Last year, the Chemical Abstracts Service reached a remarkable milestone, as it added the 100 millionth compound to its vast registry. And the pace of synthesis is accelerating: Three-quarters of those were logged in the past decade alone.

Although each compound is unique, a few stand above the rest. These are the record breakers—laying claim to chemical superlatives such as most explosive, most polar, or most twisted—that stake out new frontiers at the edges of chemical space.

What drives researchers to set these records, and what impact does it have on their field? For some, it simply starts as a chemical challenge to make something more extreme than ever before. But working at the boundaries of chemistry can also spark deeper debates about fundamental ideas, such as the nature of bonding. And even when these record breakers have no immediate use, they open up new areas of investigation, tempting others to seek applications in previously unexplored regions of the molecular universe.

Here, ACS Central Science looks at some recent record breakers and finds out how they are reshaping their corners of chemistry.

Handle With Care

“It’s a rule in our lab not to make more than 5 g in one batch,” says Jörg Stierstorfer of the Ludwig Maximilians University of Munich—a very sensible precaution, given that he spends his time as an assistant professor in Thomas Kläppel’s group making some of the world’s most explosive chemicals.

In 2011, Stierstorfer helped to create 1-diazidocarbamoyl-5-azidotetrazole (C$_2$N$_{14}$), which has been widely described as the most explosive compound ever made. In this case, the superlative actually refers to the sensitivity of the compound—just the lightest touch makes it go boom.

That means it’s difficult to say whether this is indeed the most sensitive explosive, Stierstorfer says, because his team cannot get near enough to measure the force needed to detonate it. Suffice to say, it’s fearsome stuff.

Yet Stierstorfer argues that their group has fewer injuries than a typical organic synthesis lab, thanks to the extensive precautions they take. They always wear face shields, Kevlar gloves, and other protective gear. And just in case things go wrong, right-handers carry explosive samples in their left hand, and vice versa. “We usually try to avoid making the most sensitive compounds,” Stierstorfer adds, largely because they are too ticklish for practical use.

Instead, one of their main goals is to make more powerful explosives—those that release the most energy per gram, or that generate the fastest shockwaves. For example, 1,5-di(nitramino)tetrazole contains the right proportion of oxygen atoms to boost explosive performance. The team hopes that compounds like this will help to create smaller, lighter weapons that can be carried by drones and are therefore more precisely targeted than traditional munitions, ensuring fewer unintended casualties.

Stierstorfer acknowledges that his area of research is controversial. Few chemists work in this area, but Stierstorfer says that’s not necessarily a bad thing: “We don’t have too much competition.”

Poles Apart

In February, Klaus Müllen unveiled 5,6-diaminobenzene-1,2,3,4-tetraCarbonitrile, which boasts the highest known
Itami’s work on twisted molecules began with an unexpected discovery. In 2013, his team inadvertently created warped fragments of graphene, which contain five C\(_5\) rings and a C\(_3\) ring embedded in graphene’s repeating hexagonal array. This gives the fragments a pronounced saddle shape, reducing pi-stacking interactions between the molecules and making them highly soluble in common organic solvents, unlike graphene itself.

While making analogues of this warped graphene, Itami’s team recently created a particularly twisted quadruple helicene, built with four helical lobes. Contorted by steric hindrance, the substituted naphthalene at its heart has an end-to-end twist of almost 70°, claiming the highest recorded twisting per benzene. “This twisting can be a new design principle for tuning optoelectronic properties,” Itami says, because it shifts the energy of the molecule’s molecular orbitals.

Researchers have synthesized a pentacene with a 144° twist (left) and a fully pi-conjugated porphyrin tetramer with a 300° twist (right). Credit: American Chemical Society.

Typically, researchers would change substituents or add heteroatoms to do this tuning. But Colin Nuckolls of Columbia University has been using twist to fine-tune aromatic molecules that act as electron acceptors in organic solar cells. Last year, he showed that a twisted aromatic made up of four perylene diimide units (hPDI4) gave cells an efficiency of 8.3%—pretty good for an organic solar cell, though still less than half the efficiency of a commercial silicon cell. And he has recently surpassed that with similar contorted molecules that are almost good enough to be commercializable, he says. The twist does not get in the way of electron transport needed for good solar cell performance, but since it prevents pi-stacking, the molecules can be processed in solution and readily mixed with polymers—handy traits for practical use.

