Supporting information of

\[(\text{AEDPH}_3)\cdot(\text{BtaH})\]: A novel supramolecular plaster with formaldehyde adsorption and formaldehyde/ultraviolet ray-induced luminescence switching performance

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List:

S1. Experimental Section.

Table S2. Hydrogen bonds of plaster 1 (Å and deg.).

Table S3. Concentrations of HCHO in the adsorption bottle after different times.

Figure S4. Reaction of Bta and HCHO.

Figure S5. Plaster boards (a) and chalk (b) made from plaster 1.

Figure S6. 2D supramolecular layers constructed by AEDPH$_3$ anions in plaster 1.

Figure S7. IR spectrum of plaster 1.

Figure S8. TG/DTG curve of plaster 1 in air. Real line: TG curve; Dot: DTG curve.

Figure S9. $^1$H NMR spectrum of compound 2.

Figure S10. $^{13}$C NMR spectrum of compound 2.

Figure S11. 3D supramolecular structure of compound 3 viewed at a axis.

Figure S12. Schematic diagram of experimental facility for HCHO adsorption measurement.

Figure S13. Solid-state emission spectra of pure Bta-MeOH (red) and Bta-MeOH irradiated by 254 nm ultraviolet ray for 6 hours (blue) ($\lambda_{ex} = 310$ nm).

Figure S14. PXRD patterns of pure Bta-MeOH (black) and Bta-MeOH irradiated by 254 nm ultraviolet ray for 18 hours (red).

Figure S15. 1D supramolecular chain constructed by Bta-MeOH in compound 2.

Figure S16. Proposed mechanism of the luminescence switching.

S1. Experimental Section.

**General materials and measurements.** The AEDPH$_4$ was prepared according to the DE Patent 2625767.[1]

The Bta (99 % purity) and hemihydrate gypsum (CaSO$_4$·0.5H$_2$O, 99 % purity) were purchased from Sinopharm Chemical Reagent Co., Ltd. The formalin (36 % HCHO water solution) was purchased from Hubei University Chemical Plant. The elemental analysis data (C, H, N) were obtained from a Perkin-Elmer 240B elemental analyzer. Infrared (IR) spectra were recorded as KBr pellets at a range of 400-4000 cm$^{-1}$ on a Nicolet 5700 FT-IR spectrometer with a spectral resolution of 4.00 cm$^{-1}$. Thermogravimetric analysis (TGA) was carried out with a NETZSCH STA 449C at a heating rate of 10K/min in air. The powder X-ray diffraction (PXRD) patterns were obtained with a Bruker D8 advanced diffractometer with Cu Ka radiation ($\lambda = 1.54056$
Å) at 40 kV and 40 mA at the scan speed of 4°/min (20). The photoluminescence spectra in solid state were examined with a HITACHI F-4500 Fluorescence Spectrophotometer equipped with a Xenon lamp as the excitation source in the range of 330–600 nm. The absorbances in HCHO-acetylacetone spectrophotometry were measured by a TU-1901 ultraviolet-visible spectrophotometer with a wavelength of 412 nm. \(^{1}\)H and \(^{13}\)C NMR spectra of Bta-MeOH were recorded on a Bruker Avance DRX-400 spectrometer.

**Synthesis and process of the supramolecular plaster.** Similar to other supramolecular plasters reported previously, plaster 1 is simple to synthesize and process at room temperature and atmospheric pressure:

1. **Milling:** A mixture of AEDPH\(_4\) and Bta with 1:1 mole ratio was grinded for 30 seconds, gaining a kind of white powder.

2. **Figuration:** Then with strong agitation, distilled water with 0.93 × amount (mass ratio) to the mixture was added. At this time, the mixture was a kind of milky suspension, which could be poured in a mould to shape into any forms.

3. **Induration:** After the distilled water had been added for 25 s, the suspension began to coagulate. It would indurate gradually in the following 75 seconds and finally turned into a hard and white solid, which could be made into board, artwork, coating, chalk, and etc (See Figure S5). The solid will lose almost all the water molecules gradually when placing at room temperature for 7 days, and finally form an anhydrous supramolecular plaster.

