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### Electrically conductive, tough hydrogels with pH sensitivity

Sina Naficy

*University of Wollongong, snaficy@uow.edu.au*

Joselito M. Razal

*University of Wollongong, jrazal@uow.edu.au*

Geoffrey M. Spinks

*University of Wollongong, gspinks@uow.edu.au*

Gordon G. Wallace

*University of Wollongong, gwallace@uow.edu.au*

Philip G. Whitten

*University of Wollongong, whitten@uow.edu.au*

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## Electrically conductive, tough hydrogels with pH sensitivity

### Abstract

Electrically conductive, mechanically tough hydrogels based on a double network (DN) comprised of poly(ethylene glycol) methyl ether methacrylate (PPEGMA) and poly(acrylic acid) (PAA) were produced. Poly(3,4-ethylenedioxythiophene) (PEDOT) was chemically polymerized within the tough DN gel to provide electronic conductivity. The effects of pH on the tensile and compressive mechanical properties of the fully swollen hydrogels, along with their electrical conductivity and swelling ratio were determined. Compressive and tensile strengths as high as 11.6 and 0.6 MPa, respectively, were obtained for hydrogels containing PEDOT with a maximum conductivity of  $4.3 \text{ S cm}^{-1}$ . This conductivity is the highest yet reported for hydrogel materials of high swelling ratios. These hydrogels may be useful as soft strain sensors because their electrical resistance changed significantly when cyclically loaded in compression.

### Keywords

hydrogels, tough, ph, conductive, sensitivity, electrically

### Disciplines

Engineering | Physical Sciences and Mathematics

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# Electrically Conductive, Tough Hydrogels with pH Sensitivity

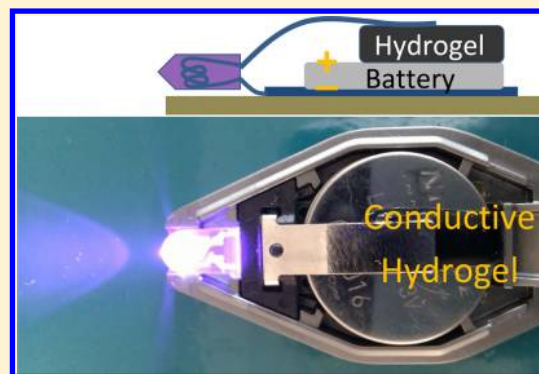
Sina Naficy, Joselito M. Razal, Geoffrey M. Spinks,\* Gordon G. Wallace, and Philip G. Whitten

ARC Centre of Excellence in Electromaterials Science and Intelligent Polymer Research Institute, University of Wollongong, Innovation Campus, Squires Way, North Wollongong, NSW, 2522, Australia

## Supporting Information

**ABSTRACT:** Electrically conductive, mechanically tough hydrogels based on a double network (DN) comprised of poly(ethylene glycol) methyl ether methacrylate (PPEGMA) and poly(acrylic acid) (PAA) were produced. Poly(3,4-ethylenedioxythiophene) (PEDOT) was chemically polymerized within the tough DN gel to provide electronic conductivity. The effects of pH on the tensile and compressive mechanical properties of the fully swollen hydrogels, along with their electrical conductivity and swelling ratio were determined. Compressive and tensile strengths as high as 11.6 and 0.6 MPa, respectively, were obtained for hydrogels containing PEDOT with a maximum conductivity of  $4.3 \text{ S cm}^{-1}$ . This conductivity is the highest yet reported for hydrogel materials of high swelling ratios. These hydrogels may be useful as soft strain sensors because their electrical resistance changed significantly when cyclically loaded in compression.

**KEYWORDS:** conductive hydrogels, mechanical properties, pH sensitivity, poly(acrylic acid), poly(ethylene glycol) methyl ether methacrylate, poly(3,4-ethylenedioxythiophene)



## INTRODUCTION

Conductive hydrogels hold significant promise in drug release, bioactive electrode coating, and actuators.<sup>1–3</sup> Combining the physical and mechanical properties of hydrogels with the electrical activity of an electroactive/conductive component can create unique opportunities for the next generation of materials. However, in many cases, conductivity is not part of the inherent characteristics of the hydrogel and is provided by other elements that are incorporated within the network of the hydrogel (e.g., conductive particles, conjugated polymers, etc.). In general, electrically conductive gels can be fabricated via several methods such as: (1) adding conductive particles to the gel matrix;<sup>4</sup> (2) producing the gel directly from conjugated polymers;<sup>5–8</sup> or (3) incorporating conjugated polymers into the network structure of the gels.<sup>9,10</sup> Except for conjugated polymer gels, electrical conductivity is achieved by a conductive network formed from the conductive elements within an insulating gel, and the gel structure simply constrains this conductive network to provide the required mechanical resistance against the external forces. However, most conventional hydrogels lack the adequate toughness required in many applications. Moreover, the swelling of the hydrogel can also suppress the electrical conductivity of the system because of the percolation phenomenon. Since the conductivity is mainly provided by the conductive network within the hydrogel, the swollen hydrogel network is essentially diluting the conductive network. As the swelling ratio increases, this effect becomes more and more significant and the system can lose its conductivity. Therefore, it is important to develop a conductive

hydrogel system that retains its conductivity at different gel swelling ratios and displays enhanced mechanical performances.

Fully swollen hydrogels with conducting particles, such as graphite,<sup>4,11–13</sup> carbon nanotubes,<sup>14,15</sup> or metallic particles,<sup>16</sup> incorporated in their structure typically have conductivity lower than  $1 \times 10^{-3} \text{ S cm}^{-1}$ , with mechanical properties similar to the constituent hydrogel matrix. In all of these examples, the conductivity is inversely affected by the swelling ratio, and the hydrogels exhibit brittle mechanical behavior.<sup>4,15</sup> To obtain suitable mechanical performance for bioapplications, researchers have widely used poly(vinyl alcohol) (PVA) (alone or with other polymers) as the hydrogel matrix. For example, PVA-graphite hydrogels were formed for use as an artificial cornea with tensile strength dropping constantly as graphite content increased.<sup>13</sup>

