Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

Supramolecular Hydrogels for Environmental Remediation: G_4-Quartet Gels that Selectively Absorb Anionic Dyes from Water

*Taylor N. Plank, Luke P. Skala, and Jeffery T. Davis**

Department of Chemistry and Biochemistry University of Maryland College Park

College Park, MD 20742 USA

Email: jdavis@umd.edu

Table of Contents

General Experimental: Chemicals and solvents were purchased from Acros, Alfa Aesar, Fisher, Santa Cruz Biotechnology, or Sigma-Aldrich and used without further purification. NMR spectra were obtained on a Bruker DRX-500, or Bruker AVIII-600 spectrometers. Chemical shifts are reported in ppm relative to the residual solvent peak. Deuterated solvents were bought from Cambridge Isotope Labs. SEM images were obtained on a Hitachi SU-70 High Resolution Analytical SEM. ICP-MS data was obtained on a Single Collector Element 2 ICP-MS. UV-Vis spectra were obtained on Varian Cary 100 spectrometer. Rheology experiments were performed on an AR200 stress-controlled rheometer from TA instruments, New Caste DE. CD spectra were obtained on a Jasco J-810 spectropolarimeter. PXRD experiments were performed with a Bruker D8 Advance Bragg-Brentano Diffractometer.

General Gel Procedure: The desired amounts of equimolar mixtures of 8-AmG and G were weighted into a vial then the appropriate amounts of salt solution and water were added and the mixtures were sonicated for ~1 minute (in the case of the $KB(OH)_4$ gels KOH and water were added, then the mixture was sonicated, and $B(OH)_3$ was added and the mixture was sonicated again). The mixture was placed in a water bath at room temperature (20 °C) and heated to 95-100 °C at a rate of ~5 °C/min until the solution was clear. The vial was then removed from the bath and was allowed to cool to room temperature (20 °C). $KB(OH)_4$ gels were made with 0.5 eq of salt, all other gels were made with various salt eqs as noted throughout the paper.

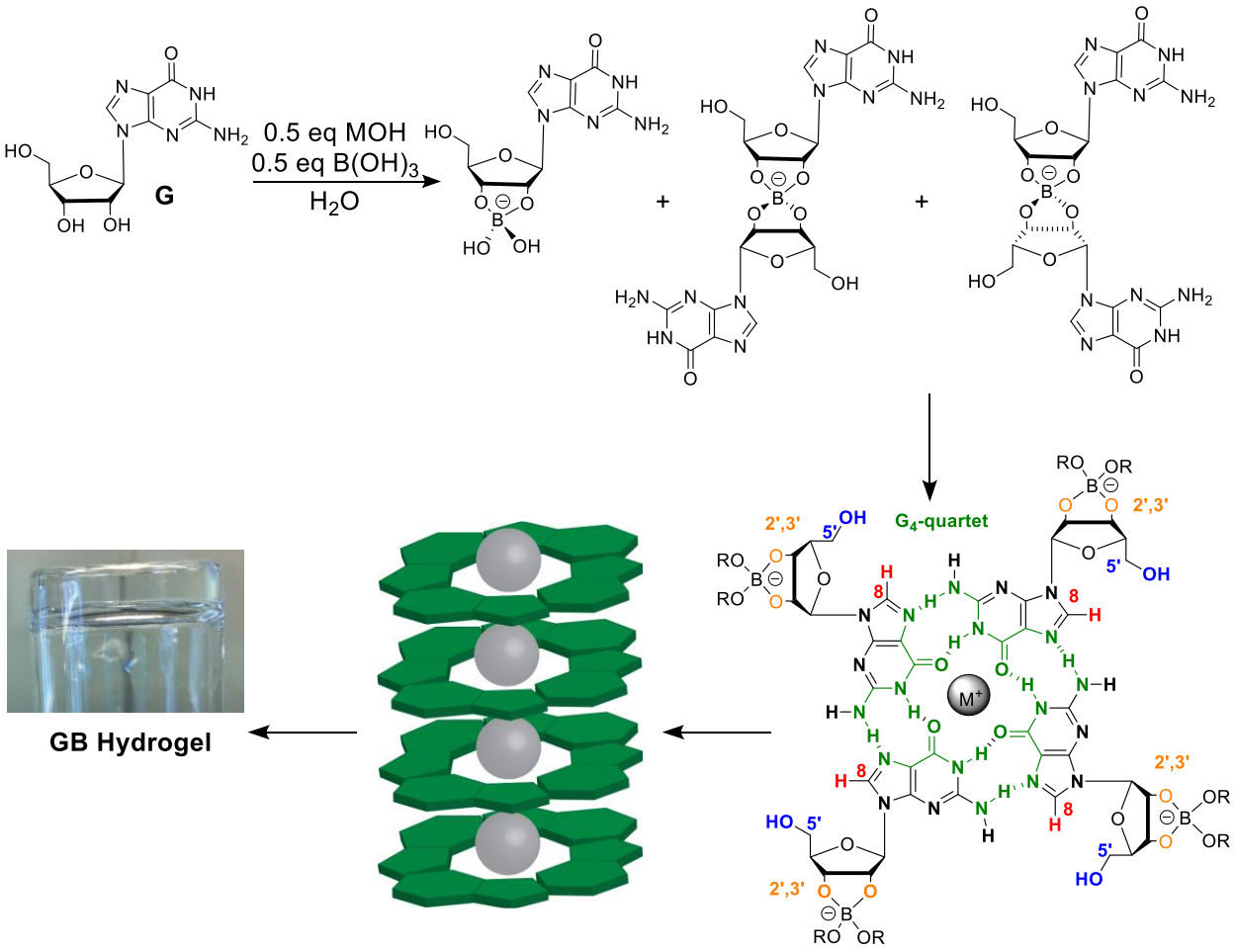


Figure S1: The mechanism of gelation for the GB hydrogels. As illustrated in the quartet the G-base (green) is needed to form the G_4-quartets, and the 2′,3′-diol (orange) is needed to form the GB esters. The 5′-OH (blue) and the H8 (red) positions open for functionalization as they seemingly play no role in the gelation mechanism.

