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Responsive ionic liquid–polymer 2D photonic crystal gas sensors†

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We developed novel air-stable 2D polymerized photonic crystal (2DPC) sensing materials for visual detection of gas phase analytes such as water and ammonia by utilizing a new ionic liquid, ethylguanidine perchlorate (EGP) as the mobile phase. Because of the negligible ionic liquid vapor pressure these 2DPC sensors are indefinitely air stable and, therefore, can be used to sense atmospheric analytes. 2D arrays of ~640 nm polystyrene nanospheres were attached to the surface of crosslinked poly(hydroxyethyl methacrylate) (pHEMA)-based polymer networks dispersed in EGP. The wavelength of the bright 2D photonic crystal diffraction depends sensitively on the 2D array particle spacing. The volume phase transition response of the EGP–pHEMA system to water vapor or gaseous ammonia changes the 2DPC particle spacing, enabling the visual determination of the analyte concentration. Water absorbed by EGP increases the Flory–Huggins interaction parameter, which shrinks the polymer network and causes a blue shift in the diffracted light. Ammonia absorbed by the EGP deprotonates the pHEMA-co-acrylic acid carboxyl groups, swelling the polymer which red shifts the diffracted light.

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Introduction

There is an ever increasing demand for simple, selective and inexpensive methods for determining the presence of chemical species in the environment. In response, we previously developed 3D and 2D polymerized photonic crystal sensors that can determine the concentrations of specific analytes in aqueous solutions.^{1–6} We designed 3D Polymerized Photonic Crystal Sensors (3DPC) for a variety of analytes such as glucose, for example, where two boronic acid side chains bind a glucose molecule, creating crosslinks that shrink the gel.

Recently we developed a 2D Polymerized Photonic Crystal Sensor (2DPC) that consists of a monolayer array of polystyrene nanospheres (450–650 nm diameter) attached to a crosslinked polymer network containing an aqueous mobile phase. These sensing materials are inexpensive and can be used for visual detection of analyte concentrations because the visible light diffracted sensitively depends on the particle spacing of the attached 2D photonic crystal array.

The polymer network is designed to undergo a volume phase transition (VPT) in response to the analyte, which in turn alters the particle spacing of the attached 2D array. For example, we recently fabricated a 2DPC sensor for surfactant detection by attaching a 2D photonic crystal array onto a poly(*N*-

isopropylacrylamide) (pNIPAM) hydrogel.¹ The polymer hydrogel undergoes a VPT;⁷ swelling when the ionic surfactant binds to the hydrogel therefore changing the 2D array particle spacing. This particle spacing change shifts the wavelengths of light diffracted from the 2D array.

The current hydrogel 2DPC and 3DPC cannot be easily used to sense analytes in the vapor phase because the mainly aqueous mobile phase has a high vapor pressure. In the work here, we demonstrate the development of an air-stable 2DPC that utilizes an ionic liquid as the mobile phase; ionic liquids generally have negligible vapor pressures. We show that these ionic liquid 2DPC (IL2DPC) can be used to measure gas phase analytes such as the water and ammonia vapor in air.

These IL2DPC consist of 2D photonic crystals attached to responsive polymer networks that are in contact with an ionic liquid mobile phase. Ionic liquid–polymer composite materials are fabricated by polymerizing the monomers within ionic liquids or by exchanging a solvent with an ionic liquid after polymerization.^{8–11} These IL2DPC are stable in air due to the ionic liquid's negligible vapor pressure.¹² Previous work utilizing polymers dispersed in ionic liquid media include that of Furumi *et al.*¹⁰ who fabricated an air-stable 3D colloidal crystal gel film that was used as a laser gain medium by exchanging the aqueous medium of the 3D polymerized crystalline colloidal array (PCCA) with the ionic liquid 1-allyl-3-butylimidazolium bromide. Kanai *et al.*¹¹ also fabricated a 3D PCCA by exchanging the aqueous media with an ionic liquid. They demonstrated the occurrence of the polymer VPT in response to changes in the free energy of mixing by utilizing ionic liquids with different solubility parameters.

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Polymer–ionic liquid systems can display VPT, where the mechanisms of response are similar to those of hydrogels. A photoinduced VPT was observed for an azobenzene-containing polymer–ionic liquid composite,¹³ similar to what we previously demonstrated in hydrogels.^{14,15} These systems contained azobenzene derivatives that reversibly switched between *cis*- and *trans*-conformations when irradiated with visible or UV light. This switching results in changes in the polymer solubility parameters, causing a VPT between these two states. In addition, an ionic liquid–polymer material using benzospiropyran switching was recently fabricated for use as a light switching microfluidic valve.¹⁶ The microfluidic valve opens when the polymer is irradiated with light. This photosensitive spiropyran ionic liquid–polymer is similar to the light responsive 3DPC hydrogel switching material we previously pioneered.¹⁷