Conjugated gels made directly from conjugated polymers were reported previously as conductive hydrogel/gel systems. Examples include ionically cross-linked poly(3,4-ethylenedioxythiophene) (PEDOT)-poly(styrenesulfonate) (PSS),<sup>17</sup> PEDOT-PSS-polypyrrole (PPy),<sup>18</sup> PPy-PSS, PEDOT-sulfonated polyaniline (SPANi), and PPy-SPANi.<sup>19,20</sup> The swelling ratio of swollen mass to dry mass of these conjugated gels was reported to range typically between 5–15 and conductivity of the order of  $10^{-2} \text{ S cm}^{-1}$ . The mechanical properties were demonstrated to vary significantly with composition. The highest compression strength reported for an ionically cross-

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linked PEDOT-PSS hydrogel was 3.3 MPa with a fracture strain of 90%, a tensile strength of  $\sim 180$  kPa and elongation at break of 64%.<sup>20</sup>

Conductivity may also be introduced to a gel by synthesizing a conjugated polymer into a preformed gel network to form an interpenetrating polymer network (IPN). Various conjugated polymers such as polyaniline (PANi)<sup>21–26</sup> have been chemically polymerized within a preformed hydrogel network (or directly added to the network) to make the hydrogel conductive. The reported conductivity for most of these hydrogels in their swollen state was on the order of  $1 \times 10^{-3}$  S cm<sup>-1</sup>. In one study, PEDOT-PSS was chemically polymerized within polyacrylamide (PAAm).<sup>27</sup> The achieved PAAm-PEDOT-PSS hydrogels were tough with compression strength as high as 1.3 MPa, fracture strain of 60–90%, and electrical conductivity on the order of  $1 \times 10^{-3}$  S cm<sup>-1</sup>. The maximum conductivity that could be achieved in this example was limited by the solubility of EDOT monomer in the aqueous solution of PSS. Interfacial polymerization has also been employed to form PANi within PAAm hydrogels where aniline monomers were chemically polymerized at the organic/water interface between the reaction media (organic phase) and PAAm hydrogel (water phase). As the polymerization reaction proceeded, the growing PANi chains became hydrophilic and migrate into the aqueous phase confined within the PAAm hydrogel.<sup>28</sup> The achieved hydrogels were reported to be tough with compression strength of up to 1.1 MPa, fracture strains from 80 to 90% (for a sample with 90% water), and electrical conductivity of up to  $3.4 \times 10^{-2}$  S cm<sup>-1</sup> (when PANi content was  $\sim 28$  wt %). Electro-polymerization was also employed to form conjugated polymers in a hydrogel network. For example, PPy and PANi were electrochemically polymerized within a PAAm hydrogel,<sup>29,30</sup> or copolymer hydrogels based on poly(hydroxyethyl methacrylate) (HEMA).<sup>31,32</sup> The measured electrical conductivity for these hydrogel films was reported to be in the order of  $\sim 1 \times 10^{-2}$  S cm<sup>-1</sup>.<sup>33</sup> Again, the mechanical performance of these hydrogels was similar to their constituent hydrogel with low tensile elongation at break and low strength.<sup>34</sup>

To overcome the inherent mechanical weakness of hydrogels, researchers have used the “double network” (DN) approach to make tough conductive hydrogels.<sup>35</sup> DN hydrogels are a type of IPNs and are typically made from a tightly cross-linked first network (usually a polyelectrolyte) and a loosely cross-linked second network (mainly a neutral polymer). Most DN hydrogels exhibit significantly improved mechanical strength and toughness without a loss in equilibrium swelling ratio.<sup>36</sup> In one recent study, a PAA-based DN was formed followed by chemical polymerization of EDOT within the hydrogel.<sup>37</sup> The tough PAA-based DN hydrogel was built from two PAA interpenetrated networks with different cross-linking ratios. The PEDOT incorporated PAA-PAA DN hydrogels were reported to be electroactive and the final gel had a compression strength as high as 1.8 MPa and a fracture strain of 80%. It was shown that this fracture strength was three times larger than that of the initial PAA-PAA DN hydrogel, and more than 20 times larger than that of PAA single network. The conductivity of these hydrogels was measured to be no higher than  $1 \times 10^{-3}$  S cm<sup>-1</sup>. In another example, PANi nanofibers were chemically polymerized within a PAA network.<sup>38</sup> Conductivities up to  $\sim 5 \times 10^{-3}$  S cm<sup>-1</sup> were reported, with improved compression strength ( $\sim 1.7$  MPa), whereas tensile

strength remained around  $\sim 25$  kPa for samples with swelling ratio around  $\sim 5$ .

Here, we report on an electronically conductive hydrogel based on a structure that comprises poly(ethylene glycol) methyl ether methacrylates (PPEGMA) as the first network and poly(acrylic acid) (PAA) as the second network.<sup>39</sup> A bottlebrush configuration was achieved by polymerization of PEGMA oligomers, which yield a hydrophobic polymethacrylate backbone with hydrophilic polyethylene glycol (PEG) side chains. It has been shown that the nonlinear PEG analogues (e.g., PEGMA) exhibit biocompatibility similar to linear PEG.<sup>40</sup> Electrical conductivity was achieved by chemically polymerizing EDOT (with PSS as the molecular dopant) within the tough PPEGMA-PAA DN hydrogel. The EDOT polymerization was carried out in sequential steps to increase the PEDOT loading and to achieve unprecedented levels of conductivity within the tough gel network.

## ■ EXPERIMENTAL SECTION

**Materials.** Poly(ethylene glycol) methyl ether methacrylate (PEGMA1100) (MW 1100 g mol<sup>-1</sup>), acrylic acid (AA), potassium persulfate (KPS) and *N,N'*-methylene bisacrylamide (MBAA) were purchased from Sigma-Aldrich and used without any further purification to fabricate the PPEGMA1100-PAA DN hydrogels. Poly(sodium 4-styrenesulfonate) (NaPSS) (MW 70 kg mol<sup>-1</sup>), ammonium persulfate (APS) and 3,4-ethylenedioxythiophene (EDOT) were purchased from Sigma-Aldrich and used to synthesize PEDOT within the DN hydrogels. Buffers (McIlvaine phosphate-citrate)<sup>41</sup> with various pHs and constant ionic strength ( $I = 0.5$  M) were prepared using citric acid (Sigma-Aldrich), sodium phosphate and potassium chloride (Ajax Finechem, Australia). To facilitate the removal of the hydrogels from the glass slide molds, we used octadecyltrichlorosilane 90% (Sigma-Aldrich), hexane, and hydrogen peroxide solution (35%) (Ajax Finechem, Australia) to make the surface of glass slides hydrophobic.<sup>42</sup> Milli Q deionized water (18.5 M $\Omega$ ) was used to make up all of the aqueous solutions.

