Electronic Supplementary Information

Multi-stimuli-responsive supramolecular gel constructed by pillar[5]arene-based pseudorotaxanes for efficient detection and separation of multi-analytes in water solution

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**Materials and physical methods**
All anions were used as tetrabutylammonium salts, which were purchased from Alfa Aesar and used as received. All metal ions were prepared from the perchlorate salts. Other reagents used in the study were of analytical grade. Fresh double distilled water was used throughout the experiment. All other reagents and solvents were commercially available at analytical grade and were used without further purification. $^1$H NMR spectra were recorded on Mercury-400BB spectrometer (400MHz) and Bruker Digital RF spectrometer (300MHz). $^1$H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, TM scale with the solvent resonances as internal standards). Mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker-FranzenAnalytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. The X-ray diffraction analysis (XRD) was performed on a Rigaku D/Max-2400 X-Ray Diffractometer. The morphologies and sizes of the xerogels were characterized using field emission scanning electron microscopy (FE-SEM, JSM-6701F) at an accelerating voltage of 8 kV. The infrared spectra were performed on a Digilab FTS-3000 Fourier transform-infrared spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). Ultraviolet-visible (UV-vis) spectra were recorded on a Shimadzu UV-2550 spectrometer. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer.
2. Synthesis and characterizations of compound PN and WP5.

Scheme S1 Synthesis of compound PN and WP5.

**Synthesis of compound BD:** A mixture of 1,8-naphthalenedicarboxylic anhydride (1.98 g, 10.0 mmol), glycine (1.13 g, 15.0 mmol) in anhydrous
DMF (20 mL) was stirred at 140 °C reflux for 24 h. After cooling to room temperature, add water and the precipitate was filtered, then with acetonitrile recrystallization get gray powder product BD. yield 65%; m.p. >300 °C; ¹H NMR (600 MHz, DMSO-d₆) δ 13.06 (s, 1H), 8.48 (m, 4H), 7.88 (t, 2H), 4.72 (s, 2H). ESI-MS m/z: [2(BD)+Na]⁺ Calcd for C₂₈H₁₈N₂NaO₈, 533.0961; Found 533.09.

Fig. S1 ¹H NMR spectrum of BD in DMSO-d₆.
Fig. S2 $^{13}$C NMR spectra (151MHz, DMSO-$d_6$) of ND.

Fig. S3 ESI-MS spectrum of BD.

**Synthesis of compound PN**: A mixture of 4-methoxyphenol (2.48 g, 20.0 mmol), K$_2$CO$_3$ (13.82 g, 100 mmol), KI (3.32 g, 20 mmol), 1,10-dibormodecane (24.01 g, 80 mmol) and acetone (400.0 mL) were added
to a 500 mL round-bottom flask under nitrogen atmosphere. The reaction mixture was stirred at 65 °C for 72 h. After the solid was filtered off, the solvent was evaporated and the residue was dissolve in CH₂Cl₂. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (V/V = 50:1) as the eluent, compound ZN as white solid (6.53 g, yield 95%) was obtained. Mp: 60-64 °C. ¹H NMR (600 MHz, CDCl₃) δ 6.83 (s, 4H), 3.90 (t, J = 6.6 Hz, 2H), 3.76 (s, 3H), 3.40 (t, J = 6.9 Hz, 2H), 1.84 (dp, J = 12.9, 7.2 Hz, 2H), 1.75 (p, J = 6.8 Hz, 2H), 1.45 – 1.42 (m, 2H), 1.39 – 1.17 (m, 10H). ¹³C NMR (CDCl₃, 151 MHz), δ/ppm: 153.64, 153.27, 115.41, 114.59, 68.62, 55.73, 34.01, 32.81, 29.42, 29.36, 29.33, 29.32, 28.72, 28.14, 26.02.  ESI-MS m/z: calcd for C₁₇H₂₇BrO₂ [ZN]: 342.12; found: 342.01.

