Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Materials

$K_{12.5}Na_{1.5}[NaP_5W_{30}O_{110}]\cdot15H_2O$ (P_5W_{30}) and SiO_2 particle were synthesized according to the published procedures.[23,24] Agarose (AG) power is biology grade, and was purchased from Beijing Chemical Reagent Ltd. Co. of China and used without further purification. Fluorescein sodium (FL) was analytical grade and used without further purification. Ulta-pure water with a resistivity of 18.2MΩr was purified by a Millipore Milli-Q water purification system.

Preparation of the self-supporting hybrid films

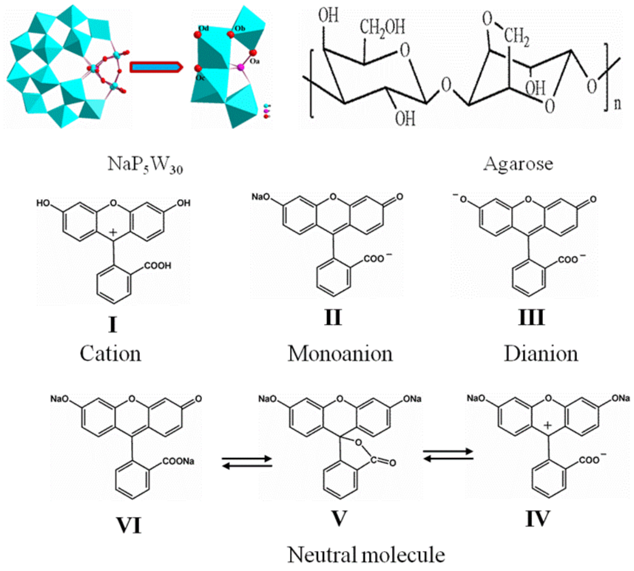
The hybrid films were fabricated by a classic hydrogel casting technique and prepared as follow process: AG powder (1 g) was added to 100 ml deionized water with vigorous stirring at room temperature to create a cloudy suspention. The mixture solution was heated until boiling for 10 minutes and the mixture became clear. Then 0.5 ml FL (1 mg/ml) was added to the above solution boiled for 5 minutes under stirring, the color of solution changed from colorless to yellow-green after FL was added (**solution 1**). Then 0.3 g P_5W_{30} and 5ml silica colloidal suspension were added respectively to 50 ml **solution 1** boiled for 5 minutes under stirring to form **solution 2** and **solution 3**, respectively. The hot mixtures of **solution 1**, **2** and **3** were casted on glass substrates respectively, followed by gelating and drying at room temperature. Then the self-supporting hybrid films were peeled from the substrates and the thickness of the films could be controlled by changing the concentration or volume of the casting solutions. Three different self-supporting hybrid films were successfully fabricated, which are named AG-FL, AG-P_5W_{30}-FL and AG-SiO_2-FL corresponding to above **solution 1**, **solution 2** and **solution 3**.

Measurement and instruments

Fourier transform infrared (FTIR) spectra were recorded in the range of 400-4000cm^{-1} with a KBr pellet for powder and film on an Alpha Centaurt FT/IR spectrometer. UV-vis spectrum was carried out by a VARIAN Cary 50 UV-VIS Spectrometer. The SEM images were collected on a JEOLFESEM 6700F electron microscope. The TEM images were obtained with a Hitachi H8100 electron microscope with an accelerating voltage of 200 kV without staining. Luminescent spectra were collected by a Horiba Jobin Yvon Fluorolog-3 Spectrofluorometer. CLSM images were obtained on Olympusfluoview FV1000. Raman spectrum was obtained with a Renishaw Raman system model 1000 spectrometer. The 514.5 nm radiation from a 6 mW air-cooled argon ion laser was used as exciting source. Powder X-ray diffraction (powder XRD) data were collected with Cu-Kα (λ = 1.542 Å) radiation on a Rigaku D/Max-2500 X-ray diffractometer.

23 I. Creaser, M. C. Hechel, R. J. Neitz and M. T. Pope, *Inorg. Chem.,* 1993, **32**, 1573.

24 X. L. Fang, Z. H. Liu, M. F. Hsieh, M. Men, P. X. Liu, N. F. Zheng, *ACSNano*, 2012, **6**, 4434.



Scheme S1 The schematic representation of chemical structure of agarose (AG)， polyhedral structure of $[NaP_5W_{30}]^{14-}$ (P_5W_{30}), and six isomer structures of fluorescein sodium (FL).