The utilization of polymerizable cations in an ionic liquid allow for the fabrication of poly(ionic liquid) materials. A poly(ionic liquid) 3DPC was fabricated by photo-copolymerization of the ionic liquid, 1-(2-acryloyloxyhexyl)-3-methylimidazolium bromide with methylmethacrylate around a 3D close packed array of monodisperse SiO₂ particles.¹⁸ An inverse opal is formed by etching away the SiO₂ particles. The polymer swells upon water absorption presumably because the ionic liquid molecules become hydrated forming free anions and immobilized cations. This polymer responds to saturated ethanol vapors if the ionic liquid anions are exchanged with SDS anions. The ionic liquid containing SDS anions is more hydrophobic, which causes the poly(ionic liquid) to preferentially absorb ethanol. Ionic liquids have been called ‘designer solvents’ because their properties can be tuned by varying the cation/anion pair.

The IL2DPC humidity sensor described in this paper consists of a pHEMA 2DPC swollen in the ionic liquid, ethylguanidine perchlorate (EGP). EGP is an excellent solvent for pHEMA; it causes the polymer to swell to more than four times its volume in pure water. The free energy of mixing between EGP and pHEMA becomes less favorable as hygroscopic EGP absorbs water from humid environments; this causes the swollen pHEMA to shrink; blue shifting the diffracted wavelengths.

There are a number of different methods for measuring humidity. The most accurate current methods include chilled mirror dew point hygrometers, capacitive and resistive humidity sensors, thermal conductivity humidity sensors and gravimetric hygrometers. These methods are very sensitive. For example the chilled mirror dew point hygrometer has an accuracy of 1.2% relative humidity (RH). All of the afore mentioned hygrometers require some power source. Here we report a humidity sensor that does not require a power source, and instead changes color in response to humidity.

We also fabricated an IL2DPC ammonia gas sensor that consists of a crosslinked pHEMA-*co*-acrylic acid polymer 2DPC. Acrylic acid carboxyls ionize in the presence of ammonia, resulting in a more favorable free energy of mixing between the polymer and EGP. This causes the IL2DPC to swell in the presence of ammonia and red shift the light diffracted.

Many industries such as fertilizer manufacturers and power plants require storage of large amounts of pressurized

anhydrous ammonia on site. Current fire and building codes require that engine rooms and refrigerated spaces have ammonia detectors. Exposure to ammonia irritates the eyes, respiratory system, and skin at concentrations as low as 30 ppm. Ammonia causes necrosis of the skin and long-term damage to the eyes and respiratory system occur at higher concentrations (>200 ppm).¹⁹ Ammonia can also become explosive at very high concentrations.²⁰

Current ammonia sensors include metal oxide sensors and conducting polymer detectors which have about 1 ppm detection limits and different optical or spectroscopic methods that are able to detect as low as 1 ppb for absorption spectroscopic methods.²¹ The inexpensive IL2DPC sensors developed here can easily detect 3 ppm NH₃ and do not require expensive electronics as it is monitored by the visual determination of color changes.

Results and discussion

IL2DPC fabrication

To fabricate 2DPC to sense gas phase species we utilized the ionic liquid EGP as the mobile phase to solvate pHEMA. EGP is a compatible co-solvent that enables polymerization of transparent pHEMA films. Compatible polymer–solvent systems do not undergo phase separations and generally have a Flory–Huggins interaction parameter, χ below 0.5.^{7,22}

χ is a function of the difference between the solubility parameters of the polymer and solvent, δ_p and δ_s (eqn (1)).

$$\chi = \frac{V_m}{RT}(\delta_s - \delta_p)^2 \quad (1)$$

where V_m is the solvent molar volume, T is the absolute temperature, and R the ideal gas constant.

Aqueous HEMA solutions undergo polymerization induced phase separations due to the large difference between the solubility parameters of pHEMA ($\delta = 26.9 \text{ MPa}^{1/2}$) and water ($\delta = 47.9 \text{ MPa}^{1/2}$).²² Phase separation is undesirable because the resulting film turbidity reduces the 2DPC light diffraction. Co-solvents can be used to alter δ_s , to minimize χ by minimizing the difference between δ_p and δ_s . For example, propylene glycol or ethylene glycol can be used as a co-solvent for aqueous HEMA solutions to produce transparent hydrogels.²²

For our sensors we find that EGP lowers the interaction parameter below $\chi = 0.5$, which produces transparent gels when EGP is used at 30 wt% (23 vol%) in a 20 wt% HEMA solution. The IL2DPC, polymerized using 23 vol% EGP, swells in pure EGP because the interaction parameter between pHEMA and the solvent decreases with increasing EGP concentrations. The very large swelling indicates that their solubility parameters are very close.

