

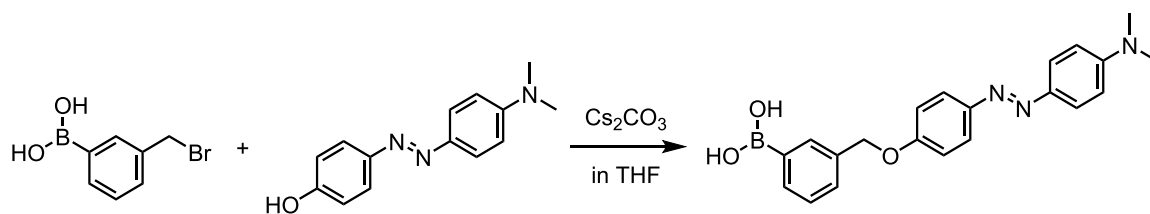
Electronic Supplementary Information

Boronic acids as molecular inks for surface functionalization of polyvinyl alcohol substrates

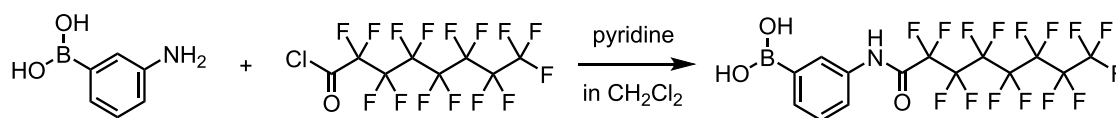
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Scheme S1 Synthetic route for a boronic acid-appended dimethylaminoazobenzene (**4**).



Scheme S2 Synthetic route for a boronic acid-appended fluoroalkane (**6**).

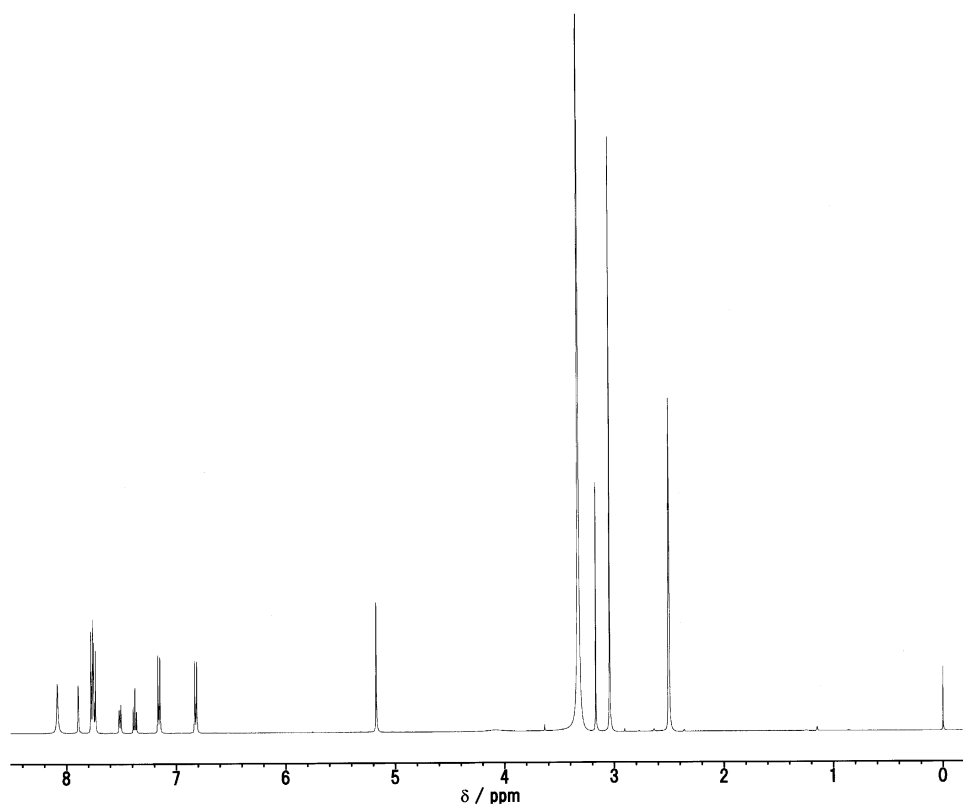


Fig. S1 ^1H NMR spectrum of **4** in $\text{DMSO}-d_6$.

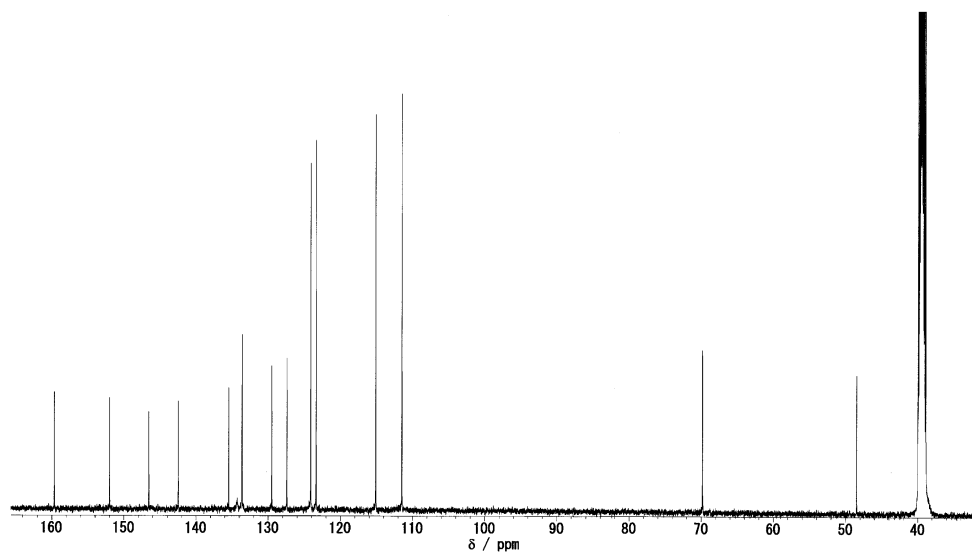


Fig. S2 ^{13}C NMR spectrum of **4** in $\text{DMSO-}d_6$.

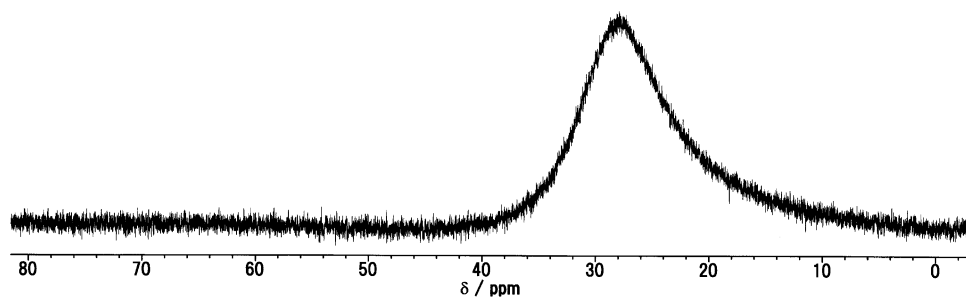


Fig. S3 ^{11}B NMR spectrum of **4** in $\text{DMSO-}d_6$.

