

Supporting Information

Fabrication of silver chalcogenolate clusters hybrid membranes with enhanced structural stability and luminescence efficiency

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S1. Chemicals and Materials.

Triethylene glycol dimethacrylate (TEGDMA), 2-methacrylic anhydride (MA), P(Cy)₃ and 2,5-dibromoaniline were purchased from Saan Chemical Technology (Shanghai) Co., Ltd. Butyl methacrylate (BMA) and Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide were supplied by J&K Chemical Technology (Beijing) Co., Ltd. Pyridine-4-boronic acid and Pd₂(DBA)₃ were purchased from Beijing HWRK Chem Co., Ltd. All reagents are of analytical grade and can be used directly after purchase. AgS^tBu was prepared by reaction of equivalent amounts of AgO and HS^tBu in the presence of Et₃N.

S2. Measurements.

Single-crystal X-ray diffraction (SCXRD) was performed on a Rigaku XtaLAB Pro diffractometer using Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$). Powder X-ray diffraction (PXRD) were collected on a Rigaku D/Max-2500PC X-ray diffractometer with Cu sealed tub ($\lambda = 1.54178 \text{ \AA}$). Morphology of all samples were carried out using Zeiss Sigma 500 on a scanning electron microscopy (SEM) measurement. The photoluminescence (PL) emission spectra were measured by using a Horiba FluoroLog⁻³ spectrofluorometer. The membrane was prepared by employing the CEL-M500/350 mercury lamp source purchased from Beijing China Education Au-light Co., Ltd. FTIR spectra were recorded in the 400-4000 cm^{-1} region on an Alpha Centaur FT/IR spectrophotometer (KBr pellets). ¹H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX spectrometer operating at 400 MHz. ¹³C NMR spectra were recorded on a Bruker DRX spectrometer operating at 600 MHz in DMSO. For liquid ¹³C NMR test, approximately 20 mg of nano-NH₂-Ag₁₂bpz, nano-MA-Ag₁₂bpz and Ag₁₂bpz membrane were degraded in d₆-DMSO with one drop of HCl, respectively. Luminescence decay profiles were measured on HORIBA Scientific Fluorolog⁻³ spectrofluorometer equipped with phosphor lamp, operating in time-correlated single photon counting mode (TCSPC) with a resolution time of 200 ps.

S3. Methods.

S3.1. Synthesis of ligand (NH₂-bpz).

The ligand 1,4-bis(pyrid-4-yl)benzenamine (NH₂-bpz) was synthesized according to the previous report.¹

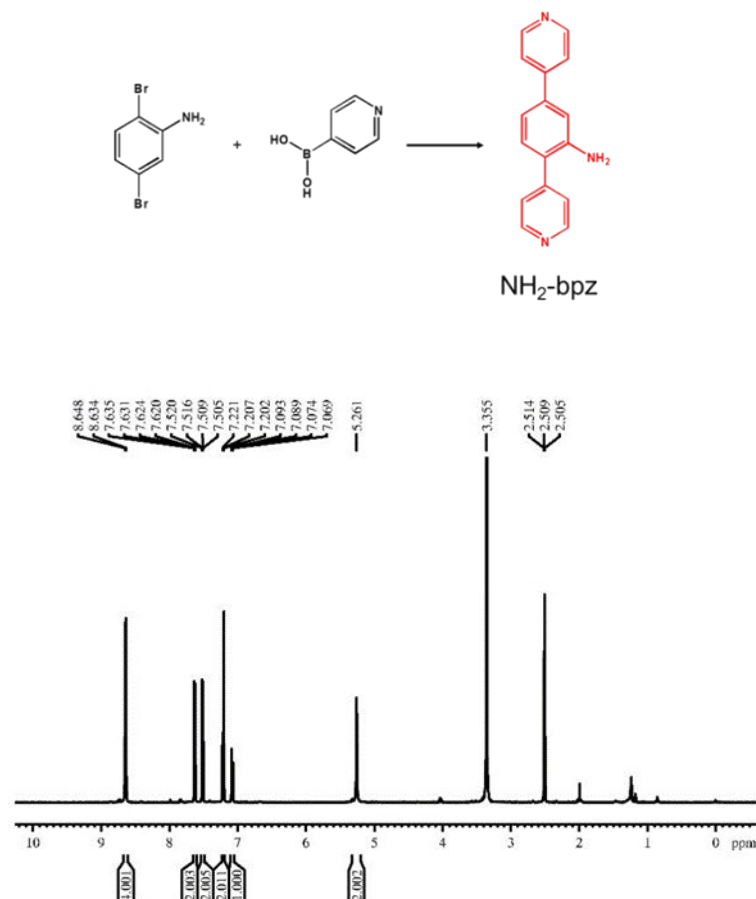


Figure S1. ¹H NMR of NH₂-bpz. (400 MHz, DMSO): δ 8.6, d, 4H; 7.6, q, 2H; 7.5, t, 2H; 7.2, t, 2H; 7.0, q, 1H; 5.2, s, 2H.