Stability of IL2DPC in air

IL2DPC are stable at room temperature in dry environments in contrast to hydrogel 2DPC and 3DPC that collapse when the water evaporates.^{10,23} Fig. 1A shows the dependence of the particle spacing upon exposure to stagnant 0.5% and 50% relative humidity environments. The particle spacing decreases

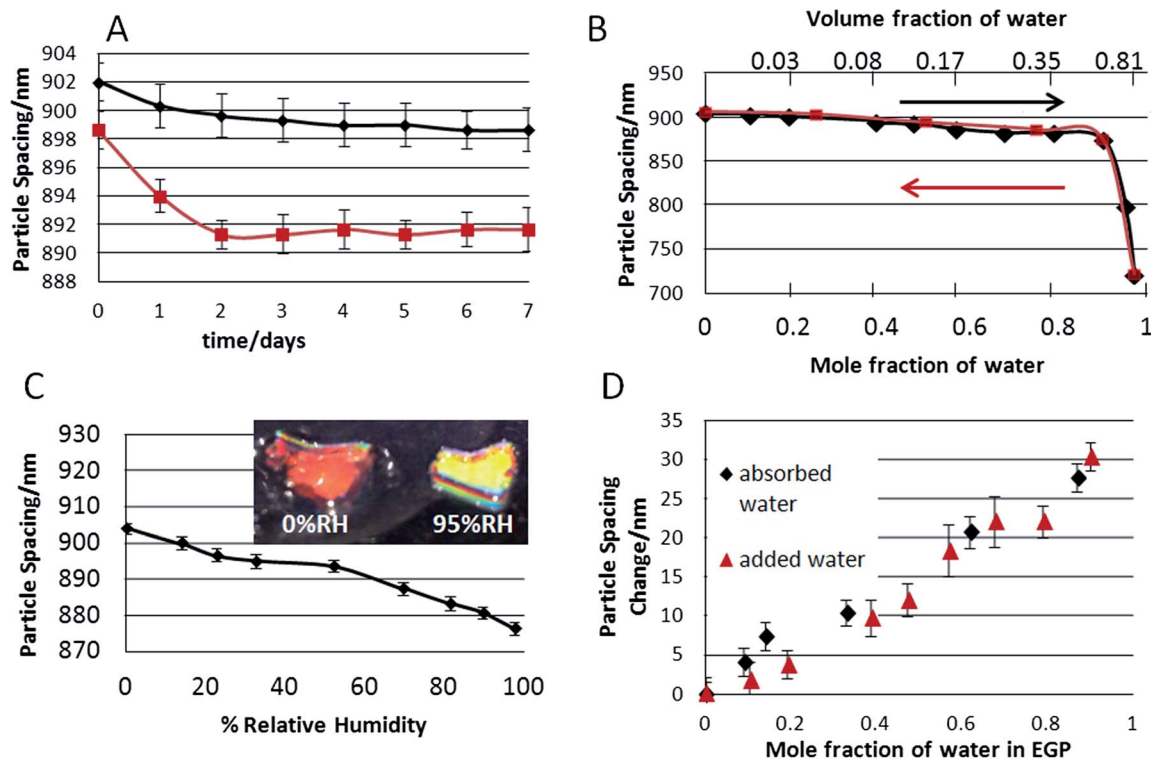


Fig. 1 (A). Stagnant air time dependence of IL2DPC particle spacing exposed to 0.5% RH (black) and 52% RH (red). (B). Particle spacing of pHEMA IL2DPC as a function of the mole fraction of water directly added to EGP. The black line shows particle spacing during increasing water concentrations, while red line shows particle spacings as water concentration decreases. The upper abscissa shows the volume fraction of water in EGP corresponding to 0.2, 0.4, 0.6, 0.8 and 0.97 water mole fractions. (C). Dependence of the particle spacing of pHEMA IL2DPC on water absorbed at different RH. The inset shows the diffraction colors of IL2DPC humidity sensors exposed to 0% RH (left) and 95% RH (right). The IL2DPC were placed on a mirror so that the forward diffracted light reflects back to the camera.²⁵ (D). Particle spacing change for pHEMA IL2DPC as a function of the water mole fraction in EGP. Water was either directly added to EGP (red) or absorbed from air (black).

as the initially dry EGP medium absorbs moisture and reaches equilibrium. The particle spacing then remains constant after equilibration. The IL2DPC particle spacing change is dependent on the relative humidity. The particle spacing change is 3 nm when the IL2DPC is exposed to the 0.5% RH while the IL2DPC particle spacing exposed to 50% RH decreases 8 nm.

IL2DPC humidity sensor

Flory Rehner solution theory models the polymer VPT as being induced by osmotic pressure within the system, Π_{Total} (eqn (2)).^{7,24} The total osmotic pressure of a non-ionic polymer is the sum of the osmotic pressures generated by changes the free energy of mixing, ΔG_{mix} (eqn (3)) and the elastic free energy, ΔG_{El} (eqn (4)). The VPT relieves the osmotic pressure in the system so that the net osmotic pressure becomes zero at equilibrium.