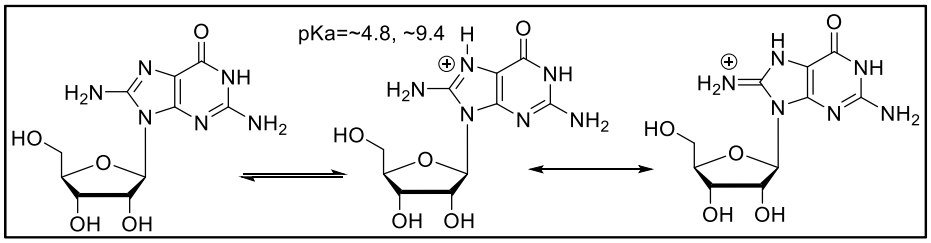
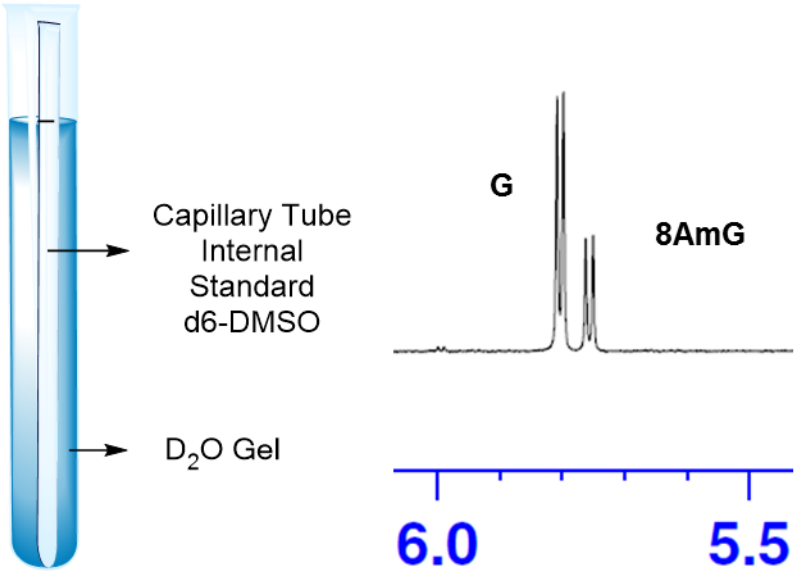


Figure S2: The potential protonation of N7 and subsequent resonance stabilization possible with 8AmG.

NMR Procedure: Gels were formed following the general gel procedure (0.5mL, 1wt%, 35mM 8AmG/G with 0.5eq salt) in D_2O. After heating the hot gel solutions were pipetted into hot NMR tubes. A capillary tube with d6-DMSO was sealed with parafilm and placed inside the NMR tube as an internal standard. ^{1}H NMR spectra were recorded on a Bruker AVIII-600 spectrometer. The DMSO peak was set to 2.5 and integrated to 1.00. The H1′ peaks for G and 8AmG were then integrated in comparison the DMSO peak. After the experiment the internal standard was removed and 10µL of DCl was added to the NMR tube to destroy the gel network. The capillary tube was re-inserted and new ^{1}H NMR spectra were obtained. The DMSO peak was again integrated to 1.00 and the H1′ peaks for G and 8AmG were integrated in comparison to the DMSO peak. The amounts of 8AmG and G in the gel and the sol were then calculated.



	KB(OH)4	KCl		KNO3		BaCl2		Ba(NO3)2		Pb(NO3)2	
	8AmG/G	8AmG	G	8AmG	G	8AmG	G	8AmG	G	8AmG	G
Gel (mM)	57	28	23	28	24	30	26	30	27	32	24
Sol (mM)	13	7	12	7	11	5	9	5	8	3	11

Figure S3: Experimental setup for the gel network quantification, a D_2O gel is made and placed in an NMR tube with a capillary tube of d6-DMSO (top left). ^{1}H NMR spectra can then be taken and the H1′ region (top right) can be used to quantify the amounts of G species in the gel and sol network. The error associated with NMR is ±10%.

