Materials scientists develop road map for designing responsive gels with unusual properties

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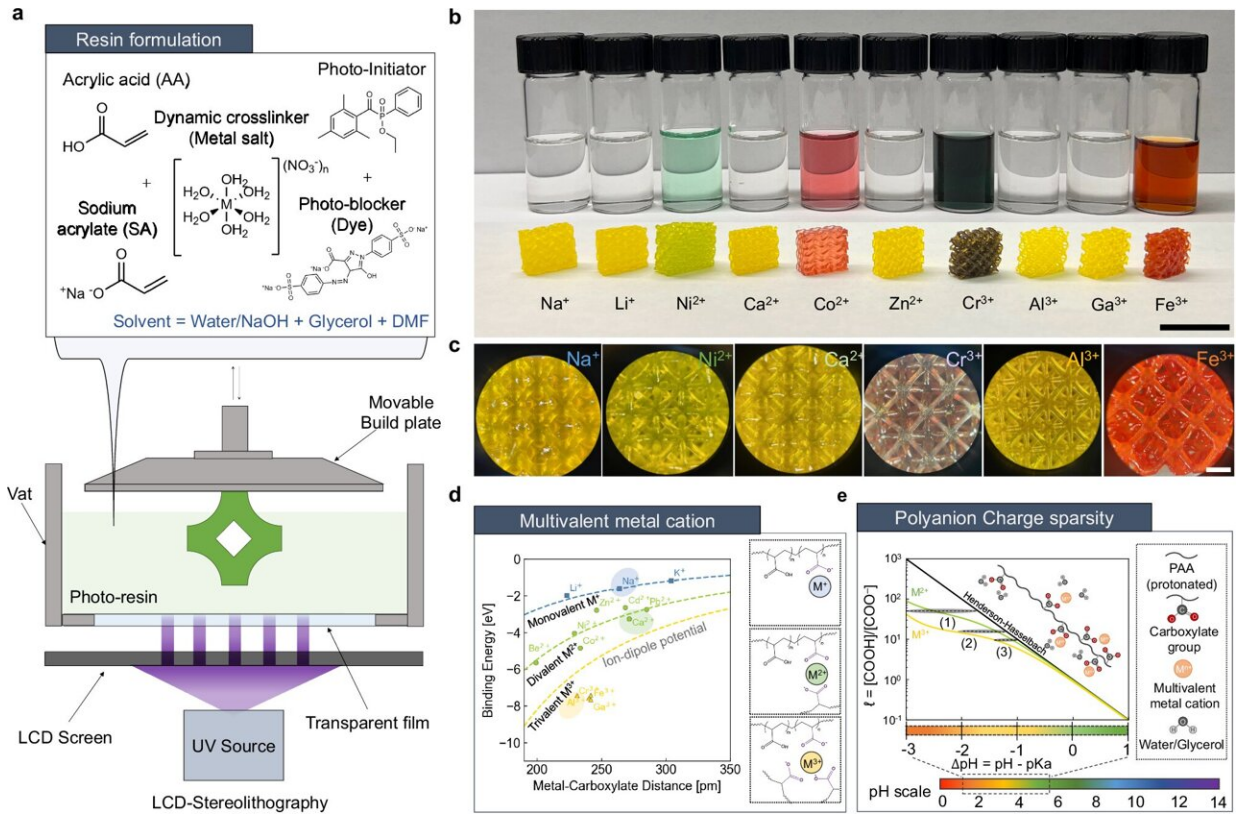

Fabrication of Metallo-polyelectrolytes with different metal ions. Credit: *Nature Communications* (2024). DOI: 10.1038/s41467-024-50860-6

Soft polymers with the combined properties of electrolytes and

traditional polymers offer some unique and desirable properties that can be drastically changed on demand.

These gels, called metallo-polyelectrolyte complexes (MPECs, pronounced "EM-pecks"), can be stimulated externally by magnetic, electrochemical, and optical stimuli, making them ideal for some energy devices, responsive actuators, and nanofiltration systems.

Metal ions within their cores provide the materials with these unique capabilities and form dynamic, "reversible" ionic bonds with polymer chains rather than much harder to break covalent bonds.

While scientists had previously identified and, in some cases, synthesized, MPECs that demonstrate unusual material properties, which vary, for example, with the pH of the solution before they form into gels, the exact source of those unusual mechanical properties had remained a mystery. In addition, earlier fabrication techniques often were not easily scaled and suffered from uneven composition.

Now, through a combination of extensive laboratory experiments, computational theoretical work, and additive manufacturing, a team of Caltech scientists has developed a complete framework for understanding a class of MPECs from the level of molecular bonds up to that of material properties.