**Sample Preparation.** *PPEGMA1100-PAA DN Hydrogels.* The method to manufacture the PPEGMA1100-PAA DN hydrogels was described in detail elsewhere.<sup>39</sup> Briefly, thermal radical polymerization was employed to prepare all networks. First, the PPEGMA1100 single network (SN) was synthesized by dissolving PEGMA1100 oligomers in deionized water (20 wt %) followed by adding MBAA as the cross-linking comonomer and KPS as the initiator (4 and 0.5 mol %, respectively, based on PEGMA1100 monomer). The solution was stirred thoroughly, purged with N<sub>2</sub> and then transferred to a mold. Thin hydrogel sheets were prepared by injecting the monomer solution between two surface-treated hydrophobic glass slides separated with a silicon spacer (1 mm). To make cylindrical hydrogels, we used plastic syringes as the polymerization container. Polymerization was carried out in a convection oven at elevated temperature (65 °C) for 6 h. After polymerization, samples were removed from the molds and rinsed thoroughly and finally kept in deionized water for 1 week, where the water was changed on a daily basis to ensure the removal of unreacted chemicals. In the second polymerization stage, the PPEGMA1100 hydrogels were soaked in an aqueous solution of AA monomer (20 wt %), MBAA (0.1 mol %), and KPS (0.1 mol %) for 3 days. The fully swollen PPEGMA1100 hydrogels were sealed in a container, followed by polymerization reaction at 65 °C for 6 h. The resulting PPEGMA1100-PAA DN hydrogels were then washed extensively in deionized water for 1 week to remove unreacted components.

*PPEGMA1100-PAA-PEDOT (PSS) Hydrogels.* To form PEDOT within the PPEGMA1100-PAA DN hydrogel structure, the starting DN hydrogels were required to absorb EDOT monomer into their structure in a swelling process. Thus, the PPEGMA1100-PAA DN hydrogels were transferred to the pH 6 buffer solution ( $I = 0.5$  M) for 3 days or until the hydrogels reached the equilibrium swelling ratio. After this period, samples were removed and washed thoroughly with

deionized water for another 3 days to remove excess ions. During this final washing process the swelling ratio of samples did not change. Hydrogel samples were allowed to fully swell at pH 6 which is above the  $pK_a$  of PAA (pH  $\sim$ 4) to facilitate the maximum uptake of EDOT monomer. Samples kept in the protonated, less-swollen state below pH 4 resulted in a small amount of EDOT uptake with most of the PEDOT confined to the outer surface of the gel. The fully swollen PPEGMA1100-PAA DN samples were soaked in EDOT-PSS dispersion for 1 week as the solution was stirred continuously. To prepare the EDOT-PSS dispersion, 10.0 g of NaPSS was dissolved in 100 mL of water followed by addition of 6.5 g of EDOT monomer. Before soaking the DN hydrogel samples, the EDOT-PSS aqueous mixture was vigorously stirred for 20 min using a homogenizer (IKA T25D, Germany) (12000 rpm) until a uniform mixture was obtained. The polymerization of PEDOT was initiated by adding 13.0 g of APS to the above EDOT-PSS dispersion in which the equilibrated DN hydrogel samples were immersed. The mixture was then left at ambient temperature under mild stirring for another 3 days. At this stage, the mixture gradually turned dark and eventually the whole system turned to a solid gel with PEDOT-PSS gel formed both outside and inside the PPEGMA1100-PAA DN gels. The PPEGMA1100-PAA-PEDOT(PSS) hydrogels were easily physically separated from the fragile surrounding PEDOT-PSS gel and washed extensively with deionized water. To increase the amount of PEDOT in the hydrogels, we repeated the PEDOT polymerization process by immersing the PPEGMA1100-PAA-PEDOT(PSS) hydrogels in pH 6 buffer solution ( $I = 0.5$  M) for 3 days. The fully swollen PPEGMA1100-PAA-PEDOT(PSS) hydrogels were then soaked in a fresh EDOT-PSS dispersion as described previously. By repeating this process the loading amount of PEDOT-PSS within the DN hydrogel was increased. To indicate the number of PEDOT polymerization steps used in this study, we referred to the PPEGMA1100-PAA-PEDOT(PSS) hydrogels as DN-PEDOT(PSS)- $X$ , where  $X$  (I, II, etc.) is the number of PEDOT polymerization steps. For example, DN-PEDOT(PSS)-I is a DN-based hydrogel in which PEDOT polymerization was performed once, whereas DN-PEDOT(PSS)-II refers to hydrogels in which PEDOT polymerization was performed two times, and so on. DN here refers to the starting PPEGMA1100-PAA double network hydrogel.

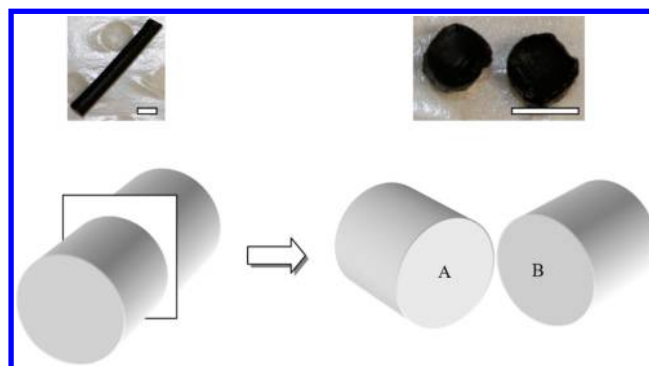
**Characterization. Swelling Ratio.** The swelling ratio of hydrogels was measured by weighing the hydrogels in their fully swollen state and after drying. Hydrogel samples were placed in pH buffer solutions at different pHs ( $I = 0.5$  M) for 1 week to reach the equilibrium. After 1 week, hydrogels were removed and weighed carefully ( $W_s$ ). Hydrogels then were dried at 75 °C for 3 days and weighed again ( $W_d$ ). The mass ratio of fully swollen hydrogels to dried hydrogels was taken to be the swelling ratio ( $Q$ ) of hydrogels:

$$Q = \frac{W_s}{W_d} \quad (1)$$

**Mechanical Tests.** Tensile and compression mechanical properties of hydrogels were measured using a EZ-S mechanical tester (Shimadzu, Japan). To investigate the effect of pH on the mechanical properties of hydrogels, samples were soaked in buffer solutions at various pHs ( $I = 0.5$  M) for 1 week, then cut into strips for tensile testing (5 mm width  $\times$  30 mm length). For compression tests, gels were cut into cylindrical-shaped samples (10 mm height). Sand paper was placed between the gels and clamp surfaces in both tensile and compression tests in order to reduce any slippage. The strain rate (tensile/compression) was set at 2 mm  $\text{min}^{-1}$  for all samples. All of the measurements were completed in air while the weight of samples was monitored before and after the test to investigate any possible water loss during the test. The change in weight during the mechanical testing measured for each sample revealed that the water loss was not significant during the course of such tests.