Fig. S4 ¹H NMR spectrum of compound ZN in CDCl₃.
Fig. S5 $^{13}$C NMR spectrum of compound ZN in CDCl$_3$.

Fig. S6 ESI-MS spectrum of compound ZN.
In a 100 mL round bottom flask, compound ZN (0.43 g, 1.25 mmol), K$_2$CO$_3$ (1.55 g, 11.25 mmol), KI (0.08 g, 0.5 mmol), BD (0.26 g, 1.0 mmol) and acetonitrile (75 ml) was added and the reaction mixture was stirred for 48 h at 85 $^\circ$C. After removal of the inorganic salt by filtration, the solvent was evaporated and afford the crude product, which was isolated by flash column chromatography using petroleum ether/ethyl acetate (10:1). The fractions containing the product were combined and concentrated under vacuum to give PN (0.45 g, yield 85%) as a white solid. Mp: 90 - 91 $^\circ$C. $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 8.51 (dd, J = 12.7, 7.8 Hz, 4H), 7.91 – 7.86 (m, 2H), 6.81 (d, J = 1.4 Hz, 4H), 4.80 (s, 2H), 4.07 (t, J = 6.4 Hz, 2H), 3.84 (t, J = 6.5 Hz, 2H), 3.65 (d, J = 3.6 Hz, 3H), 1.65 – 1.59 (m, 2H), 1.54 – 1.49 (m, 2H), 1.35 – 1.29 (m, 2H), 1.23 – 1.10 (m, 10H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 168.55 , 163.74 , 154.01 , 153.47 , 135.54 , 131.79 , 127.98 , 122.14 , 116.10 , 115.34 , 68.71 , 65.60 , 56.10 , 41.91 , 29.41 , 29.12 , 25.88 . ESI-MS m/z: [PN+Na]$^+$ Calcd for C$_{31}$H$_{35}$NNaO$_6$, 540.24; Found 540.26.
Fig. S7 $^1$H NMR spectra (600 MHz, DMSO-$d_6$) of PN.

Fig. S8 $^{13}$C NMR spectra (151 MHz, DMSO-$d_6$) of PN.
Fig. S9 ESI-MS spectrum of PN.

**Synthesis of 1, 4-bis(4-bromohexyloxy)benzene ZM:** Hydroquinone (2.3 g, 20.0 mmol), K₂CO₃ (16.6 g, 120 mmol), KI (6.6 g, 40 mmol), 1, 4-dibromobutane (34.6 g, 160 mmol) and acetone (400.0 mL) were added in a 500mL round bottom flask stirred at room temperature. The reaction mixture was stirred at reflux for 1.5 days. After the solid was filtered off, the solvent was evaporated and the residue was dissolved in CH₂Cl₂. Column chromatography (silica gel; petroleum ether: CH₂Cl₂ = 10:1) afforded a white solid (6.0 g yield 70%). m.p.: 87 °C. ¹H NMR (600 MHz, CDCl₃) δ 6.81 (s, 4H), 3.90 (t, 4H), 3.42 (t, 4H), 1.89 (m, 4H), 1.77 (m, 4H), 1.49 (m, 8H). ESI-MS m/z: [ZM+H]⁺ Calcd for C₁₈H₂₉Br₂O₂, 437.05; Found 437.01.
**Fig. S10** $^1$H NMR spectra (600 MHz, CDCl$_3$) of ZM.

**Fig. S11** $^{13}$C NMR spectra (151 MHz, CDCl$_3$) of ZM.
Fig. S12 ESI-MS spectrum of ZM.

**Synthesis of Copillar[5]arene CP5.** To a solution of 1, 4-bis (4-bromohexyloxy) benzene (1.9 g, 5.0 mmol) and 1,4-dimethoxybenzene (2.76 g, 20.0 mmol) in 1, 2-dichloroethane (200 mL), paraformaldehyde (0.75 g, 25.0 mmol) was added under nitrogen atmosphere. Then boron trifluoride diethyl etherate (6.75 mL, 25 mmol) was added to the solution and the mixture was stirred at room temperature for 4 h and concentrated by rotary evaporation. The resultant oil was dissolved in CH₂Cl₂ and washed twice with H₂O. The organic layer was dried over anhydrous Na₂SO₄ and evaporated to afford the crude product, which was isolated by flash column chromatography using petroleum ether/ethyl acetate (20:1,v/v) to give CP5 2.0219 g (38.66%) as a white solid. m.p.:185-189 °C. 

