

Supporting Information

A Recyclable hydroxyl functionalized polyindole hydrogel for sodium hydroxide extraction via synergistic effects of cation- π interaction and hydrogen bonding

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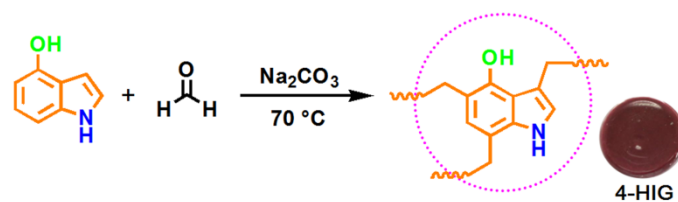
1. General remarks

4-hydroxyindole was purchased from J & K Technology Co., Ltd., and was purified by column chromatography on 100-200 mesh silica gel with petroleum ether (PE) : ethyl acetate (EA)=3.5 : 1. Formaldehyde (HCHO, 37 wt% in H₂O) was purchased from J & K Technology Co., Ltd., and used without further purification. The rest of the materials and reagents were obtained from different commercial sources and used without further purification. FTIR spectra were recorded on a Nicolet 6700 FTIR spectrometer. Solid-state cross-polarization magic-angle-spinning (CP/MAS) NMR spectrum was recorded on a Bruker Avance III 400 NMR spectrometer. The scanning electron microscopy (SEM) image of the 4-HIG hydrogel was made on an Ultra 55 microscope system. Digital photos were taken using a Cannon 600D camera. Absorption spectra were detected on a SHIMADZU UV-3150 UV-vis-NIR spectrophotometer. UV-vis diffuse reflectance spectra (DRS) of the 4-HIG hydrogel were carried out on a Solidspec-3700 spectrometer using BaSO₄ as the background.

2. Synthesis of 4-HIG hydrogel

4-HIG hydrogel was synthesized by the typical sol-gel process as follows: 0.532 g 4-hydroxyindole (4.0 mmol) was dissolved in 6 mL NMP, and 650 μ L HCHO (37 wt% in H₂O) (8.0 mmol) were mixed at room temperature under vigorously stirred at 800 rpm for 10 min. Then, 4 mL 10 mM Na₂CO₃ aqueous solution was added dropwise. The mixture was stirred for 20 min and then was transferred into 2 mL ampoule bottles and aged at 70 °C for 10 hours. The obtained

4-HIG hydrogel was washed with acetone and deionized water, respectively, until the pH of the aqueous solution was 7.0. And the final purple-red hydrogel was prepared.



Scheme S1. Synthesis of 4-HIG hydrogel. Purple-red hydrogel was obtained by reacting 4-hydroxyindole with formaldehyde at 70 °C in the presence of Na₂CO₃ under air conditions.

3. The structure characterization of 4-HIG hydrogel

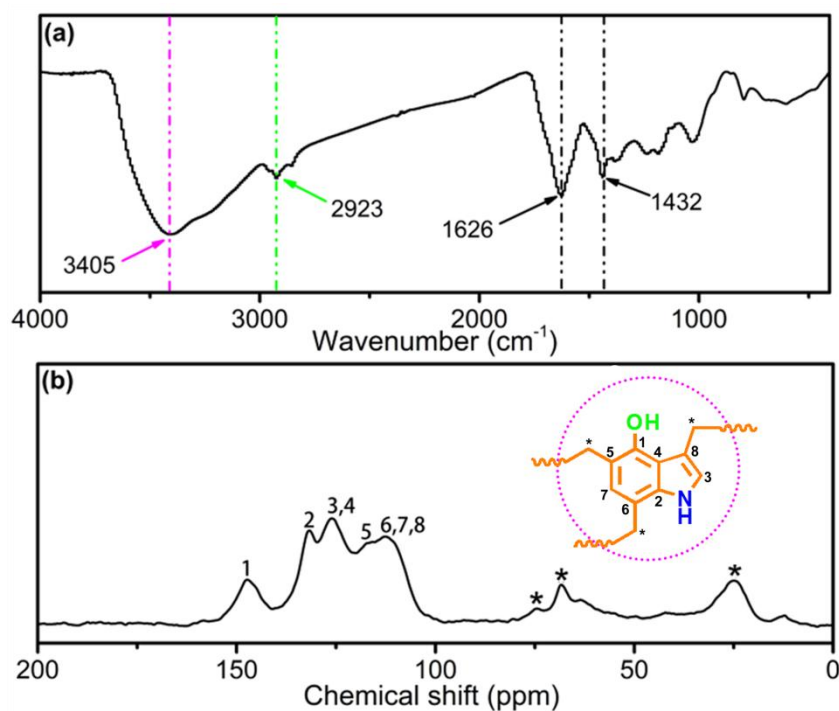


Fig. S1 (a) FTIR spectrum and (b) ¹³C CP/MAS NMR spectrum of 4-HIG hydrogel.