**Example of the synthesis of plaster 1.** A mixture of 20.50 g AEDPH\(_4\) (0.1 mol) and 11.91 g Bta (0.1 mol) was grinded in a muller for 30 seconds. Then 30 mL distilled water was added to the mixture with a strong agitation to form suspension. The suspension was poured in 0.5×1×10 cm and 2×2×2 cm moulds and completely coagulated after 100 seconds. The samples produced in this method were preserved in the laboratory condition for 24 h. After this period, they were demoulded and deposited at room temperature for 7 days, and then tested for flexion and compression.

**Synthesis of single crystal of (AEDPH\(_3\))(BtaH)-(H\(_2\)O) (1).** A mixture of 0.1025 g AEDPH\(_4\) (0.5 mmol), 0.1190 g Bta (1 mmol) and 3 mL distilled water was sealed in a small glass vial and heated in an oven at 100 °C for 3 days. Then this vial was taken out and the mixture was filtrated immediately as it was hot. Colorless crystals for X-ray crystallographic analysis were obtained and dried in air. Yield: 27 % (based on Bta). Elemental analysis calculated (%) for C\(_{8}\)H\(_{14}\)N\(_{4}\)O\(_{6}\)P\(_{2}\): C 29.64, H 4.35, N 17.28, found: C 29.59, H 4.25, N 17.27.

The single crystals of 1 were obtained from the reaction of 1 mmol Bta and 0.5 mmol AEDPH\(_4\). However, because the selectivity in the crystallization process, only 0.5 mmol Bta could access the crystal lattice of 1, while the other 0.5 mmol Bta was remained in the solution. In fact, reaction of 0.5 mmol Bta and 0.5 mmol AEDPH\(_4\) at 100 °C could also afford compound 1, but compound 1 synthesized by this method was a kind of micro-crystal which could not characterized by single crystal diffraction (SCD).

Based on the PXRD patterns of the supramolecular plaster and single crystal 1 (See Figure 1a), the locations of the diffraction peaks are completely the same for the as-synthesized supramolecular plaster and single crystal 1. So the structure of supramolecular plaster is the same as single crystal 1.

**Synthesis of crystalline phase A and Bta-MeOH crystal (2).** A mixture of 1 g supramolecular plaster powders and 1mL formalin was sealed in a small glass vial, and then placed at room temperature for 24 hours. The result powders were crystalline phase A and characterized by PXRD. And then, 10mL acetone was added.
to phase A and stirred for 10 minutes. The mixture was filtrated and the filtrate was vaporized at room temperature for 1 day. Colorless single crystals were obtained and characterized. $^1$H NMR (300 MHz, acetone-d$_6$) $\delta = 8.25$ (d, 1H, $J = 8.7$ Hz), 7.89 (d, 1H, $J = 8.1$ Hz), 7.58 (t, 1H, $J = 7.7$ Hz), 7.43 (t, 1H, $J = 7.7$ Hz), 6.26 (bs, 1H, hydrogen bonded –OH), 6.17 ppm (s, 2H, $-\text{CH}_2$), 2.90 ppm (bs, free –OH); $^{13}$C NMR (75.5 MHz, acetone-d$_6$) $\delta =$ 146.5, 132.9, 127.7, 124.2, 119.6, 110.9, 70.9 ppm. Elemental analysis calculated (%) for C$_7$H$_7$N$_3$O: C 56.37, H 4.73, N 28.17, found: C 56.19, H 4.69, N 27.32.

Synthesis of anhydrous AEDPH$_4$ crystal (3). A mixture of 0.1025 g AEDPH$_4$ powder (0.5 mmol), 0.0390g 2,2'-bipyridyl (0.25 mmol) and 1mL distilled water was sealed in a small centrifuge tube, and then heated at 80°C for 5 days. Colorless crystals for single crystal diffraction analysis were obtained. Yield: 76 % (based on the AEDPH$_4$ powder). Elemental analysis calculated (%) for C$_2$H$_9$NO$_6$P$_2$: C 11.71, H 4.42, N 6.83, found: C 11.70, H 4.45, N 6.89.

