Supporting Information for:

Ion pair Induced Environmental Responsive Metal-Organic Gel: en Route to Smart Material for Volatile Salt-Based Nitrogen (VBN) Sensing

Chao-Ping Hou, ^[a] *Ming-Rui Leng*, ^{[a][b]} *Qiong-Yu Yang*, ^[a] *Jun-Feng Xiang* ^{[c][d]} *and Han-Yuan Gong* ^{*[a]}

^aCollege of Chemistry, Beijing Normal University, Xinjiekouwaidajie 19, Beijing, 100875 (China);

^bDepartment of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, Wisconsin 53706 (USA);

^cInstitute of Chemistry, Chinese Academy of Sciences, Zhongguanchunbeiyijie 2, Beijing, 100190 (China);

^dUniversity of Chinese Academy of Sciences, Beijing 100049 (China)

*e-mail: hanyuangong@bnu.edu.cn

Materials and Methods

Section S1: General considerations. (pp. S3)

Section S2: Synthesis of $1^{2+} \bullet PF_6^-$ and $1^{2+} \bullet NO_3^-$.(pp. S4-S11)

Section S3: The characterization and mechanism of $1^{2+}-Ag^+-NO_3$ gel construction. (pp. S12-S23)

Section S4: The Ag^+ - NO_3^- ion pair selectivity in gel construction with $\mathbf{1}^{2+}$. (pp. S24-S26)

Section S5: The stability characteriation of $I^{2+}-Ag^+-NO_3^-$ gel. (pp. S27)

Section S6: The adductive response of 1^{2+} - Ag^+ - NO_3^- gel. (pp. S28-S31)

Section S7: The fish freshness detection via VBN sensing. (pp. S31)

Section S8: References. (pp. S32-33)

Section S1: General considerations.

All reagents were purchased commercially (Aldrich, Acros, or Fisher) and used without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). NMR spectra were recorded on Bruker Avance 600 or Bruker Avance III 500WB instruments. The ¹H chemical shifts are reported relative to the residual solvent (¹H: acetonitrile- d_3 at 1.94 ppm, DMSO- d_6 at 2.50 ppm; ¹³C: DMSO- d_6 at 39.52 ppm).^[1] Electrospray ionization high resolution mass spectrometry (ESI-HRMS) was carried out with a Bruker Solarix XR FTMS instrument. The concentration dependent dynamic light scattering (DLS) test was detected on ZetaPlus. A SU8010 scanning electron microscope (SEM) was used for taking the pictures. Single crystal X-ray diffraction was achieved with XtaLAB SuperNova. 1,4-Bis((1-(6-(1H-imidazol-1-yl)pyridin-2-yl)-1Himidazol-3-yl)methyl)benzene ($\mathbf{1}^{2+}$) was studied with its PF₆ - salt (*i.e.*, $\mathbf{1}^{2+}$) •2PF $_{6}$). Unless otherwise indicated, tested anions included in this study were either used in the forms of their corresponding tetrabutylammonium (TBA⁺) salts. For the bicarbonate anion species, tetraethylammonium (TEA^{+}) was the counter cation.

Section S2: Synthesis of $1^{2+} \bullet PF_6^-$ and $1^{2+} \bullet NO_3^-$.

Synthesis of 2,6-di(1H-imidazol-1-yl) pyridine (2)

Follow the reported procedure ^[2], 2,6-dibromopyridine (947 mg, 4.0 mmol) afforded **2** as a white solid (801 mg; yield: 95%). ¹H NMR (600 MHz, DMSO- d_6) δ 8.76 (s, 1H), 8.19 (t, *J* = 8.0 Hz, 1H), 8.14 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.16 (s, 1H). The characterization data of this product matches that found in the literature.



300 K (600 MHz).

Synthesis of 1,4-bis((1-(6-(1*H*-imidazol-1-yl)pyridin-2-yl)-1*H*-imidazol -3-yl)methyl)benzene hexafluorophosphate [1²⁺•2PF₆⁻](1²⁺).

