

CHEMICAL



In recent years, great interest is being focused on exotic materials such as two-dimensional sheet-type layers, caged atoms/molecules, and three-dimensional assemblies of small molecules or polymers, as well as on conventional gas, liquid, and solid state materials. Many excellent articles have been published this year by SPring-8 users. Some representative topics are selected in this Chemical Science category. First, the photoelectron-recoil-induced rotational excitation following photo-ionization of gas molecules is introduced. When a photoelectron is ejected from a molecule, recoil momentum is imparted to the remaining ions. In general, the recoil energy is shared among translational, rotational, and vibrational motions. The research team of Prof. K. Ueda (Tohoku University) has shown that the degree of rotational excitation depends on the type of molecular orbital. Their technique, employed at BL27SU, provides information on the atomic orbital composition of molecular orbitals. A JAEA joint research team has successfully studied water under the multiply-extreme conditions of high pressure and high temperature – similar conditions to the Earth's interior. The structural and dynamical properties of water under these conditions were investigated with *in situ* X-ray diffraction experiments at BL14B1, backed up by advanced first principles molecular dynamics simulations. A crossover from a hydrogen-bonded liquid to a simple-liquid-like liquid was observed when the temperature of the molecular liquid phase was raised to 400 K - 500 K. As a typical 2D material, graphene, a honeycomb network constructed by

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sp^2 -bonded carbon atoms, has attracted considerable attention as a potential material for electronics and photonics. Epitaxial graphene formation on an SiC thin film on an Si substrate (graphene-on-silicon), developed by the research team of Prof. M. Suemitsu (Tohoku University), has been proved to be effective for forming high quality and large area graphene films. Graphene formation was confirmed using real-time *in situ* photoemission spectroscopy of the C 1s core level at BL23SU, probing the sp^2 -bonded carbon atoms. The encapsulation of a Li cation inside a C_{60} cage was observed by the research team of Prof. H. Sawa (Nagoya University) using X-ray diffraction at BL02B1. A single crystal of $[Li@C_{60}](SbCl_6)$ was grown by the diffusion of CS_2 vapor, and the positively charged $Li@C_{60}$ ions were found to be periodically assembled on a 2D negatively-charged sheet of $SbCl_6$ ions. Since the Li cation can move within the C_{60} cage, an external field can be used to control its position, suggesting applications such as single molecular switches and ferroelectric sheets. Controlling the size of porous objects on the nanoscale and aligning them on various substances is currently a hot topic. The fabrication of a preferentially-oriented metal-organic framework nanofilm was achieved by the research teams of Prof. R. Makiura (Osaka Pref. University) and Prof. H. Kitagawa (Kyoto University). Detailed insight into the crystallinity was obtained from X-ray diffraction at BL13XU. The versatility of the solution-based growth strategy is expected to allow the fabrication of various well-ordered metal-organic nanofilms. The large-area 3D molecular ordering of a graft polymer sandwiched between Teflon sheets lead to photo-actuating capability. Exposure to light releases the strain within the material, resulting in a photo-mechanical bending motion. This discovery provides a new design concept for photomechanical soft materials. To determine the structure of the polymer, small-angle X-ray scattering measurements were made at BL45XU by the research team of Prof. N. Hosono (The University of Tokyo/RIKEN). Porous coordination polymers (PCPs), or metal-organic frameworks possessing design-ability that provides host-guest interactions, as well as flexibility that allows guest-responsive dynamic accommodation, have attracted attention as candidates for enhancing molecular recognition ability. A PCP with selective sorption properties for O_2 and NO has been found by the research team of Prof. S. Kitagawa (Kyoto University/RIKEN) at BL02B2. PCPs are expected to provide a new platform for developing selective adsorption systems for small gas molecules. Liquid crystal semiconductors attract increasing attention due to their potential applications in solution-processable and self-repairable organic electronics. Triphenylene derivatives carrying paraffinic side chains with ionic liquid termini were applied to form a liquid crystal mesophase. The relevant phase diagrams have been re-investigated at BL02B2 and BL44B2 by the research team of Prof. Y. Yamamoto (University of Tsukuba). They found that the optically isotropic phase is not amorphous, but a liquid crystal mesophase. This unexpected observation has led to the design of new triphenylene derivatives with different paraffinic spacers and ionic liquid pendants. A combination of neutron and X-ray diffraction techniques has been applied to measure the full set of partial structure factors for liquid and glassy $ZnCl_2$ by the research team of Prof. P. S. Salmon (University of Bath, UK). The high energy X-ray diffraction measurements were conducted at BL04B2. The diffraction patterns were used to construct three-dimensional models for liquid and glassy $ZnCl_2$ by employing the reverse Monte Carlo method. Finally, several kinds of textile fabrics containing silk fibers have recently been found from archaeological sites in Japan. The characteristics of the degraded fibers have been analyzed using FTIR micro-spectroscopy at BL43IR by the research team of Prof. N. Akada (Kyoto Institute of Technology). This research on organic archaeological samples demonstrates the power and usefulness of synchrotron radiation infrared spectroscopy.

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