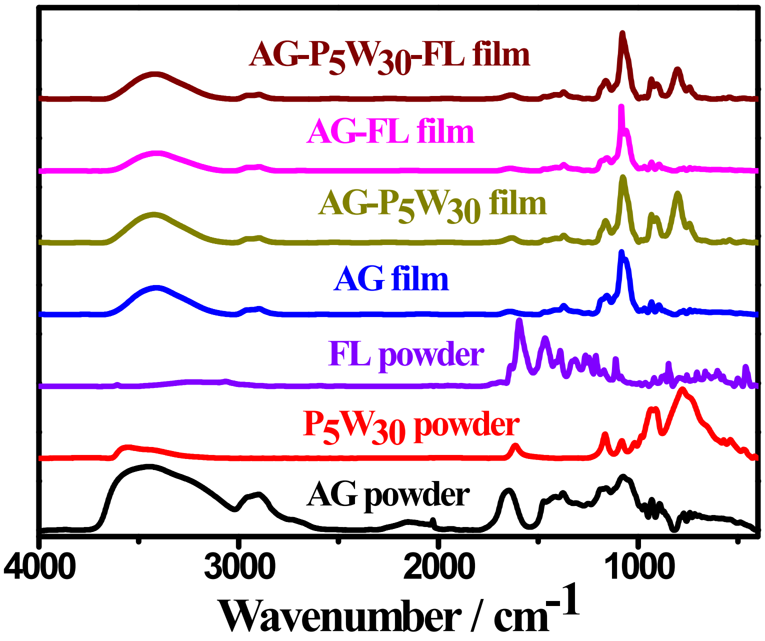


Fig. S1. FT-IR spectra of AG powder (black line), P_5W_{30} powder (red line), FL powder (violet line), AG film (blue line), AG-P_5W_{30} film (dark yellow line), AG-FL film (magenta line) and AG-P_5W_{30}-FL film (wine line).

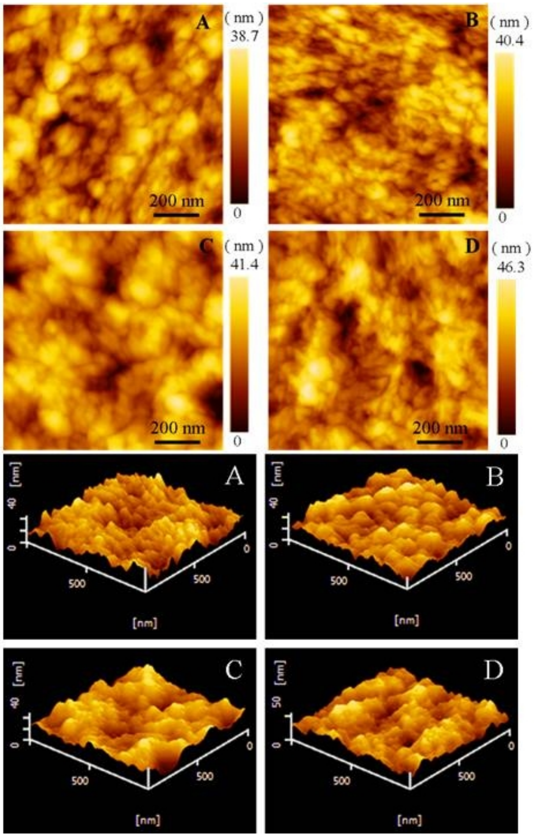


Fig. S2. AFM images (top) and 3D AFM images (bottom) of AG film (A), AG-FL film (B), AG-P_5W_{30}-FL film (C) and AG-SiO_2-FL film (D) on silicon substrates.

