The identification of supramolecular synthons in the solid-state is a key activity of crystal engineering. It is only through acquiring such knowledge that the ultimate goal of crystal engineering can be achieved, namely the rationale design of crystal structure. Accordingly, significant effort has been devoted over the years to evaluate, in a systematic fashion, the large number of crystal structures available in the Cambridge Structural Database in order to identify repeat patterns in supramolecular association. The most popular form of supramolecular association is provided by conventional hydrogen-bonds, which occur between electronegative elements, e.g. O–H…O. These, along with halogen-bonding, are preeminent in crystal engineering and afford readily recognisable points of contact between molecules in crystals, often leading to predictable supramolecular aggregates. A case in point is the design of co-crystals, a major step forward towards the realisation of deliberately constructing crystal structures.

Complementing hydrogen- and halogen-bonding are a diverse array of other, usually expected to be weak, modes of supramolecular association. Prominent examples of these include π…π (face-to-face) stacking, their off-set (edge-to-edge) counterparts, C–H…π interactions, C–H…O, C–H…X, etc. These interactions can function in co-operation with hydrogen- and halogen-bonding but, become more important when hydrogen- and/or halogen-bonding alone does not lead to a three-dimensional architecture. For example, well-defined halogen-bonding may link molecules into a supramolecular chain but, how are the chains connected? The evaluation of supramolecular association in instances where hydrogen- and halogen-bonding arranges molecules into one- or two-dimensional aggregates, or even when hydrogen- and halogen-bonding does not exist, reveals much about so-called second tier interactions. The purpose of this presentation is to provide an overview of some less appreciated, i.e. emerging, intermolecular interactions, found in crystals. A particular focus will be upon interactions involving π-systems. Just as π…π interactions can occur between arene rings, similar interactions can involve chelate rings in organometallic compounds, i.e. π(chelate ring)...π(arene) and π(chelate ring)...π(chelate ring). Chelate rings, both as donors and acceptors can form C–H…π contacts, i.e. C–H…π(chelate ring). Utilising the polar gap at the tip of a lone-pair of electrons, lone-pairs can also form interactions with arene rings, i.e. M(lone-pair)...π(arene) interactions, in both light- and heavy-element crystals. The aforementioned often lead to well-defined points of contact between molecules leading to specific supramolecular aggregation patterns, usually, but not always, zero- and one-dimensional. Crucially, structural observations made in this presentation will augmented by theoretical considerations as to the nature of the interaction and the energy of stabilisation it imparts.
Keywords: crystal engineering, supramolecular synthons, pi-interactions