Controlled tuning of the properties in optoelectronic self-sorted gels


Published in:
Journal of the American Chemical Society (JACS)

Document Version:
Publisher's PDF, also known as Version of record

Queen's University Belfast - Research Portal:
Link to publication record in Queen's University Belfast Research Portal

Publisher rights
Copyright 2018 the authors.
This is an open access article published under a Creative Commons Attribution License (https://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution and reproduction in any medium, provided the author and source are cited.

General rights
Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.
Controlled Tuning of the Properties in Optoelectronic Self-Sorted Gels

Emily R. Cross,† Stephen Sproules,† Ralf Schweins,‡ Emily R. Draper,*,†‡ and Dave J. Adams*,†‡

†School of Chemistry, University of Glasgow, Glasgow G12 8QQ, U.K.
‡Large Scale Structures Group, Institut Laue-Langevin, 71 Avenue des Martyrs, CS 20156, F-38042 Grenoble Cedex 9, France

ABSTRACT: Multicomponent supramolecular gels have great potential for optoelectronics. Ideally, we could control the self-assembly of multiple components across many length scales, from the primary assembled structures to how these are arranged in space. This would allow energy transfer between p-type and n-type fibers to be controlled. Usually, a single network is formed and analyzed. It is not clear how most networks could be modified, and certainly not how these might be differentiated. Here, we address both of these issues. We show how the different components in a multicomponent gel can be differentiated by small-angle neutron scattering using contrast-matching experiments. The rate of self-assembly can be used to vary the networks that are formed, leading directly to changes in the efficiency of electron transfer. The assembly kinetics can therefore be used to prepare different networks from the same primary building blocks and primary self-assembled structures. We expect that these advances will allow multicomponent systems to become effective electronic materials.

Low-molecular-weight gelators (LMWGs) are molecules that can self-assemble into supramolecular fibers.1,2 Gels result from the entanglement and/or cross-linking of these fibers. Mixing LMWGs offers an opportunity to prepare useful networks and materials that cannot be achieved with a single component.2−6 If two different LMWGs are mixed, different outcomes are possible, all of which have potential opportunities.2,3,7−9 The LMWGs can mix such that any one supramolecular fiber contains both the gelators. Alternatively, self-assembled systems can be formed; here, each fiber contains only one of the LMWGs. Conceptually, it is possible to have cases where neither extreme occurs. Mixed LMWGs can be used therefore to prepare different network types, for example, where one LMWG forms the host fiber, while the second LMWG provides the active site.6

While this primary assembly level is used to define the system, useful properties often arise out of the next level of hierarchy, namely how these fibers interact.2 Bulk heterojunctions have been formed using self-sorted LMWGs.10−12 One LMWG forms n-type fibers and the other p-type fibers. Where these touch, a p−n heterojunction is formed.10 This method therefore allows the formation of useful electronic materials from cheap and easily synthesized molecules.11,13,14

We are investigating a system where an n-type perylene bisimide (PBI) LMWG (1, Figure 1) gels in the presence of a p-type stilbene-based LMWG (2, Figure 1).15 A self-sorted system can be formed using a slow pH change. Electron transfer was shown by transient absorption spectroscopy (TAS); incorporating the p-type LMWG resulted in a change in the wavelength response of the photoconductivity of the system.15 1 alone is only photoconductive when irradiated with a wavelength below 400 nm, whereas the inclusion of the stilbene-based LMWG results in activity above 400 nm.

The challenge here is that the properties of the final material are controlled by the interactions between the fibers. A real hurdle to exploiting mixed LMWG systems is that there is no way of controlling or predicting in advance these interactions. It is conceptually possible for the fibers to not interact at all (giving the supramolecular equivalent of an interpenetrating polymer network), or interaction strongly leading to fibers intimately wrapping around each other, or somewhere in between (Figure 1b).2 On top of the lack of predictability, many of these materials are kinetically trapped, and multiple states are possible from the same mixtures. It is also extremely difficult to tell what has been formed.16 For example, in many cases, the fibers are very similar and so imaging fibers and proving the network type is rarely achieved. This is a major

Received: May 22, 2018
Published: June 26, 2018
stumbling block for developing and using mixed LMWGs for useful materials. Here, we show the networks can be modified and the result on their photoresponsive behavior.