S3.2. Synthesis of NH₂-Ag₁₂bpz crystal.

AgS^tBu (20 mg, 0.1 mmol) and CF₃COOAg (22 mg, 0.1 mmol) were dissolved in N,N-dimethylacetamide (DMAc, 3 mL), followed by a mixture of NH₂-bpz (20 mg, 0.08 mmol) with 1 mL DMAc being added into the above solution. The obtained mixture was slowly evaporated in air for 10 min. The resultant NH₂-Ag₁₂bpz crystals were collected with 68.54 % yield based on NH₂-bpz.

S3.3. Synthesis of nano-NH₂-Ag₁₂bpz.

Nanocrystals of NH₂-Ag₁₂bpz (nano-NH₂-Ag₁₂bpz) were prepared by stirring method. AgS^tBu

(20 mg, 0.1 mmol) and CF_3COOAg (22 mg, 0.1 mmol) was first dissolved in 3 mL DMAc, the resulting solution was then added dropwise to a solution consisting of 20 mg $\text{NH}_2\text{-bpz}$ and 1 mL DMAc. Under vigorous stirring for 1 min, the pale yellow product was obtained by filtration.

S3.4. Synthesis of nano-MA- Ag_{12}bpz .

Nano- $\text{NH}_2\text{-Ag}_{12}\text{bpz}$ (20 mg) were soaked in the mixture solution of 2-methacrylate anhydride (MA, 14.7 μL) and dichloromethane (CH_2Cl_2 , 1 mL) for 2 days at room temperature. Afterwards, nano-MA- Ag_{12}bpz was obtained and separated by filtration.

S3.5. Preparation of membrane.

S3.5.1. Preparation of Ag_{12}bpz membrane.

TEGDMA (100 μL), BMA (100 μL) and phenylbis-(2,4,6-trimethylbenzoyl) phosphine oxide (0.8 mg) were uniformly mixed together, and then different amounts of nano-MA- Ag_{12}bpz were added into the mixture under sonication until the solutions were well-dispersed. The resulting suspension was dripped into a glass plate, and another glass slide was covered over the suspension. The interfacial polymerization was occurred upon irradiated by the UV-lamp source. After 5 min, the obtained Ag_{12}bpz membrane can be easily peeled off from the glass slide.

S3.5.2. Preparation of $\text{NH}_2\text{-Ag}_{12}\text{bpz}$ membrane.

The nano- $\text{NH}_2\text{-Ag}_{12}\text{bpz}$ (35.3 mg) were dispersed in the mixture of TEGDMA (100 μL), BMA (100 μL) and phenylbis-(2,4,6-trimethylbenzoyl) phosphine oxide (0.8 mg), and formed a homogeneous suspension. Through the same photo-polymerization method mentioned above, we obtained the $\text{NH}_2\text{-Ag}_{12}\text{bpz}$ membrane

S3.5.3. Preparation of Ag_{12} membrane.

The Ag_{12} membrane was obtained by directly mixing Ag_{12} clusters (22.2 mg) particles with BMA (100 μL) and TEGDMA (100 μL) in the presence of phenylbis-(2,4,6-trimethylbenzoyl) phosphine oxide (0.8 mg), then via the same photo-polymerization method.

S3.6. Nitrobenzene detection by Ag₁₂bpz membrane.

S3.6.1. Liquid phase detection.

We prepared a solution of nitrobenzene with the concentration ranging from 1 μ M to 10 μ M. And then the NB solution were dripped onto the Ag₁₂bpz membrane. During the fluorescence measurements, the samples were excited at 454 nm.

S3.6.2. Vapor-phase detection.

2 mL of nitrobenzene solution was placed in a capped glass vial for a week to ensure that the equilibrated vapor pressure of nitrobenzene was reached. To conduct a test, the Ag₁₂bpz membrane were put into the vial for a specified time for exposure to the NB vapors, and then taken out quickly to measure the corresponding fluorescence spectra.

For the cycle test, after each luminescence quenching by NB, Ag₁₂bpz membrane was vacuumed at 40 °C for 5 hours, then used for the next round of testing.