A solution of 1,4-bis-bromomethylbenzene (264 mg, 1.09 mmol) in acetonitrile (100 mL) was added dropwise to a solution of 2,6-di(1Himidazol-1-yl)pyridine (422 mg, 2.09 mmol) in acetonitrile (150 mL) over a period of 6 h. The mixture was heated under reflux for 48 h. After cooling to room temperature, the solvent was removed *via* rotary evaporation. The residue was dissolved in water (200 mL) and NH_4PF_6 (10.0 mmol, 1.63 g) was added to the solution. This gave rise to a light yellow precipitate, which was filtered off and washed with 200 mL water. The crude product was recrystallized from acetonitrile and water to give out 637 mg of $1^{2+\bullet}2PF_6^ (1^{2+})$ in the form of colourless crystals in 78% yield. ¹H NMR (600 MHz, DMSO- d_6) δ 10.45 (s, 1H), 8.88 (s, 1H), 8.72 (s, 1H), 8.41 (t, J = 8.0 Hz, 1H), 8.22 (s, 1H), 8.06 (s, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 8.0Hz, 1H), 7.61 (s, 2H), 7.23 (s, 1H), 5.57 (s, 2H). ¹³C NMR (150 MHz, DMSO- d_6) δ 148.1, 145.6, 144.4, 136.3, 136.2, 135.5, 130.9, 129.5, 124.1, 120.4, 117.4, 113.5, 111.7, 52.8. HRMS (ESI) Calc. for C₃₀H₂₆F₆N₁₀P₁ (M+H⁺): 671.1978; found: 671.1966.



Figure S3. ¹³C-NMR spectrum of $\mathbf{1}^{2+}$ in DMSO-*d*₆ at 300 K (150 MHz).



Figure S4. ESI-HRMS spectrum of 1^{2+} .

Synthesis of 1,4-bis((1-(6-(1*H*-imidazol-1-yl)pyridin-2-yl)-1*H*-imidazol -3-yl)methyl)benzene nitrate [1²⁺•2NO₃⁻].

 $1^{2+} \cdot 2PF_6^-$ (1.0 mmol, 816 mg) was dissolved in CH₃CN (200 mL) and the acetonitrile solution (10 mL) of TBA⁺ • NO₃⁻ (10.0 mmol, 1.63 g) was added to the solution. This gave rise to a white precipitate, which was filtered off and washed with 200 mL acetonitrile. The crude product was recrystallized from acetonitrile and water to give 768 mg of $1^{2+} \cdot 2NO_3^-$ in the form of white solid in 94% yield. ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.44 (s, 1H), 8.86 (s, 1H), 8.72 (s, 1H), 8.40 (t, *J* = 8.0 Hz, 1H), 8.21 (s, 1H), 8.06 (s, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.61 (s, 2H), 7.22 (s, 1H), 5.57 (s, 2H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 148.2, 145.7, 144.4, 136.3, 136.2, 135.5, 131.1, 129.5, 124.1, 120.4, 117.4, 113.5, 111.7, 52.7. HRMS (ESI) Calc. for C₃₀H₂₆N₁₁O₃ (M+H⁺): 588.2215; found: 588.2206.



Figure S6. ¹³C-NMR spectrum of $1^{2+} \cdot 2NO_3^{-}$ in DMSO-*d*₆ at 300 K (150 MHz).



Figure S7. ESI-HRMS spectrum of $1^{2+} \cdot 2NO_3^-$

Single crystal X-ray structural analysis of 1²⁺.

The single crystal sample used to obtain the X-ray diffraction structure was grew as clear light colourless prism. The .cif document is available as separate supporting information file; it provides details regarding the specific crystal used for the analysis, along with the structure in question. Diffraction grade crystals were obtained by slow evaporation from solution of 1^{2+} in the mixture of water/acetonitrile (1:1, ν/ν).