**Electrical Conductivity.** The four-point probe technique was used to measure the conductivity of hydrogels using a linear probe head (JANDEL, UK). The bulk resistance of samples ( $R$ ) was calculated from the applied current ( $I$ ) and recorded voltage ( $V$ ), using Ohm's

law:  $R = I/V$ , with at least five separate measurements made for each sample. To avoid any possible interference from any PEDOT-PSS remaining on the gel surface, cylindrical-shaped samples were cut transversely and the inner cross section of the cut samples was used in all of the conductivity measurements (Figure 1). Before each measurement, the surface water on the samples was carefully tapped dry.



**Figure 1.** Photographs and schematic illustration of a conducting hydrogel cut into two pieces (A and B). Electrical conductivity tests were performed on the cross sections A and B. Pictures show a cylindrical-shaped DN-PEDOT(PSS)-I hydrogel before and after cut. Scale bar is 10 mm in both images.

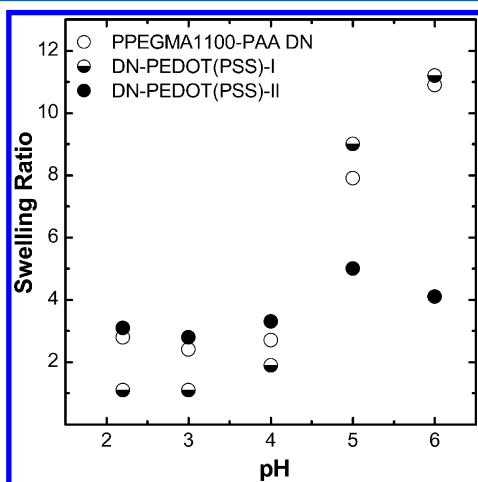
## RESULTS

**Hydrogel Formation.** The PPEGMA1100-PAA DN hydrogels were mechanically robust and pH sensitive. Typical compression behavior of a DN structure was observed for PPEGMA1100-PAA DN hydrogels with enhancements more than 15 and 270 times in compression strength compared to PAA and PPEGMA1100 SN hydrogels, respectively (see below and reference 37). The PPEGMA1100-PAA DN hydrogels were pH sensitive, with their swelling ratio and hydrophobicity changing extensively with pH. Hydrogen bonding between ethylene glycol units of PPEGMA1100 side chains and carboxylic acid groups in PAA were considered to be responsible for this pH sensitivity. As the pH increases, the hydrogen bonding between PPEGMA1100 side groups and PAA dissociates and subsequently the PPEGMA1100-PAA DN hydrogels swelling ratio and hydrophilicity increase significantly. The as-prepared gels were opaque and had a swelling ratio around 2.5 due to the acidic pH of the polymerization mixture. The fully swollen PPEGMA1100-PAA hydrogel at pH 6 was transparent with a swelling ratio of  $\sim$ 11.

The formation of PEDOT throughout the PPEGMA1100-PAA hydrogels required preconditioning at neutral pH. When as-prepared DN hydrogels were placed in EDOT-PSS dispersion for 1 week, only a small amount of EDOT-PSS could be absorbed and the resulting polymerization yielded PEDOT only at the surface of the hydrogels. Consequently, to allow EDOT monomers to diffuse into the PPEGMA1100-PAA DN structure, as-prepared DN hydrogels were first soaked in pH 6 buffer solution. After EDOT polymerization the pH of the reaction solution had decreased to below 4 and yet optical microscopy inspection of thinly sliced hydrogels showed that the PEDOT was formed evenly through the hydrogel with no apparent difference observed along the cross section of DN-PEDOT(PSS) hydrogels (see pictures in Figure 1). Micro-Raman spectroscopy (see the Supporting Information) also

confirmed the presence of PEDOT throughout the entire volume of the DN hydrogel.

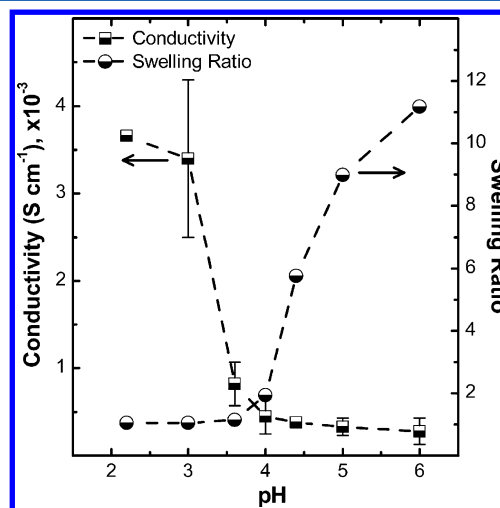
**pH Sensitivity.** The swelling ratio of the PPEGMA1100-PAA DN hydrogel was shown to vary considerably with pH. Thus, it was expected to observe similar pH sensitivity for DN-PEDOT(PSS) hydrogels where PEDOT was incorporated in the PPEGMA1100-PAA DN hydrogels. The swelling ratio of the starting PPEGMA1100-PAA DN hydrogel, DN-PEDOT(PSS)-I and DN-PEDOT(PSS)-II hydrogels are plotted in Figure 2 as pH ranges from 2.2 to 6 ( $I = 0.5$  M).



**Figure 2.** Swelling ratio of PPEGMA1100-PAA DN, DN-PEDOT(PSS)-I, and DN-PEDOT(PSS)-II hydrogels as a function of pH of the buffer solution ( $I = 0.5$  M). Error bars are smaller than the size of symbols.