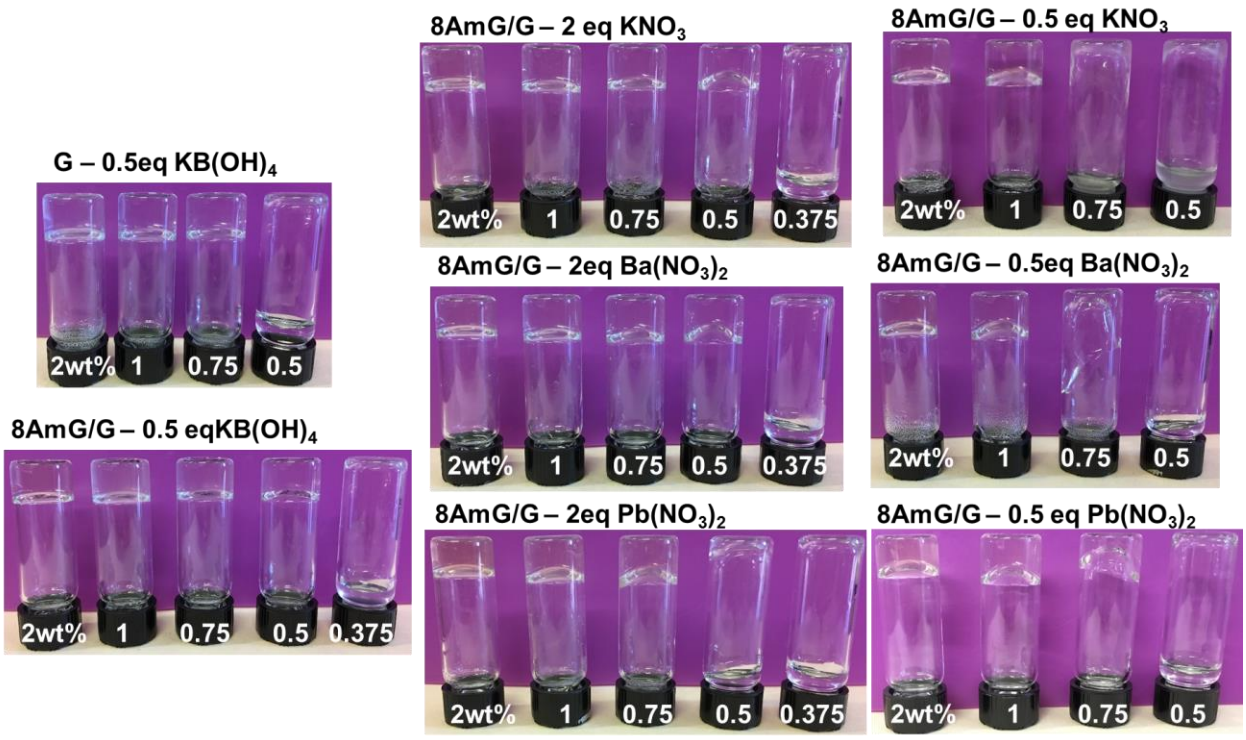


Figure S4: The critical gelation concentration (CGC) for 8AmG/G $KB(OH)_4$ gels is lower (~18mM) than the CGC of GB gels (~27mM). The CGC of NO_3^- gels depends upon the amount of salt and the cation used. Gels with 2eq of K^+ and Ba2+ have a CGC of 18mM whereas the CGC for the Pb^{2+} gel is 26mM. Gels with only 0.5eq of salt have higher CGCs.

CD Procedure: Gels were prepared following the general gel procedure. $KB(OH)_4$ gels were prepared at 2wt% with 0.5eq of salt. KNO_3 and $Pb(NO_3)_2$ gels were prepared at 1wt% with 0.5eq salt. The gels were allowed to sit for 1-2 hours prior to the experiments. The CD spectra were recorded at 25 °C in a Hellma 106-QS quartz cell with an optical path length of 0.01nm. Experiments were run on a Jasco J-810 spectropolarimeter with a scanning speed of 200 nm/min, response time of 2sec, and a bandwidth of 1nm. Each experiment was repeated at least 3 times, and the signals were averaged.

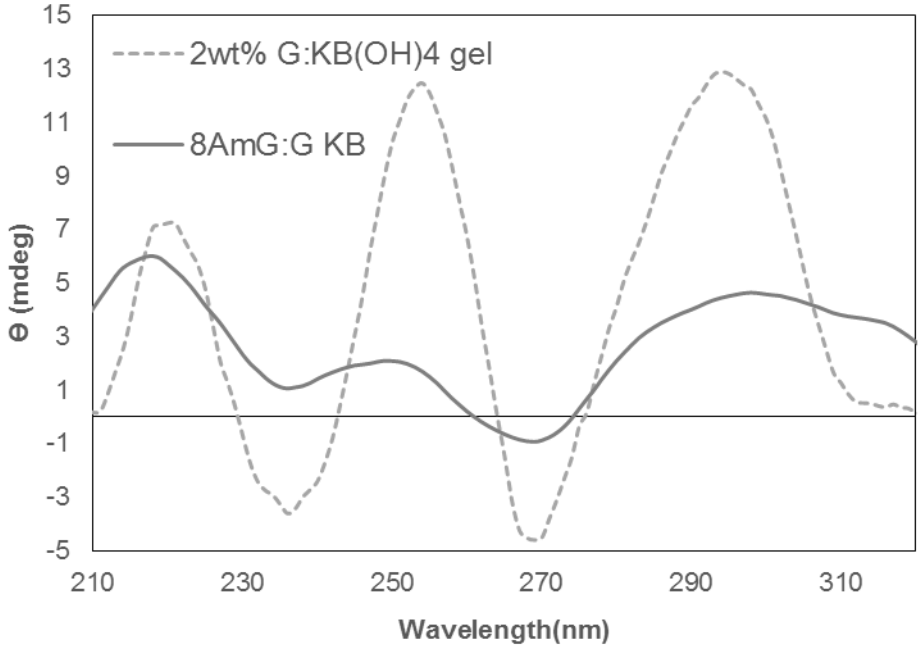


Figure S5: Both G (dotted line) gels and binary 8AmG/G gels (solid line) made with 0.5eq $KB(OH)_4$ show CD signatures indicating the presence of G_4-quartets.

PXRD Procedure: Gels were prepared according the general gel procedure (1wt%, 35mM 8AmG/G with 0.5eq salt). After sitting at 20 °C overnight the gels were lyophilized to form white powders. Powder X-ray diffraction measurements were performed with a Cu radiation source at 20 °C using a Bruker D8 Advance Bragg-Brentano Diffractometer equipped with a LynxEye detector.