The data crystal was cut from a cluster of crystals and had the approximate dimensions given in the .cif document. The data were collected on SuperNova, Dual, Cu at zero, AtlasS2. Data reduction was performed using CrystalClear. The structures were refined by full-matrix least-squares on F2 with anisotropic displacement parameters for the nonH atoms using SHELXL-2014.^[3] R(F), Rw(F2) and the goodness of fit, S, are given below and in the .cif document.^[4] All ellipsoid figures were generated using SHELXTL/PC.^[5] Positional and thermal parameters, bond lengths and angles, torsion angles, figures and lists of observed and calculated structure factors are located in the .cif document available from the Cambridge Crystallographic Data Centre (CCDC) by quoting the CCDC reference number 1909312. The .cif document also contains details of crystal data, data collection and structure refinement.

The crystallographic information and structural parameters for $1^{2+} \cdot 2PF_6^$ are as follows: $C_{30}H_{26}F_{12}N_{10}P_2$; clear light colourless prism, $0.12 \times 0.03 \times$ 0.02 mm^3 ; monoclinic, space group P 2₁/c; a = 11.094(2), b = 9.7187(19), c = 14.962(3) Å; $\alpha = 90$, $\beta = 98.144(17)$, $\gamma = 90$; V = 1596.9(5) Å^3; Z = 2; $\rho_{calcd} = 1.698 \text{ g} \cdot \text{cm}^{-3}$; T = 100.00(10) K; 2524 reflections collected, 274 parameters, 0 restraints; R₁ = 0.1016, wR₂ =0.2016 [I > 2.0\sigma(I)]; R₁ = 0.2733, wR₂ = 0.2448 (all data); good of fit = 1.011; CCDC number: 1909312.





Figure S8. The single crystal structure of 1^{2+} is shown in a top view in ellipsoid form (a). Also shown are a top view (b), side view (c), and front view (d) in capped stick forms. Selected atomic distances (Å): C(2)-H(2)···F(3) 3.325(7), C(10)-H(10)···F(4) 3.051(6) and C(12)-H(12)···F(1) 3.455(6). Selected interatomic angles: C(2)-H(2)··· F(3) 145.32(3)°, C(10)-H(10)···F(4) 149.02(4)° and C(12)-H(12)···F(1) 166.60(3)°.

Section S3: The characterization and mechanism of $I^{2+}-Ag^+-NO_3^-$





Figure S9. ¹H-NMR Job-plots (600 MHz) corresponding to the binding between 1^{2+} and AgPF₆. $[1^{2+}] + [Ag^+] = 1.00 \times 10^{-3}$ M. The maximum value was found at 0.5, a finding consistent with a 1:1 (host:guest) binding stoichiometry.^[6]



Figure S10. ¹H-NMR spectroscopic titration of $\mathbf{1}^{2+}$ (1.00 × 10⁻³ M) with AgPF₆ in the mixture of DMF- d_7 and acetonitrile- d_3 (1:1, ν/ν) at 300 K (600 MHz).



Figure S11. ¹H-NMR binding isotherms corresponding to the interaction between 1^{2+} and AgPF₆ in the mixture of DMF- d_7 and acetonitrile- d_3 (1:1, ν/ν) at 300 K (600 MHz). The chemical shift changes of H(2-9) on 1^{2+} were used for the calculation of $1gK_a = 3.0(2)$, corresponding to the formation of $[1^{2+} \cdot Ag^+]^{3+}$, using the Hyperquad 2003 program.^[7] The red dashed lines show the non-linear curve fit of the experimental data to the appropriate equation.



Figure S12. ¹H-NMR Job-plots (600 MHz) corresponding to the binding between 1^{2+} and AgClO₄. $[1^{2+}] + [Ag^+] = 1.00 \times 10^{-3}$ M. The maximum value was found at 0.5, a finding consistent with a 1:1 (host:guest) binding stoichiometry. ^[6]



Figure S13. ¹H-NMR spectroscopic titration of $\mathbf{1}^{2+}$ (1.00 × 10⁻³ M) with AgClO₄ in the mixture of DMF-*d*₇ and acetonitrile-*d*₃ (1:1, *v*/*v*) at 300 K (600 MHz).