At equilibrium the interaction parameter, χ can be related to the swelling ratio, $q = V/V_0$ (eqn (5)).⁷ Here V is the volume of the swollen polymer, V_0 is the volume of the dried polymer gel, V_r is the volume of the relaxed polymer and n_{CL} is the number of crosslinks.

$$\frac{\partial \Delta G_{\text{Total}}}{\partial V} = \Pi_{\text{Total}} = \Pi_{\text{Mix}} + \Pi_{\text{El}} \quad (2)$$

$$\Pi_{\text{Mix}} = -\frac{\partial \Delta G_{\text{Mix}}}{\partial V} = -\frac{RT}{V_m} \left[\ln \left(1 - \frac{V_0}{V} \right) + \frac{V_0}{V} + \chi \left(\frac{V_0}{V} \right)^2 \right] \quad (3)$$

$$\Pi_{\text{El}} = -\frac{\partial \Delta G_{\text{El}}}{\partial V} = -\frac{RTn_{\text{CL}}}{V_r} \left[\left(\frac{V_r}{V} \right)^{1/3} - \frac{V_r}{2V} \right] \quad (4)$$

$$\chi = - \left[\frac{\ln \left(1 - \frac{V_0}{V} \right) + \frac{V_0}{V} + \frac{n_{\text{CL}}}{V_r} \left[\left(\frac{V_r}{V} \right)^{1/3} - \frac{V_r}{2V} \right]}{\left(\frac{V_0}{V} \right)^2} \right] \quad (5)$$

We monitor the particle spacing changes, which disclose the swelling behavior that results from interaction parameter changes due to solvent composition changes. The addition of water to EGP increases the interaction parameter, shrinking the polymer as shown in Fig. 1B. Unfavorable changes in the free energy of mixing between pHEMA and the solvent occur as the increasing water content increases the solvent solubility parameter (eqn (6)). This process is fully reversible as shown in Fig. 1B.

$$\delta_s = \sum_i \phi_i \delta_i \quad (6)$$

Stagnant air response

The dependence of the particle spacings of pHEMA IL2DPC in EGP on the %RH is shown in Fig. 1C. The particle spacing decreases as humidity increases as EGP absorbs more water at higher %RH. The mole fraction of water absorbed by EGP was directly measured using the near IR absorption overtones of water at 1420 nm and 1915 nm. The IR spectra used to generate the calibration curve and the IR spectra of EGP at different %RH are shown in the ESI.†

The mole fraction of water absorbed by EGP is less than expected for an ideal solution indicating that the activity of water in EGP is higher than in pure water. This is similar to the increased water activity observed for many cholinium based ionic liquids.²⁶ Fig. 1D shows similar particle spacing changes for our pHEMA IL2DPC when water was either directly added (red) *versus* being absorbed from the air (black).

Flowing air response

The data in Fig. 1A was taken in stagnant air conditions where equilibration was limited by diffusion of water into the head space of the vials and by slow diffusion of water into the 2 mL EGP reservoir. This slow two day equilibration time was significantly decreased to 100 minutes by flowing humid air over the sensor in the presence of minimal excess EGP as shown in Fig. 2A. The equilibration time in flowing air is much faster but we observe a transient swelling event in the first 20 minutes before the pHEMA gel relaxes and returns to equilibrium.

This short time transient behavior is observed both when water is absorbed from the air and when water is directly added to EGP as shown in Fig. 2B. The initial swelling is driven by equilibration of the water concentration which causes the gel to swell because water diffuses in before the EGP can escape. The subsequent shrinking is due to slower diffusion of the bulky EGP as the system comes to equilibrium. This transient behavior also occurs in the reverse direction when the water concentration is decreased. The network initially shrinks as water leaves the polymer network to mitigate the chemical potential difference across the membrane then subsequently swells as the polymer relaxes to equilibrium and EGP diffuse into the gel.

Ammonia detection

The IPN-IL2PCS ammonia sensor utilizes a pH sensitive interpenetrating network (IPN) made by polymerizing acrylic acid. Ammonia absorbed by the ionic liquid deprotonates the acrylic acid carboxyl groups, localizing anionic carboxylates on the polymer. Ammonia selectively deprotonates the poly(acrylic acid).

In low ionic strength solutions, localization of charges on the polymer creates a Donnan potential that causes polymer swelling. However, these charges have little impact on polymer