S4. Crystallographic data of NH₂-Ag₁₂bpz.

Table S1. Crystal data and structure refinements.

NH₂-Ag₁₂bpz	
CCDC number	1956711
Empirical formula	C ₈₄ H ₉₆ Ag ₁₂ F ₁₈ N ₁₂ O ₁₂ S ₆
Formula weight	3294.51
Temperature / K	293(2)
Crystal system	hexagonal
Space group	P6/mmm
<i>a</i> / Å	23.5654(5)
<i>b</i> / Å	23.5654(5)
<i>c</i> / Å	11.2007(3)
<i>α</i> / °	90
<i>β</i> / °	90
<i>γ</i> / °	120
Volume / Å³	5386.7(3)
<i>Z</i>	1.00008
<i>ρ</i>_{calc} g / cm³	1.016
<i>μ</i> / mm⁻¹	9.477
F(000)	1602.0
Crystal size / mm³	0.2 × 0.05 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection / °	4.33 to 132.98
Index ranges	-16 ≤ <i>h</i> ≤ 28, -27 ≤ <i>k</i> ≤ 19, -13 ≤ <i>l</i> ≤ 9
Reflections collected	18296
Independent reflections	1779 [R _{int} = 0.0419, R _{sigma} = 0.0220]
Data / restraints / parameters	1779 / 48 / 107
Goodness-of-fit on F²	1.099
Final R indexes [<i>I</i> ≥ 2σ (<i>I</i>)]	R ₁ = 0.0896, wR ₂ = 0.2569
Final R indexes [all data]	R ₁ = 0.0959, wR ₂ = 0.2665
Largest diff. peak/hole / e Å⁻³	1.71/-0.69

$$R_1 = \sum | |F_o| - |F_c| | / \sum |F_o| \quad . \quad wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

S5. Supplementary Figures.

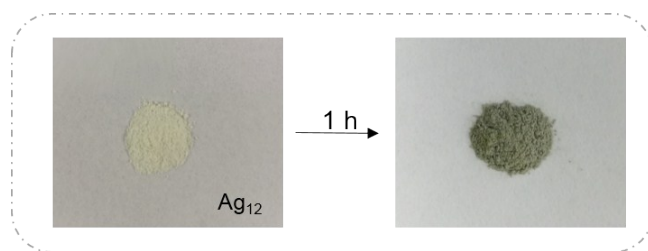


Figure S2. Photographs of Ag₁₂ clusters before and after exposure in air for 1 hour.

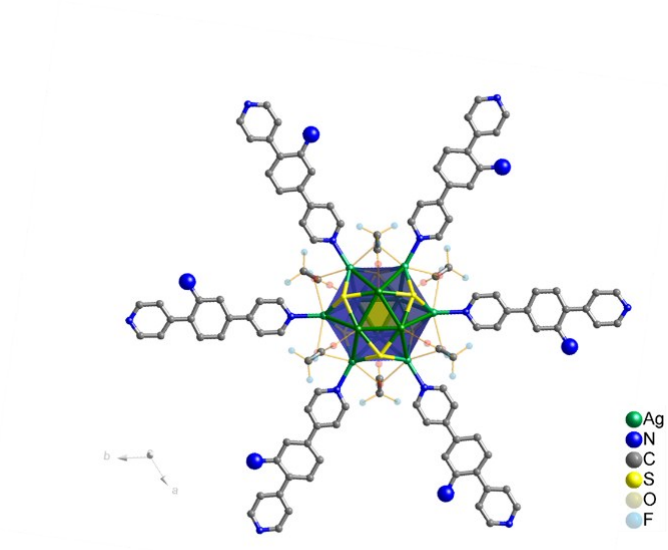


Figure S3. Single crystal structure of NH₂-Ag₁₂bpz.

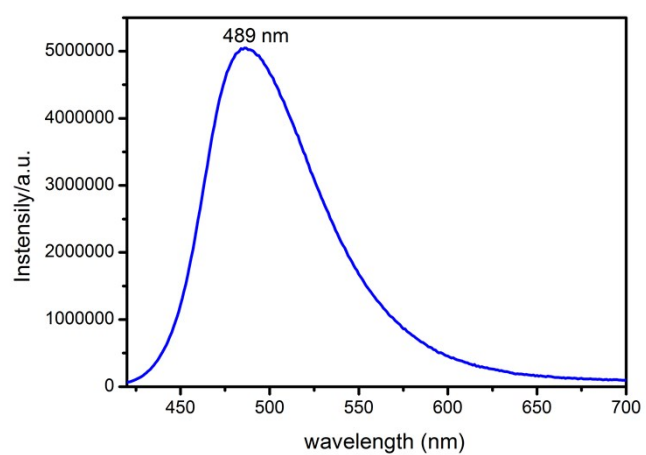


Figure S4. Fluorescence emission spectra of NH₂-Ag₁₂bpz (single crystals).