Figure S14. ¹H-NMR binding isotherms corresponding to the interaction between 1^{2+} and AgClO₄ in the mixture of DMF- d_7 and acetonitrile- d_3 (1:1, v/v) at 300 K (600 MHz). The chemical shift changes of H(2-9) on 1^{2+} were used for the calculation of $lgK_a = 3.2(2)$, corresponding to the formation of $[1^{2+} \cdot Ag^+]^{3+}$, using the Hyperquad 2003 program.^[7] The red dashed lines show the non-linear curve fit of the experimental data to the appropriate equation.



Figure S15. ¹H-NMR spectroscopic titration of $\mathbf{1}^{2+}$ (1.00 × 10⁻³ M) with AgNO₃ in the mixture of DMF-*d*₇ and acetonitrile-*d*₃ (1:1, *v*/*v*) at 300 K (600 MHz).



Figure S16. ¹H-NMR Job-plots (600 MHz) corresponding to the binding between a mixture consisting of 1^{2+} and AgPF₆ ($1^{2+} \cdot Ag^+$ as host) with TBA⁺NO₃⁻ (guest). [$1^{2+} \cdot Ag^+$] + [NO₃⁻] = 1.00 × 10⁻³ M. The maximum value was found at 0.67, a finding consistent with a 1:2 (host:guest) binding stoichiometry. ^[6]



Figure S17. ¹H-NMR spectroscopic titration of a mixture consisting of 1 molar equiv. of $\mathbf{1}^{2+}$ (1.00 × 10⁻³ M) and 1 molar equiv. of AgPF₆ with increasing TBA⁺•NO₃⁻ in the mixture of DMF- d_7 and acetonitrile- d_3 (1:1, v/v) at 300 K (600 MHz).



Figure S18. ¹H-NMR binding isotherms corresponding to the interaction between 1^{2+} (1 × 10⁻³ M) and 1 molar equiv. of AgPF₆ with increasing TBA⁺NO₃⁻ in the mixture of DMF-*d*₇ and acetonitrile-*d*₃ (1:1, *v/v*) at 300 K (600 MHz). The chemical shift changes of H(1-9) on 1^{2+} were used for the calculation of $1gK_a = 3.3(3)$, corresponding to the formation of $[1^{2+} Ag^+ NO_3^-]^{2+}$ and $1gK_a = 2.7(2)$ corresponding to the further formation of $[1^{2+} Ag^+ 2NO_3^-]^{+}$ on the basis of $1gK_a = 3.0(1)$ of $[1^{2+} Ag^+]^{3+}$ using the Hyperquad 2003 program.^[7] The red dashed lines show the non-linear curve fit of the experimental data to the appropriate equation.

Concentration dependent Uv-vis spectroscopic study of 1²⁺-Ag⁺-NO₃⁻

Concentration dependent Uv-vis spectroscopic study of the mixture containing 1^{2+} and 1 molar equiv. of AgPF₆ and 5 molar equiv. of TBA⁺• NO₃⁻ was carried out. Uv-vis absorbance of the mixture increases stepwise from 1.4 mM to 2.0 mM at 290 nm (Figure S19a). The values of \mathcal{E} at 290 nm starts to decline at 1.40 mM (Figure S19b). The results suggested that the Ag⁺-NO₃⁻ ion-pair interact with 1^{2+} induced the gel formation with the CGC as $[1^{2+}] = 1.40$ mM, a finding consistent with the result in DLS study.



Figure S19. (a) Original Uv-vis spectra of the solution containing 1^{2+} , 1 molar equiv. of AgPF₆ and 5 molar equiv. of TBA⁺•NO₃⁻ in the mixture of DMF-*d*₇ and acetonitrile*d*₃ (1:1, *v/v*) at 300 K (600 MHz) (insert: the plot of Abs at 290 nm vs. [1^{2+}]); (b) The plot of \mathcal{E} (290 nm) *vs*. [1^{2+}] from concentration dependent Uv-vis spectroscopic study.