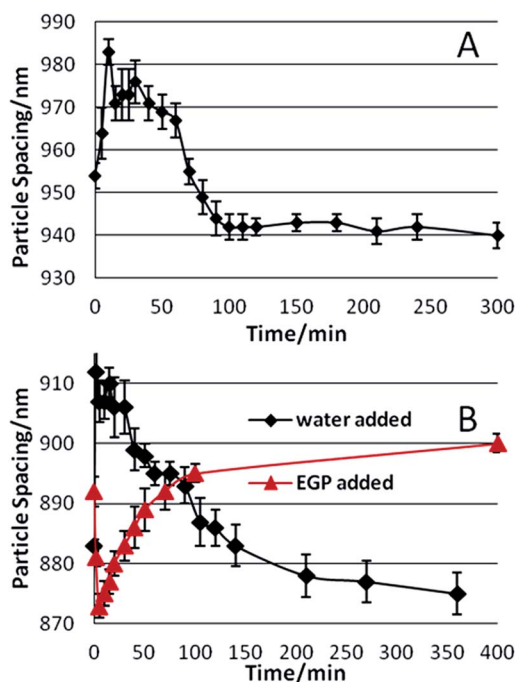


Fig. 2 Flowing air time dependence of IL2DPC particle spacing. (A). Swelling when gel is exposed to 70% RH. (B). Swelling when water is directly added to EGP (black diamonds) and when EGP is directly added to a EGP/water mixture (red triangles).

swelling in very high ionic strength solutions such as in ionic liquids. Thus, the VPT observed due to polymer deprotonation by ammonia derives mainly from a change in the free energy of mixing. The localization of charges on the polymer increases favorable interactions between the polymer and ionic liquid therefore lowering the interaction parameter and swelling the polymer (Fig. 3). This deprotonated polymer swelling that stems from a change in the free energy of mixing was previously described in our creatinine sensor designed for use in high ionic strength blood or serum samples.²⁷

The IPN-IL2DPC response to ammonia is irreversible; the sensor acts as a dosimeter. The IPN-IL2DPC response measured after 24 h saturates when all of the carboxyl groups are deprotonated by the absorbed ammonia. The sensor is irreversible since the equilibrium lies far towards NH_4^+ and carboxylates, neither of which have significant vapor pressures.

The IPN-IL2PCS is very sensitive to low ammonia concentrations. The particle spacing increases 25 nm for 3 ppm ammonia in stagnant air after 24 hours. The 24 h observed red shift saturates above 18 ppm ammonia. The Fig. 3 inset shows the visually evident color change associated with ammonia exposure.

The ammonia concentrations in air determine the rate of change of the particle spacings. The transport rate of NH_3 into the system depends on the NH_3 concentration at the sensor. Fig. 4A shows the particle spacing change for an IPN-IL2DPC exposed to 10 ppm and 90 ppm NH_3 . The particle spacing of the IPN-IL2DPC exposed to the higher NH_3 gas concentration increases faster than the IPN-IL2DPC exposed to 10 ppm NH_3 .

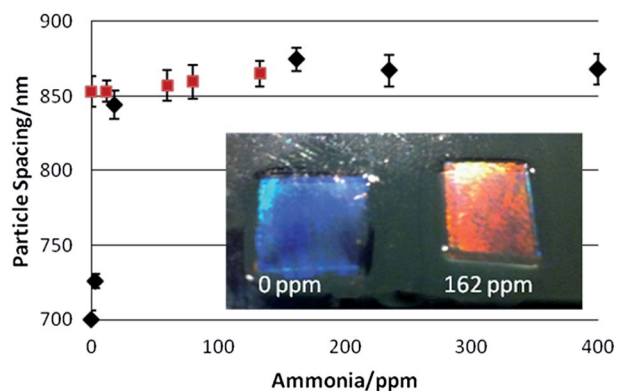


Fig. 3 Dependence of particle spacing of IPN-IL2DPC on air ammonia concentration. The black diamonds indicate the particle spacing as the ammonia concentration increases, while the red squares indicate the particle spacing as the ammonia concentration decreases. The inset shows the diffraction colors of IPN-IL2DPC ammonia sensors exposed to 0 ppm (left) and 162 ppm (right) ammonia. The IPN-IL2DPC were placed on a mirror so that the forward diffracted light reflects back to the camera.²⁵

Fig. 4B shows the particle spacing change that occurs during the first 15 minutes of exposure. The slope of the particle spacing change for the IPN-IL2DPC exposed to 10 ppm NH_3 is 0.9 nm min^{-1} . The slope increases to 1.8 nm min^{-1} when the IPN-IL2DPC is exposed to 90 ppm NH_3 .

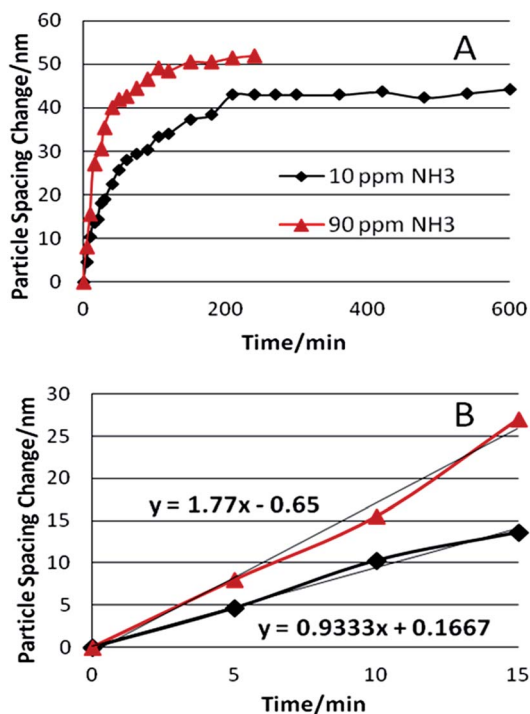


Fig. 4 (A). The particle spacing change, $(d-d_0)$ over time for IPN-IL2DPC exposed to 10 ppm NH_3 (black diamonds) and 90 ppm NH_3 (red triangle). (B). Particle spacing change during the first 15 minutes. Equations for the linear trendlines are included for both 10 ppm and 90 ppm NH_3 .