As a result, the work, reported in the journal *Nature Communications*, provides a road map of sorts for designing and tailor-making gels with desired functionality and mechanical properties.

"Our lab typically works on interesting materials, which respond to external stimuli because of the way we build them into specific micro- or nano-architectures. What's so interesting and exciting about MPECs is that they can be actuated even without that kind of architecture," says

Julia R. Greer, the Ruben F. and Donna Mettler Professor of Materials Science, Mechanics and Medical Engineering; and the Fletcher Jones Foundation Director of the Kavli Nanoscience Institute at Caltech.

She explains that these materials can exhibit vastly different properties and responses. For example, by choice of metal ion and pH, a sample can be made that bends to the left or to the right depending on how fast a force is applied to it. In another case, a sample can fully dissolve in water or remain solid for several days, with the only difference being the metal's ionic charge.

"This opens the door for 'training' an entire suite of new materials—both computationally and experimentally—that can enable previously challenging technologies, from self-monitoring autonomous filters to advanced ion-exchange membranes and catalysts, and even artificial muscles," Greer says.

"We were really focused on making a bridge between the molecular level interactions to the mechanical properties on a global scale, providing insight into phenomena that we can't necessarily see," says Seola Lee, co-lead author of a new paper about the work and a Ph.D. student in mechanical engineering in the Greer lab who is currently a research scientist intern at Meta.

"We hope that the guidelines we've demonstrated will help people tap into the design territory in terms of what they will be able to make with these materials."

Central to the changeability of MPECs are the metal ions at their cores and the connections they make to charged polymer chains. Many transition metals are multivalent, meaning they can have more than one possible charge. Valency is determined by an atom's outer shell of electrons. Iron, for example, can be present as Fe^{2+}, a form in which it

would likely attach to two polymer chains, or Fe^{3+}, which would be more likely to bind with three chains.

The Caltech team determined that the metal ions' valency is one of several levers that can be adjusted to tune the properties of MPECs, with the others being the pH of the solution and the solvent used.

For their investigation, the group used a process called stereolithography, a type of 3D printing where a light-induced polymerization creates a solid structure layer by layer. Carrying out this printing process with a resin that includes various metal ions, it is possible to print out a stable polymer called polyacrylic acid (PAA) with these metal ions bound to it.

Next, they conducted exhaustive thermal and mechanical experiments on those materials to probe the material responses at different length scales. Pierre Walker, co-lead author of the paper and a graduate student in chemical engineering in the lab of Zhen-Gang Wang, the Dick and Barbara Dickinson Professor of Chemical Engineering, analyzed the data and calculated how to model the details from the molecular level up to the full material scale.

"A lot of this investigation was kind of like walking around in the dark, where there were many different levers that at the time we had no idea were present," Walker says. "Other papers have looked at one or two effects at most in their study.

"The fact that we were able to couple all three, and the fact that we are able to not only understand how each of them interacts with each other, but how they then impact the global property really makes it much easier for future users of MPEC gels to navigate the space."

In the new paper, the authors describe a few examples of MPECs they were able to design using their new framework. One, a shape-memory

polymer, looks like a yellow gummy flower that has bloomed and is lying flat. After heating the flower to 90°C, Lee manually lifted the petals, closing the flower into a bud shape. She then cooled the whole thing to –5°C. When she brought the temperature back to 90°C, the flower bloomed and returned to its original shape.

Here, the valency of the metal dictated how well the material "remembered" its original shape. The gel made with aluminum (Al^{3+}) returned to the open flower position much more quickly and completely than either calcium (Ca^{2+}) or sodium (Na^{+}).

In a second example, the scientists made a gel strip where one side was fabricated with a high pH and the other with a lower pH. Based on the theoretical modeling, the scientists knew how the two sides should behave when submerged in different solutions. And just as expected, when the bilayer was submerged in water, it buckled to the left; when in an aluminum solution, it buckled to the right.

"We now have a really robust explanation for if you change some of these small molecular levers, here's what comes out at the global scale," says Seneca Velling, a former graduate student in the Greer group who is now completing his studies in the Origins and Habitability Lab at JPL, which Caltech manages for NASA.

"Therefore, if you want a global scale property, you can back it out by thinking about what starting conditions make that global property a reality, which is a really cool way to design a material. You can now explain it top-down or bottom-up."

More information: Seola Lee et al, Molecular control via dynamic bonding enables material responsiveness in additively manufactured metallo-polyelectrolytes, *Nature Communications* (2024). DOI: 10.1038/s41467-024-50860-6

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