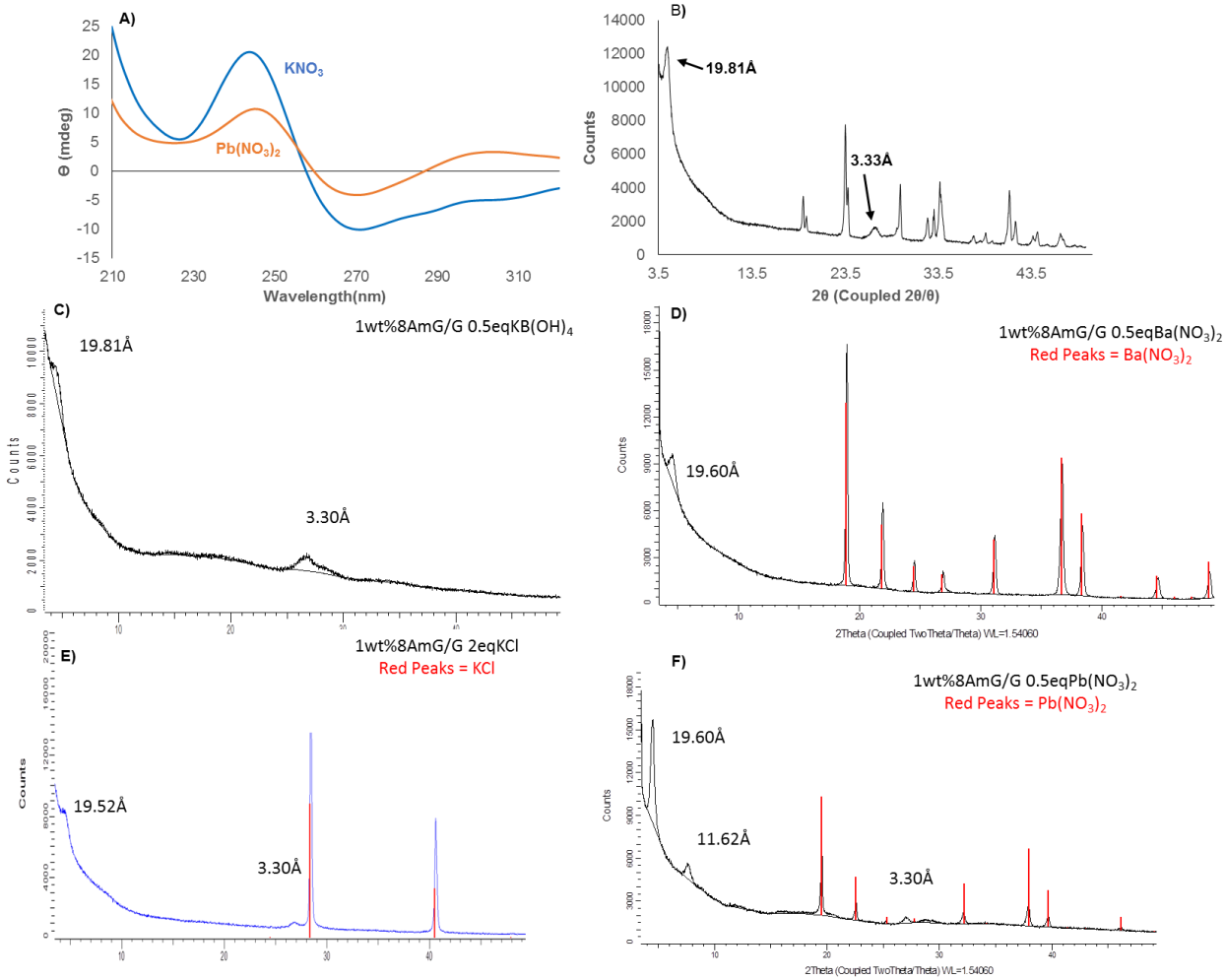
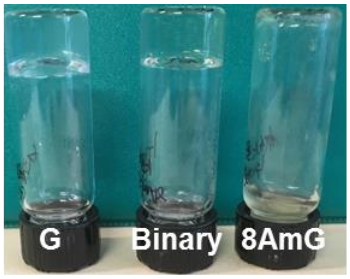
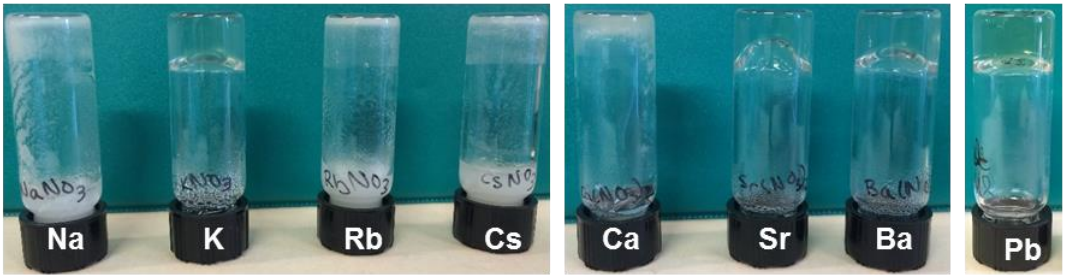


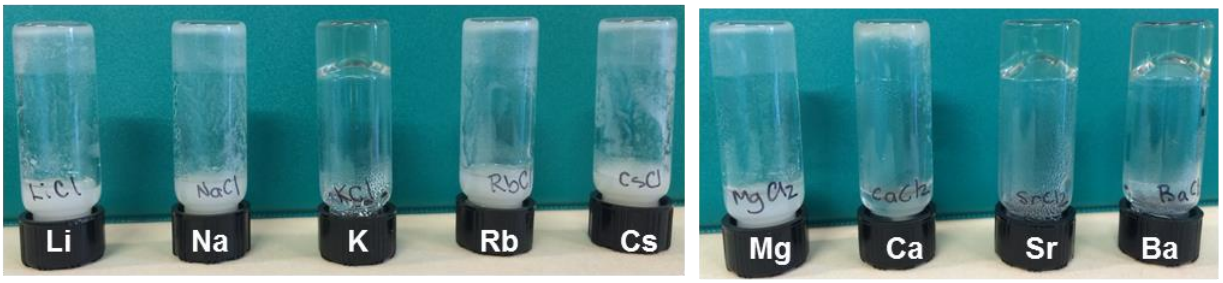
Figure S6: A) The CD spectra for KNO_3 (blue) and $Pb(NO_3)_2$ (orange) hydrogels show signatures of G-helices. This matches B) PXRD data of a KNO_3 gel with peaks corresponding to ~20Å, which is the diameter of a G_4-layer, and ~3.3 Å, which is the π-π stacking distance between two G-layers. PXRD of C) $KB(OH)_4$, D) KCl, E) $Ba(NO_3)_2$, and F) $Pb(NO_3)_2$ gels.



2wt% G-Species 0.5eq $KB(OH)_4$



2wt% 8AmG/G with 2eq $M(NO_3)_n$



2wt% 8AmG/G with 2eq $M(Cl)_n$

Figure S7: We attempted to form gels with all of the salts shown above following the general gel procedure. Gels were only able to form with K^+, Sr^{2+}, Ba^{2+}, and Pb^{2+} salts.