X-ray crystallographic analysis. Crystallographic measurements of compounds 1-3 were manipulated on a Bruker SMART CCD area-detector diffractometer. All the structures were analyzed at 273 K using graphite monochromated Mo Kα radiation ($\lambda =$ 0.71073 Å) and solved by direct methods using SHELXS-97 program.\textsuperscript{[4]} Non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on $F^2$ using SHELXL-97 program. Hydrogen atoms H2, H4, H9 and H10 in compound 1, as well as H1, H2, H3 and H6 in compound 3 were obtained from difference Fourier maps, and the other hydrogen atoms were geometrically fixed. Crystal data of 1 (C$_8$H$_{14}$N$_4$O$_6$P$_2$): M$_w =$ 324.17, Triclinic, space group P-1, $a =$ 5.448(2) Å, $b =$ 9.366(3) Å, $c =$ 12.918(4) Å, $\alpha =$ 94.059(4) º, $\beta =$ 95.706(4) º, $\gamma =$ 99.278(4) º, $V =$ 644.8(3) Å$^3$, $Z =$ 2, $D_{\text{calc}} =$ 1.670 g·cm$^{-3}$, $\mu =$ 0.370 mm$^{-1}$, $R_1 =$ 0.0674, $wR_2 =$ 0.1753 (all data), GOOF = 1.030. Crystal data of 2 (C$_7$H$_7$N$_3$O): M$_w =$ 149.16, Monoclinic, space group P2(1)/c, $a =$ 7.503(2) Å, $b =$ 9.923(3) Å, $c =$ 9.413(3) Å, $\alpha =$ 90 º, $\beta =$ 95.388(4) º, $\gamma =$ 90 º, $V =$ 697.7(3) Å$^3$, $Z =$ 4, $D_{\text{calc}} =$ 1.420 g·cm$^{-3}$, $\mu =$ 0.101 mm$^{-1}$, $R_1 =$ 0.0627, $wR_2 =$ 0.1347 (all data), GOOF = 1.091. Crystal data of 3 (C$_2$H$_9$NO$_6$P$_2$): M$_w =$ 205.04, Triclinic, space group P-1, $a =$ 5.5780(4) Å, $b =$ 5.9177(4) Å, $c =$ 11.399(2) Å, $\alpha =$ 82.368(2) º, $\beta =$ 82.198(2) º, $\gamma =$ 78.166(8) º, $V =$ 362.72(5) Å$^3$, $Z =$ 2, $D_{\text{calc}} =$ 1.877 g·cm$^{-3}$, $\mu =$ 0.586 mm$^{-1}$, $R_1 =$ 0.0334, $wR_2 =$ 0.0878 (all data), GOOF = 1.073. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Centre as Supplementary Publication No. CCDC 782031 (1), 805173 (2), and 682746 (3).

Measurements of the mechanical properties. The bending strength and compressive strength were measured by a MZ-400B universal material testing machine. The test of bending strength was carried out on the samples of dimensions 0.5×1×10 cm. The test of compressive strength was carried out on the samples of dimensions 2×2×2 cm. All tests were carried out in a laboratory condition at 20±2 °C and around 65 % relative humidity. Each result given in Table 1 represents the average measurement performed on three samples of the same composition.

In order to investigate the mechanical properties of plaster 1 after adsorbing formaldehyde, sample of plaster 1 were sealed in a 15 cm desiccator with 100 μL formalin for 24 hours, and then tested for flexion and compression.

Measurements of the formaldehyde (HCHO) adsorption performance. The HCHO adsorption experiment was carried out in a facility which is shown in Figure S11. The experimental facility mainly includes the following parts: (1) a compressed air cylinder, which can provide air flow; (2) a gas generating bottle, which can generate gaseous HCHO by the thermal decomposition reaction of triformol with phosphoric...
acid; (3) three 500mL adsorption bottles with gas sampling tube, which are used for HCHO adsorption. Before the experiment, 16 g plaster and 16 g gypsum plaster (CaSO₄·2H₂O) were spin-coated onto the side wall of one adsorption bottle and dried, respectively; (4) several two-way valves, which can control the sealing/unsealing of the adsorption bottle.

At the beginning of the experiment, all the two-way valves were open. A certain amount of triformol and phosphoric acid were added to the gas generating bottle, and then heated at 90 °C in an oil bath for 10 minutes. The triformol was completely decomposed and formed pure gaseous HCHO. Then compressed air passed through the gas generating bottle for 20 minutes. With the help of compressed air, the gaseous HCHO passed through the three adsorption bottles with equal flow velocity. After that, all the two-way valves were closed at the same time, and all the adsorption bottles were sealed. At this time, there was a certain amount of gaseous HCHO in the adsorption bottle, and the initial concentrations of HCHO in the three adsorption bottles were the same. By controlling the velocity of air flow and the quality of triformol, the initial concentration of HCHO could be changed.