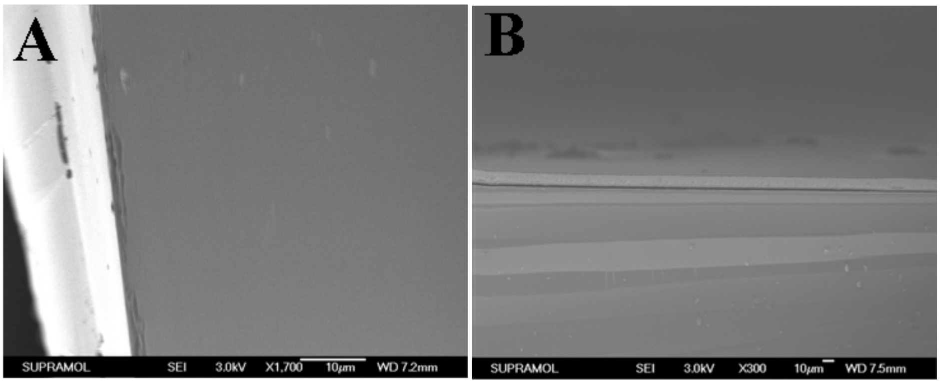


Fig. S3. SEM images with different thickness of 6.5 nm (A) and 11nm (B).

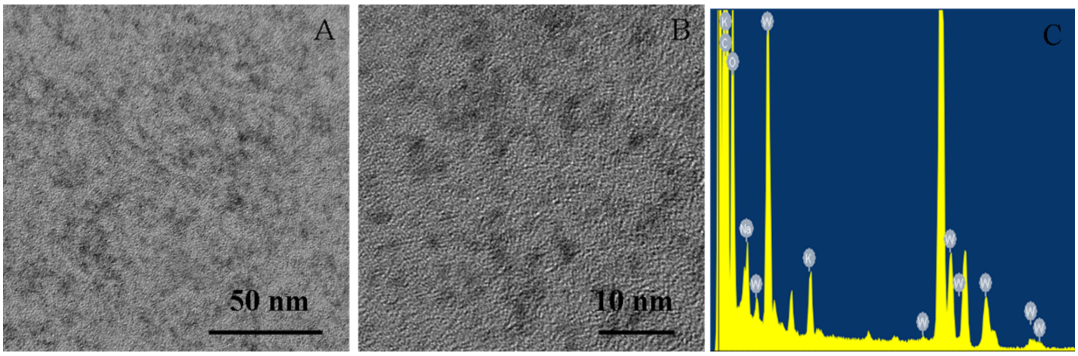


Fig. S4. TEM images of AG-P_5W_{30}-FL film: (A) low magnification image, (B) high magnification image and (C) EDX analysis.

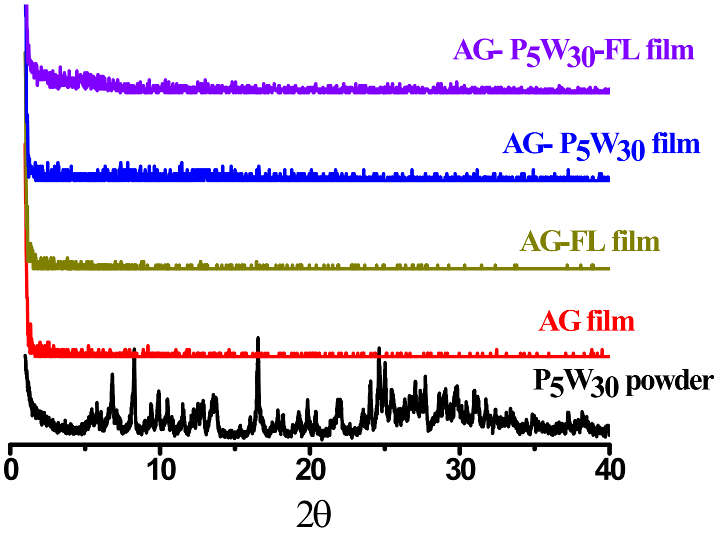


Fig. S5. XRD patterns of P_5W_{30} powder, AG film, AG-FL film, AG-P_5W_{30} film, and AG-P_5W_{30}-FL film.