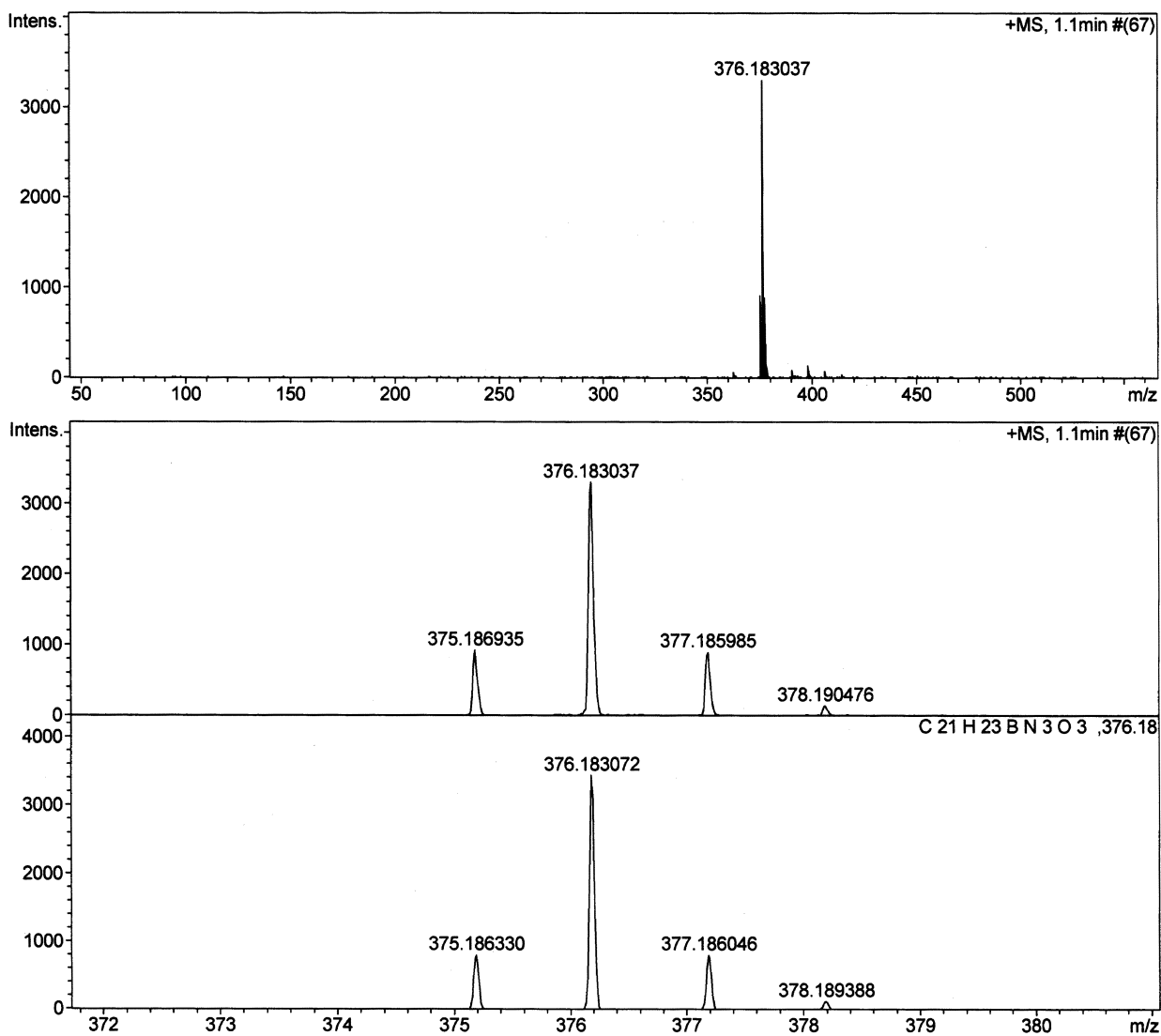


Fig. S4 HRMS (ESI) of the isolated product (top and middle) and simulated (bottom) isotope patterns of $[4 + H]^+$.

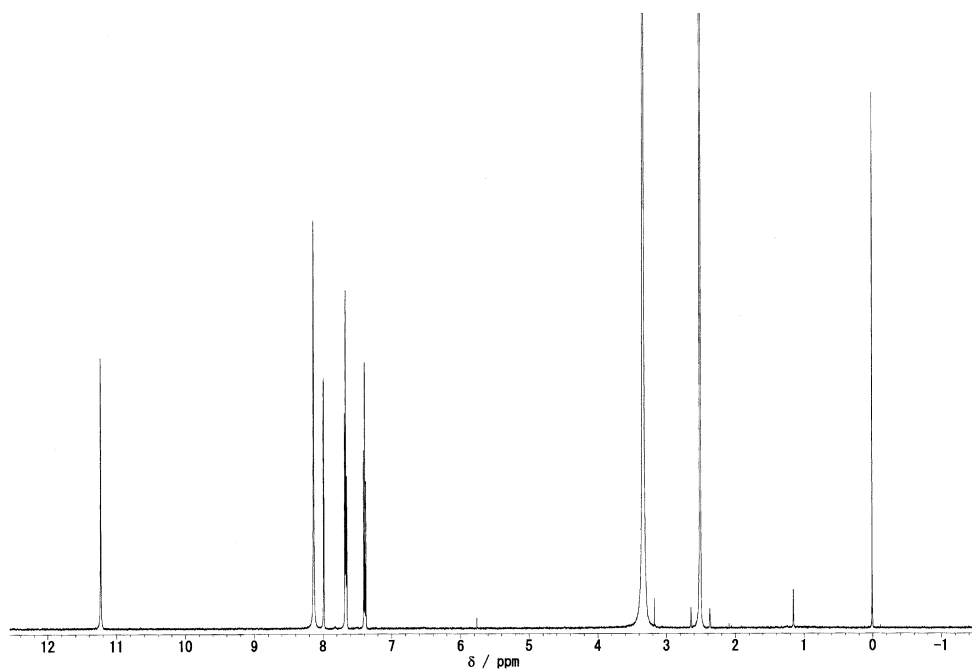


Fig. S5 ^1H NMR spectrum of **6** in $\text{DMSO-}d_6$.

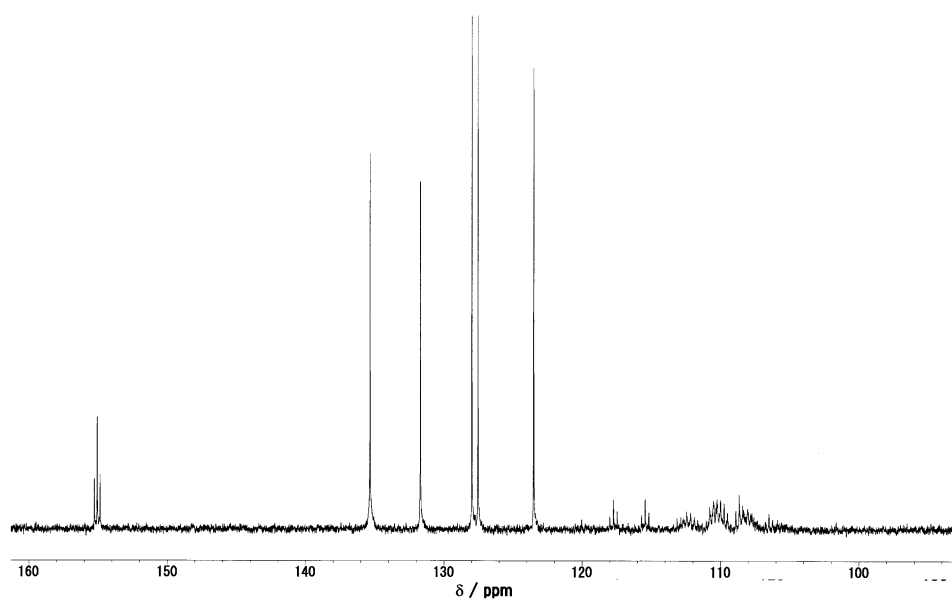


Fig. S6 ^{13}C NMR spectrum of **6** in $\text{DMSO-}d_6$.

