

In this issue

Chemistry: Structure, synthesis and dynamics

In this issue, *Current Science* brings out a special section on 'Chemistry: Structure, synthesis and dynamics' to celebrate the International Year of Chemistry 2011. It gives a glimpse of the current areas of research in chemistry and covers topics ranging from crystallization to the development of reusable bactericidal agents.

Bhattacharyya and co-workers (page 861) have studied how the replacement of water by D₂O affects the solvation dynamics in a protein (lysozyme) and protein–surfactant (lysozyme–CTAB) aggregate. The average solvation time in the lysozyme and lysozyme–CTAB aggregate becomes about two times slower in D₂O. The deuterium isotope effect confirms that the water molecules are the main source of solvation dynamics and the role of polar residues of protein is minor.

Dastidar and co-workers (page 869) exploited the *in situ* crystallization of coordination polymers to separate an important anion sulphate (SO₄²⁻) from a complex mixture of oxoanions (SO₄²⁻, NO₃⁻, ClO₄⁻ and CF₃SO₃⁻). Selective separation of an anion from a complex mixture of anions via *in situ* crystallization of coordination compounds is one of the current research interests and is highly relevant to environmental issues. In this technique, an organic ligand and metal salts having various counter anions are allowed to crystallize together. Ligands having multiple hydrogen-bonding functionalities such as amide, urea, etc. may attract anions via hydrogen bonding. Separation of sulphate from an aqueous solution containing a complex mixture of anions including other oxoanions such as nitrate (NO₃⁻), is an important issue in cleaning up radioactive waste tanks. Since urea functionality can form a stable hydrogen-bonded structure with the anion resulting in the so-called urea–sulphate

supramolecular synthon, ligands having urea moiety have been exploited to recognize/bind/separate sulphate anion using *in situ* crystallization of coordination compounds.

Angiotensin converting enzyme (ACE) inhibitors are an important class of antihypertensive drugs. ACE is a Zn(II)-dependent metalloenzyme which catalyses the conversion of angiotensin I (Ang I) to angiotensin II (Ang II), and the vasodilator hormone, bradykinin to its inactive form (bradykinin (1–7)). The formation of Ang II and depletion of bradykinin result in the elevation of blood pressure. Furthermore, Ang II-mediated hypertension is also known to be closely associated with oxidative stress. Therefore, inhibition of ACE is important in the treatment of hypertension. Muges and Bhuyan (page 881) present a review of the literature on ACE inhibitors in the treatment of hypertension. This article includes the structure of ACE, association between ACE and hypertension, different inhibitors for ACE and their role in the treatment of hypertension, mode of binding of these inhibitors at the active site of ACE, and interdependence of hypertension and oxidative stress. These inhibitors coordinate to the Zn(II) ion in the active site and interact with different binding pockets in the active site. Therefore, the stereochemistry and the functional group of the inhibitors play a crucial role in the inhibition of ACE. Recent development regarding the association of hypertension and oxidative stress leads to the conclusion that ACE inhibitors having antioxidant activity may be suitable candidates for hypertension.

3,4-Disubstituted maleimide framework constitutes an important structural organization in heterocyclic chemistry as this skeleton is present in a number of natural products and bioactive molecules. The Baylis–Hillman (B–H) reaction provides diverse classes of densely functionalized molecules in an operationally

simple one-pot atom-economical process via the coupling of activated alkenes with electrophiles under the influence of an appropriate catalyst or a catalytic system. These densely functionalized molecules are usually referred to as the B–H adducts and have been systematically and extensively used as valuable substrates in various organic transformations and synthons for obtaining a number of heterocyclic and carbocyclic compounds. Basavaiah *et al.* (page 888) describe an important application of 3-ethoxycarbonyl-3-hydroxy-3-aryl(alkyl)-2-methylenepropanenitriles, the B–H adducts, derived from α -keto esters and acrylonitrile, for synthesis of 3,4-disubstituted maleimide derivatives. We have developed a simple and facile synthesis of 3-(alkylcarbonyloxy)methyl-4-aryl(alkyl)-1H-pyrrole-2,5-diones via the treatment of 3-ethoxycarbonyl-3-hydroxy-3-aryl(alkyl)-2-methylenepropanenitriles with carboxylic acids (propanoic and acetic acids) in the presence of FeCl₃. A plausible mechanism for the formation of 3,4-disubstituted maleimide derivatives is also provided. We have also demonstrated applications of these maleimide derivatives (with two examples) as substrates for the Friedel–Crafts reaction with benzene in the presence of methanesulphonic acid to provide 3-benzyl-4-aryl-1H-pyrrole-2,5-dione derivatives in high yields.