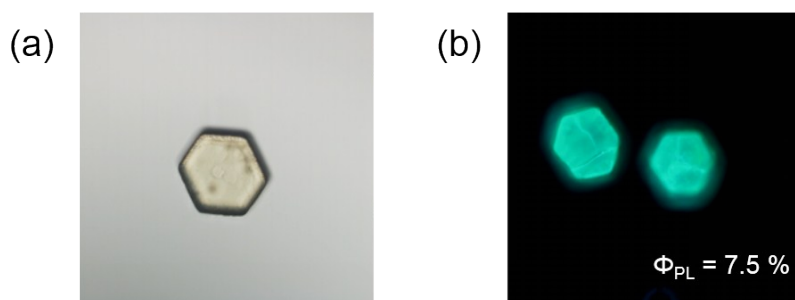


Figure S5. Optical microscope images of $\text{NH}_2\text{-Ag}_{12}\text{bpz}$ (single crystals) (a) under normal light and (b) under UV light.

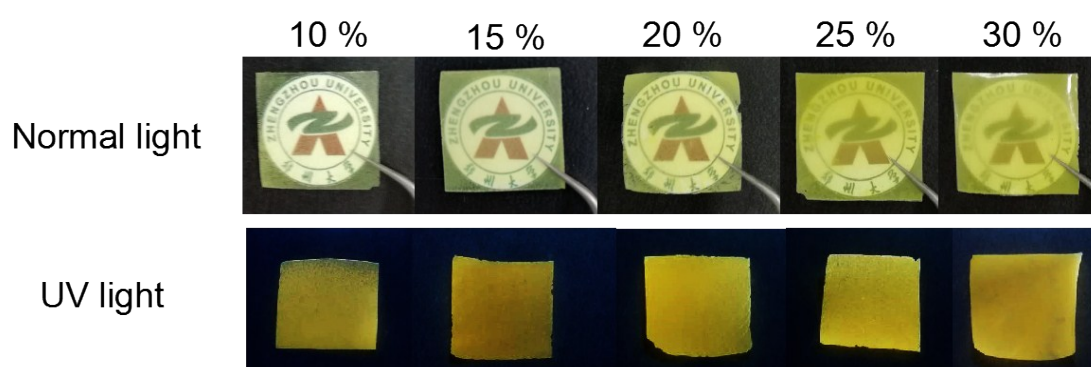


Figure S6. Photographs of Ag_{12}bpz membrane loaded with increasing (left-to-right) concentrations of nano-MA- Ag_{12}bpz under normal light and UV light.

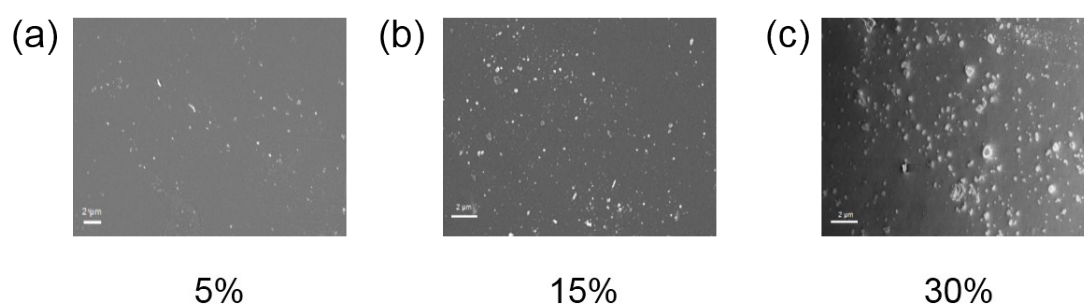


Figure S7. SEM images Ag_{12}bpz membrane with different loadings (a) 5%, (b) 15%, and (c) 30%.