¹H NMR (600 MHz, CDCl₃, room temperature) δ (ppm): 6.93(m, 10H),
3.82(m, 34H), 3.69(s, 4H), 1.49(m,16H), 0.87(m, 4H). ESI-MS m/z: 
\[\text{[C}_{55}\text{H}_{68}\text{O}_{10}\text{Br}_{2} + \text{NH}_{4}^+]\] Calcd for 1066.3493; Found 1066.3496.

**Fig. S13** $^1$H NMR spectra (600 MHz, CDCl$_3$) of CP5.

**Fig. S14** $^{13}$C NMR spectra (151 MHz, CDCl$_3$) of CP5.
Fig. S15 High resolution mass data of compound CP5.

Synthesis of host compound WP5: Copillar[5]arene CP5 (0.5 g, 0.5 mmol) and trimethylamine (33 % in ethanol, 1.0 mL, 3.7 mmol) were added to ethanol (80 mL). The solution was refluxed overnight. Then the solvent was removed by evaporation, you can afford a white solid. After white solid was washed by diethyl ether to obtain WP5 as a white solid (0.52 g, 93 %). Mp 176–178 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.00 – 6.67 (m, 10H), 3.95 (d, $J = 70.8$ Hz, 4H), 3.83 – 3.53 (m, 34H), 3.43 (t, $J = 7.0$ Hz, 4H), 3.07 (d, $J = 6.1$ Hz, 18H), 1.71 (s, 8H), 1.56 (s, 4H), 1.40 – 1.29 (m, 4H). $^{13}$C NMR (151 MHz, DMSO-$d_6$) $\delta$ 150.34, 149.61, 128.04, 113.77, 68.08, 65.68, 55.99, 55.93, 55.91, 55.84, 52.61, 36.16, 31.18, 29.48, 26.17, 25.83, 22.54. ESI-MS m/z: [C$_{61}$H$_{86}$ BrN$_2$O$_{10}$]$^+$ Calcd
for 1087.27; Found 1087.3384.

**Fig. S16** $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of WP5.

**Fig. S17** $^{13}$C NMR spectra (151 MHz, DMSO-$d_6$) of WP5.
Fig. S18 ESI-MS spectrum of compound WP5.
Table S1. Gelation Property of supramolecular gel WP5-PN-G.

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<th>Entry</th>
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<th>CGC&lt;sup&gt;b&lt;/sup&gt; (%)</th>
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State: \( n_{WP5}/n_{PN} = 1/1 \)

<sup>a</sup>G, P and S denote gelation, precipitation and solution, respectively.

<sup>b</sup>The critical gelation concentration (wt%, 10mg/ml = 1.0%).

<sup>c</sup>The gelation temperature (°C).
Table S2. Optimum water content of gelation conditions

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<th>Water content</th>
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<sup>a</sup> G, P and S denote gelation, precipitation and solution, respectively.

<sup>b</sup> The critical gelation concentration (wt%, 10mg/ml = 1.0% ).

<sup>c</sup> The gelation temperature (°C). C = 90 mM.

Fig. S19 Fluorescence spectra of supramolecular gel WP5-PN-G (in gelated state, 10.5 %, w/v) and solution in the DMSO-H<sub>2</sub>O (1:1, v/v) system (λ<sub>ex</sub> =365 nm).
Fig. S20 Fluorescence spectra of WP5 (c = 90 mM), PN (c = 87 mM), WP5-PN sol (c = 90 mM, T = 85 °C > T_{gel}) and the WP5-PN-G (in the DMSO-H$_2$O (1:1, v/v) system, c = 90 mM, T = 20 °C < T_{gel}, $\lambda_{ex}$ =365 nm).