4. Procedure for NaOH absorption

According to the general preparation procedure given above, 4-HIG gel was obtained in an ampoule bottle. A spatula was used to scrape the purple red, stiff gel and form a “ball” of gel to maximize the surface area. The composition of this taken out 0.1 mL of hydrogel was approximately 5 mg polymer synthesizing by the hydroxymethylation of 4-hydroxyindole. Then, we washed the gel with acetone and deionized water for many times to ensure that any residue base Na_2CO_3 was removed. Next, the hydrogel was added to the 2 mL of 25 mM aqueous NaOH. After soaking at various time points, the 4-HIG gel was separated from solutions using 0.45 μm polypropylene syringe filters. Then, aliquots of the NaOH solution (1.5 mL) were removed at different time points and combined with 0.5 mL of a 10 mM solution of phph in MeOH. The concentration of NaOH was evaluated by the UV-vis absorption spectra by recording the intensity of the phph λ_{max} at 554 nm. Spectra were obtained using a quartz cell of 1 cm of optical path length. The pH was also confirmed using litmus paper and a pH probe. These experiments were done in triplicate.

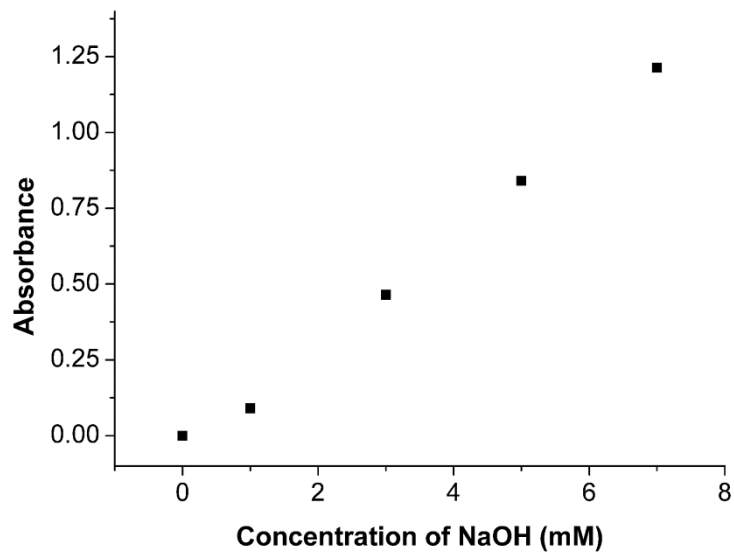


Fig. S2 changes in the UV-visible absorbance intensity of phph (10 mM in 50:50 H₂O:MeOH) at 554 nm as a function of different concentration of NaOH.

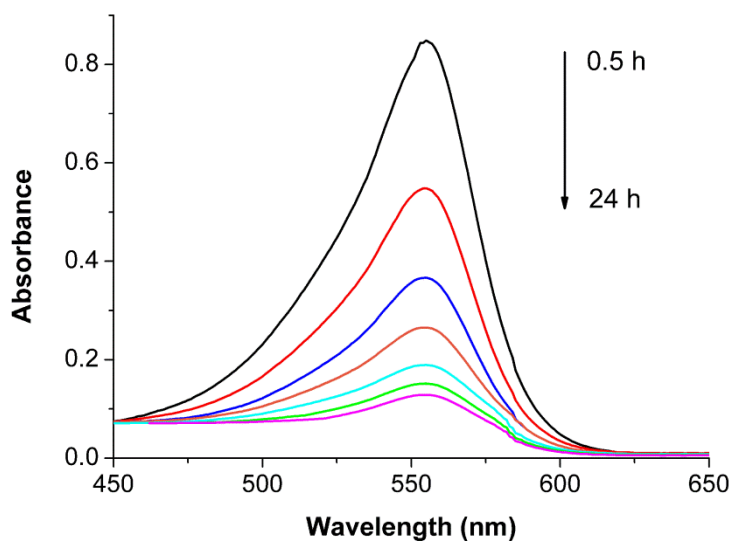


Fig. S3 UV-visible spectra of mixtures of 0.5 mL phph (10 mM in MeOH) and 1.5 mL aliquots of the NaOH aqueous solution after exposure to the 4-HIG gel for the indicated times.