Diffusion-ordered NMR spectroscopy (DOSY) study of 1²⁺-Ag⁺

Concentration dependent DOSY experiment⁸ of the mixture containing 1^{2+} and 1 molar equiv. of AgPF₆ were carried out. The diffusion coefficient decreases with increasing concentration, which implied that supramolecular aggregators with higher order construct.



Figure S20. DOSY (600 MHz, 298 K) plot of solutions in acetonitrile- d_6 /DMF- d_7 (1:1, v/v) containing $\mathbf{1}^{2+}$ and 1 molar equiv. of AgPF₆.

However, due to the critical gel concentration (CGC) of our present system is as low as 0.1 wt%, 5 molar equiv. of additional $TBA^+ \cdot NO_3^-$ can form a gel even [1²⁺] as low as 1.40 mM. The concentration is too low for DOSY detection resolution limit. We also try DOSY detection of the gel system at high temperature. However, our gel is heating stable and can't change into a clear solution in the temperature scale from 298 K to 413 K. So the DOSY detection of the gel was unsuccessful.



Concentration dependent ¹H NMR spectroscopic study of 1²⁺-Ag⁺.

Figure S21. Concentration dependent ¹H NMR spectra recorded for 1^{2+} in the presence of 1 molar equiv. of AgPF₆ in the mixture containing DMF- d_7 and acetonitrile- d_3 (1:1, ν/ν) at 300 K over the indicated spectral ranges (600 MHz).

Mass spectroscopic study of 1²⁺-Ag⁺ and 1²⁺-Ag⁺-NO₃⁻

A white precipitate was obtained via adding AgPF₆ (10.1mg, 0.04 mmol) dissolved in 1 mL acetonitrile to a solution of 1^{2+} (16.3mg, 0.02 mmol) in 1 mL acetonitrile. Electrospray ionization high resolution mass spectrometry (ESI-HRMS) using a Bruker Solarix XR FTMS instrument analysis revealed a peak corresponding to $[1^{2+}+Ag^++PF_6^-+2H]^{2+}$ (Cal. m/z = 390.0596 Found. m/z = 390.0517) in the gas phase. A white precipitate was obtained *via* adding the mixture of AgPF₆ (10.1mg, 0.04 mmol) and TBA⁺ • NO₃⁻ (60.9mg, 0.20 mmol) into a solution of 1^{2+} (16.33mg, 0.02mmol) in 1 mL acetonitrile. Instrument analysis revealed a peak corresponding to $[1^{2+}+Ag^++PF_6(10.1mg, 0.04 mmol)$ and TBA⁺ • NO₃⁻ (60.9mg, 0.20 mmol) into a solution of 1^{2+} (16.33mg, 0.02mmol) in 1 mL acetonitrile. Instrument analysis revealed a peak corresponding to $[1^{2+}+Ag^++NO_3^--H]^{+}$ (Cal. m/z = 694.1193 Found. m/z = 694.1186) in the gas phase. Several ions corresponding to the existence of

host/guest complexes, especially the aggregation of $1^{2+} \cdot Ag^+$ in the gas phase were seen as presented below (Table S1).

Table S1. Summary of ESI-HRMS results. Peak assignments were confirmed by collisional activation (fragmentation) experiments, which produced ions corresponding to the free host $\mathbf{1}^{2+}$ in all cases.

Presumed	Observed	Calculate	Proposed m/z Assignment
Compound	Peak	m/z,	
$1^{2+\bullet}Ag^{+\bullet}3PF_6^-$	891.0868	891.0395	$[1^{2+}+2Ag^{+}+PF_{6}^{-}+4H]^{+}$
	925.0629	925.0753	$[(1^{2+})_2+2Ag^++4PF_6^-+2H]^{2+}$
	1023.6029	1023.6948	$[(1^{2+})_3+3Ag^++PF_6^-+H]^{2+}$
$1^{2+} \cdot Ag^+ \cdot 3NO_3^-$	632.1242	632.1229	$[(1^{2+})_2+2Ag^+-4H]^{2+}$
	694.1185	694.1193	$[1^{2+}+Ag^{+}+NO_{3}^{-}-H]^{+}$
	716.5718	716.5699	$[(1^{2+})_2+3Ag^++NO_3^4H]^{2+}$



Figure S22. Full view (a) and expanded views (b, c, d) of the ESI-HRMS of $1^{2+} \cdot Ag^{+} \cdot 3PF_6^{-}$.