Fig. S21 Partial $^1$H NMR spectra of WP5 (0.017 mol/L) in DMSO-$d_6$ with increasing amounts of PN, (a) Free WP5; (b) 0.5 equiv. (c) 2.0 equiv. (d) Free PN.
**Fig. S22** 2D NOESY NMR spectrum (600 MHz, 298 K) of 50.0 mM WP5 and PN in DMSO-$d_6$ solution.
Fig. S23 ESI-MS spectrum of the host-guest complex formed between WP5 and PN.
Fig. S24 $^1$H NMR spectra (600 MHz, 298 K) of WP5-PN in DMSO-$d_6$ at various concentrations: (a) 1.0 mM; (b) 2.0 mM; (c) 5.0 mM; (d) 10.0 mM; (e) 20.0 mM.

Fig. S25 XRD diagrams of xerogel of WP5-PN-G, metallogel of WP5-PN-FeG, xerogel of WP5-PN-FeG+F⁻.
Fig. S26 XRD diagrams of xerogel of WP5-PN-G, metallogel of WP5-PN-CuG and xerogel of WP5-PN-CuG +CN−.

Fig. S27 Partial ¹H NMR spectra (600 MHz, DMSO-d₆, 298 K) of WP5-
PN and CH₃COOH at various concentrations: (a) 5.0 mM; (b) 8.0 mM; (c) 10.0 mM; (d) 15.0 mM; (e) 20.0 mM.

**Fig. S28** Photographs of organogel of **WP5-PN-G** (10.5% w/v) in DMSO-H₂O (1:1, v/v) system and organogels of **WP5-PN-G** in the presence of various metal ions (Zn²⁺, Pb²⁺, Cd²⁺, Al³⁺, Cr³⁺, Ni²⁺, Co²⁺, Cu²⁺, Hg²⁺, Fe³⁺, Ba²⁺, Ag⁺, Mg²⁺, Ca²⁺, Tb³⁺, La³⁺ and Eu³⁺) under UV light.
**Fig. S29** Fluorescence spectra of supramolecular gel (a) WP5-PN-G and WP5-PN-FeG (10.5%, in DMSO-H₂O (v:v = 1:1) binary solution, WP5-PN = 1:1). (b) The fluorescence spectra of WP5-PN-G (10.5%, in DMSO-H₂O (v:v=1:1) binary solution, WP5-PN = 1:1) with increasing concentration of Fe³⁺ (using 0.1 mol L⁻¹ Fe³⁺ water solution as the Fe³⁺ sources), λ_{ex} = 365 nm.
Determination of the detection limit

We use the $3\delta$ way to figure out the detection limit. The process of the analysis as follows.

![Graph of fluorescence intensity vs. [Fe$^{3+}$]/[Host]](image)

**Fig. S30** Plot of the intensity at 492 nm for a mixture of WP5-PN-G and Fe$^{3+}$ ($\lambda_{ex} = 365$ nm).

Linear Equation: $Y = -11977.75079X + 629.812$ \hspace{1cm} $R^2 = 0.98555$

$S = 11977.75 \times 10^6$

$$\delta = \sqrt{\frac{\sum (F_i - F_0)^2}{N-1}} = 2.505324 (N=20)$$

$K = 3$

$LOD = K \times \delta / S = 6.27 \times 10^{-10}$ M

Fi is the fluorescence intensity of WP5-PN-G; F0 is the average of the Fi.
Fig. S31 Plot of the intensity at 492 nm for a mixture of WP5-PN-G and Cu$^{2+}$ in DMSO-H$_2$O (1:1, v/v) solution ($\lambda_{ex} = 365$ nm).

Linear Equation: $Y=−2192.72501X+665.07778 \quad R^2=0.99203$

$S=2192.73\times10^6$

$$\delta = \sqrt{\frac{\sum (F_i - F_0)^2}{N-1}} = 3.326178 \quad (N=20)$$

$K=3$

$LOD = K\times\delta/S = 4.55\times10^{-9}$ M

Fi is the fluorescence intensity of WP5-PN-G; F0 is the average of the Fi.

