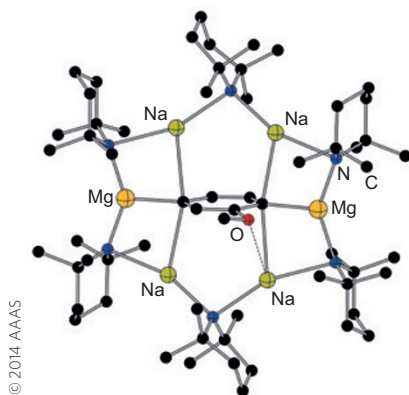


DIRECTED METALATION

Not just for *ortho*

Science **346**, 834–837 (2014)



Directed *ortho*-metalation is a powerful and widely employed method for functionalizing aromatic molecules in which an organometallic base is used to deprotonate one position on the ring. It works through the presence of a directing group on the substrate — typically a Lewis base such as a methoxy or dimethylamino group — that enables the deprotonation of an adjacent C–H bond either through coordination to the incoming

metal or by weakening the C–H bond through induction. This opens the door to site-specific addition of electrophiles. On the downside, this regioselectivity is heavily skewed towards the *ortho* positions, and while some reports have shown the possibility of activating non-*ortho* sites, these were based on clever design of the substrate rather than fundamentally changing the metalating reagent.

Charles O'Hara, Robert Mulvey and colleagues, from the University of Strathclyde, have shown that they can override this innate selectivity by using organosodium–magnesium complexes, giving access to different functionalization patterns on the aromatic substrate. The tetrasodium–dimagnesium complex acts as a template and its structure helps to guide subsequent chemistry, leading to metalation at two possible sites on the molecule, with the exact regiochemistry determined by the nature of the directing group. Ethers, amides and carbamates are metalated at both the regular *ortho* site and the *meta'*-position as shown by X-ray crystallography, and the subsequent addition of electrophiles gave the 2,5-disubstituted products.

Amino-directing groups, however, gave a different substitution configuration

— a *meta,meta'* (that is, 3,5) pattern was observed, showing a fundamental break from *ortho*-metalation protocols. X-ray crystallography gives some insight into the reasons for this, showing that the nitrogen atom within the dimethylamino group is sp^2 -hybridized and in the plane of the aromatic ring. Thus the lack of any *ortho*-metalation could be due to steric blocking by the methyl substituents. Overall, this new-found control in regioselectivity is likely to find many applications in synthesis. And although the metalating agent is not yet as easily available as butyllithium and the like, it can be made in a one-step process and stored in solution for extended periods of time. *EB*

LI-S BATTERIES

Activating additives

J. Phys. Chem. Lett. **5**, 3986–3991 (2014)

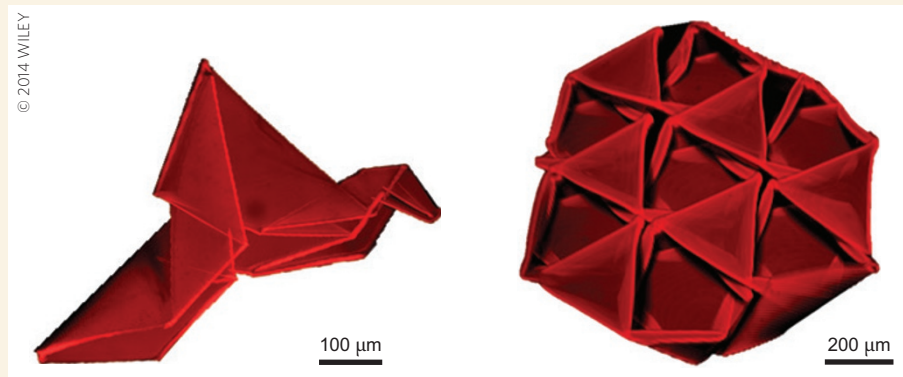
Li-ion batteries have served us well since their commercial introduction in the 1990s. Their versatility allows them to be used not only in portable devices, but also in electric vehicles and in electrical grid applications. However, the demand for more powerful electronics, longer battery-life and cheaper, more-sustainable batteries has

RESPONSIVE MATERIALS

At the crease

Structures made from materials that can alter their shape in response to changes in their local environment could find use in soft robotics, amongst other applications. Flat, easily fabricated films that can fold up to form 3D structures may be particularly useful from a synthetic standpoint, and such materials can take inspiration from the elegant simplicity of traditional origami.

Now, a team from the University of Massachusetts Amherst and Western New England University led by Ryan Hayward has developed a material that can be pre-programmed to fold and unfold itself into complex origami shapes on cooling and heating. The material consists of a crosslinked poly(*N*-isopropylacrylamide) (PNIPAM)-based hydrogel copolymer that can swell and contract in response to external stimuli. The hydrogel is sandwiched between, and covalently bonded to, two thin layers of rigid poly(*para*-methylstyrene) (PpMS). When the material is immersed in a buffer solution, the hydrogel swells but is constrained by the top and bottom layers. Creating gaps in



the two PpMS layers using photolithography results in folding of the material at those lines — and whether the gap is in the top or bottom film determines the direction of the fold. The radius of curvature of the fold is determined by the width of the gap, with folding angles between 0 and 180° possible.

Several traditional origami designs were patterned onto the trilayer material and shown to fold into recognizable origami objects, such as a bird, with sizes of

around 1 mm. As the PNIPAM becomes hydrophobic above a certain temperature, the hydrogel contracts on heating — this phenomenon means that the origami can be reversibly unfolded and refolded. One limitation of the material is that all folds occur at once, rather than being able to fold along the patterned lines in a specific order. Nonetheless, this approach could be used to form structures or small-scale soft robots with function as well as beauty. *CH*

Adv. Mater. <http://doi.org/f2v2b4> (2014)