Pachfule and Banerjee (page 894) have represented synthesis and gas adsorption study of a 2D metal–organic framework (MOF) with square-shaped 1D channels. The resulting MOF shows 0.69 wt% H₂ (at 77 K, 1 atm) and 1.65 mmol/g CO₂ (at 298 K, 1 atm) uptake. Thermal gravimetric analysis performed on as-synthesized Cu-TBA-3 revealed that this compound also has high thermal stability. Although hydrogen uptake shown by Cu-TBA-3 is moderate, it is comparable with hydrogen adsorption of highest capacity zeolites, carbon-containing materials like carbon

nanotubes, activated carbon, etc. The authors believe MOFs synthesized using a mixed ligand system will be of great interest to chemists involved in the design and synthesis of new materials for hydrogen storage and carbon capture. They believe that these findings will not only be useful at the basic level in the crystal engineering of coordination networks, but also enrich the database of MOFs having non-carboxylate organic building units.

Anomalous properties of water have drawn the attention of physicists, chemists and biologists for a long time. Notable anomalies include low temperature, divergent-like growth of specific heat and isothermal compressibility of bulk water, dynamics of water around proteins and DNA, and also within reverse micelles. There is, however, a unity among diversity in these problems which Bagchi and co-workers (page 900) discuss in detail. In short, the hydrogen bond network and its disruption near the DNA and reverse micelles are shown to be responsible for much of the observed behaviour.

2-Aminotetralin-2-carboxylic acid (Atc) is a constrained analogue of phenylalanine (Phe), where the amino acid side chain has been fixed by the bridging methylene units. Incorporation of these unusual α -amino acids (AAAs) into biologically active peptides is known to enhance their selectivity and efficacy. Tetralin unit is a core structural element which can fix the relative position of functional groups to impart greater specificity in biological activity. Recently, Atc derivatives have been used as immunosuppressants. Towards the development of new methodologies for the synthesis of constrained AAA derivatives via the 'building block approach', here Kotha and Gopal Krishna (page 923) report a short route for the synthesis of linearly annulated Atc derivatives using the Diels–Alder (DA) reaction as a key step. This strategy can deliver a series of tetralin-based AAAs with varying shapes and sizes within a short period of time. They have prepared building blocks based on sultine

intermediates using inexpensive and readily available starting materials such as indane (or tetralin) and rongalite. Sultine derivatives are useful building blocks to generate the *o*-xylylene intermediate, which can be trapped with methyl-2-acetamidocrylate in a DA fashion to generate Atc derivatives.

Radhakrishnan and co-workers (page 927) have developed an efficient and reusable bactericidal agent using a polymer–metal nanocomposite thin film fabricated through soft chemistry carried out within the polymer matrix. Silver nanoparticles are generated through *in situ* reduction of silver ions in a poly(vinyl alcohol) film. Experiments on *Escherichia coli* with the nanoparticle-embedded polymer film reveal very low minimum inhibitory and minimum bactericidal concentrations. Extensive reuse of the thin-film bactericidal agent and its facile monitoring between the multiple reuses through spectroscopy and microscopy are demonstrated. Preliminary studies demonstrate effective deployment of the thin film as a coating on stirring rods.

Optical tweezers have found many applications due to the minuscule forces that light exerts on micron-sized particles to perform important studies on cells, colloids, etc. without inflicting damage. Continuous efforts exist in this area for trying to trap smaller and smaller particles so as to reach the goal of trapping single molecules. Typically, a trapped particle is detected through light-scattering schemes. However, the capability to observe smaller and smaller particles by light scattering becomes increasingly difficult due to signal-to-noise considerations, which makes this a serious bottleneck for single-molecule-trapping experiments. Femtosecond optical tweezers can be effective in trapping particles of any size at low average powers and can additionally induce two-photon fluorescence signal with built-in confocality. Two-photon fluorescence signal from the trapped particle is shown as an effective detection

scheme irrespective of size restrictions by Goswami and co-workers (page 935). A comparison between the back-scattering and two-photon fluorescence demonstrates that such a nonlinear signal can be an effective and fruitful diagnostic tool for laser tweezers. Development of such a nonlinear detection scheme to directly detect and visualize trapping events, even at sub-diffraction length scales, shows new directions to spectroscopy at the single-molecule level in solution.

Crystallization is a way of purification of an impure organic compound. Most often, it capitalizes on the preferential tendency of a given compound to interact better with itself to yield nuclei that eventually transform into crystals. Although homogeneous mixing of two or more different atoms of metals into alloys is well known, crystallization of two or more organic compounds together as the so-called cocrystals or multicomponent crystals is an arduous task, and the growth of multicomponent crystals remains challenging. It is of fundamental importance to understand as to how and when one may engineer the growth of crystals with two or more components in a well-defined stoichiometry. Of course, this knowledge is of direct relevance and invaluable importance in the pharmaceutical industry and organic materials chemistry. With the exception of the strategy based on acids and organic bases that leads to cocrystals/salts, there is seemingly no viable approach to access multicomponent crystals. Moorthy and co-workers (page 939) describe an approach based on rational molecular design towards engineering multicomponent crystals in a rational manner. It is shown that a tetraarypyrene host with distinct topological features exhibits site-selective recognition and binding of guests (small versus large). While larger-sized guests are found to be accommodated in a region termed 'trough', small-sized guests are shown to be trapped in 'basin/concave' domains of the host system.