05.12.2016 - Tokyo Tech researchers show dendrimers that mimic the electron valency of atoms can also mimic polymerisation yielding controlled one and two-dimensional arrays of nanocontainers.

In nanotechnology control is key. Control over the arrangements and distances between nanoparticles can allow tailored interaction strengths so that properties can be harnessed in devices such as plasmonic sensors. Now researchers at Tokyo Institute of Technology use dendrimers that mimic the electron valency of atoms and link them into arrays using molecules that coordinate with the dendrimer as they would form a covalent electron pair in their valence shell – “electron pair mimicry”.

Kimihisa Yamamoto, Ken Albrecht, and colleagues at Tokyo Tech considered the dendritic polyphenylazomethine (DPA), which has a structure that branches out from a central core. “Lewis acid” molecules coordinate to the “Lewis base” sites of DPA. Analysis of the ratio of SnCl2 Lewis acid molecules coordinating with each dendrimer revealed step increases from 2 to 4 to 8 to 16, which mimics the valency of the Bohr atom that has 2, 8, 18, and 32 electrons in the 1st, 2nd, 3rd, and 4th orbitals. This reflects the increase in the number of molecules that can coordinate with the dendrimer with increasing distance from the core, as the number of dendrimer branches and electron density increases.

Yamamoto’s team analysed the coordination of DPA with a stronger binding Lewis acid – triphenylmethylium (TPM) – bound to the rod-like molecule phenylene ethynylene. The phylene ethynylene backbone is rigid enough that the acid cations at either end cannot then bind to the same dendrimer. Instead a polymer chain of dendrimers forms. Using a different starting dendrimer (ZnPG4 instead of DPAG4) - which has a core valency of four instead of two - led to the formation of two dimensional polymerisation of the dendrimers, producing a 2D array of nanocontainers for that can accumulate other Lewis acids into the outer orbitals.

The work describes “a new aspect of atom mimicry” conclude the researchers. “The geometry and pitch can be controlled by the design of the dendrimer and the linker and are potentially applicable to plasmonics (after seed-mediated growth) and nanoelectrode grids (which are also useful as electrocatalysts).”

Original publication:

Albrecht, Ken and Hirabayashi, Yuki and Otake, Masaya and Mendori, Shin and Tobari, Yuta and Azuma, Yasuo and Majima, Yutaka and Yamamoto, Kimihisa; “Polymerization of a divalent/tetravalent metal-storing atom-mimicking dendrimer”; Science Advances; 2016