Figure S23. Full view (a) and expanded views (b, c, d) of the ESI-HRMS of $1^{2+} \cdot Ag^{+} \cdot 3NO_3^{-}$.

The scanning electron microscope study of $1^{2+}-Ag^+-NO_3$ gel

A SU8010 scanning electron microscope (SEM) was used for taking the pictures at 10.0 kV (**Figure. S24a**) or 3.0 kV (**Figure. S24b S24c and S24d**). The preparation of sample for SEM photos was as bellow: the gel in DMF-CH₃CN was frozen by liquid nitrogen, and the frozen specimen was then evaporated by a vacuum pump at -38 °C for 1 day. The obtained xerogel was shielded with gold and then examined.



Figure S24. SEM images of the xerogel under different scale bars.

Section S4: The selectivity of 1^{2+} - Ag^+ - NO_3^- gel with ion pair.

In all the study, the gel construction tests were in the mixture of CH₃CN and DMF (1:1, v/v).



Figure S25. The mixture containing 1^{2+} (5 mM), 1 molar equiv. of AgPF₆ and 5 molar equiv. of tested anions (*i.e.*, F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, N₃⁻, HSO₄⁻, H₂PO₄⁻, HP₂O₆⁻ and ClO₄⁻ in the forms of their corresponding tetrabutylammonium (TBA⁺) salts. The counter cation of HCO₃⁻ were tetraethylammonium (TEA⁺)). Only NO₃⁻ can induced the gel construction.



Figure S26. The mixture containing 1^{2+} (5 mM), 1 molar equiv. of lanthanide (*i.e.*, Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺, Yb³⁺, Lu³⁺ in the forms of their corresponding NO₃⁻ salts) and 5 molar equiv. of TBA⁺ • NO₃⁻. All cases were no response.



Figure S27. The mixture containing 1^{2+} (5 mM), 1 molar equiv. of alkali metals (*i.e.*, Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ in the forms of their corresponding NO₃⁻ salts) and 5 molar equiv. of TBA⁺•NO₃⁻. All cases were no response.



Figure S28. The mixture containing 1^{2+} (5 mM), 1 molar equiv. of transition metals (*i.e.*, Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Pd²⁺, Cd²⁺ and Hg²⁺ in the forms of their corresponding NO₃⁻ salts) and 5 molar equiv. of TBA⁺ • NO₃⁻. All cases were no response.

More experiments to study the counter cation effect of nitrate are carried out. 1^{2+} (5 mM), 1 molar equiv. of AgPF₆ and 5 molar equiv. of KNO₃, NaNO₃, LiNO₃ and TEA⁺ • NO₃⁻ were mixed in solution of DMF/acetonitrile (1:1, v/v). The experimental results showed that nitrate (e.g., TEA⁺•NO₃⁻, NaNO₃ and LiNO₃) could form gels no matter with the counter cation species (note: the gel formation is unsuccessful in the case of KNO₃ due to its limited solubility in the solution)



Figure S29 (a) KNO₃ is almost insoluble in solution of DMF/acetonitrile (1:1, ν/ν); (b) 1^{2+} , 1 molar equiv. of AgPF₆ and 5 molar equiv. of NaNO₃, LiNO₃, TEA⁺•NO₃⁻ or TBA⁺•NO₃⁻ can form gels.

Section S5: The stability of 1^{2+} - Ag^+ - NO_3^- gel.



Figure S30. After exposing under visible light for two weeks, gel has little change.



Figure S31. After adding 1000 molar equiv. (relative to 1^{2+}) of TFA or TEA⁺•OH⁻ (3.2 g dissolved in the mixture of DMF and CH₃CN (1:1, v/v, 2 mL)), gel has little change.



Figure S32. After exposing at 413 K or 153 K for 30 mins, gel has little change.