Clearly, both DN-PEDOT(PSS)-I and DN-PEDOT(PSS)-II hydrogels exhibited swelling ratios that were pH dependent. At pHs below  $\sim 4$  all three systems exhibited a low swelling ratio which then increased between pH 4 and 5 corresponding to the  $pK_a$  of PAA (4.25).<sup>43</sup> This increase was much more pronounced in the case of PPEGMA1100-PAA DN and DN-PEDOT(PSS)-I. Both the PPEGMA1100-PAA DN and the DN-PEDOT(PSS)-I hydrogels reached a maximum swelling ratio of around 11 at pH 6, whereas the maximum swelling ratio of the DN-PEDOT(PSS)-II hydrogel was only  $\sim 4$  at this pH. Moreover, at pHs below  $\sim 4$  both PPEGMA1100-PAA DN and DN-PEDOT(PSS)-II had similar swelling ratios ( $Q \approx 2.8-3.3$ ), while the DN-PEDOT(PSS)-I hydrogel showed smaller swelling ratios ( $Q \approx 1.1$ ). In the DN-PEDOT(PSS)-II case where PEDOT polymerization was performed two times, more PEDOT was present in the system which consequently resulted in hydrogels which were less pH-sensitive with a swelling ratio ( $Q \approx 3-5$ ) closer to that of previously reported PEDOT-PSS hydrogels ( $Q \approx 5$ ).<sup>20</sup> These results suggest that although the DN-PEDOT(PSS) hydrogels remained pH-sensitive, their overall response to pH decreased as more PEDOT was introduced to the system. It is likely that PEDOT network in the DN-PEDOT(PSS)-II system is continuous, thereby limiting expansion and contraction of the hydrogels. Of note, the PPEGMA1100 SN hydrogel was not pH sensitive with the swelling ratio remaining around 10 over the pH range studied here. The PAA SN hydrogel was, on the other hand, pH sensitive with the swelling ratio increasing from 5 at pH 2.2 to 23 at pH 6 (data not included in Figure 2).

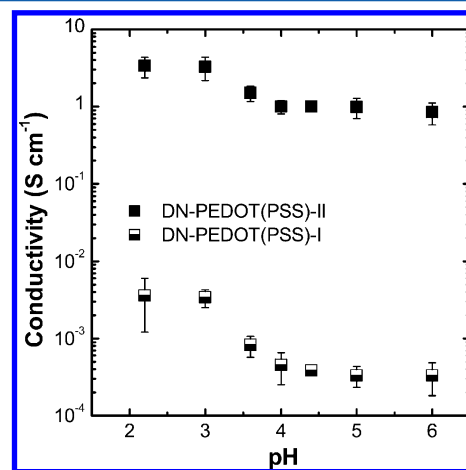
**Electrical Conductivity.** PEDOT was incorporated into the hydrogels to enhance the electrical properties of the system. The DC electrical conductivity of DN-PEDOT(PSS)-I samples was measured using a four point probe. Figure 3 illustrates the



**Figure 3.** Conductivity and swelling ratio of fully swollen DN-PEDOT(PSS)-I as a function of pH ( $I = 0.5$  M). Lines are to guide the eye only.

conductivity and swelling ratio of DN-PEDOT(PSS)-I hydrogels as pH changes from acidic to neutral (pH 2.2–6). Clearly, the conductivity decreased with increasing pH while swelling ratio increased with pH. As the swelling ratio increased from 1.1 to 11.2 with pH increasing from 2.2 to 6, the conductivity dropped almost 1 order of magnitude from  $3.7 \times 10^{-3}$   $S\ cm^{-1}$  to  $2.8 \times 10^{-4}$   $S\ cm^{-1}$ .

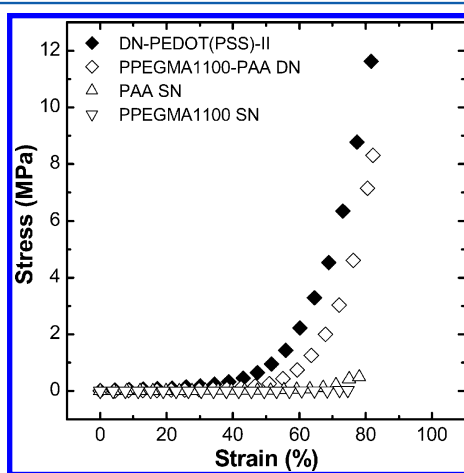
The conductivity was improved significantly by repeating the polymerization of EDOT to form the DN-PEDOT(PSS)-II. After the second polymerization, electrical conductivity was enhanced by 3 orders of magnitude, increasing from  $3.7 \times 10^{-3}$   $S\ cm^{-1}$  for DN-PEDOT(PSS)-I to  $3.4$   $S\ cm^{-1}$  for DN-PEDOT(PSS)-II (pH 2.2). The effect of pH on the conductivity of DN-PEDOT(PSS)-I and DN-PEDOT(PSS)-II hydrogels is shown in Figure 4. Both systems show a decrease in conductivity as the pH increases above  $\sim 4.5$ , corresponding to the pH-induced swelling transition in Figure 2. However, at



**Figure 4.** Conductivity of fully swollen DN-PEDOT(PSS)-II and DN-PEDOT(PSS)-I as a function of pH ( $I = 0.5$  M).

all pHs the DN-PEDOT(PSS)-II hydrogel had a conductivity at least 3 orders of magnitude larger than the DN-PEDOT(PSS)-I hydrogels. The conductivity change was observed to be reversible as pH changed from acidic to neutral and vice versa. The PEDOT(PSS) content in dried samples was measured to be around 24 wt % for the DN-PEDOT(PSS)-I hydrogel, and 38 wt % for the DN-PEDOT(PSS)-II hydrogel based on the dry mass. The ratio of PSS to PEDOT was not determined; however, it was observed that DN-PEDOT hydrogels prepared in the same manner but without PSS were poorly conducting ( $1 \times 10^{-5} \text{ S cm}^{-1}$ ), indicating that PSS is important for forming highly conducting PEDOT and the PSS is likely incorporated as dopant inside the hydrogels.