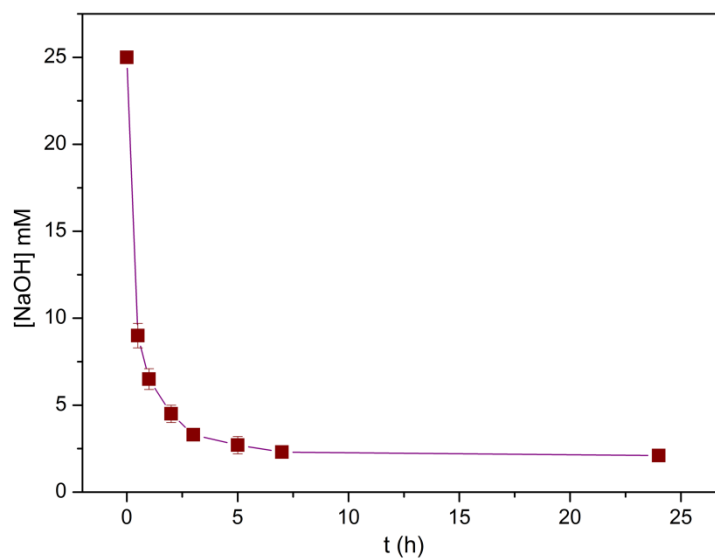


Fig. S4 The concentration of NaOH decreases as a function of time in the presence of the 4-HIG gel. The changes were monitored for up to 24 h. These concentrations were determined by measuring the absorbance intensity of phph at 554 nm as a function of time.

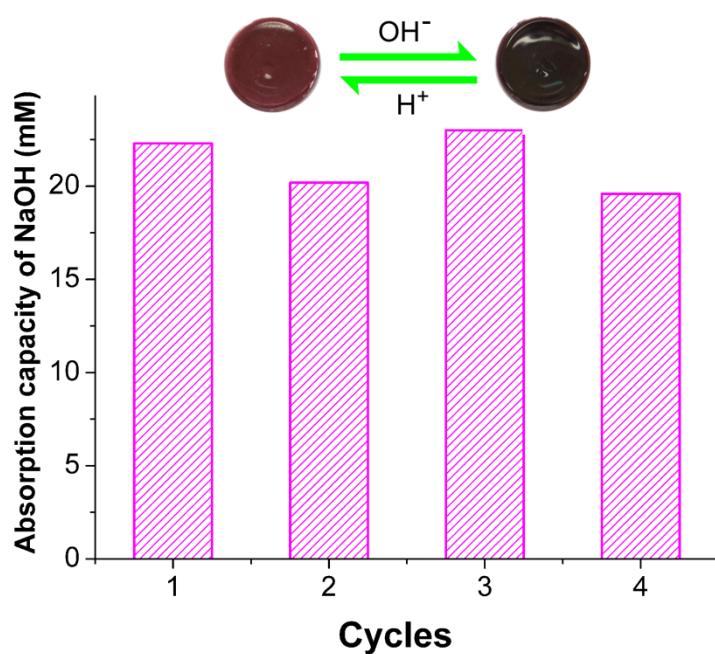


Fig. S5 Reversibility tests showing that the absorption are reversible via a gentle aqueous treatment (H^+ or OH^-).