Experimental

Materials

Barium perchlorate (97% Sigma), 1-ethylguanidine sulfate (98% Sigma), *N,N'* methylene bisacrylamide (BIS) (98% Sigma), 2,2-diethoxyacetophenone (DEAP) (>95% Sigma), 1-propanol ($\geq 99.5\%$ Sigma), and ammonium hydroxide (28.0–30.0% Sigma) were used as received. Hydroxyethylmethacrylate (HEMA) (97%A Sigma) and acrylic acid (AA) (98% Sigma) were distilled under reduced pressure and stored at 4°C . A Fischer Scientific Traceable Dew point/Wet bulb/Humidity and Thermometer and Dri-Rite was purchased from Fischer Scientific. The BW Honeywell GasAlert Extreme Ammonia 0–400 ppm Monitor and the calibration gas (50 ppm) were purchased from Honeywell. Stericup GP Filter Units ($0.22 \mu\text{m}$) were purchased from Millipore. The nanopure water was obtained from a Barnstead Infinity Nanopure water purifier.

Ionic liquid ethylguanidine perchlorate (EGP) synthesis

100 mL of 0.4 M barium perchlorate in water was added to 100 mL of 0.4 M ethylguanidine sulfate in water with vigorous stirring. The barium sulfate precipitate was separated by centrifugation followed by vacuum filtration of the supernatant liquid using a stericup filter unit. Water was evaporated under reduced pressure at 60°C by using a Rotovap. The ionic liquid, ethylguanidine perchlorate (Fig. 5) was further dehydrated by exposing it to a high vacuum pump for several days. It was then stored in a desiccator. Humidity inside the desiccator was 0.5% Relative Humidity (RH).

Fabrication of IL2DPC humidity sensors

The polymerizable monomer solutions used to fabricate the IL2DPC humidity detectors contained 20 wt% HEMA, 1 wt% BIS as the crosslinker, and 30 wt% EGP (density = 1.4 g mL^{-1}) in water. 20 μL of a photoinitiator solution consisting of 30 wt% DEAP in DMSO was added per 1 mL of monomer solution. The co-solvent, EGP, functions in a way similar to that of propylene glycol, preventing pHEMA polymerization induced phase separation in order to produce transparent polymer films.²²

The monomer solution was sandwiched between two glass slides with a spacer in between to produce 500 μm thick films. One of the slides had the 2D array on its surface. Fabrication of monodisperse polystyrene spheres as well as deposition of 2D arrays onto water and glass microscope slides were previously described.^{4,28}

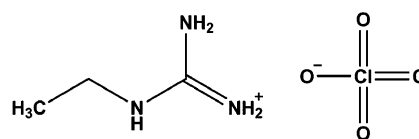


Fig. 5 Structure of ethylguanidine perchlorate ionic liquid.

The monomer solution was UV polymerized, by using 365 nm UV light from a 6 Watt Handheld UV Lamp (UVP UVGL-55 365 nm) to catalyze the free radical polymerization. After UV light polymerization for 15 min, the polymer film with the 2D array attached to the surface was peeled from the slides and cut into pieces ($\sim 1 \text{ cm}^2$). The IL2DPC pieces were washed with pure EGP several times to remove any unreacted monomers and water. IL2DPC were sealed in a vial with fresh EGP and stored in a desiccator until use.

Humidity sensor response

Stagnant air response. IL2DPC sensor pieces ($1 \text{ cm} \times 1 \text{ cm} \times 0.04 \text{ cm}$) were placed in a small dish with 2 mL pure EGP. The particle spacing was measured before exposing the films to humid environments. Humidity was controlled inside a closed desiccators using the supersaturated salt solutions listed in Table 1. The relative humidity (RH) and temperature in the desiccators were monitored using the Fisher Scientific hygrometer. The pHEMA IL2DPC was exposed to each humidity for 48 hours before the particle spacing was measured, after which the supersaturated salt solution was exchanged to increase the humidity inside the chamber. We directly monitored the water concentration absorbed by EGP using near IR absorption measurements as described in the ESI.†

The particle spacings of the pHEMA IL2DPC samples in small dishes with 2 mL EGP were measured daily for 1 week. Samples were exposed to either 0.5% RH or 53% RH.

