How does one place atoms where one wants? For chemists and materials scientists, this continues to be an outstanding question that drives new synthetic efforts. With the development of 2D materials, new strategies are emerging for building 3D materials one atomic layer at a time. These layers are usually separated by 3 to 4 Ångstroms, a distance at which van der Waals forces attract adjacent layers. Although tuning this distance—from covalent or ionic bonding at 2 Å to weakly interacting at >4 Å—would yield 3D materials with new properties, few methods provide this control. In this talk, I will describe two strategies to address this challenge. The first strategy—an approach to reduce interlayer distance—utilizes “2D electrenes,” a new 2D material with an electrical conductivity that rivals silver (JACS 138, 16089 (2016)). 2D electrenes have radically different electronic structures: they have planes of electrons that are physically separated from planes of cations. Using DFT calculations and preliminary experiments, we show that electrenes act as electron donors to 2D metals, semiconductors, and insulators. These materials are 2D analogs of donor-acceptor systems and have interlayer distances that approach those of covalent or ionic materials. I will describe these structures and their fascinating properties—from ferrimagnetism to superlubricity. The second strategy—an approach to increase interlayer distance—also results in semiconducting materials with unique optoelectronic properties. When held at a slightly increased distance, electrons may still tunnel between 2D flakes but electronic coupling diminishes. Such materials may be considered as the 2D analogue of “confined-yet-coupled” quantum dot materials. These two strategies, and the materials they enable, highlight the virtues of building 3D materials one atomic layer at a time.