After a certain time, 5 mL gas in the adsorption bottle was taken suction from the gas sampling tube. The HCHO in the sample gas was absorbed by distilled water, and then quantitatively measured by acetylacetone spectrophotometry.

The acetylacetone spectrophotometry is a regular method for measuring HCHO. In this method, HCHO reacts with acetylacetone and ammonia, forming 1,1’-(2,6-dimethyl-1,4-dihydropyridine-3,5-diyl)-diethanone as a yellow product, whose absorbance at a wavelength of 412 nm can be quantitatively measured by spectrophotometry. The concentration of HCHO can be calculated from the value of absorbance. The concentrations of HCHO in the adsorption bottle after different times are given in Table S3. The HCHO adsorption rate is calculated as follows:

\[ R = \left( 1 - \frac{C}{C_0} \right) \times 100\% \]

- \( R \) = the HCHO adsorption rate (%)
- \( C \) = the concentrations of HCHO in the adsorption bottle after different times (10⁻⁶ g/L)
- \( C_0 \) = the initial concentrations of HCHO in the adsorption bottle (10⁻⁶ g/L)

**Ultraviolet irradiation experiment.** The ultraviolet irradiation experiment of plaster 1 with adsorbed HCHO was carried out in a light-tight box, at the top of which was a 20W/254nm UV lighting tube. The plaster samples were produced as cylindrical blocks of dimensions \( \Phi 1 \times 0.3 \) cm, and then, one drop of formalin was added to the surface of the cylindrical block, on which HCHO solution diffuses the whole surface. The processed plaster blocks were placed under the UV lighting tube with a distance of 20 cm. After a certain time, one plaster block was taken out to measure the solid state photoluminescence spectra with an excited wavelength of 310 nm.

**Example of formalin served as invisible ink for the supramolecular plaster.** This experiment was also carried out in the light-tight box with a 20W/254nm UV lighting tube at top. We chose a Chinese writing brush soaked with formalin to paint an “A” pattern on the surface of a supramolecular plaster board of dimensions \( 5 \times 5 \times 0.5 \) cm. Then the plaster board was placed under the UV lighting tube with a distance of 20 cm, and irradiated for 2 hours. After that the plaster board was taken out. In natural light, the processed plaster board didn’t seem to be changed and remained pure white; however, when placed under ultraviolet lamp (365 nm), the “A” pattern displayed strong blue luminescence and could be seen by naked eyes.
Example of plaster 1 served as a HCHO sensor. In order to detect HCHO with plaster 1, the plaster was produced as cylindrical block of dimensions Φ 1×0.3 cm. And then, 0.25 mL sample solution was slowly added to the surface of the cylindrical block, and placed at room temperature for 1 hour. The processed plaster block was placed under a 20W/254nm UV lighting tube with a distance of 20 cm, and irradiated for 10 hours. If the sample solution contained HCHO, the processed plaster blocks could display blue luminescence. The limit of detection was obtained by this method, which was defined as the signal plus three times of the standard deviations of the blank sample.

Preliminary investigation on the mechanism of the luminescence switching. It was observed that the pure Bta-MeOH (2) can generate similar luminescence switching phenomenon when irradiating by 254 nm ultraviolet ray (See Figure S13). So the luminescence switching phenomenon can be attributed to a photochemical change of compound 2.

As shown in Figure S14, the PXRD patterns of Bta-MeOH (2) before and after ultraviolet ray irradiation are almost the same, which indicates that the atomic arrangements in the structure of 2 (except the hydrogen atoms) before and after ultraviolet ray irradiation are almost the same.