To prepare self-sorted systems from 1 and 2, a solution at pH 10.5 is first prepared (we use both H2O and D2O, but for convenience refer only to pH) which contains both LMWGs at a concentration of 5 mg/mL. This solution is then acidified by the addition of glucono-δ-lactone (GdL). GdL slowly hydrolyzes to gluconic acid, resulting in a slow, uniform, reproducible change in the pH. The self-assembly can be followed using different techniques with time, allowing us to show self-sorting by NMR (by sequential disappearance of the signals from each gelator), pH measurements (allowing us to link the different structures to the pKₐ of the LMWG), and rheology (showing evolution of the gel structure). We have previously used these approaches to show that 1 and 2 self-sort on gelation. It is unlikely that either 1 or 2 is unimolecularly dissolved at high pH before gelation, as this class of gelator tends to form micellar aggregates at high pH.

While self-sorting occurs, this shows only that the fibers contain each of the individual LMWG. It does not inform about the network; self-sorting of the primary fibers is entirely consistent with either of the cartoon networks in Figure 1b, for example. However, to understand the electronic properties, we need to be able to understand the networks since the p-n heterojunctions are formed where the fibers interact. It is extremely difficult to do this. The examples where self-sorting has been demonstrated (as opposed to implied) at the network level often rely on drying. This can lead to significant changes. Rare examples of imaging in the solvated state require selective staining of the LMWG.

An alternative approach is to use small-angle neutron scattering (SANS) combined with contrast matching. SANS has been used previously to probe the self-assembled networks formed by a number of LMWGs. SANS has the advantage over microscopy of being a bulk measurement and so does not just probe a small fraction of the sample. The scattering intensity in SANS is determined by the contrast difference between the LMWG and the solvent. This can be changed by varying the ratio of D2O to H2O. Each LMWG will have a different scattering length density (SLD) depending on its chemical composition, and hence the ratio of H2O to D2O at which the contrast of the LMWG and the solvent are matched will be different. It is therefore possible to choose one solvent ratio such that 1 effectively does not scatter but 2 does, and a different ratio where 1 scatters but 2 does not. These data can be compared to the sample in pure D2O where both scatter. Hence, it should be possible to probe the individual networks (cartoon in Figure 2).

Gels were prepared from either 1 or 2 in a range of ratios of D2O to H2O. As expected from the calculated SLD values for 1 and 2, 1 was essentially contrast matched in a mixture of 60% D2O in H2O (v/v) (Figures 2 and S2). Similarly, 2 was essentially contrast matched at 45% D2O in H2O (v/v). Hence, we collected data for the gel of 1 only, the gel of 2 only and the mixed gel of 1 and 2 in 45% D2O and 60% D2O.

In 45% D2O, the gel of 1 alone scatters well (Figures 2 and S4). The data can be fitted to a cylinder model coupled with a power law to take into account the scattering at low Q (Figure S4 and Table S1). The fits imply that the structures have a radius of 7.2 ± 0.1 nm, and a length that is outside the meaningful range of the fit (>1000 nm). Similarly, in 60% D2O, 2 alone scatters well and the data can be fitted to a flexible cylinder model (Figure S5 and Table S2). The fit implies that the structures have a radius of 3.2 ± 0.2 nm, a Kuhn length of 6.0 ± 0.3 nm, and a length that is again outside the meaningful range of the fit.

From our previous data, changing the pH leads to sequential assembly of 1 and 2 to form the self-sorted system. Conceptually, templating of structures could occur for either system, and fibers of either 1 or 2 might be affected by the presence of the other. For the mixed gel in 45% D2O, the scattering is very similar to that of the gel of 1 alone (Figure 2). The data can again be fitted to a cylinder model coupled with a power law, with the fit implying that the structures have a radius of 6.1 ± 0.1 nm, and a long length. These values are extremely close to the data for 1 alone (Table S1) implying that 1 forms the same structures when self-assembled in the mixed system as in the pure system.

In the mixed gel at 60% D2O, we expect only 2 to scatter. The scattering is however very different to that of 2 alone. The fit to the data using a flexible cylinder model shows that the structures have a radius of 6.1 ± 0.4 nm, a Kuhn length of 11.8 ± 0.4 nm, and a long length (Table S2). Hence, in the mixed system, the structures formed by 2 are heavily affected by having formed in the presence of 1. We believe this is first example that has determined differences in the fibrous structures formed in a self-sorted system at this length scale.