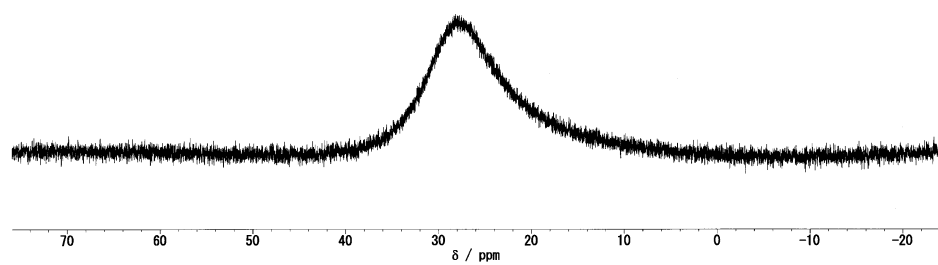


Fig. S7 ^{11}B NMR spectrum of **6** in $\text{DMSO-}d_6$.

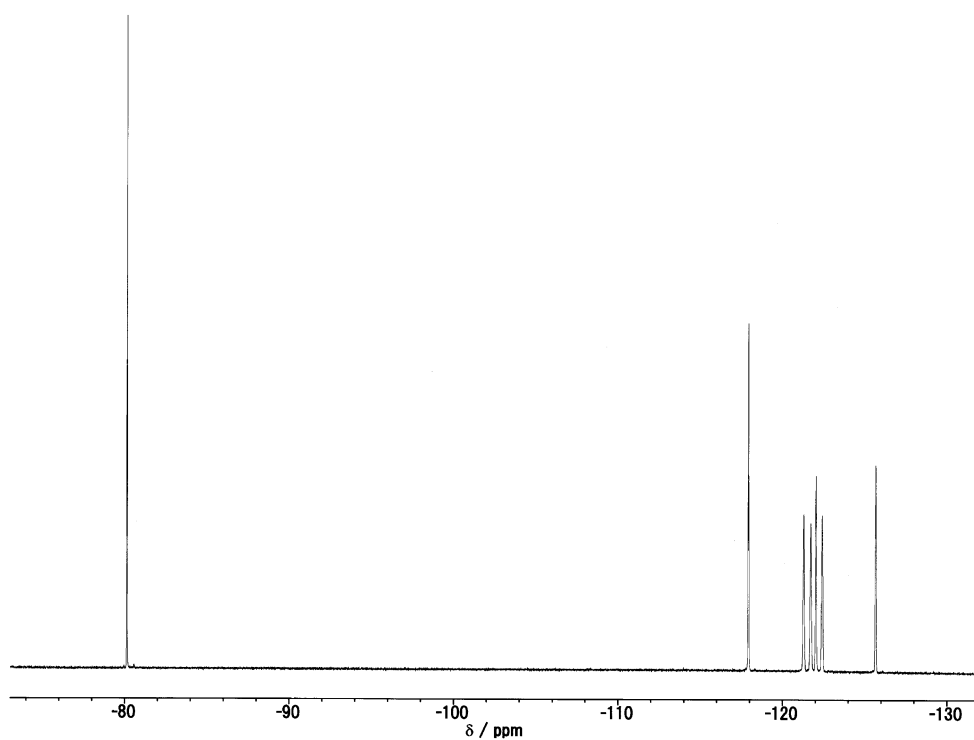


Fig. S8 ^{19}F NMR spectrum of **6** in $\text{DMSO-}d_6$.

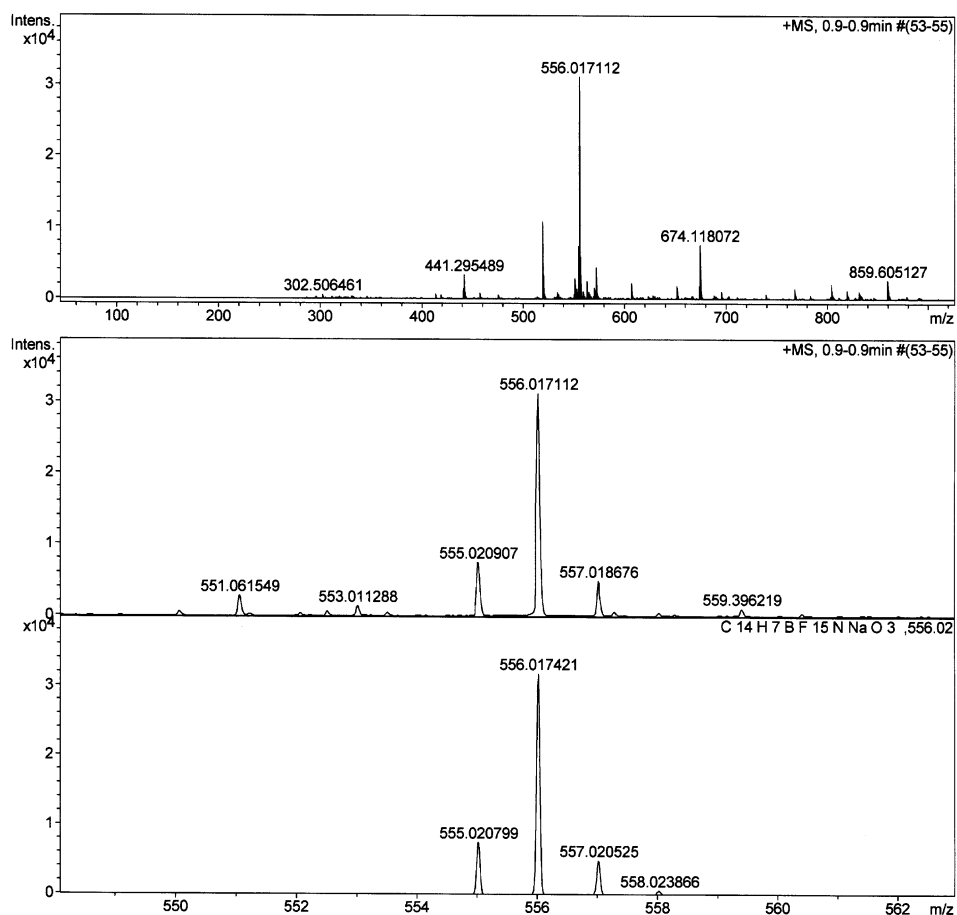


Fig. S9 HRMS (ESI) of the product (top and middle) and simulated (bottom) isotope patterns of $[6 + Na]^+$.

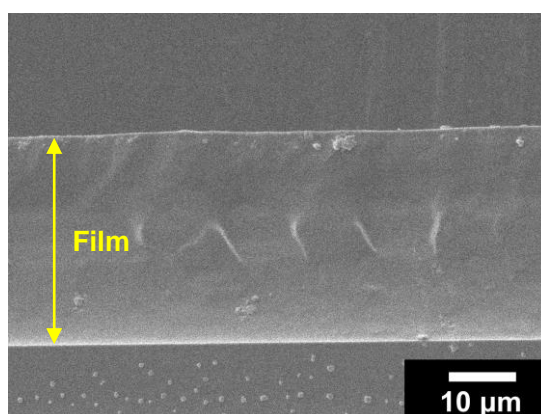


Fig. S10 SEM image of the cross-section of the PVA film.