Section S6: The adductive response of $I^{2+}-Ag^+-NO_3^-$ gel.

For all the study, the gel was inverted after adding solvent for one minute.



Figure S33. Small molecular response of 1^{2+} -Ag⁺-NO₃⁻ gel. 15% gel's volume of liquid were added, only H₂O and DMSO decompose the gel.

Figure S34. Anion response of 1^{2+} -Ag⁺-NO₃⁻ gel. One molar equiv. (5.00 mM) of anions (study as their TBA⁺ salts, except TEA⁺ form in the case of HCO₃⁻) dissolved in the mixture of CH₃CN and DMF (1:1, v/v, 1 mL). Only Cl⁻, Br⁻, I⁻ and HSO₄⁻ break the gel to white suspension.

Figure S35. Amine response of 1^{2+} -Ag⁺-NO₃⁻ gel. 1% gel's volume of ethane-1,2diamine can break down the gel to form clear colorless solution less than 10 seconds. Diethylamine with 10% gel's volume are needed to decomposed the gel. Triethylamine and ethyldiisopropylamine with 20% gel's volume are needed to decomposed the gel.

Further gas adductive response study of the gel 1^{2+} -Ag⁺-NO₃⁻ was carried out. Herein, the gel was prepared with the Congo red for clarity (mixing 1^{2+} •2PF₆⁻ (5 mM), AgPF₆, TBA⁺•NO₃⁻ and the Congo red with 1:1:5:0.1 molar ratio. The gel was treated with amine vapour as Figure S36 and broken down to clear solution in 5 seconds.

Figure S36. Schematic representation of the amine vapour response of the gel.

Figure S37. $NH_3 \cdot H_2O$ vapour response of $1^{2+}-Ag^+-NO_3^-$ gel.

Figure S38. CH_3NH_2 vapour response of 1^{2+} -Ag⁺-NO₃⁻ gel.

Figure S39. Ethane-1,2-diamine vapour response of 1^{2+} -Ag⁺-NO₃⁻ gel.

Section S7: The fish freshness detection via VBN sensing

Figure S40. (a) Schematic representation of the fish freshness detection. (b) Actual picture of the fish freshness detection *via* VBN sensing property of gel 1^{2+} -Ag⁺-NO₃⁻.

Section S8: References:

[1] H. E. Gottlieb, V. Kotlyar and A. Nudelman, NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities, *J. Org. Chem.* 1997, 62, 7512-7515.

[2] H. -Y. Gong, B. M. Rambo, E. Karnas, V. M. Lynch and J. L. Sessler, A 'Texas-sized' molecular box that forms an anion-induced supramolecular necklace, *Nat. Chem.* 2010, 2, 406-409.

[3] G. M. Sheldrick, SHELXL97. Program for the Refinement of Crystal Structures.University of Gottingen, Germany, 1994.

[4] $R_w(F^2) = \{w(|Fo|^2 - |Fc|^2)^2/w(|Fo|)^4\}^{1/2}$ where w is the weight given each reflection. $R(F) = (|Fo| - |Fc|)/|Fo|\}$ for reflections with Fo > 4((Fo)). S = $[w(|Fo|^2 - |Fc|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

[5] G. M. Sheldrick, SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA, 1994.

[6] P. Job, Studies on the formation of complex minerals in solution and on their stability, *Ann. Chim. Paris.* 1928, **9**, 113-203.

[7] Hyperquad 2003: P. Gans, A. Sabatini and A. Investigation of equilibria in solution. Determination of equilibrium constants with the HYPERQUAD suite of programs, Vacca, *Talanta*, 1996, **43**, 1739-1753.

[8] Z.-Y. Li, Y. Zhang, C.-W. Zhang, L.-J. Chen, C. Wang, H. Tan, Y. Yu,

X. Li and H.-B. Yang, Cross-Linked Supramolecular Polymer Gels

Constructed from Discrete Multi-pillar[5]arene Metallacycles and Their Multiple Stimuli-Responsive Behavior, *J. Am. Chem. Soc.*, 2014, **136**, 8577-8589.