Generally, for self-sorted gels, a single set of conditions is used. It is important to be able to affect and control the properties of the system. Ideally, one would be able to change a specific system and observe the outcome. The assembly here is driven by the change in pH. The rate of hydrolysis of GdL is temperature dependent, allowing control over the assembly.

While gelation at 25 °C results in sequential assembly of the gelators as shown by the rates at which the peaks disappear from the NMR spectra for 1 and 2 (Figure 3a), at 30 °C the results are less clear (Figure 3b). The signals for 1 and 2 disappear simultaneously throughout the gelation process, although as a fraction 1 still assembles before 2. These data are consistent with either co-assembly, self-sorting (assuming the structures would rather self-sort even when they assemble at the same rate), or a mixture of co-assembly and self-sorting.
occurring. Using SANS, the structures formed at 30 °C are essentially identical to those formed at 25 °C (Figures S4 and S5, Tables S1 and S2), implying that self-sorting is still occurring. The gels formed from 1 or 2 alone are stiffer when prepared at 30 °C as compared to 25 °C, as is the mixed gel (Figures S9 and S10). Therefore, at the primary fiber level, the structures are similar at 25 and 30 °C, but there are differences in the networks.

When this system is used as a bulk heterojunction, the heterojunctions are where the fibers of 1 and 2 are sufficiently close in space to allow electron transfer. Hence, it is the network level assembly that is important. To probe differences, we used electron paramagnetic resonance (EPR). On irradiating 1 with UV light, the radical anion is formed, which is EPR active.30 Adding 2 means that the radical anion can be formed by irradiating at higher wavelengths15. As expected, no radical anion is formed when gels of 1 formed at either temperature are irradiated at 420 nm (Figure 4).15 In comparison, the radical anion was formed in the mixed gel of 1 and 2. Despite the primary structures being very similar (see above), there are differences in the amount of radical anion that is formed from the gels. Significantly more radical anion is formed from the gel prepared at 30 °C. This strongly implies that the networks are different, with more opportunity for electron transfer from 2 to 1 at 30 °C.

Hence, we have addressed two key issues which are currently hindering the use of multicomponent supramolecular gels. We show how the kinetics can be manipulated to optimize the specific properties of the system and, importantly, how such systems can be characterized. The underlying self-assembled structures are very similar; instead, it is the organization of these structures that is affected. We expect that these advances will allow multicomponent systems to become effective electronic materials.

Figure 3. Monitoring the gelation of (1+2) over time at (a) 25 °C and (b) 30 °C by changes in peak intensity from 1H NMR spectroscopy (full squares are the data for 1, hollow squares are for 2) compared to the change in pH (black). Alongside are photographs of the final gels.

Figure 4. Growth in EPR signal during irradiation with a 420 nm LED light source for (1+2) in full circles, and 1 only in hollow squares at 25 °C (orange) and 30 °C (green).

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b05359.

Full experimental details and further rheology, NMR, SANS, and EPR data, including Figures S1−S12 and Tables S1 and S2 (PDF)
The data which underpin this work are available at http://dx.doi.org/10.5525/gla.researchdata.631 and the SANS data at DOI: 10.5291/ILL-DATA.9-11-1823.

AUTHOR INFORMATION
Corresponding Authors
*dave.adams@glasgow.ac.uk
*emily.draper@glasgow.ac.uk

ORCID
Emily R. Cross: 0000-0002-6628-6166
Stephen Sproules: 0000-0003-3587-0375
Emily R. Draper: 0000-0002-3900-7934
Dave J. Adams: 0000-0002-3176-1350

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
E.R.C. thanks the University of Glasgow for a studentship. E.R.D. thanks the Leverhulme Trust for an Early Career Fellowship (ECF-2017-223) and the University of Glasgow for a LKAS Leadership Fellowship. D.J.A. thanks the EPSRC for a Fellowship (EP/L021978/1). We thank Dr. Steve King (Rutherford Appleton Laboratory) for helpful discussions around contrast matching. The experiment at the Institut Laue Langevin was allocated beam time under experiment number 9-11-1823 (DOI: 10.5291/ILL-DATA.9-11-1823) and collected on D11. This work benefitted from the SasView software, originally developed by the DANSE project under NSF award DMR-0520547.

REFERENCES
(29) https://www.ncnr.nist.gov/resources/activation/