**Table S3.** A part of the literatures about the LOD (mol/L) of cations and anions (Fe$^{3+}$, Cu$^{2+}$, F$^-$ and CN$^-$) were provided in the followed table.
### Table S4 Adsorption percentage of WP5-PN-G for Fe^{3+} and Cu^{2+}.

<table>
<thead>
<tr>
<th>Ions</th>
<th>Initial concentration (M)</th>
<th>Residual concentration (M)</th>
<th>Adsorption percentage %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe^{3+}</td>
<td>1×10^{-4}</td>
<td>1.93×10^{-6}</td>
<td>98.07</td>
</tr>
<tr>
<td>Cu^{2+}</td>
<td>1×10^{-4}</td>
<td>4.62×10^{-6}</td>
<td>95.38</td>
</tr>
</tbody>
</table>

Calculation method of adsorption percentage:

\[
\text{Adsorption percentage(\%)} = \left(1 - \frac{C_R\times V_R}{C_I\times V_I}\right) \times 100\%
\]

(state: \(C_R\) is the residual concentration of Fe^{3+}, \(C_I\) is the initial concentration of Fe^{3+}, \(V_R=V_I\))
Fig. S32 (a) Photographs of WP5–PN-CuG in the DMSO-H₂O (1:1, v/v) system (10.5 %, w/v) and WP5–PN-CuG in the presence of various anions under UV light. (b) Fluorescence spectra of WP5–PN-CuG and WP5–PN-CuG (in gelated state) in the presence of various anions, ($\lambda_{ex}$ = 365 nm).

Fig. S33 Fluorescence spectra of supramolecular metallogel WP5-PN-
CuG (10.5%, w/v) with increasing concentration of CN⁻ (using 1.0 M NaCN water solution as the CN⁻ source), $\lambda_{ex} = 365$ nm.

Fig. S34 FT-IR spectra of xerogel of WP5-PN-G, metallogel WP5-PN-FeG and WP5-PN-FeG +F⁻.

Fig. S35 FT-IR spectra of xerogel of WP5-PN-G, metallogel WP5-PN-CuG and WP5-PN-CuG +CN⁻.
Fig. S36 ESI-MS spectrum of WP5-PN-Fe$^{3+}$.

Fig. S37 ESI-MS spectrum of WP5-PN-Cu$^{2+}$. 
Fig. S38 Absorbance spectra of WP5-PN-G (2.0 × 10⁻⁵ M) in DMSO-H₂O (1:1, v/v) solution upon the addition of Fe³⁺ (5.0 equiv.) and F⁻ (20.0 equiv.). Inset: photograph showing the change in color of the solution of WP5-PN-G in DMSO-H₂O (1:1, v/v) solution after addition of Fe³⁺ and F⁻ at room temperature.
**Fig. S39** Partial $^1$H NMR spectra (600 MHz, DMSO-$d_6$, 298 K) of (a) WP5-PN in the presence of varying amounts of Cu$^{2+}$ and (b) WP5-PN + Cu$^{2+}$ in the presence of varying amounts of CN$^-$.  

![Graph showing NMR spectra](image1)

**Fig. S40** Emission spectra showing the reversible evidence between WP5-PN-G and Fe$^{3+}$ by introduction of F$^-$ ($\lambda_{ex} = 365$ nm).  

![Graph showing emission spectra](image2)

**Fig. S41** Fluorescent ‘‘Off–On–Off’’ cycles of WP5-PN-G controlled by the alternating addition of Cu$^{2+}$ and CN$^-$, ($\lambda_{ex} = 365$ nm).  

![Graph showing fluorescent cycles](image3)
**Fig. S42** (a) Recyclable separation of Fe$^{3+}$ ($\lambda_{ex} = 365$ nm), (b) Recyclable separation of Cu$^{2+}$ ($\lambda_{ex} = 365$ nm).

**References:**