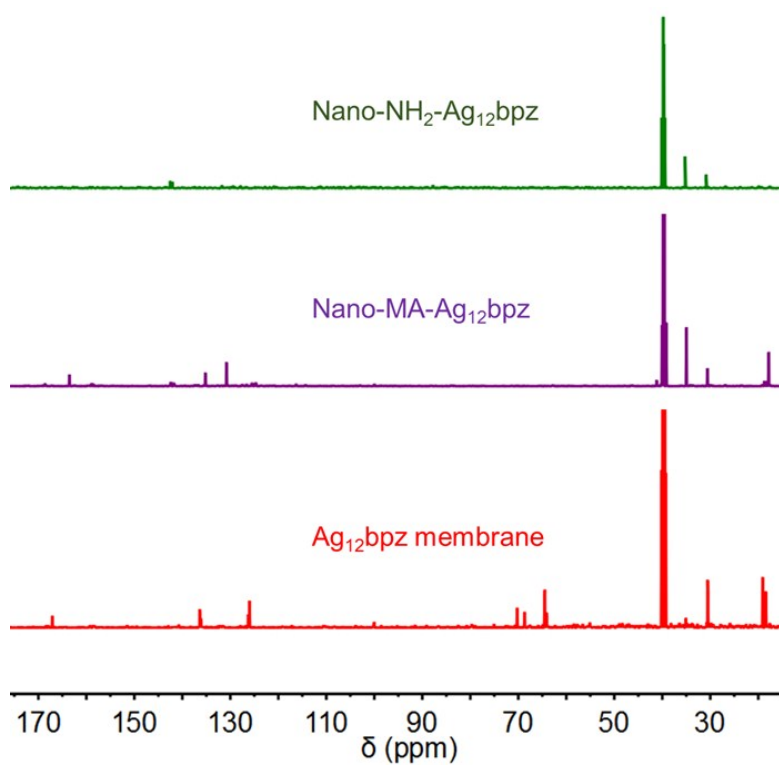


Figure S8. ^{13}C NMR spectrum of nano- $\text{NH}_2\text{-Ag}_{12}\text{bpz}$, nano- $\text{MA-Ag}_{12}\text{bpz}$ and Ag_{12}bpz membrane in $\text{d}_6\text{-DMSO}$.

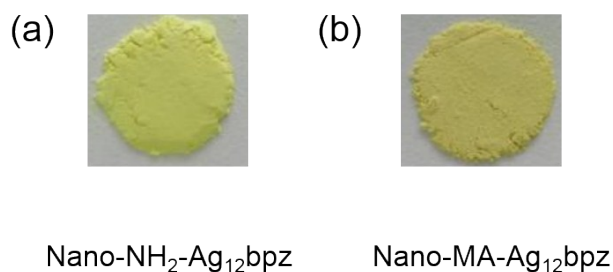


Figure S9. Photographs of (a) nano- $\text{NH}_2\text{-Ag}_{12}\text{bpz}$ and (b) nano- $\text{MA-Ag}_{12}\text{bpz}$ under normal light.

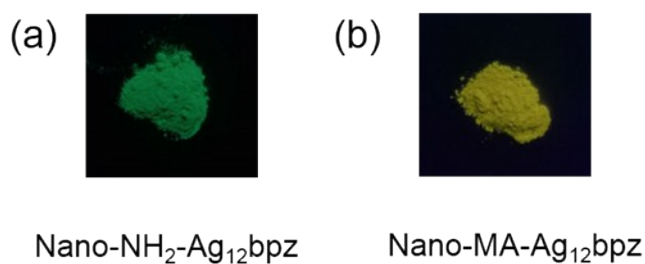


Figure S10. Photographs of (a) nano- $\text{NH}_2\text{-Ag}_{12}\text{bpz}$ and (b) nano- $\text{MA-Ag}_{12}\text{bpz}$ under UV light.