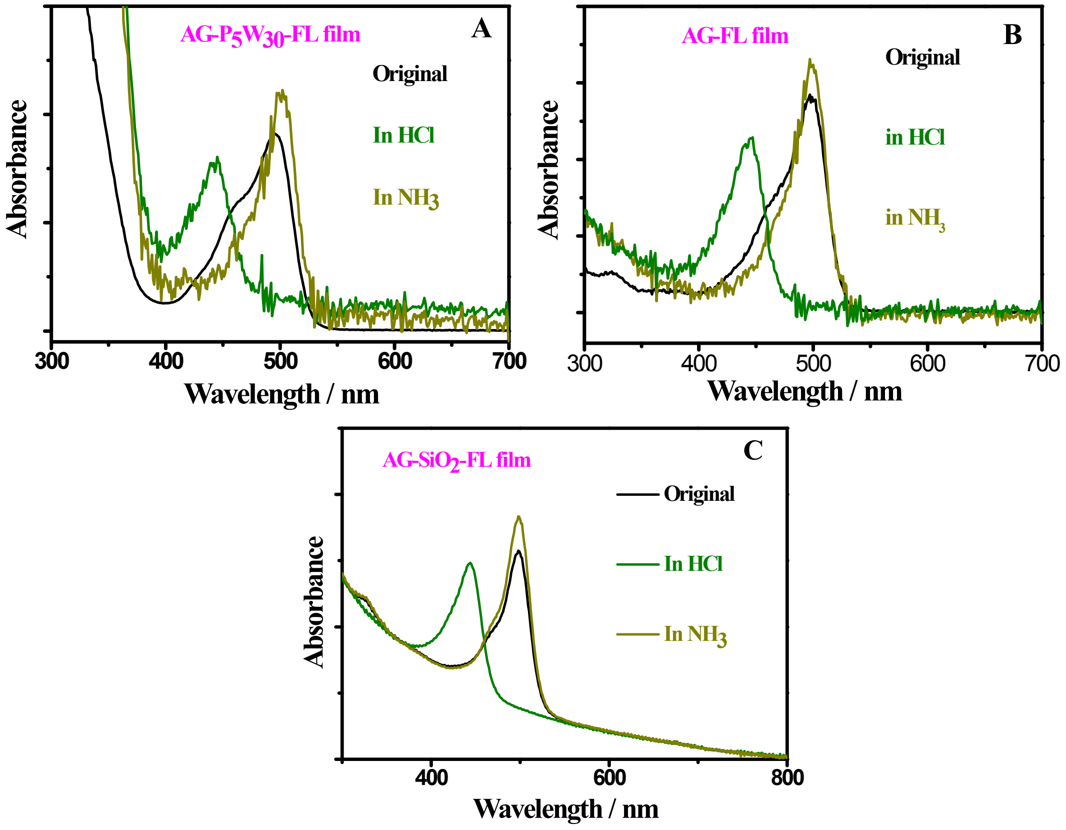


Fig. S6. UV-vis spectra of AG-P_5W_{30}-FL film (top left), AG-FL film (top right) and AG-SiO_2-FL film (bottom) at original state (black line), in HCl gas (olive line) and NH_3 gas (dark yellow line).

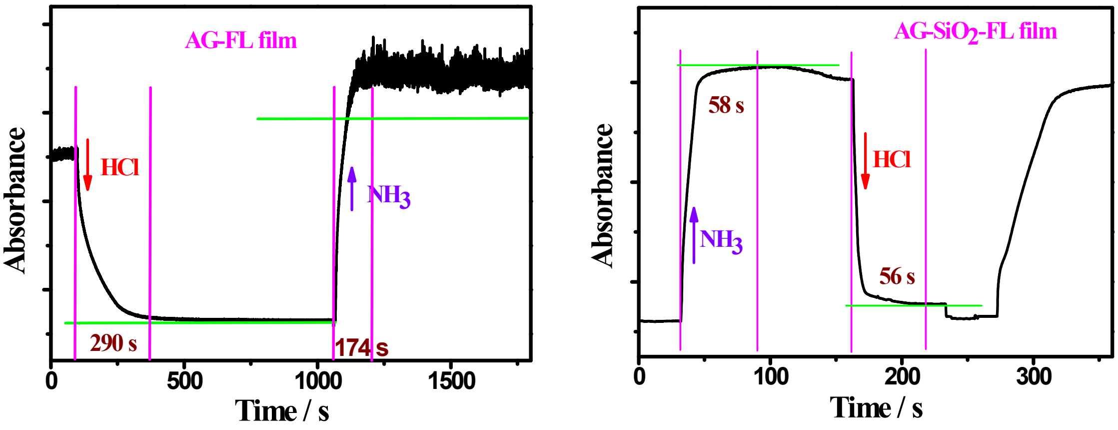


Fig. S7. Kinetic curves of absorbance with time for AG-FL film (left) and AG-SiO_2-FL film (right) under HCl and NH_3 gases using the UV-vis spectra for films A-P_5W_{30}-F (top) and A-F (bottom).