For those who simply seek peak twist, though, bigger is usually better. “If you make the system longer and longer, and keep the same twisting unit, you get more and more twist overall,” Itami explains. In 2004, Robert Pascal, now at Tulane University, made a pentacene with a 144° end-to-end twist without destroying its aromaticity, still the largest twist for a polyaromatic hydrocarbon. And last year, Itami’s Nagoya colleague Hiroshi Shinokubo made a fully pi-conjugated porphyrin tetramer with an astonishing twist...
There’s lots of interest now in these nonplanar systems,” Itami says.

**Good Neighbors**

What is the largest number of atoms that can coordinate to a central metal cation? For Klaus-Richard Pörschke at the Max Planck Institute for Kohlenforschung, the answer is 16—and he has just created a compound that reaches that lofty goal.

Pörschke’s complex emerged from studies of a weakly coordinating anion, bis(perfluoro-triphenylborane)amide, which bears a single negative charge. Combined with cesium, it forms crystals of Cs[H2NB2(C6F5)6] in which the cesium ion is coordinated to 16 fluorine atoms. At first, they were puzzled by the X-ray crystal structure, Pörschke says. His team had to feed the data into a 3-D printer to create a model of the structure, just so they could wrap their heads around it.

Last year, another team of researchers made a 16-coordinate complex, CoB16−, which they described as having “the highest coordination for a metal atom known in chemistry.” Pörschke points out that its drumlike structure was produced in the gas phase by laser vaporization and was inferred from a mixture of photoelectron spectroscopy and quantum-chemical calculations. In contrast, Cs[H2NB2(C6F5)6] “is easily prepared in any amount and the structure is proven by X-ray diffraction”, he says.

Pörschke suggests that his anion’s coordinating abilities could make it useful in separating radioactive cesium from solutions. But the compound also raises interesting questions about the concept of coordination number, says Santiago Alvarez of the University of Barcelona. The term was originally coined by Swiss chemist Alfred Werner in the late 19th century to describe complexes between transition metals and ligands, such as [Co(NH3)6]3+, which are bound together by two-electron bonds.

But at higher coordination numbers, neighboring atoms spread further away from the central cation, and the coordinating bonds become weaker. “Then we get to the stage where it’s not really clear if it’s a bond or not,” Pörschke says. “Coordination number becomes a bit of a gut feeling.”

So, for some chemists, coordination number simply denotes the number of neighbors close enough to have some interaction with the central ion. By this definition, Alvarez points to a clathrate compound, Cs8Na16Si136, in which the metal ions are trapped in silicon cages. Here, cesium has a coordination number of 28, he says.

But Pörschke is adamant that without distinct two-electron bonds between cesium and silicon, that doesn’t count as a coordination record: “Coordination number 16 is likely to remain unparalleled for a long time,” he says.

**Atomic String**

In April, Thomas Pichler of the University of Vienna announced that he had created the longest atomic chain made of nothing but carbon atoms. With more than 6000 atoms, some say that the polyacetylene chain deserves to be classed as carbyne, a one-dimensional—and effectively infinite—string of pure carbon with alternating single and triple bonds. Carbyne has attracted considerable controversy since it was first predicted in 1885. In theory, these atomic strings would be immensely strong—and also highly reactive, which is why previous claims have been hotly disputed.

So Pichler took a different approach. He created the chains within a protective carbon nanotube sheath, growing them up to 800 nm long—more than enough to qualify as carbyne, he says. “The properties don’t change any more beyond 1000 atoms, so after that you can treat it as an infinite chain.”
Pichler’s team hopes to stabilize the chains so that they can be removed from the nanotubes. But even trapped inside, they offer interesting and potentially useful properties. For example, they give a huge Raman resonance enhancement to the nanotube, which could make it useful as a tracer in biological systems, he says.

Record-breaking wasn’t their goal. Instead, Pichler was trying to validate a model describing the relationship between the length of carbon chains inside nanotubes and their Raman frequency. “We were very surprised when we got these incredibly long chains—which perfectly agreed with our model, by the way,” he says.

And it certainly shows that in chemistry, records are sometime a matter of sweet serendipity, Pichler says. “All the most interesting results I’ve had in the past 25 years have been like that—not planned.”

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