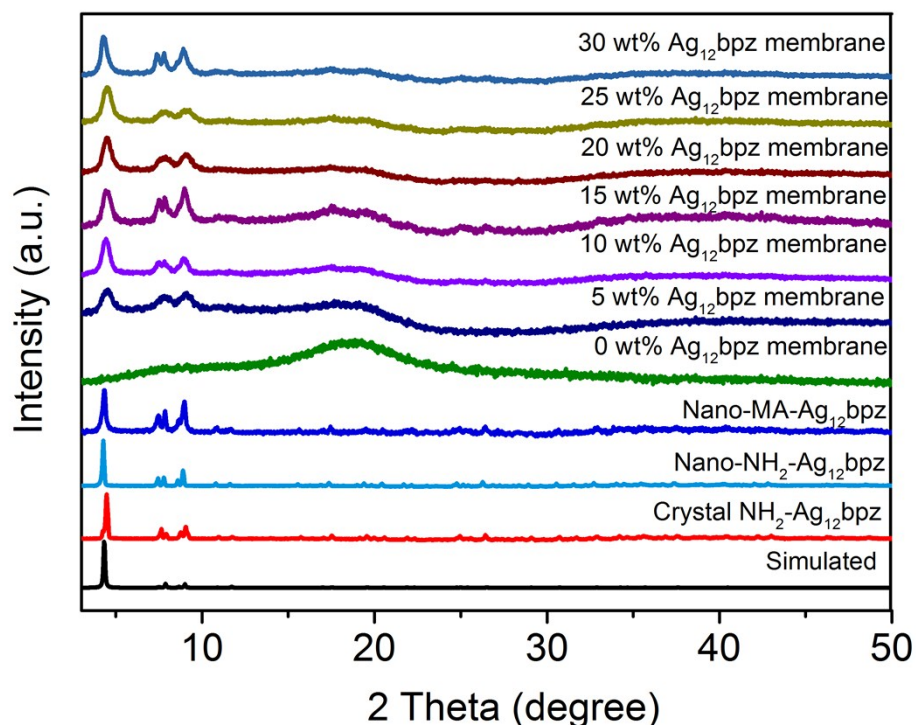


Figure S11. PXRD patterns of simulated NH₂-Ag₁₂bpz, single crystal of NH₂-Ag₁₂bpz, nano-NH₂-Ag₁₂bpz, nano-MA-Ag₁₂bpz and Ag₁₂bpz membrane with different Ag₁₂bpz loading.

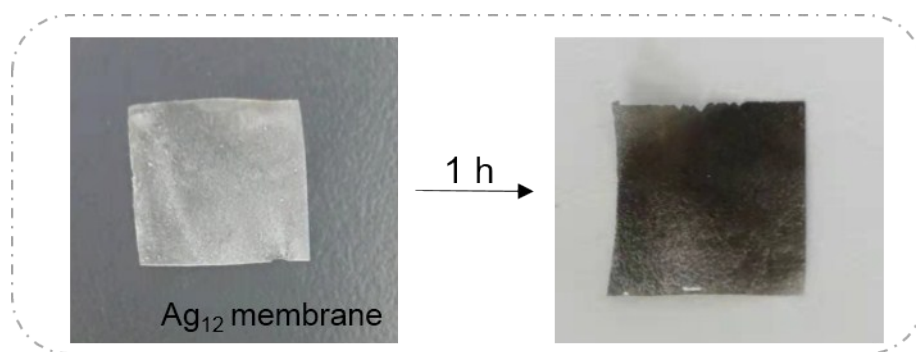


Figure S12. Corresponding photographs before and after exposure of Ag₁₂ membrane in air for 1 hour.

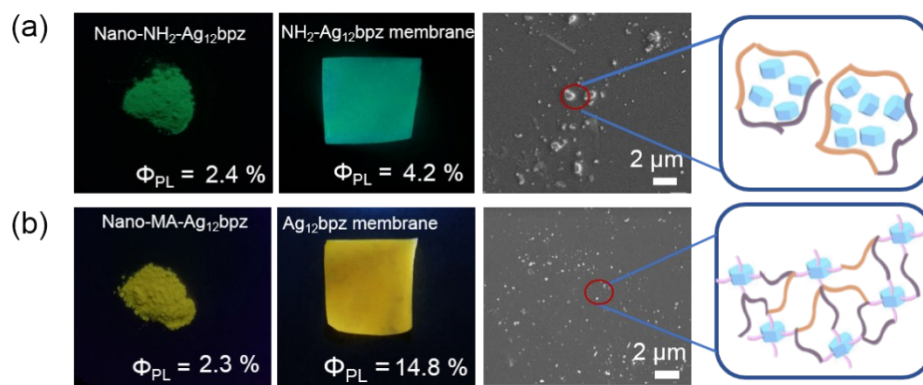


Figure S13. Photographs of nano-NH₂-Ag₁₂bpz, NH₂-Ag₁₂bpz membrane, nano-MA-Ag₁₂bpz and Ag₁₂bpz membrane under 365 nm UV light as well as their corresponding SEM images.