Flowing air response. pHEMA IL2DPC pieces ($5 \text{ mm} \times 5 \text{ mm} \times 0.4 \text{ mm}$) are placed on a glass cover slip, then placed in a desiccator to equilibrate to 0.5%RH. This desiccator is placed inside a glove box that contains a large dish of a supersaturated NaCl solution and three small fans to gently circulate the air surrounding the Debye ring measurement apparatus. The humidity inside the glove box is 70% RH. The samples on the cover slips are removed from the desiccator and the Debye ring is measured over the course of 5 hours.

Direct water addition. The particle spacings were measured for solutions with defined mole fractions of water in EGP after equilibrium is reached. The particle spacings were monitored while being cycled through increasing and decreasing concentrations of water in EGP. The particle spacings were also measured for samples over shorter time intervals. A pHEMA IL2DPC sample is placed in a vial with 500 μL of EGP and the

Debye ring is measured through the vial. 85 μL of water (~ 0.5 mole fraction) is added and the vial is swirled until the two liquids mix completely. The Debye ring is then measured over the course of 5 hours. Then 250 μL of EGP is added to the solution to decrease the water concentration. Again the Debye ring is measured over the course of 5 hours.

Fabrication of 2D IL2DPC ammonia sensors

An IL2DPC containing carboxyl groups was fabricated for ammonia detection. A 500 μm thick pHEMA IL2DPC was fabricated in the same manner as described above by using a monomer solution containing 17 wt% HEMA, 1 wt% BIS, and 30 wt% EGP in water. After UV polymerization for 15 min, the polymer films with the imbedded 2D array were peeled from the slides and swollen in a second monomer solution containing 15 wt% HEMA, 7 wt% AA, 1 wt% BIS and 50 wt% EGP in water. UV polymerization of the second monomer solution results in an interpenetrating network (IPN) of the pH sensitive polymer. The IPN-IL2DPC film was peeled from the glass slide and cut into pieces ($1 \text{ cm} \times 1 \text{ cm} \times 0.04 \text{ cm}$). The IPN-IL2DPC films were then washed in pure EGP several times to remove unreacted monomers and water and then sealed in a vial with fresh EGP and stored in a desiccator until use.

Testing the ammonia sensor

Stagnant NH_3 . The IPN-IL2DPC pieces were placed in a small dish in contact with 2 mL of EGP in an air tight glass desiccator along with the GasAlert Extreme NH_3 sensor. A beaker with 40 mL of NH_4OH solution was utilized as the NH_3 source. The concentration of gas phase NH_3 was directly measured using the GasAlert Extreme NH_3 sensor. The IL2DPC were initially equilibrated to the humidity inside the desiccator for 48 hours prior to ammonia measurements; the beaker contained 40 mL of pure water. The NH_3 concentration was increased by increasing the NH_4OH concentration, using freshly made NH_4OH solutions. The particle spacings of the IPN-IL2DPC were measured after 24 h exposure to the ammonia.

Flowing NH_3 . IPN-IL2DPC pieces are placed in a small dish with 250 μL of EGP and allowed to equilibrate inside the 60% RH glove box with three small fans that gently circulate the air. We very roughly adjusted the equilibrium NH_3 concentrations by mixing the air of a small reservoir of high NH_3 concentration with air in a large reservoir. The Debye ring is measured over the course of 4 or 10 hours.

Monitoring particle Spacings of IL2DPC sensors

The magnitude of the VPT of the IL2DPC polymer was monitored by the shift in the diffracted light wavelength due to changes in the particle spacing of the embedded 2D array, which depends upon the amount of analyte present.

When a laser pointer irradiates the 2D array at normal incidence, the light is strongly forward diffracted. If the laser irradiated a single 2D array domain, six spots corresponding to the longest six reciprocal 2D array lattice vectors would be observed. In our case, the beam is diffracted by multiple randomly oriented crystalline domains. The locus of forward

Table 1 Salts used to make supersaturated solutions and their % Relative Humidities at 23 °C

Salt	%Relative humidity at 23 °C
Lithium chloride	11.3
Potassium acetate	22.5
Magnesium chloride	32.8
Magnesium nitrate	52.9
Sodium chloride	75.3
Potassium chloride	84.3
Potassium sulfate	97.3