From the results of SCD, in compound 2, each Bta-MeOH molecule forms hydrogen bond O1–H1⋯N3#1 (2.818(2) Å) to the neighboring Bta-MeOH molecule, generating a 1D zigzag supramolecular chain along c axis (See Figure S15). It can be expected that, by irradiating with ultraviolet ray, a proton transfer process may occur in the O1–H1⋯N3#1 hydrogen bond. In this process, the hydrogen atom (H1) of the hydroxyl group transfers to the nitrogen atom (N3#1) of the neighboring Bta-MeOH molecule, which can result a zwitterion, i.e BtaH⁺-MeO⁻ (4). It can be concluded that the PXRD patterns of 2 and 4 are almost the same because their arrangements of non-hydrogen atom are the same. Compared with 2, zwitterion 4 displays larger degree of charge transfer, so it can be expected that the luminescence emission of 4 will occur a red shift compared with that of 2.\[^{[5]}\]

In sum, we propose the luminescence switching may take place as follows: after the adsorption of HCHO, Bta-MeOH (2) is formed. By ultraviolet ray irradiation, compound 2 undergoes a proton transfer process, in which the hydrogen atom of the hydroxyl group transfers to the nitrogen atom of the neighboring Bta-MeOH molecule. Thus, zwitterion 4 (BtaH⁺-MeO⁻) is formed, and can display blue luminescence (λ\text{max} = 475 nm). However, by adding ethanol, the zwitterion 4 retransfers the proton and regenerates compound 2, so the blue luminescence disappears and the luminescence peak at ultraviolet range reappears (See Figure S16).

Table S2. Hydrogen bonds of plaster 1 (Å and deg.).

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<tr>
<th>Donor–H⋯Acceptor</th>
<th>D(Donor⋯Acceptor)</th>
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<tr>
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<td>O(6)-H(9)...O(1)#2</td>
<td>2.567(3)</td>
<td>160(4)</td>
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</table>
N(4)-H(4)...O(4)#4 2.623(3) 163(4)
N(2)-H(2)...O(5)#5 2.574(3) 164(4)

Symmetry transformations used to generate equivalent atoms: #1 x-1,y,z; #2 -x+1,-y+2,-z+1;
#3 –x+1,-y+1,-z+1; #4 x-1,y,z+1; #5 –x,-y+2,-z+1

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**Table S3.** Concentrations of HCHO in the adsorption bottle after different times.

<table>
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<th>Time(h)</th>
<th>Concentrations of HCHO in the adsorption bottle (10⁻⁶ g/L)</th>
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</table>

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**Figure S4.** Reaction of Bta and HCHO.

**Figure S5.** Plaster boards (a) and chalk (b) made from supramolecular plaster 1.
**Figure S6.** 2D supramolecular layers constructed by AEDPH$_3^-$ anions in plaster 1.

**Figure S7.** IR spectrum of plaster 1.
Figure S8. TG/DTG curve of plaster 1 in air. Real line: TG curve; Dot: DTG curve. Because plaster 1 is anhydrous, it is expected to have good thermal reliability. Thermogravimetric analysis (TGA) reveals that plaster 1 can be stable up to 184 °C in air, which is much higher than that of other supramolecular plasters. The BtaH\(^+\) cation begins to decompose at that temperature till 277 °C with a weight loss of 37.18 % (Calc. 37.04 %). Then the AEDPH\(_3\)\(^-\) anion decomposes and ends at 547 °C. The final product in 800 °C is probably assumed to be 0.5 P\(_2\)O\(_5\), and the observe total weight loss (78.04 %) is similar to the calculated value (78.11 %).

Figure S9. \(^1\)H NMR spectrum of compound 2.
Figure S10. $^{13}$C NMR spectrum of compound 2.
Figure S11. 3D supramolecular structure of compound 3 viewed at a axis.

Figure S12. Schematic diagram of experimental facility for HCHO adsorption measurement.
**Figure S13.** Solid-state emission spectra of pure Bta-MeOH (red) and Bta-MeOH irradiated by 254 nm ultraviolet ray for 6 hours (blue) ($\lambda_{ex} = 310$ nm).

**Figure S14.** PXRD patterns of pure Bta-MeOH (black) and Bta-MeOH irradiated by 254 nm ultraviolet ray for 18 hours (red).
Figure S15. 1D supramolecular chain constructed by Bta-MeOH in compound 2. In compound 2, each Bta-MeOH molecule forms hydrogen bond O1–H1···N3#1 (2.818(2) Å, dashed line) to the neighboring Bta-MeOH molecule, resulting in a 1D zigzag supramolecular chain along c axis.

Figure S16. Proposed mechanism of the luminescence switching.

Reference