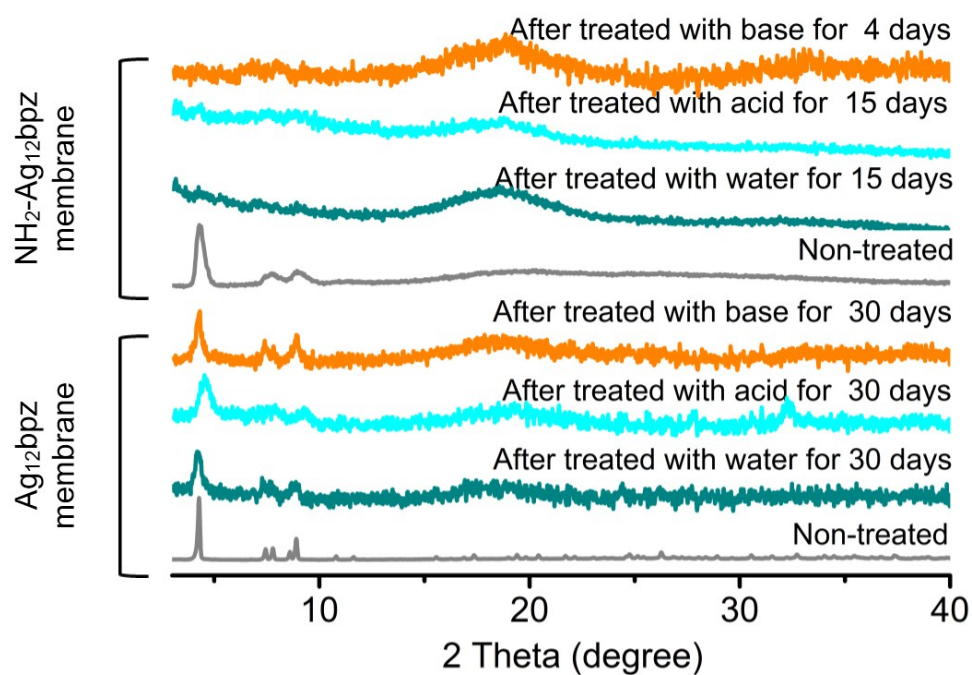


Figure S14. PXRD patterns of Ag₁₂bpz membrane and NH₂-Ag₁₂bpz membrane upon treated by water, base and acid with different time.

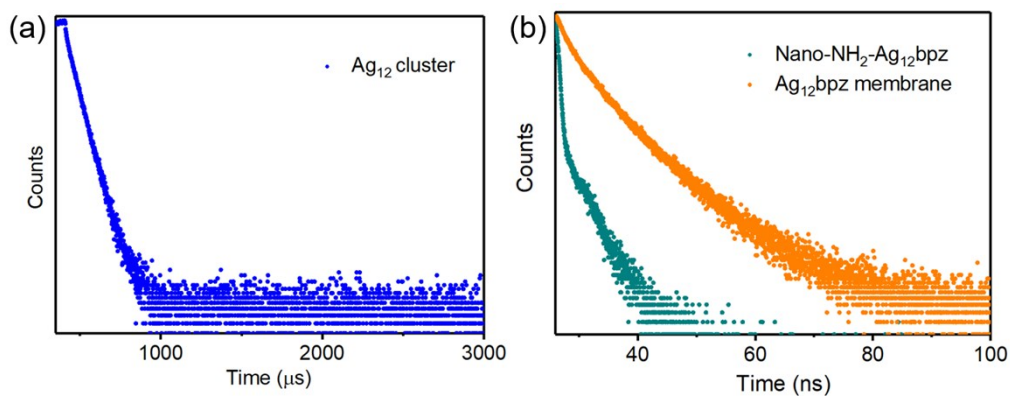


Figure S15. Time-resolved fluorescence-decay profiles of (a) Ag₁₂ cluster, (b) nano-NH₂-Ag₁₂bpz and Ag₁₂bpz membrane.

Ag₁₂ cluster showed a lifetime of 5.7 μs, which can be attributed to the metal-centered transitions. On the other hand, due to the luminescence mainly derived from the ligand-centered emission, nano-NH₂-Ag₁₂bpz and Ag₁₂bpz membrane exhibited nanoseconds lifetime. It is worth mention that the lifetime of Ag₁₂bpz membrane (4.6 ns) is longer than nano-NH₂-Ag₁₂bpz (0.44 ns). The relatively slower exciton energy release of Ag₁₂bpz membrane can be accounts for the covalent linkages between nanocrystal and polymer binder, which effectively restricted Ag₁₂bpz moieties motions in the polymer matrix.