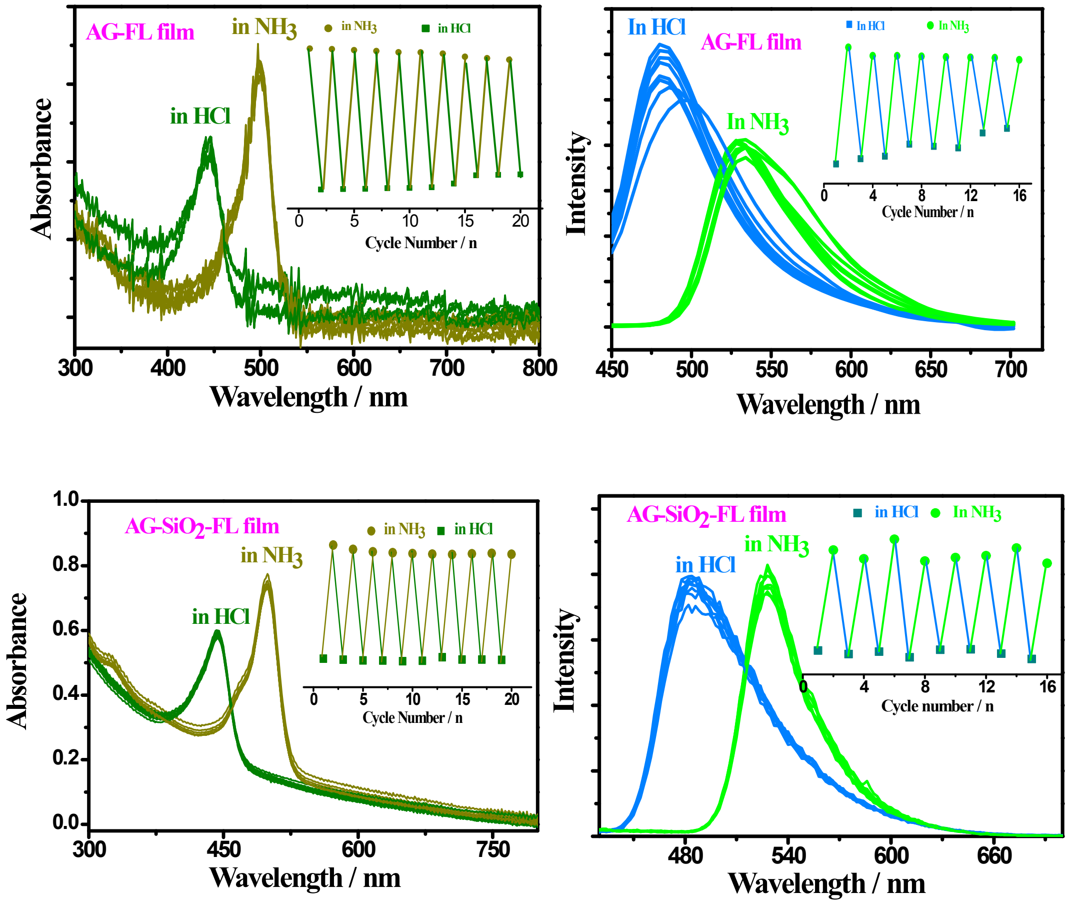


Fig. S8. (top) UV-vis spectra of AG-FL film in HCl gas (olive line) and NH_3 gas (dark yellow line), and the insert is the curve of the absorbance with cycle number; luminescent spectra of AG-FL film in HCl gas (blue line) and NH_3 gas (green line), and the insert is the curve of the luminescent intensity with cycle number. (bottom) UV-vis spectra of AG-SiO_2-FL film in HCl gas (olive line) and NH_3 gas (dark yellow line), and the insert is the curve of the absorbance with cycle number; luminescent spectra of AG-SiO_2-FL film in HCl gas (blue line) and NH_3 gas (green line), and the insert is the curve of the luminescent intensity with cycle number.

