity originated from the recombination of excitons in state $E_j$.

**Table S4** Fitting parameters and excited states in mHBA and mHBA-L.

| Sample   | Exciton label | $E_{ij}$ (emV) |
|----------|---------------|----------------|
|          | 1             | 1              | 0             |
|          | 2             | 0.93           | 2.1           |
|          | 3             | 0              | 17            |
|          | 4             | 1107           | 104           |
| HBA      | 1             | 1              | 0             |
|          | 2             | 4.16           | 1.5           |
|          | 3             | 0              | 22            |
|          | 4             | 0              | 142           |
| mHBA-L   | 1             | 1              | 0             |
|          | 2             | 2.3            | 24            |
|          | 3             | 24             | 22            |
|          | 4             | $2.9 \times 10^4$ | 142           |

**Figure S8.** Percentages of the three types of excitons in mHBA (a) and mHBA-L (b) vs. temperature according to equation (2) in the Supporting Information S5.
Figure S9. Temperature dependence of the temperature-sensitive (Sint) of mHBA, which is calculated according to the equation 
\[ S_{\text{int}}(T) = \left| \frac{\partial (I_{\text{exc}} / I_{\text{tot}})}{\partial T} \right|. \]

Figure S10. The image of products with mHBA nanobelts and magnetite nanoparticles.
References

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