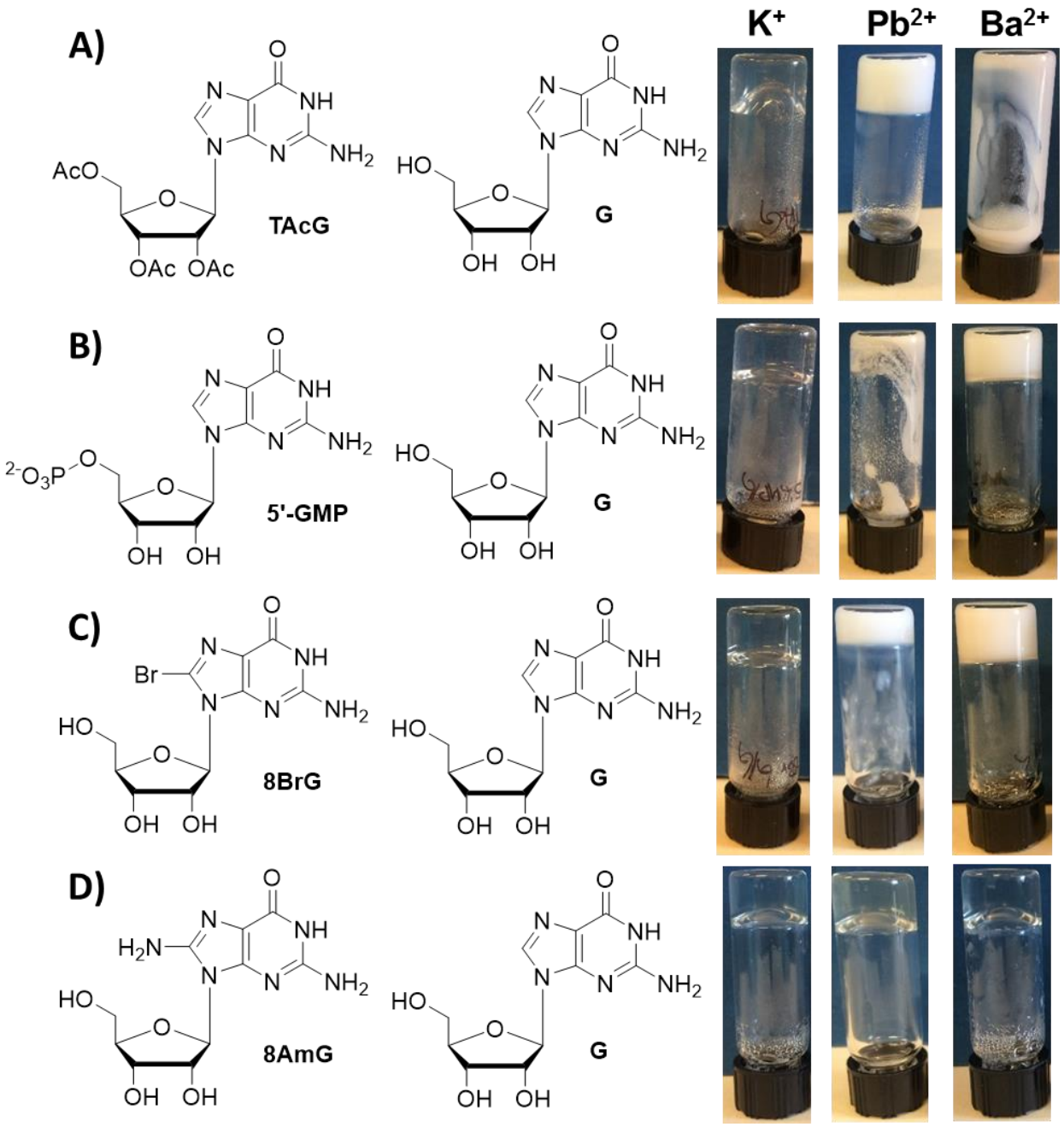


Figure S8: While the gels in A, B, and C have been previously reported to form gels with K^+ salt, they do not gel with Pb^{2+} or Ba^{2+}, only 8AmG (D) gels with all 3 cations.

SEM Procedure: A 2wt% (70mM) binary 8AmG/G hydrogel was prepared according to the general gel procedure. A small portion of the gel was scooped up with a small spatula and placed on an AL stub with a small dimple. A 0.3µL aliquot of 3% ionic liquid (HILEM 1000 for Hitachi EM) was pipetted onto the gel sample and set in the air for 10 minutes prior to SEM examination.

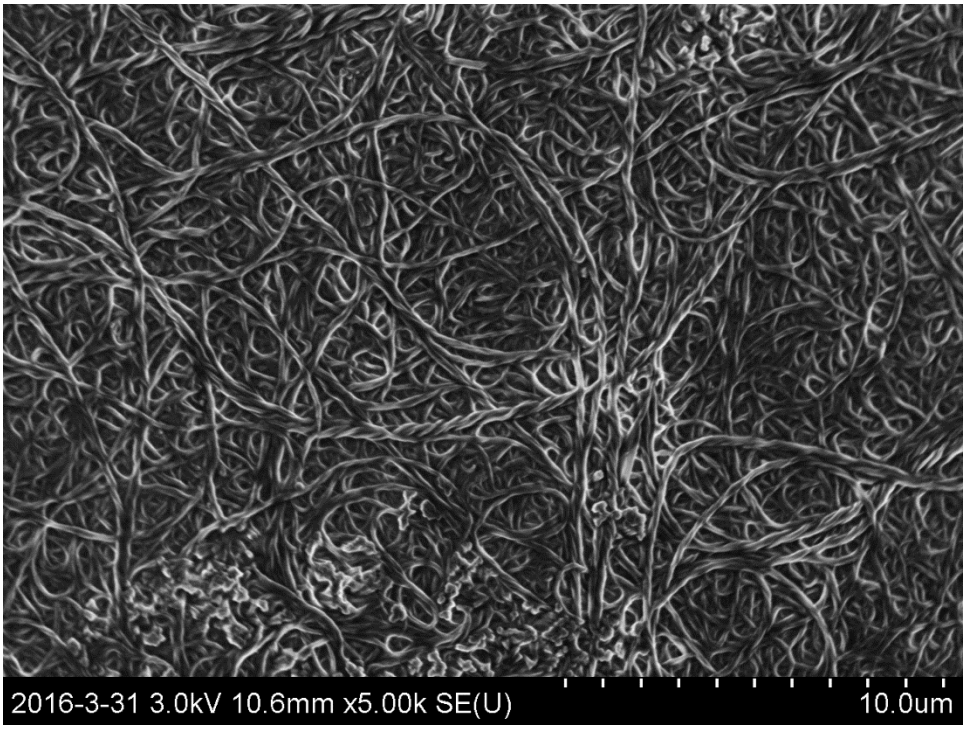


Figure S9: An SEM image of a 2wt% (70mM) 1:1 8AmG/G hydrogel with 2eq of $Pb(NO_3)_2$ clearly shows an entangled, fibrous, gel network.