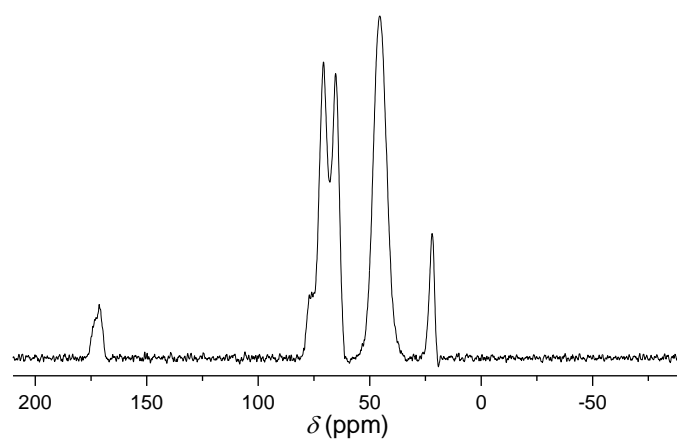


Fig. S11 Solid state ^{13}C CP/MAS NMR spectrum of the **PVA** film.

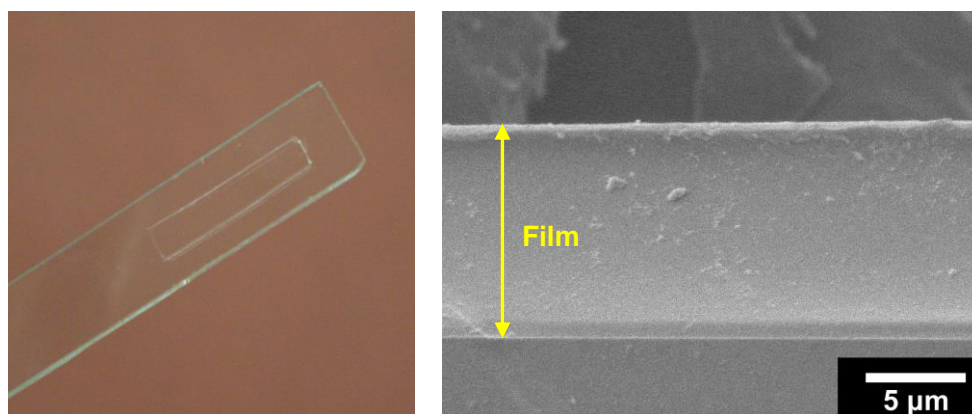


Fig. S12 Photograph of the **PVA-GA** film on the glass slide (left) and SEM image of the cross-section of the **PVA-GA** film (right).

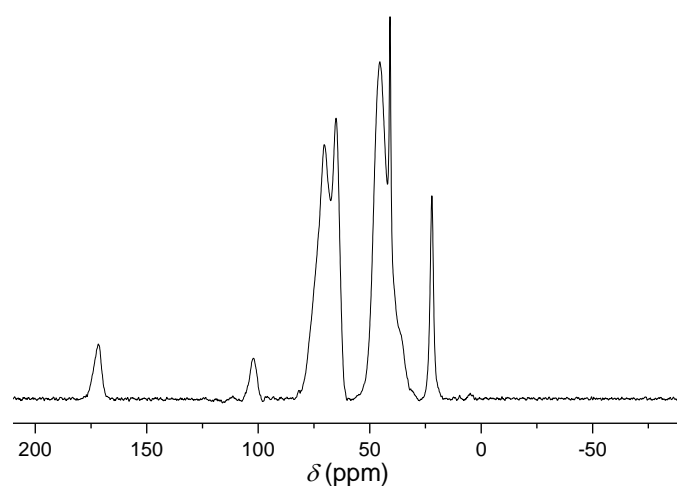


Fig. S13 Solid state ^{13}C CP/MAS NMR spectrum of a **PVA-GA** film.

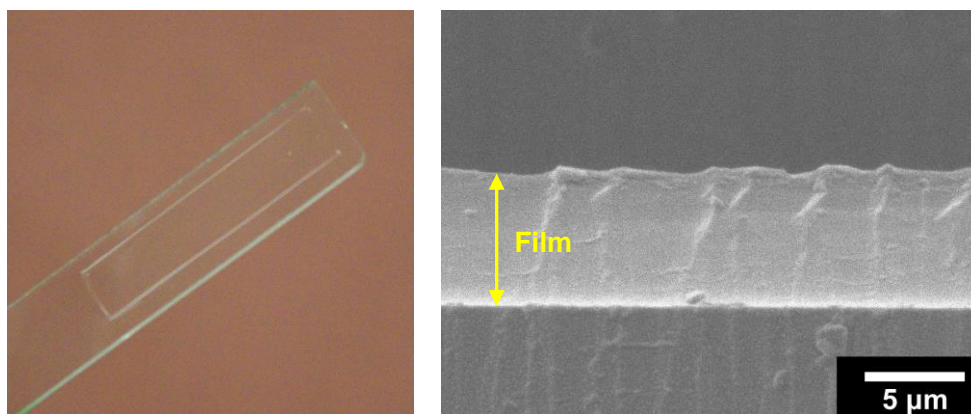


Fig. S14 Photograph of the **PVA-BA** film on the glass slide (left) and SEM image of the cross-section of the **PVA-BA** film (right).

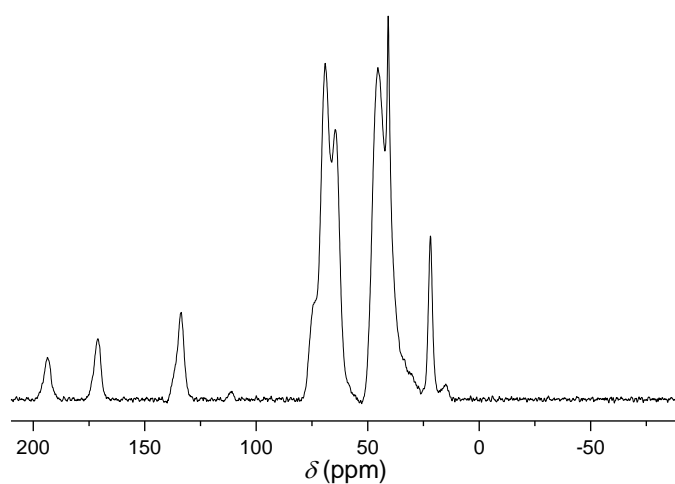


Fig. S15 Solid state ^{13}C CP/MAS NMR spectrum of the **PVA-BA** film.



Fig. S16 Photographs of (a) the empty marker pen and (b) the marker pen filled with methanol solution containing **1a**.



Fig. S17 Photographs of the **1a/PVA** film on the glass slide (a) before and (b) after washing with methanol.

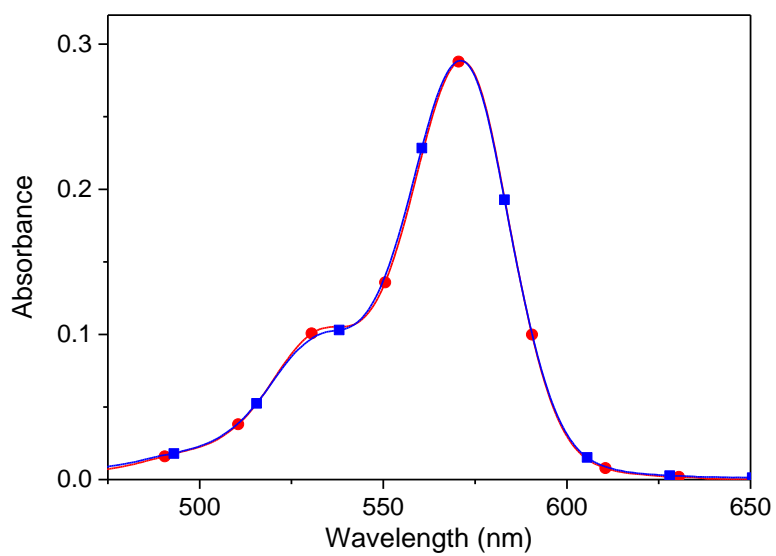


Fig. S18 UV-vis absorption spectra of the **1a/PVA** film before (circle) and after (square) washing with methanol.