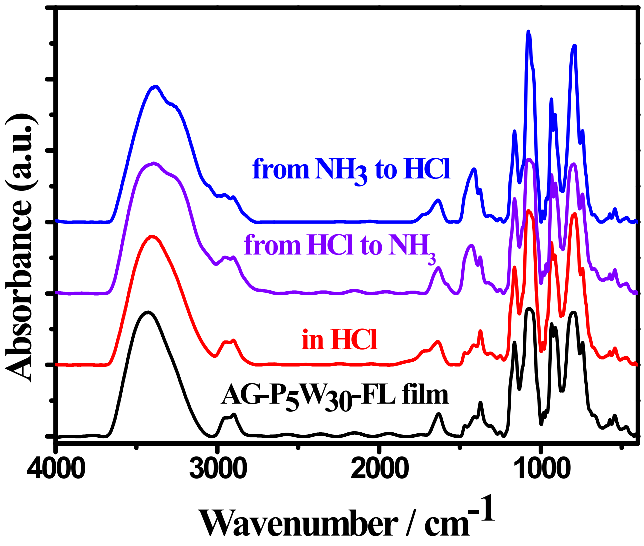


Fig. S9. FT-IR spectra of AG-P_5W_{30}-FL film (black line), film alternately exposed in HCl and NH_3 gases for many times.

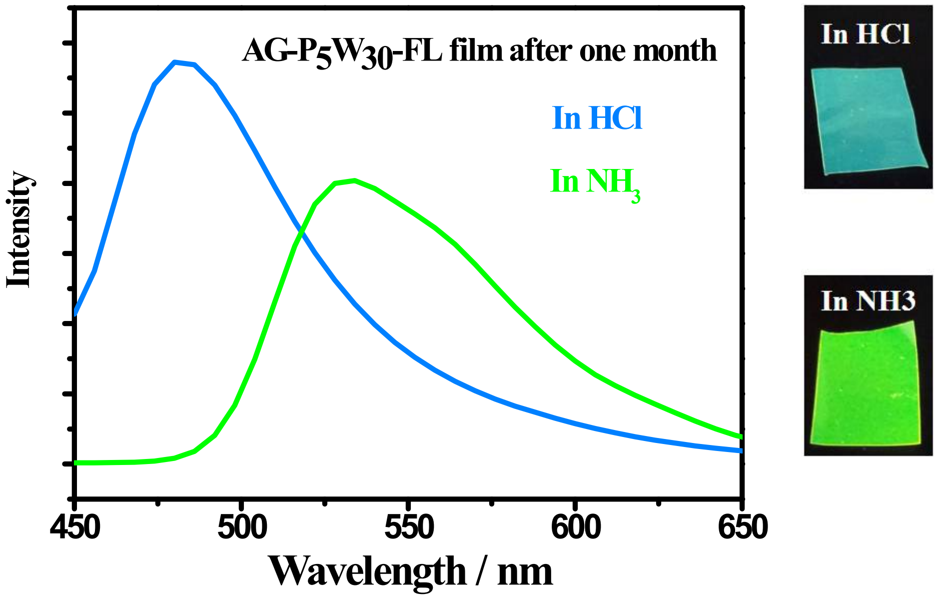


Fig. S10. Luminescent spectra of AG-P_5W_{30}-FL film in HCl (blue line) and NH_3 (green line) gases and the corresponding photographs under UV light irradiation ($\lambda = 365$nm) after one month.

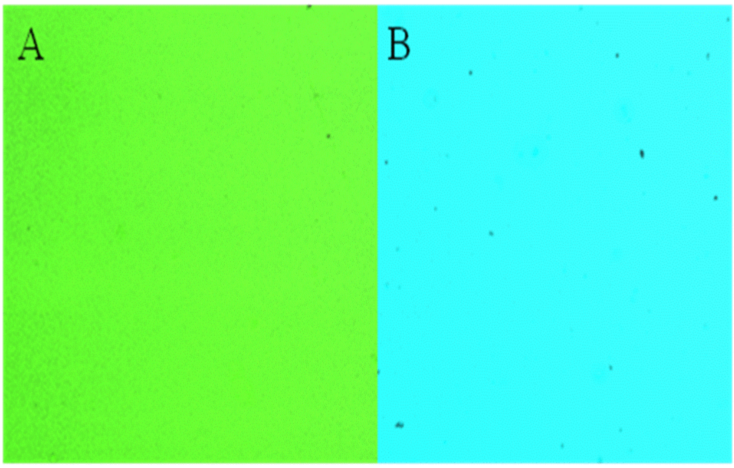


Fig. S11. Confocal fluorescence microscopy images of AG-P_5W_{30}-FL film in NH_3 gas (A) and HCl gas (B).