Abstract

Metal–organic frameworks (MOFs), comprised of metal ions/clusters and linkers, have been regarded as one of the most important classes of materials in the past 10-15 years. On the other hand, covalent-organic frameworks (COFs) have attracted much interest in recent years due to the enormous potential design space offered by the atomically precise spatial assembly of molecular organic building blocks. Both MOFs and COFs exhibit high porosity, crystallinity, large surface area, tunable pore size, tailorable functionality, high chemical and thermal stability. These characteristics of MOFs and COFs have been widely exploited for their applications in gas storage, separation and conversion, catalysis, drug delivery, chemical sensing, etc. Furthermore, the luminescent MOFs and COFs have been ideal for high sensitivity, fast response time, real-time monitoring, and easy portability in their applications towards health hazards, national/international security issues and environmental pollution. Thus, the selective sensing of toxic and harmful substances, such as nitro-explosives, organic effluents, metal ions and volatile organic compounds, is an important research field. Similarly, the sensing of bio-relevant parameters, like pH and temperature, by such materials is being currently pursued by many research groups. The rapid climate change by global warming due to extensive CO_2 emission into the atmosphere by anthropogenic activities, e.g., industrialisation, fossil-fuel power plants, deforestation and automobile toxic emissions has been a serious issue in the present day world. Under this canvas, porous MOFs and COFs play a crucial role to tackle this urgent global issue by the selective capture, separation and conversion process. On the other hand, the industrially important separation of liquid phase hydrocarbons, such as benzene (Bz) and cyclohexane (Cy), is an emergent challenge as the conventional methods cannot be feasible due to their markedly similar physical properties. Furthermore, MOFs as drug-delivery nano-carriers have been reported in recent times.

This thesis work focused on the strategic design and synthesis of new triazine-based functional MOFs (using four different metal ions and several custom-designed triazine-based functional carboxylic acid linkers) and COFs (poly-condensation reaction of aldehydes and amines in a 3:2 or 3:4 ratio) under ambient or solvothermal conditions in good to high yields. These have been extensively studied by numerous sophisticated analytical techniques: (i) structural characterization by single crystal and powder X-ray diffraction, SAX/WAX, solid state NMR and HRMS, (ii) thermal behaviour by TGA, VT-PXRD and VT-FTIR, (iii) photophysical properties by UV-vis,

fluorescence spectroscopy, fluorescence microscopy and confocal microscopy, and (iv) surface analysis by FE-SEM, STEM, HRTEM and AFM. Their applications in above-mentioned fields are listed below:

(1) fluorescent sensing of nitro-explosives (TNP and Dunnite), organic pollutants (Dichloran and 4-nitroaniline), and toxic metal ions (Cu(II) and Cd(II)) at the ppb level; (2) switch on-off fluorescent sensing of pH and temperature; (3) molecular recognition of a) small molecules (the decoding of solvents based on solvent polarity parameters and an unprecedented 2D readout of life-time and quantum yield has allowed to distinguish protic and aprotic solvents with similar physical properties), and b) volatile organic compounds (the recognition was based on an unprecedented 2D readout of life-time and quantum yield); (4) extraordinary carbon dioxide capture, separation over N_2 (flue gas) and CH_4 (landfill gas) and its chemical conversion into value-added cyclic carbonates; (5) separation of benzene (Bz) over cyclohexane (Cy); (6) nano-scale drug delivery of Fluorescein, Calcein and 5-Fluorouracil.