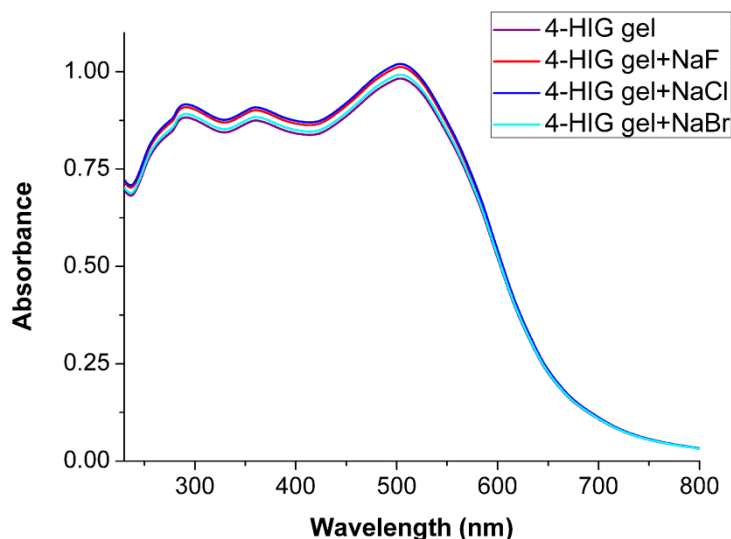


Fig. S6 UV-vis spectra of the 4-HIG gel for soaking 5h in aqueous NaF, NaCl or NaBr, respectively.

5. Simulations

Molecular dynamics (MD) MD simulation was performed using the amorphous cell module of Materials Studio (Accelrys Software Inc.) with a dreiding force field whose intermolecular parameters were optimized using quantum mechanics. A parent 4-HIG (as described in Fig. 1 in the main text) with a five-generation dendrimer was built that consists of indole and hydroxyl groups. Although size of the parent 4-HIG chain is not sufficiently long to represent conformations of a real polymer chain, a previous study has reported a good agreement between experiments and simulations when simulated Li-CMP chains are short (merely five-generation dendrimer on average).^[1] Moreover, a periodic boundary condition were imposed and an initial density of 0.9 g/cm^3 was used to simulate the polymer conformation in bulk under an equilibrium state. The 4-HIG dendrimer in simulation box was relaxed through NVT for 1 ns at 800 K with time steps of 0.2 fs. The simulation of high-temperature relaxation was closely followed a protocol

suggested previously.^[2] After 1 ns of simulated relaxation at 800 K, the system temperature is decreased to 273 K. In order to obtain a suitable structure for further analysis, ten different initial structures for each system were built and relaxed according to the procedure mentioned previously. The one with the lowest system energy was selected as the MD result for further analysis. The MD simulation was performed to analyze the conformation of the complex between 4-HIG and NaOH under an equilibrium state. For example, it is clear that the Na⁺ cation is close to an indole group. The correlation distance is 3.180 Å. To see this in a quantitative way, the radial distribution function, $g_{AB}(r)$, was introduced to describe how density of designated particles varies as a function of distance from a reference particle. Usually, $g_{AB}(r)$ is determined by measuring the ensemble averaged distance between all particle pairs, as follows,

$$g_{AB}(r) = \frac{\langle n_{AB}(r) \rangle}{4\pi r^2 \Delta\rho_{AB}} \quad (1)$$

where, $n_{AB}(r)$ is the distance of each pair between A (Na⁺) and B (indole) in the simulation box. $\langle \dots \rangle$ represents an ensemble average. $\Delta\rho_{AB}$ is the rate of change in the average number density of Na⁺ over distance from an indole ring. The plot of $g_{AB}(r)$ gives the local density of B around A at a distance r . $g_{AB}(r) = 1$ indicate the particles are completely uncorrelated. A positive peak of $g_{AB}(r)$ reflects a definite correlation between atoms at r . As shown in Fig. 3g, a noticeable peak is observed at $r = 3.18$ Å, consistent with the characteristic length of the cation- π interaction.^[3] Meanwhile, the fluctuation of $g_{AB}(r)$ at distances over 5~7 Å indicated the absence of a long-range interaction in the system. To conclude, the analysis of the radial distribution function indicated the presence of a large number of indole-Na⁺ complexes with a correlation distance of 3.18 Å between

the 4-HIG and NaOH. In addition, the electrostatic interactions and hydrogen bonds also confirmed by the same calculation methods.

Density functional theory (DFT) The molecules were optimized with density functional theory (DFT) at the M062x/6-311+g** level theory, using the Gaussian-09 package. The electrostatic potential (ESP) of the model were analyzed using Multiwfn 3.3.5.^[4] The simulation procedure was closely followed a previously suggested one.^[5]

6. References

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