**Mechanical Properties.** To investigate the effect of PEDOT formation on the mechanical behavior of the hydrogels, both compression and tensile tests were performed on hydrogels fully swollen at different pHs. Figure 5 compares

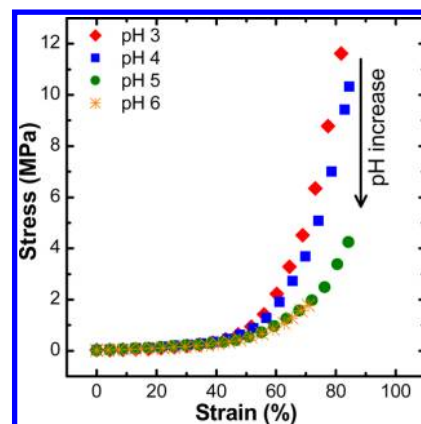


**Figure 5.** Compression stress–strain curves of DN-PEDOT(PSS)-II, PPEGMA1100-PAA DN, PAA, and PPEGMA1100 hydrogels at pH 3 ( $I = 0.5 \text{ M}$ ).

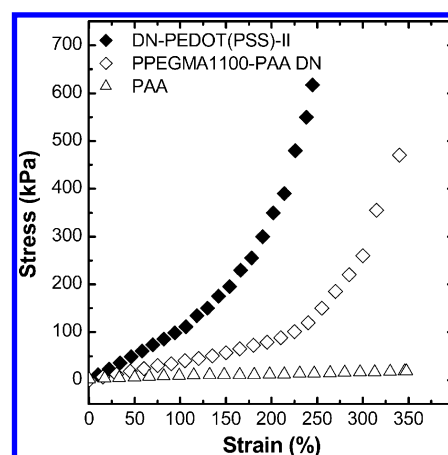
the compression stress–strain curves of DN-PEDOT(PSS)-II hydrogel with PPEGMA1100-PAA DN, PPEGMA100 SN and PAA SN hydrogels at pH 3. The maximum compression strain among these networks did not vary significantly. However, the compression strength of the PPEGMA1100-PAA DN hydrogel was enhanced by a factor of more than 15 and 250 times compared with the PAA and PPEGMA1100 single networks, respectively. The introduction of PEDOT provided a further significant enhancement in compression strength without compromising the swelling ratio.

The effect of pH on the compression strength was investigated (Figure 6). As the pH increased from 3 to 6, the compression strength of all hydrogels decreased particularly around the swelling transition point at pH 4.5. Over the entire pH range studied here the DN-PEDOT(PSS)-II hydrogel had significantly higher compression strength than the starting DN and the individual SN constituents (i.e., PPEGMA1100 and PAA) at the same pH.

The tensile strength, Young's modulus and elongation at break of PPEGMA1100-PAA DN and DN-PEDOT(PSS)-II hydrogels were investigated as a function of pH (Figures 7 and 8). For all gels tested, the tensile strength, Young's modulus and the elongation at break decreased with increasing pH through the swelling transition region as more highly swollen gels are usually softer and more brittle (Figure S2). The tensile



**Figure 6.** Compression stress–strain curves of fully swollen DN-PEDOT(PSS)-II hydrogels at various pHs ( $I = 0.5 \text{ M}$ ).

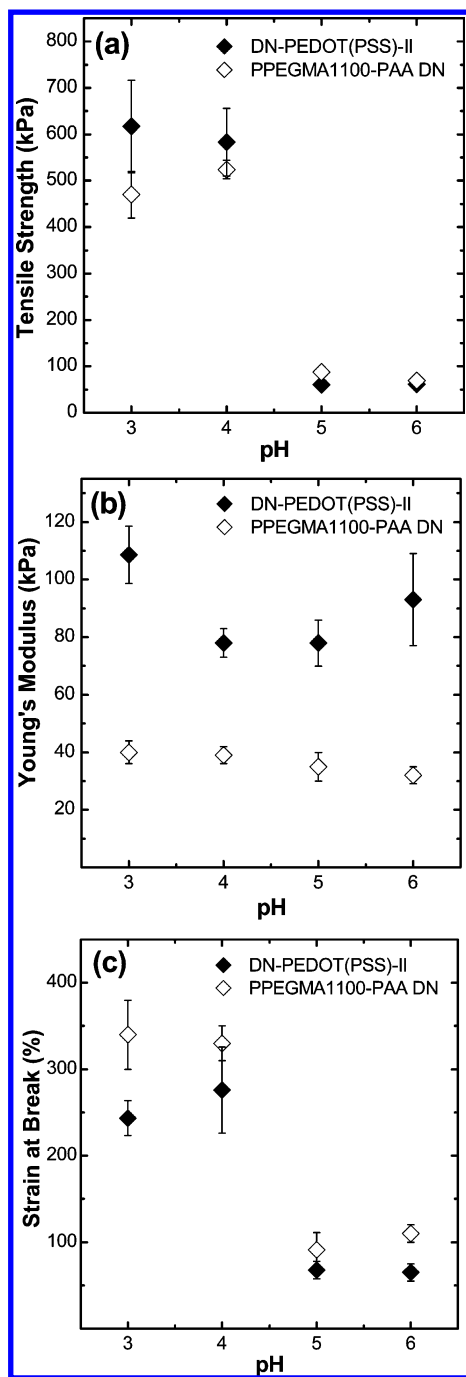


**Figure 7.** Tensile stress of DN-PEDOT(PSS)-II, PPEGMA1100-PAA DN and PAA hydrogels (pH 3,  $I = 0.5 \text{ M}$ ) as a function of strain.

strength of DN-PEDOT(PSS)-II hydrogels was slightly higher than PPEGMA-PAA DN at low pHs, then decreased to similar values at pHs above the swelling transition point (Figure 8a). Interestingly, the Young's modulus of the DN-PEDOT(PSS)-II hydrogels was 2–3 times higher than that of the starting PPEGMA1100-PAA DN hydrogels over the pH range investigated (Figure 8b).