Rheology Procedure: Gels were made following the general gel procedure (2wt%, 70mM 8AmG/G with salt concentrations as indicated in **Fig S13** and **Fig S14**). Gels were allowed to cool overnight before rheology was performed. Experiments were performed on an AR2000 stress-controlled rheometer from TA instruments in New Castle, DE at 20 °C with a 20mm diameter parallel plate geometry. The gels were allowed to equilibrate on the plate for 10 minutes. Frequency sweeps were performed at 0.5% strain.

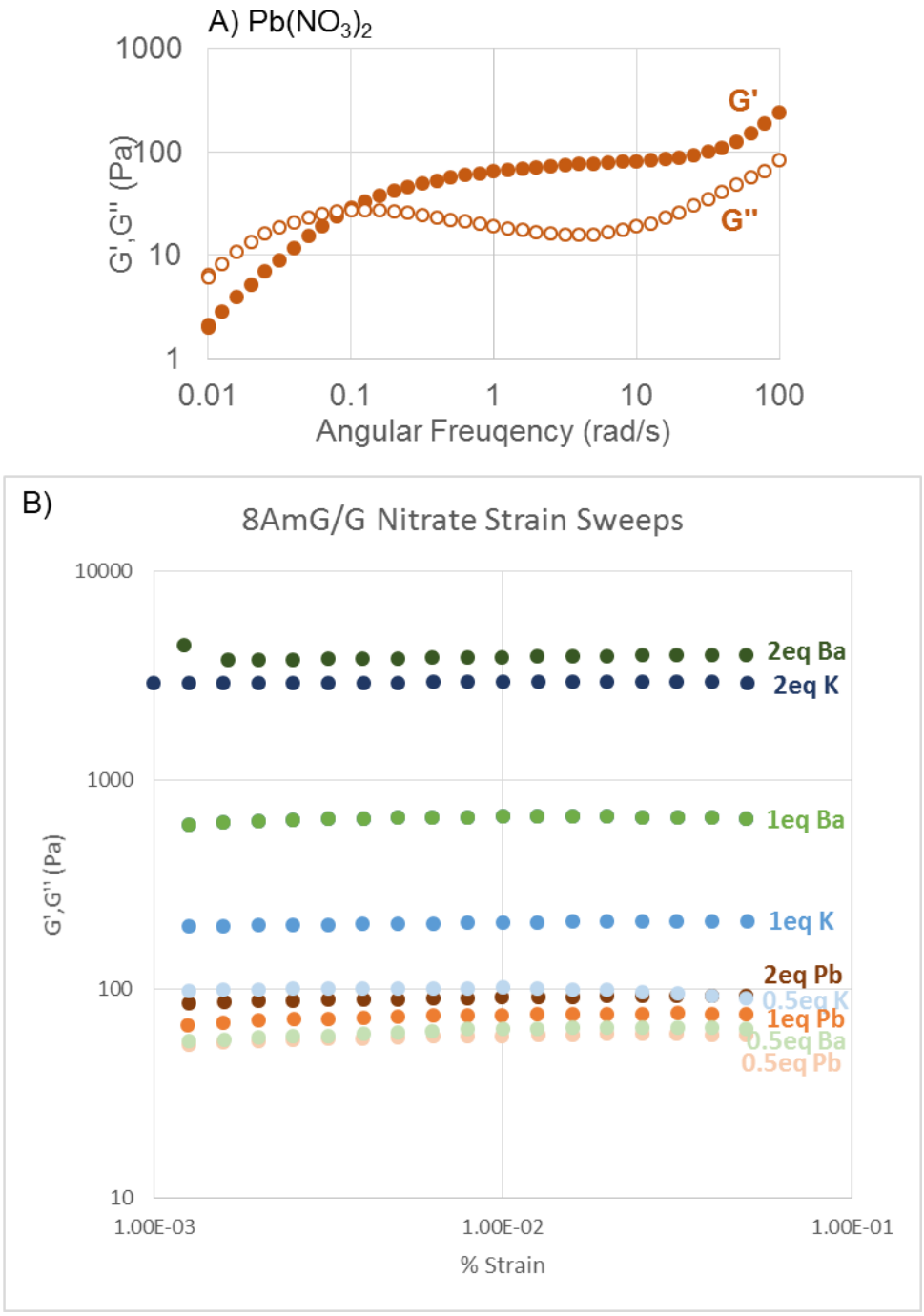


Fig S10: A) Frequency sweep of a 2wt% (70mM) 8AmG/G-$(NO_3)_2$ B) Strain sweeps of 2wt% (70mM) 8AmG/G gels with varying eqs of salt show that Ba^{2+} (green) gels are strongest, followed by K^{+} (blue), and Pb^{2+} (orange) gels, which are much weaker. Adding more salt results in stronger hydrogels.

Dye Release Procedure: Gels were prepared following the general gel procedure (2wt%, 70mM 8AmG/G, 0.5eq $KB(OH)_4$ or 2eq KCl or 2eq $BaCl_2$) with the following alterations. After heating to ~95 °C both MB and RB were added (25μM each) and the vials were shaken to distribute the dyes. The vials were returned to the heat bath for ~2 mins. After the 2 min heating 0.5mL of the hot dyed gel solution was pipetted into a parafilm lined cube mold. After cooling for 1 hour at room temperature the gel cubes were suspended in 3mL of 155mM KCl solutions. The systems were monitored visually for dye release.