Fig. S19 Photographs of the **1b/PVA** film on a glass slide (a) before and (b) after washing with methanol.

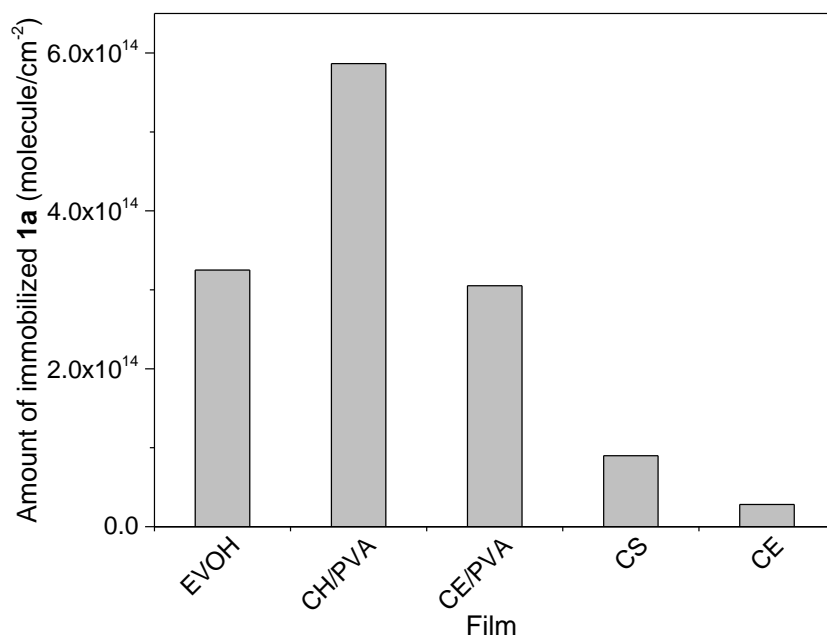


Fig. S20 The amounts of **1a** immobilized on the surface of **EVOH**, **CH/PVA**, **CE/PVA**, **CH** and **CE** films.

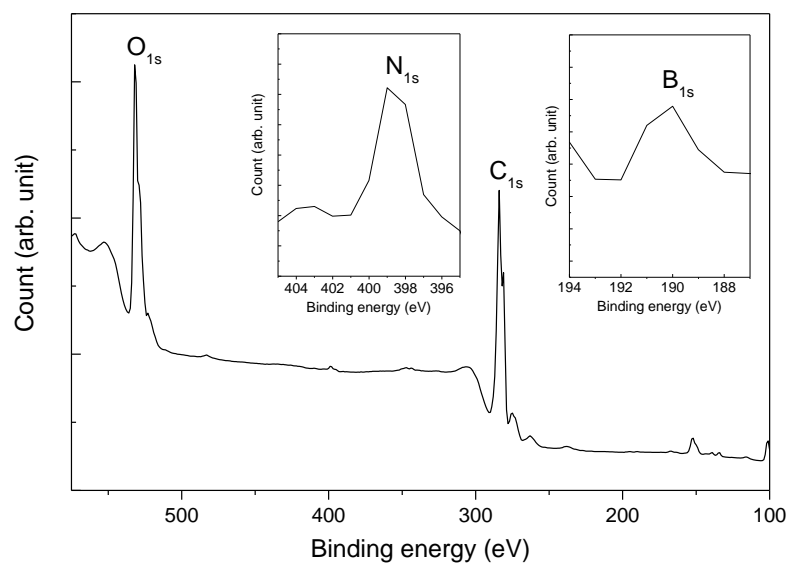


Fig. S21 X-ray photoelectron spectrum of the **1a/PVA** film.

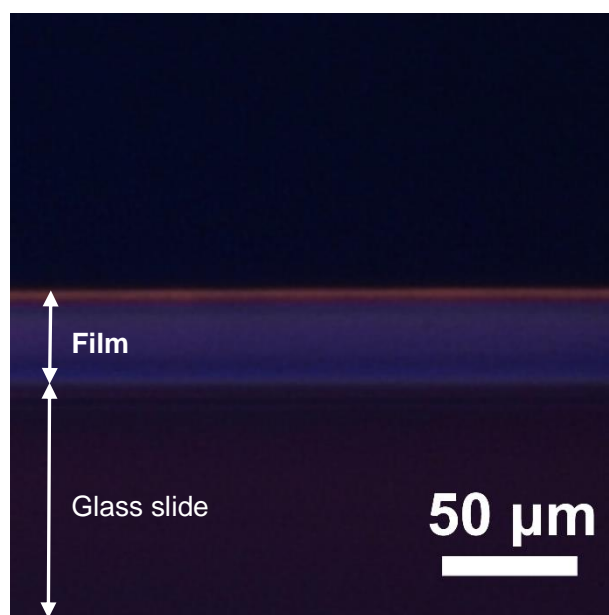


Fig. S22 Fluorescence microscopic image of the cross-section of the **1/PVA** film.

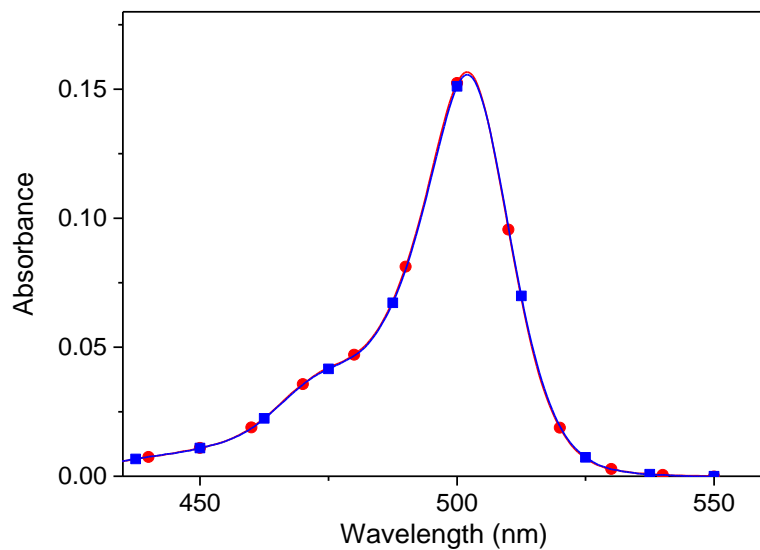


Fig. S23 UV-vis absorption spectra of the **2/PVA** film before (circle) and after (square) washing with methanol.

