

diiodoperfluoroalkanes (DIPFAs). These compounds are produced on an industrial scale as monomers for a wide range of fluoropolymer products.

DIPFAs are typically made by telomerization, a process of building up perfluoro-carbon chains from tetrafluoroethylene, Metrangolo explained. The resulting mixture of C₂ to C₁₂ species must be separated and purified by fractional distillation, he noted, which is an energy-intensive process and is limited to the volatile C₈ and shorter compounds. To find an improved method to separate the entire mixture, the Italian team used bis(trimethylammonium) alkane diiodides of different chain lengths as host molecules with which to cocrystallize DIPFAs of matching chain lengths.

This “size-matching” allows a DIPFA to just fit into a void space in the ammonium compound’s nonporous crystal lattice, where I...I halogen bonds hold the molecule in place, Metrangolo said. DIPFAs too small for the space fall out, and those too large simply can’t enter. Heating the cocrystals liberates the purified DIPFA. Metrangolo said that an array of cocrystals with size-matched void spaces could be used like a filter to separate the mixtures.

ANOTHER FRUITFUL area for halogen bonding is the development of solid-state materials for electronics applications. Hiroshi M. Yamamoto of RIKEN’s Condensed Molecular Materials Laboratory, in Saitama, Japan, provided an overview of the use of halogen bonding to control the properties of organic semiconductors, metals, and superconductors. One project he is particularly excited about is constructing supramolecular insulating sheaths to separate conducting organic nanowires from each other.

Yamamoto and colleagues used stacks of planar ethylenedithiotetrathiafulvalene radical cations as the nanowire. The researchers then surrounded the wire with bromine and iodine counterions and tetraiodoethylene. The counterions serve as a halogen bond clamp to hold the insulating tetraiodoethylene molecules against the conducting core via Br...I and I...I bonds. The insulating ability of the supramolecular sheath is similar to that of epoxy resins commonly used in circuit boards, he added.

Yamamoto believes that controlling conducting properties by constructing an insulating network is a key development. “Scientists tend to pay the most attention to the conducting molecules in their development of conducting materials,” he said. “But I find

that the insulating moiety can play just as big a role when you consider an application.”

Halogen bonding also holds vast potential for novel biomedical applications. Patrick Y. S. Lam of Bristol-Myers Squibb (BMS) related efforts to use halogen-bonding interactions in rational drug design. Medicinal chemists, he said, typically utilize the three classical interactions—hydrogen bonding,

Coulombic interactions between charged groups, and hydrophobic interactions. But when BMS scientists were optimizing a potential anticoagulant drug a decade ago, halogen bonding was just gaining recognition. The team decided to give it a try as a parallel approach in the discovery pathway that led to the oral anticoagulant apixaban, which is now in Phase III clinical trials.