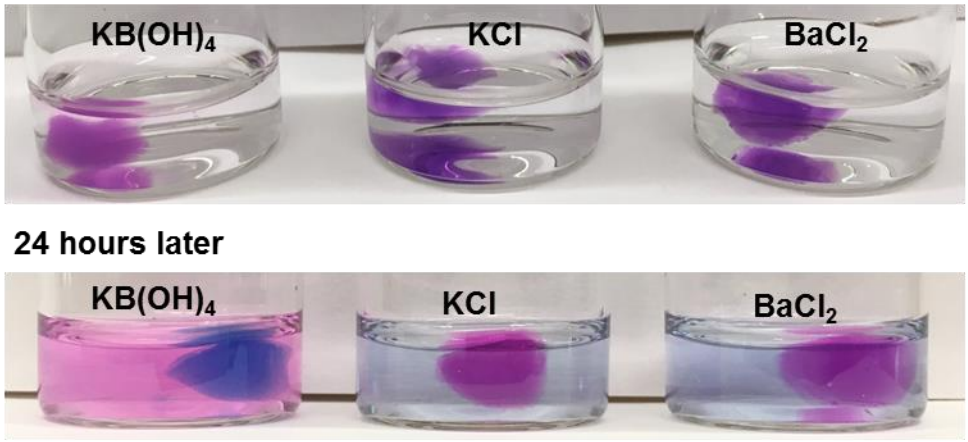


Figure S11: Gels loaded with MB and RB (25μM each) suspended in 155mM KCl buffer will release different dyes based on their charge. Borate containing gels retain cationic MB and release anionic RB, presumably due to the negative charge of the borate esters. Chloride gels follow the opposite trend, which could be due to the potential positive charge on the N7 of 8AmG.

Dye Uptake Procedure: Gels were prepared according to the general gel procedure (2wt%, 70mM, 8AmG/G with 0.5eq $KB(OH)_4$ or 2eq KCl or 2eq $BaCl_2$). After heating 0.5mL aliquots of the hot gel solution were pipetted into parafilm lined cube molds and allowed to cool at RT for 1hr. The cubes were then suspended in 3mL of 155mM KCl with 12.5μM dye. The outside solution was monitored overtime via UV-Vis spectroscopy.

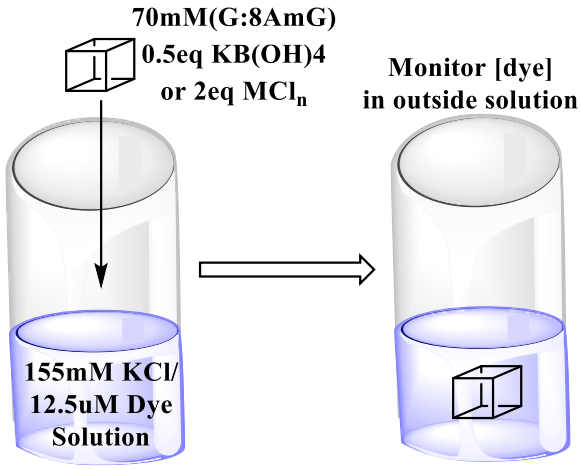


Figure S12: Illustration of the dye uptake experiments, see dye uptake procedure for more details.

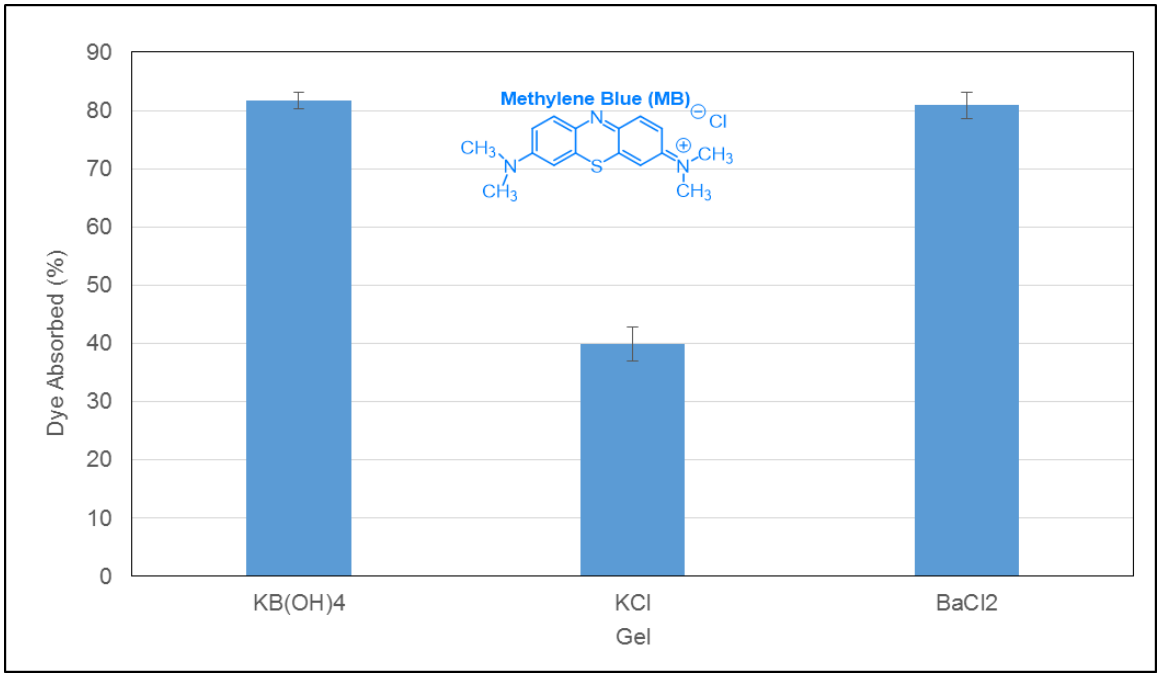


Figure S13: Gels were suspended in a 155mM KCl solution with 12.5µM MB dye and the amount of dye in the outside solution was monitored using UV-Vis. The graph shows the amount of MB absorbed by the gel after 24 hours.

NBB Max Procedure: Gels were prepared according to the general gel procedure (2wt%, 70mM, 8AmG/G with 0.5eq $KB(OH)_4$ or 2eq KCl or 2eq $BaCl_2$). After heating 0.5mL aliquots of the hot gel solution were pipetted into parafilm lined cube molds and allowed to cool at RT for 1hr. The cubes were then suspended in 3mL of 155mM KCl with 100µM NBB. The outside solution was monitored overtime via UV-Vis spectroscopy.