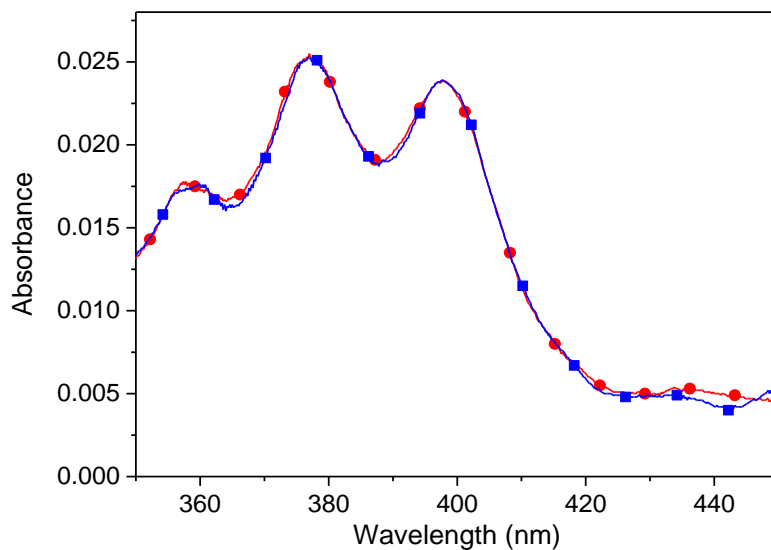


Fig. S24 UV-vis absorption spectra of the **3/PVA** film before (circle) and after (square) washing with methanol.

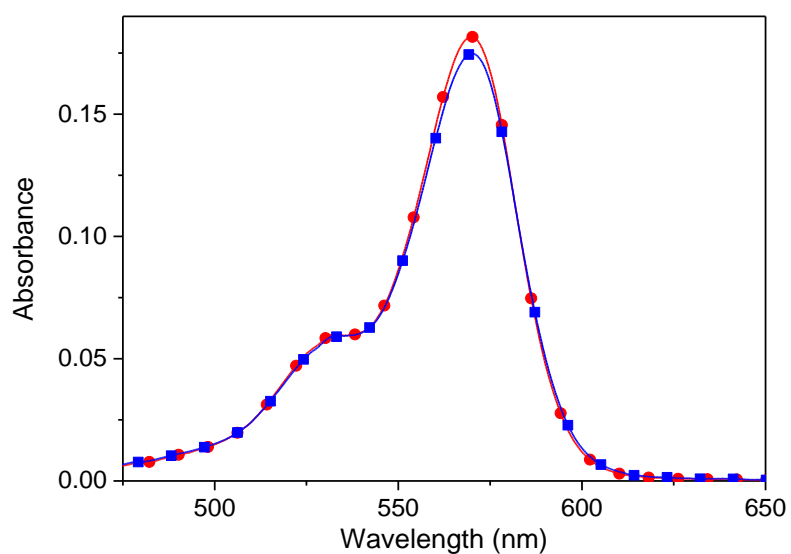


Fig. S25 UV-vis absorption spectra of the **1a/PVA-GA** film before (circle) and after (square) washing with methanol. The amount of immobilized **1a** was determined to be 8.1×10^{14} molecule/cm².

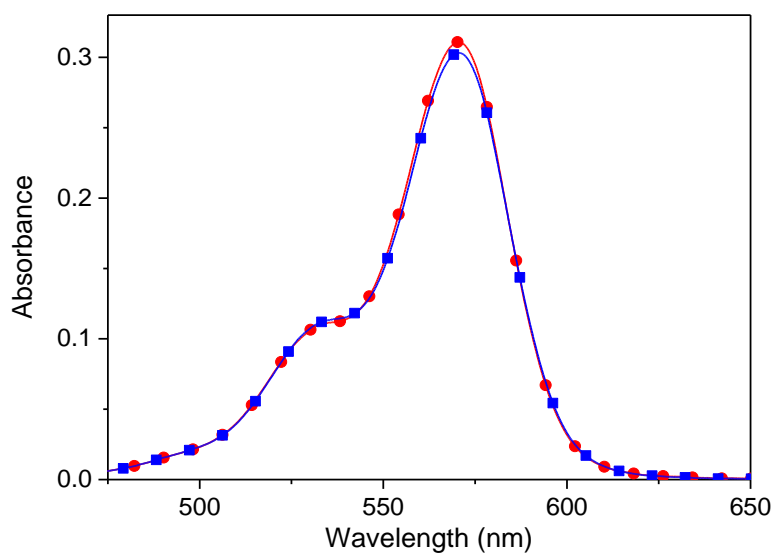


Fig. 26 UV-vis absorption spectra of **1a/PVA-BA** film before (circle) and after (square) washing with methanol. The amount of immobilized **1a** was determined to be 1.4×10^{15} molecule/cm².

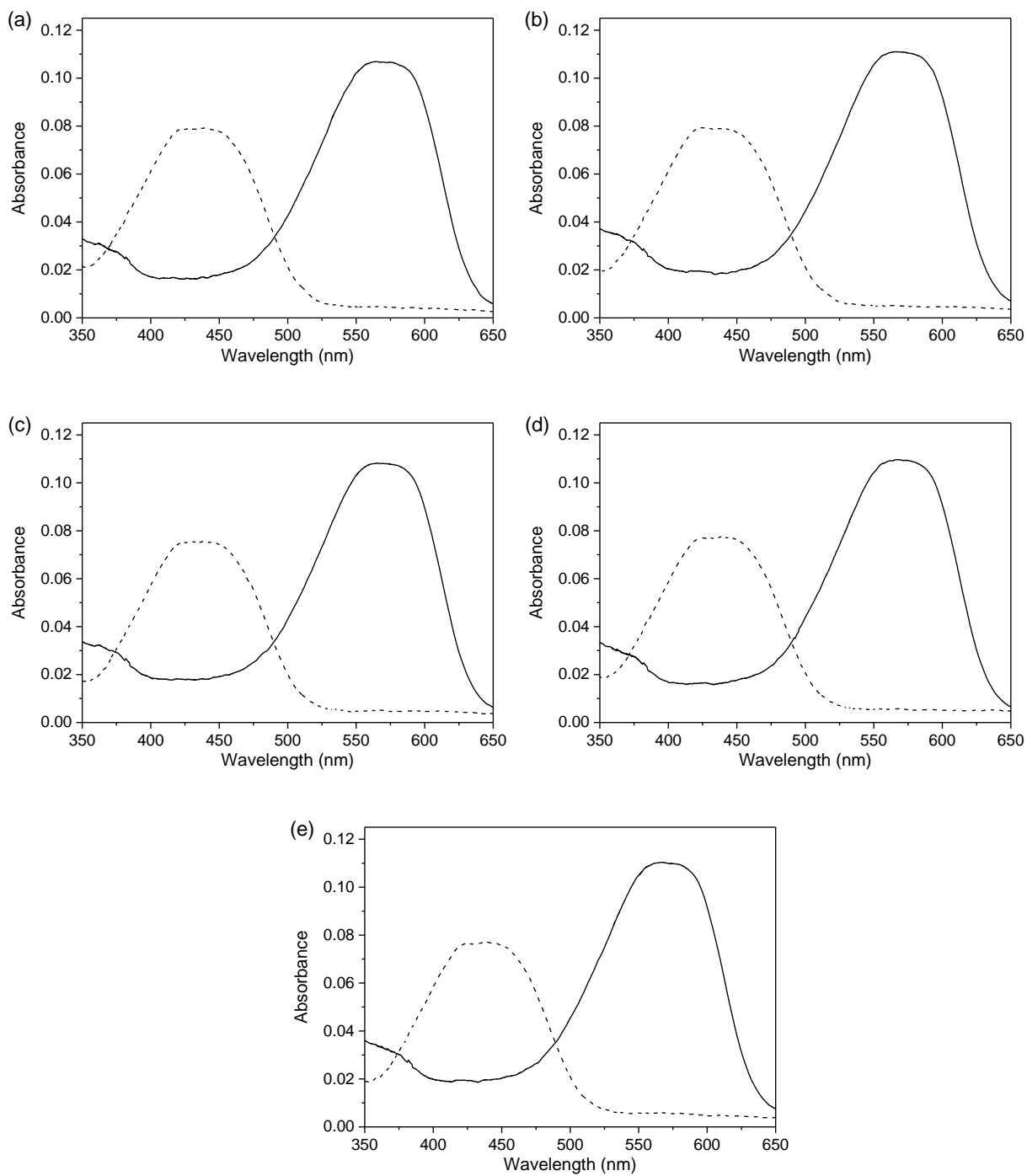


Fig. S27 Absorption spectral changes of the 4/PVA-BA film after repetitive immersion (5 min) in acidic (solid line) and basic (dashed line) aqueous solutions. (a) First, (b) second, (c) third, (d) fourth and (e) fifth cycles.