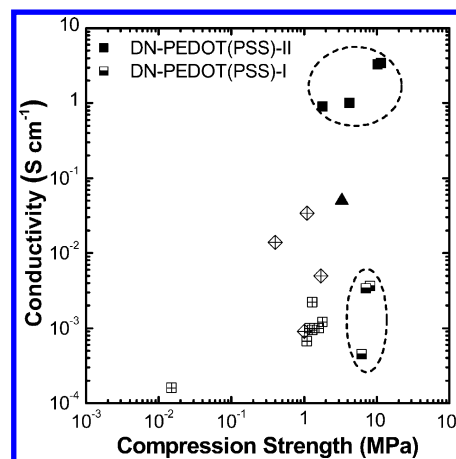
## DISCUSSION

The swelling ratios and mechanical properties of hydrogels containing PEDOT were comparable with other DN hydrogels. In fact, some improvement was observed in the mechanical properties of DN-PEDOT(PSS) hydrogels compared to the starting PPEGMA1100-PAA DN hydrogels. In terms of compression strength, the DN-PEDOT(PSS)-II hydrogels exhibited high strengths (11 MPa at acidic pHs), which places them among the strongest hydrogels developed (for comparison see Table 1 in ref 35). High electrical conductivity was attained by increasing the amount of PEDOT within the network via repeating chemical polymerization of EDOT. To compare the electrical conductivity and mechanical performance of DN-PEDOT(PSS) hydrogels obtained in this study with various gel systems available in the literature, Figure 9 shows the conductivity and compressive strength of fully swollen conductive hydrogels. Many more hydrogel systems have been described in the literature as electrically conductive,



**Figure 8.** Tensile mechanical properties of fully swollen DN-PEDOT(PSS)-II and PPEGMA1100-PAA DN hydrogels as a function of pH ( $I = 0.5\text{ M}$ ): (a) tensile strength, (b) Young's modulus, and (c) strain at break.

but not enough information is available on their mechanical properties. The results we obtained here for conductivity ( $3.4\text{ S cm}^{-1}$  for DN-PEDOT(PSS)-II at acidic pH) is slightly higher than that of the untreated PEDOT-PSS films ( $\sim 1\text{--}2\text{ S cm}^{-1}$ ),<sup>44</sup> and similar to dehydrated PEDOT-PSS gels prepared via ionic cross-linking.<sup>19</sup> As for DN-PEDOT(PSS)-I, the measured electrical conductivity ( $3.7 \times 10^{-3}\text{ S cm}^{-1}$  at pH 2.2 to  $2.8 \times 10^{-4}\text{ S cm}^{-1}$  at pH 6) is comparable with the highest conductivity previously described for IPN hydrogel-conjugated polymer systems and other filled gels.

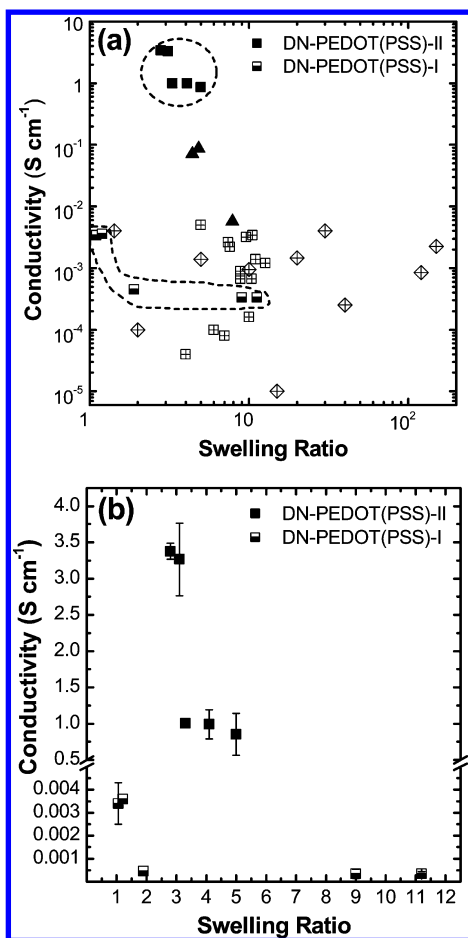


**Figure 9.** Conductivity of various hydrogels and their compression strength in fully swollen state. Conductivity is achieved by incorporating PEDOT<sup>27,34,37</sup> (squares) or PANi<sup>28,38</sup> (diamonds) into a hydrogel matrix. Neat ionically cross-linked PEDOT-PSS hydrogel<sup>20</sup> is shown for comparison (filled triangle). The DN-PEDOT(PSS) hydrogels of the present study are highlighted by dashed lines.

The extent of swelling strongly affects all hydrogel properties, including the conductivity as summarized in Figure 10. From these studies it is apparent that the conductivity tends to decrease with increasing swelling ratio. In the present study, it was shown that the conductivity of DN-PEDOT(PSS) hydrogels significantly decreased as pH changed from acidic to more neutral values corresponding to an increase in swelling ratio. A threshold swelling ratio around  $Q_c \approx 1.9$  and  $3.3$  was observed for DN-PEDOT(PSS)-I and DN-PEDOT(PSS)-II, respectively, where the conductivity dramatically dropped from higher values to a lower plateau. This behavior may suggest that the swelling disrupts the percolation network of conductive pathways within the gel. At all swelling ratios, the conductivity of DN-PEDOT(PSS)-II hydrogels was at least 3 orders of magnitude higher than the conductivity of DN-PEDOT(PSS)-I hydrogels. It seems, therefore, that after the second PEDOT polymerization in the already-formed DN-PEDOT(PSS)-I hydrogels, the amount of PEDOT has reached a critical threshold to cause a significant enhancement in the conductivity. This hypothesis is likely valid because after the second PEDOT polymerization the conductivity did not change considerably when a third PEDOT polymerization was performed ( $4.3\text{ S cm}^{-1}$  at pH 3 for DN-PEDOT(PSS)-III). Moreover, The conductivity of the DN-PEDOT(PSS)-II hydrogels above their percolation threshold point ( $0.8\text{ S cm}^{-1}$ ,  $Q \approx 4$ ) was almost 10 times higher than the next highly conductive hydrogel based on the ionically cross-linked PEDOT and PSS.<sup>19,20</sup>

The conductivity of DN-PEDOT(PSS) hydrogels was also observed to be sensitive to the applied external strain. The resistance of the DN-PEDOT(PSS)-II hydrogel (pH 6) under a reciprocal compression strain was measured with a digital multimeter (Agilent 34410A) connected to two stainless steel foils that were sandwiched between the ends of a cylindrical gel sample and insulated clamps of the mechanical tester. The hydrogel was compressed to a strain of  $\sim 50\%$  held for 120 s and then unloaded to a strain of  $\sim 30\%$ . Sample remained in this state for another 120 s. The change in the height and force was recorded along with the resistance of the sample as a