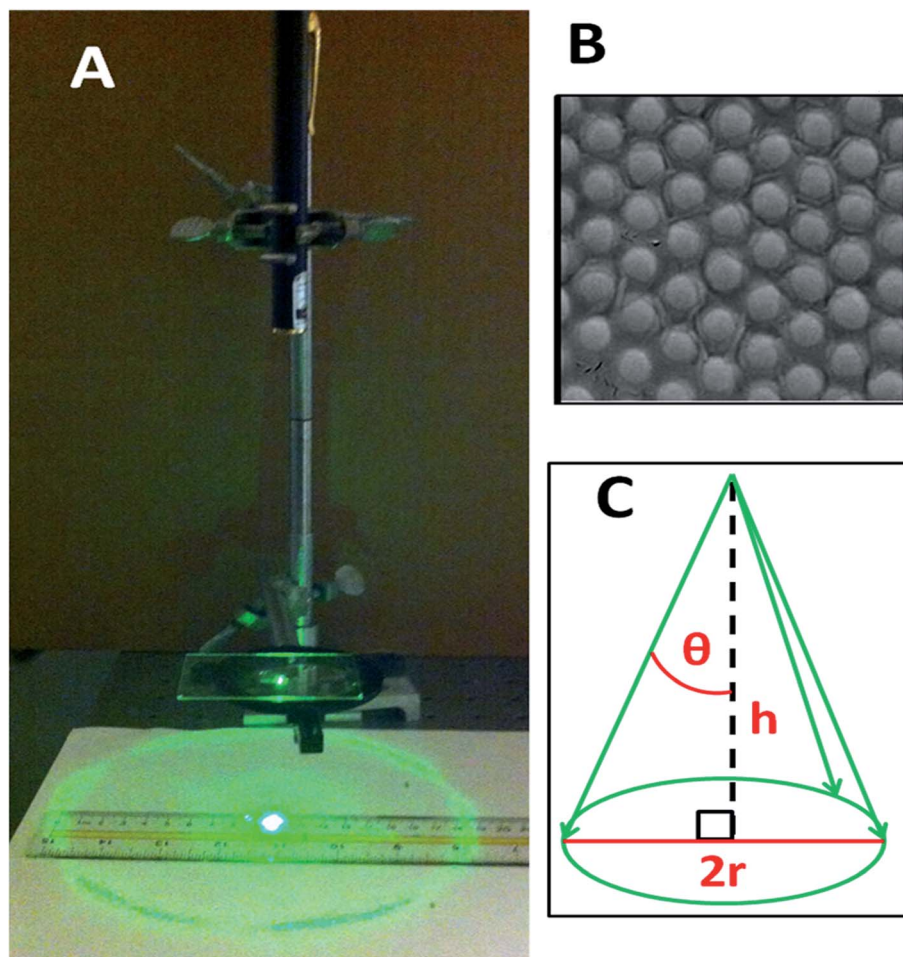


Fig. 6 Debye ring diffraction measurement. (A). The laser pointer beam (532 nm light) incident along the array normal is diffracted, producing a Debye ring. (B). SEM image of the 2D array 2DPC containing ~ 500 nm particles. (C). Illustrates the relationship between the diffraction angle, θ and the radius of the Debye ring, r .

diffraction occurs in a Debye ring (Fig. 6). The diameter of the Debye ring depends on the particle spacing of the IL2DPC.²⁵

Our IL2DPC sample was placed on a microscope slide parallel to the bench top, 8.9 cm above the surface. A 532 nm laser pointer irradiated the sample at normal incidence and the diameter of the Debye ring was measured below on a piece of paper. The diffraction angle, θ , was determined from the Debye ring radius as shown in Fig. 6C (eqn (7)). The particle spacing was calculated from the 2D Bragg diffraction condition (eqn (8)).^{25,29,30} This equation can be simplified for the normal incidence angle $\theta^\circ = 0$. The equation is therefore rearranged to solve for the lattice spacing, d (eqn (9)).

$$\theta = \tan^{-1} \frac{r}{h} \quad (7)$$

$$\lambda = \frac{\sqrt{3}d}{2} (\sin \theta^\circ + \sin \theta) \quad (8)$$

$$d = \frac{2\lambda}{\sqrt{3} \sin \theta} \quad (9)$$

Conclusion

We developed a photonic crystal responsive material for the visual determination of gas phase analytes such as water vapor and ammonia. The ionic liquid ethylguanidine perchlorate (EGP) was utilized as the mobile phase for poly(hydroxyethylmethacrylate) (pHEMA) organogel networks. The ionic liquid-polymer system undergoes a volume phase transition in response to changes in the Gibbs free energy of mixing. This volume change shifts the wavelength of light diffracted from the embedded photonic crystal. The humidity sensor blue shifts when water is absorbed by EGP due to the change in the solubility parameter of the mobile phase. A transient volume phase transition at small time scales is observed due to fast diffusion of water into the EGP-polymer network. The ammonia sensor red shifts when NH_3 is absorbed because the NH_3 deprotonates the polymer carboxylate groups, localizing charges on the polymer. The rate at which the particle spacing changes reports on the concentration of ammonia present.

This novel IL2DPC gas sensing demonstrates proof of concept for a new generation of 2DPC air sensors that use ionic

liquids as their mobile phases. There is a great need for detecting airborne analytes such as environmental toxins, chemical warfare agents, *etc.* Our IL2DPC can provide visually evident determination of atmospheric chemical threats. The sensors demonstrated here are far from optimized in their sensitivity and optical response. These IL2DPC sensors are easily fabricated and should be inexpensive to manufacture.

Acknowledgements

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