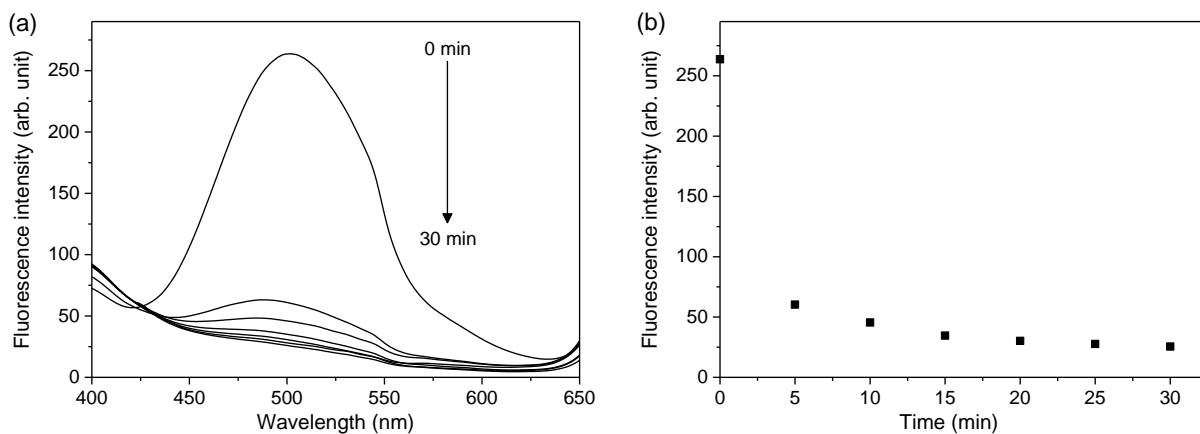
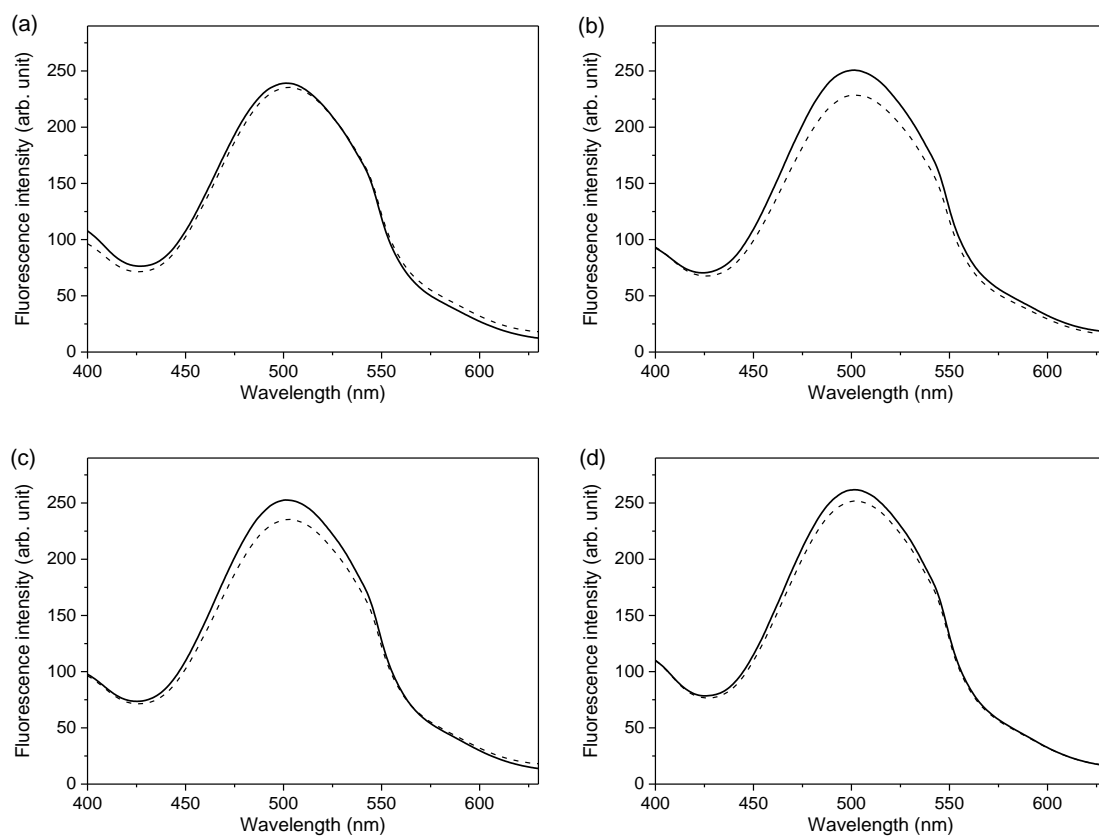
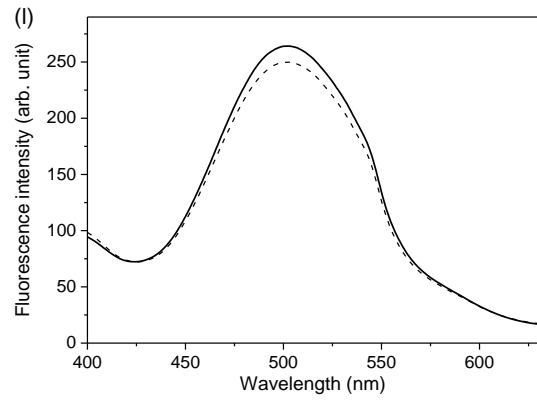
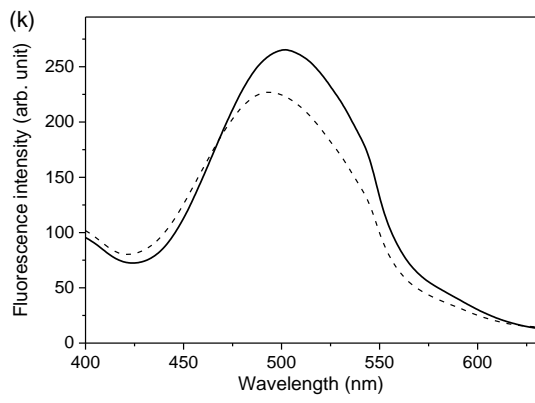
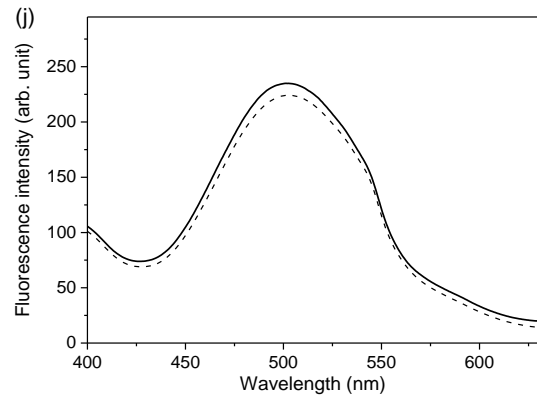
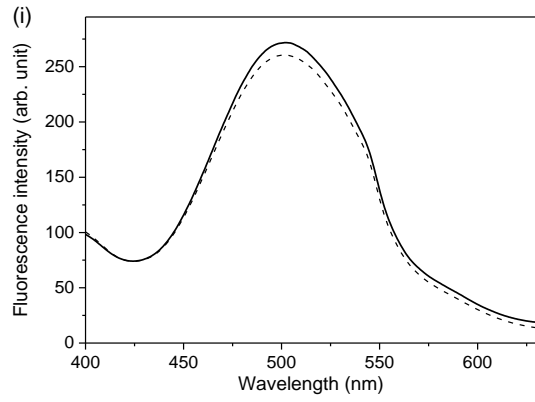
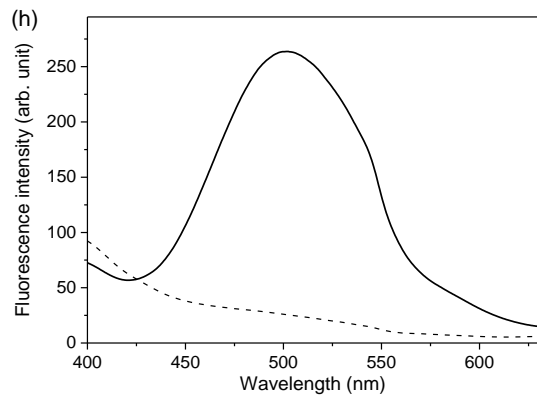
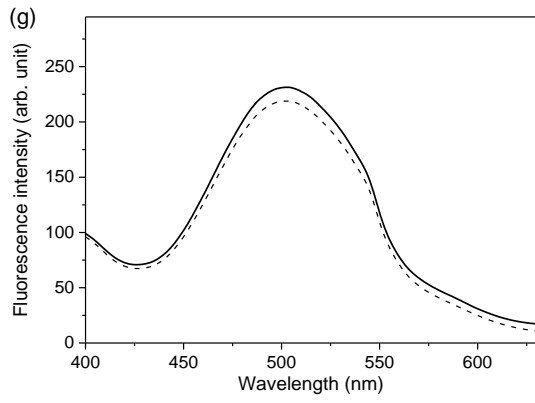
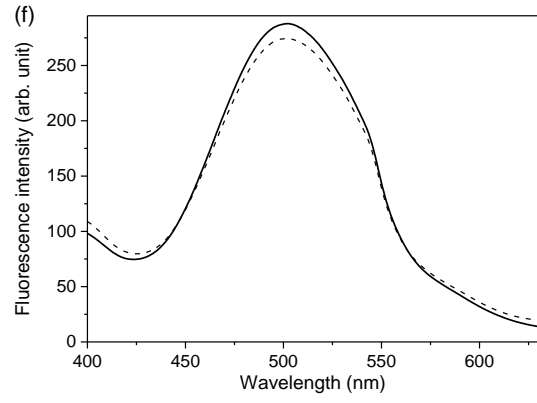
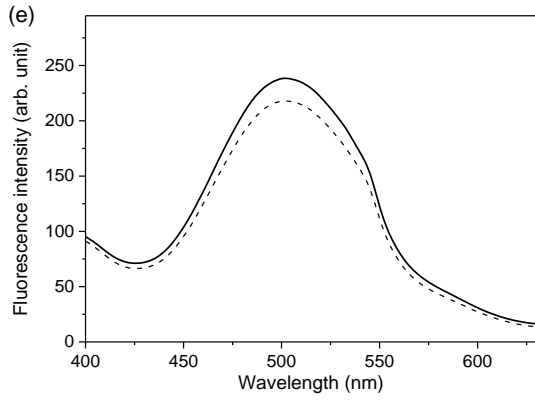