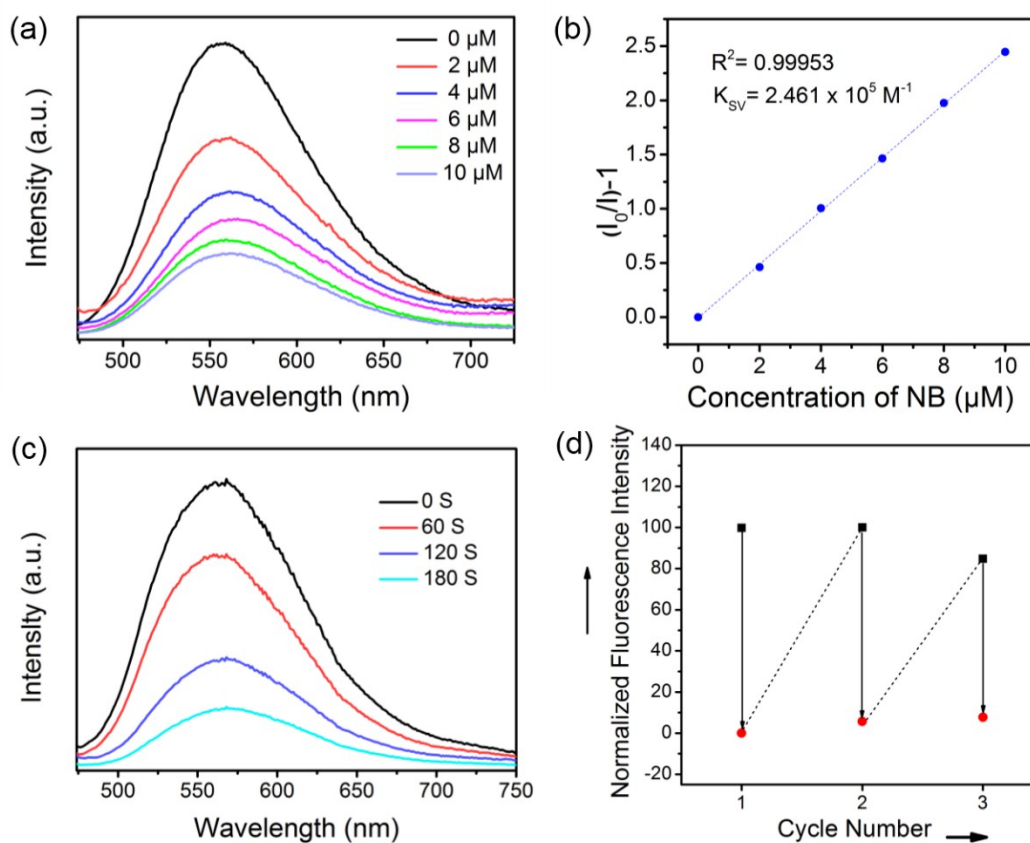


Figure S16. (a) Fluorescence spectra showing response on the incremental addition of the solution of NB on Ag₁₂bpz membrane. (b) SV plot with the addition of NB to 10 μM. (c) Fluorescence intensity changes of Ag₁₂bpz membranes exposed to nitrobenzene vapor at different time. (d) Cycling test of the Ag₁₂bpz membrane upon exposure to vapors of NB.

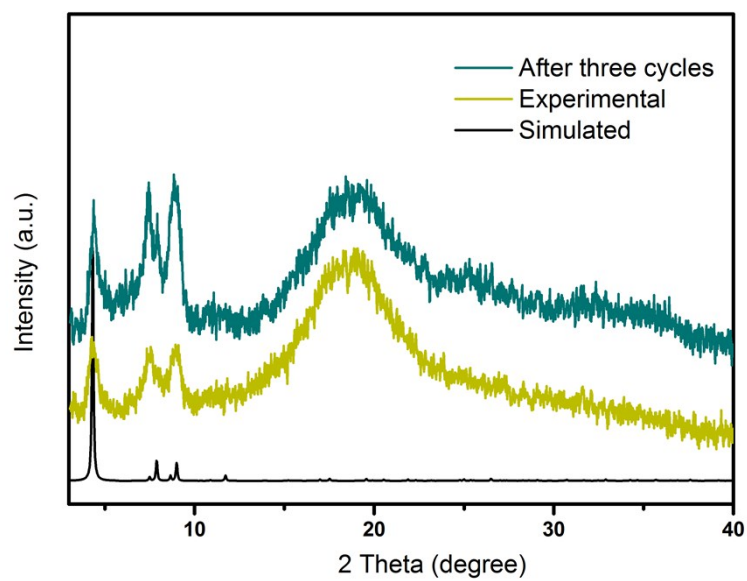


Figure S17. PXRD patterns of Ag_{12}bpz membrane before and after exposure to the NB vapor for three cycles.

- 1 X. G. Guo, Z. Y. Zhang, S. Qiu, X. Su, Y. B. Wang and X. Sun, *Chem. Eur. J.*, 2017, **23**, 17727-17733.