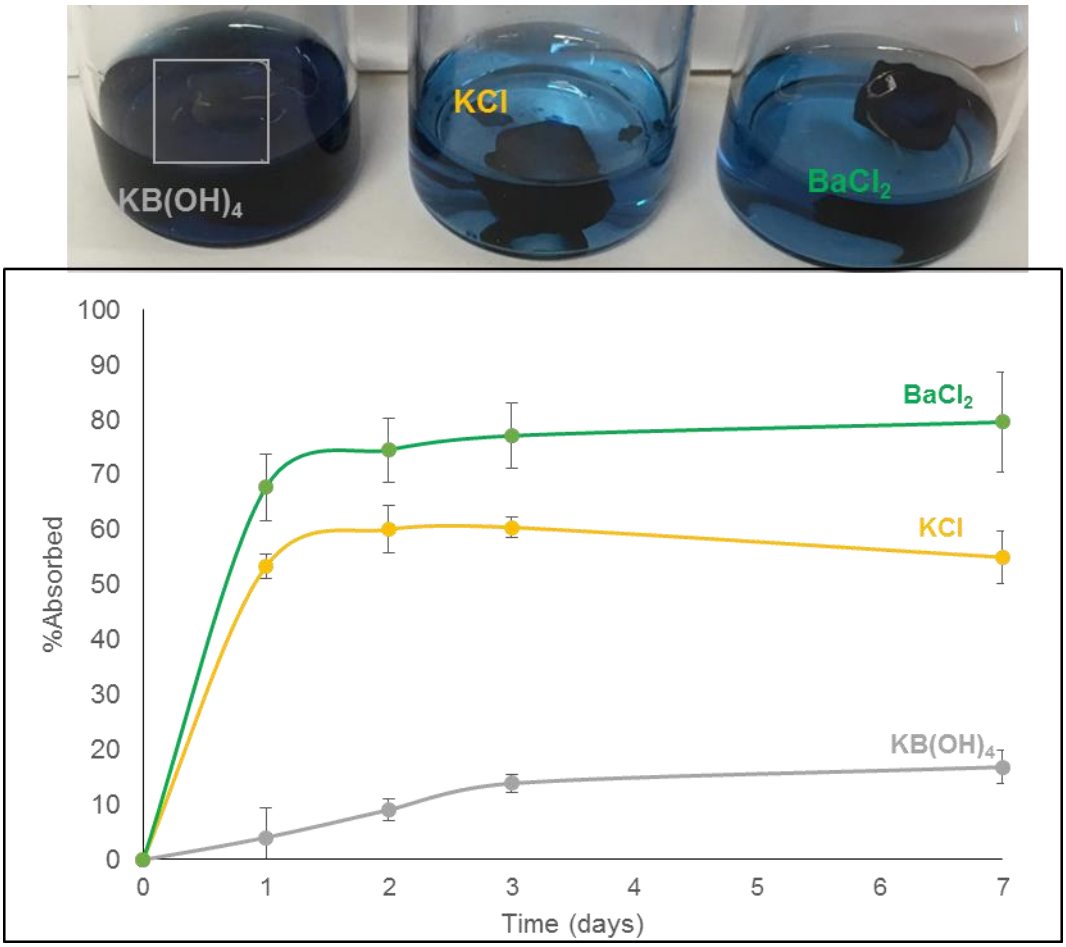


Figure S14: Gels soaking in 100µM NBB solution for 24 hours (top) absorb different amounts of NBB depending on the salt they are made with. $BaCl_2$ gels absorb ~80% of the dye after one week whereas $KB(OH)_4$ gels absorb less than 20%.

Qualitative Dye Procedure: Gels were prepared following the general gel procedure (2wt%, 70mM 8AmG/G with 0.5eq $KB(OH)_4$ or 2eq KCl or 2eq $BaCl_2$). The hot gel solution was pipetted into parafilm lined cube molds in 0.5mL increments. The gel cubs were allowed to cool for 1hr before being suspended in 3mL of 155mM KCl solution.

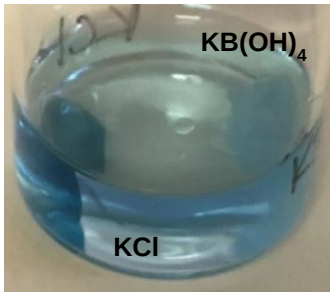


Figure S15: Qualitative dye uptake experiments show 8AmG/G-KCl vs 8AmG/G-$KB(OH)_4$ gels after soaking in 12.5μM NBB **3** for 24 hours. The 8AmG/G-KCl gel absorbs the anionic NBB **3** much more than the 8AmG/G-$KB(OH)_4$ gel, likely due to the electrostatic repulsion between the dye and the anionic borate esters.

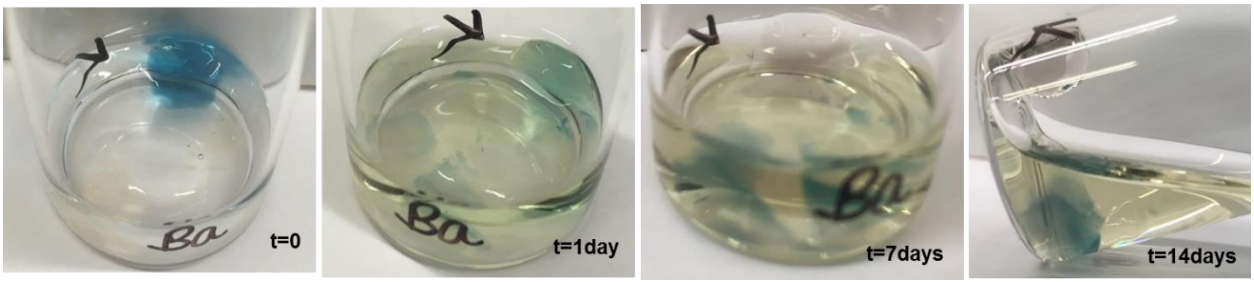


Figure S16: This qualitative dye experiment shows how a KCl gel loaded with 25μM NBB will release the dye into solution. The NBB will then be absorbed by a $BaCl_2$ gel in the same vial over the course of 2 weeks.