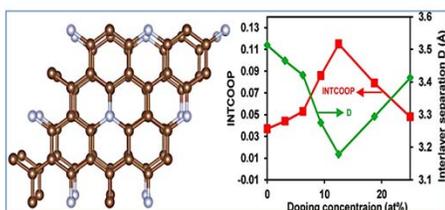


## New chemistry for graphene



Bi-layer graphene with 12.5% carbon atoms substituted with nitrogen (**left**) in an AA stacked configuration. **Right**, crystal orbital overlap population (COOP) analysis as a function of nitrogen doping. A positive value of INTCOOP is indicative of the overall bonding orbital overlap of two chemical fragments.

Work was performed as User Project at the Center for Nanophase Materials Sciences.

### Scientific Achievement

Theoretical simulations identify a tunable and new type of chemical bonding in graphene-based materials.

### Significance and Impact

A tunable covalent-like bonding enables a new way to assemble 2D graphenes into functional layered materials with distinctive properties.

### Research Details

- Theoretical discovery of a new type of graphene chemistry, interlayer covalent-like bonding.
- Demonstrated tunability of covalent-like chemical bonding between graphene layers as a function of nitrogen doping.
- A detailed electronic structure and crystal orbital overlap population analysis provide solid evidence for this new tunable chemical bonding.

Y. Tian, et. al. *Nano Letters*. (2015), DOI: 10.1021/acs.nanolett.5b01940



**Narrative Highlight Text:** A new aspect of graphene chemistry in terms of a special chemical bonding between the giant graphene “molecules” is demonstrated through rigorous theoretical calculations. Nitrogen-doped graphenes (NGPs) with various doping levels (replacing C atoms with N atoms) can form an unusual two-dimensional (2D) pi-pi bonding in bi-layer NGPs leading to interlayer binding energies that are enhanced by up to 50% compared to the pristine graphene bilayers. Such an unusual chemical bonding arises from the pi-pi overlap across the van der Waals gap while the individual layers maintain their in-plane pi-conjugation and are accordingly planar. Due to the interlayer pi-pi bonding, an electrical conduction pathway is formed in the solid state along the stacking direction. Overall this new finding may open a way to assemble 2D NGPs into novel layered materials with distinctive properties associated with the novel covalent-like pi-pi bonding, e.g., electronic and magnetic properties in solid-state materials such as magneto-optoelectronic bistability and thermochromism.

### Reference

“Nitrogen-Doping Enables Covalent-Like  $\pi$ - $\pi$  Bonding between Graphenes”

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