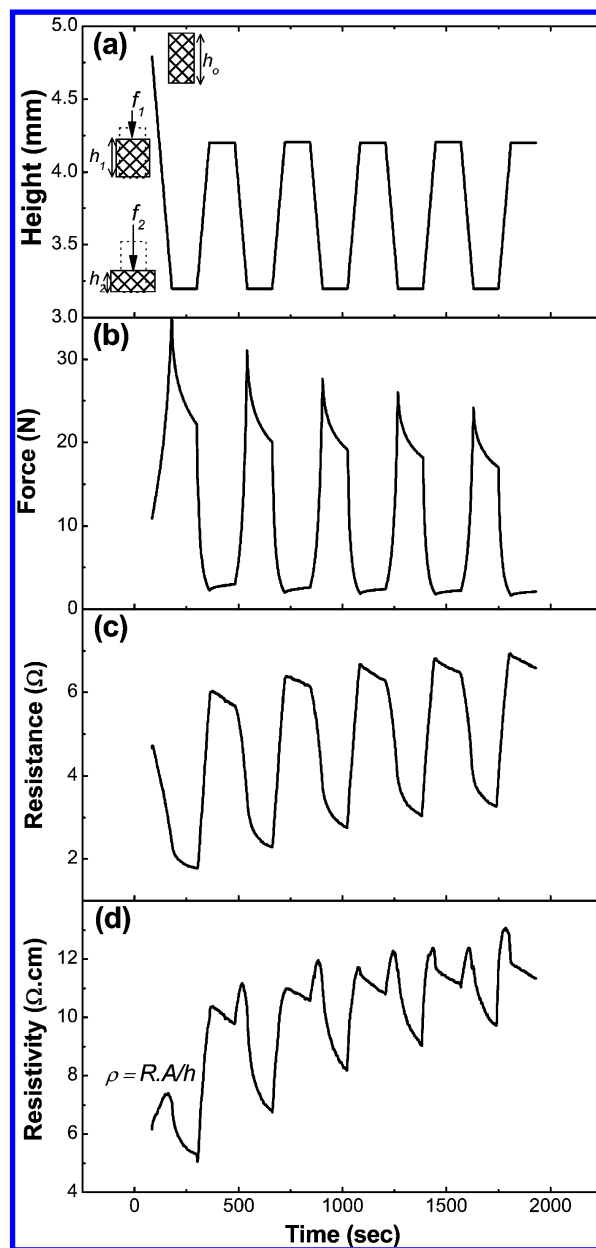
**Figure 10.** (a) Conductivity of various conductive hydrogels and their swelling ratios. Conductivity is produced by addition of conductive fillers<sup>4,11,12,15,16</sup> (diamonds) or conducting polymers<sup>27,28,34,37,38</sup> (squares). Neat ionically cross-linked PEDOT-PSS hydrogel<sup>19,20</sup> is shown for comparison (filled triangles). The DN-PEDOT(PSS) hydrogels of the present study are highlighted by dashed lines. (b) Conductivity of DN-PEDOT(PSS)-I and DN-PEDOT(PSS)-II hydrogels as a function of swelling ratio caused by a pH change.

function of time (Figure 11). Since the resistance is related to the cross section surface area ( $A$ ) and height ( $h$ ) of the hydrogel, and both  $A$  and  $h$  were variables when hydrogel was under the pressure, resistivity ( $\rho$ ) was calculated based on the constant volume assumption ( $A_1h_1 = A_2h_2$ ). This equation is valid only if the friction between hydrogel surface and contacting clamps surface is assumed to be negligible and sample remains cylindrical all the time. The resistivity of hydrogel can be calculated as

$$\rho = RA/h \quad (2)$$

where  $R$  is the measured resistance,  $A$  is the calculated surface area based on the constant volume assumption, and  $h$  is the recorded height of sample.

The cyclic compression loading showed some irreversibility in the mechanical behavior of the DN-PEDOT gels. From Figure 11 it is seen that a stress relaxation occurs during the hold period at constant strain (Figure 11b). Also the peak compression stress decreased gradually in each subsequent cycle, which may suggest permanent change in the height of sample (permanent setting) probably because of permanent



**Figure 11.** Electrical behavior of a cylindrical-shaped DN-PEDOT(PSS)-II hydrogel (pH 6) under a (a) reciprocal displacement, (b) recorded force and (c) resistance, (d) calculated resistivity using eq 2.

damage that was introduced in each loading cycle and as previously described for DN gels.<sup>45</sup>

As expected, the electrical resistance decreased as the sample was more compressed (Figure 11c). In addition, an overall increasing trend in resistance was noted for each loading cycle. To understand the source of changes in resistance under the pressure, we plotted sample resistivity for each cycle in Figure 11d, using eq 2. Because the sample resistivity changes with compression in each cycle, the geometrical changes in sample length and area cannot fully account for the changes in sample resistivity. The pattern is similar in each cycle, which starts with a rise in resistivity at small compressive strains, followed by a decrease in resistivity when the sample was fully compressed. There was also an overall increase in resistivity with continued strain cycling, with the calculated resistivity doubling compared to the starting values after five cycles. To

ensure the overall water content of the hydrogel did not change during the test, we weighed the sample before and after the test, with no significant difference being observed. Considering the gradual decrease in the maximum stress over the time (Figure 11b) at each cycle, a possible explanation for the increase in resistivity could be that network damage caused in each cycle interrupts the electrical conductivity pathway as well. As a result of this permanent change in the network structure, the resistivity of material increases in each cycle. Because the conductivity of the hydrogels developed here is sensitive to pH and external strains, they are a candidate for wet environment sensor applications.

## CONCLUSION

Electronic conductivity within the DN hydrogels investigated here was significantly enhanced by sequential introduction of PEDOT. The properties of the gels formed here were dependent on pH in a manner expected for PAA containing materials. With the introduction of PEDOT the hydrogels remain pH sensitive, where a distinct swelling transition occurred between pH 4 and 5. This transition correlated with the transformation between highly conductive/less swollen hydrogels (pH < 4) to less conductive/more swollen hydrogels (pH > 4). Also, a dramatic decrease in tensile and compression strength occurred when pH exceeded the transition point (pH ~4.5). Electrical resistivity of PEDOT incorporated DN hydrogels was also studied under a reciprocal displacement and the permanent changes in resistivity was attributed to the permanent damage caused in the network structure.

## ASSOCIATED CONTENT

### Supporting Information

Additional figures and information (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [gspinks@uow.edu.au](mailto:gspinks@uow.edu.au).

### Notes

The authors declare no competing financial interest.

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