Fig. S28 (a) Fluorescence spectra and (b) intensity ($\lambda_{em} = 502$ nm) of the **5/PVA-BA** film at different immersion time in aqueous solution containing Cu^{2+} ions (2.0×10^{-5} M). Conditions: 5 mM HEPES buffer (30 mL, pH 7.0), $\lambda_{ex} = 340$ nm. Stock solution of copper perchlorate (1.0×10^{-2} M, 60 μL) dissolved in distilled water were added to 5 mM HEPES buffer solutions (30 mL, pH 7.0) in the presence of the **5/PVA-BA** film.





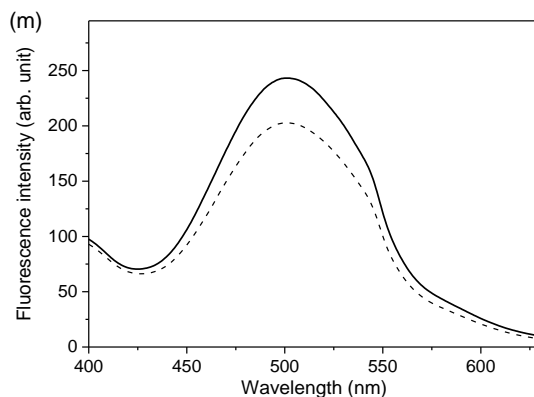


Fig. S29 Fluorescence spectra of **5/PVA-BA** films after immersion in aqueous solution in the absence (solid line) and the presence (dashed line) of (a) Na^+ , (b) K^+ , (c) Mg^{2+} , (d) Ca^{2+} , (e) Fe^{3+} , (f) Co^{2+} , (g) Ni^{2+} , (h) Cu^{2+} , (i) Zn^{2+} , (j) Cd^{2+} , (k) Hg^{2+} , (l) Al^{3+} , and (m) Pb^{2+} ions. Conditions: 5 mM HEPES buffer (30 mL, pH 7.0), $[\text{M}^{n+}] = 2.0 \times 10^{-5}$ M, $\lambda_{\text{ex}} = 340$ nm. Solutions of metal perchlorates dissolved in distilled water (1.0×10^{-2} M, 60 μL) were added to 5 mM HEPES buffer solutions (30 mL, pH 7.0) in the presence of the **5/PVA-BA** films.

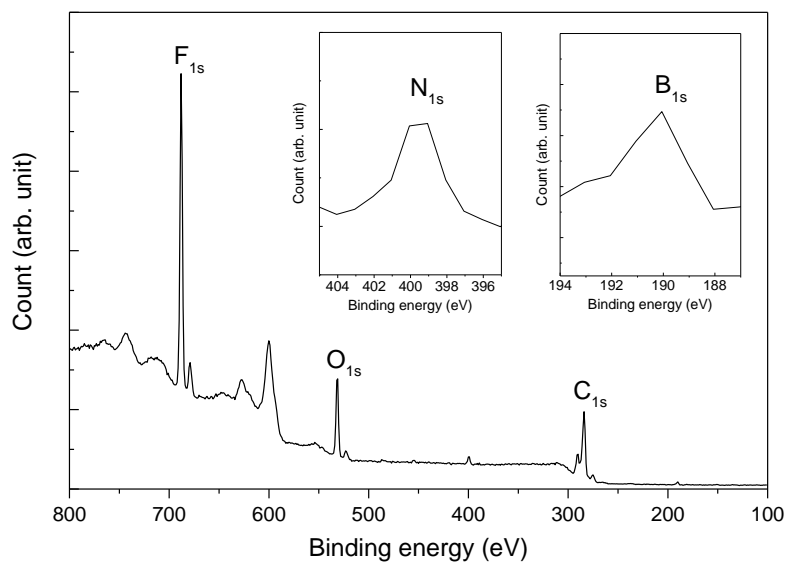


Fig. S30 X-ray photoelectron spectrum of the **6/PVA** film.