# **Photoabsorption and Photoionization Studies of Fullerenes and Development of High-Efficiency Organic Solar Cells**

### **Department of Photo-Molecular Science Division of Photo-Molecular Science III**



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As the first topic, we have observed the formation of singly- and multiply-charged photoions from gaseous fullerenes irradiated with synchrotron radiation at hv = 25 to 200 eV. We thus studied the mechanisms and kinetics of consecutive C2-release reactions on the basis of (i) the yield curves for the fragments  $C_{60(70)-2n}^{z+}$   $(n \ge 1, z = 1-3)$  as a function of the primary internal energy of the parent  $C_{60(70)}^{z+1}$ and (ii) the three dimensional velocity distributions of the fragment carbon clusters.

In the second topic we have fabricated dye-sensitized solar cells (DSSC) containing ruthenium dye and iodide electrolyte and measured their short current and the intensity of the transmitted light to estimate the wavelength dependence of the incidence photon-to-current conversion efficiency (IPCE) and photoabsorbance (ABS) in the range of 300 to 1000 nm. In addition, we evaluated the quantum yield (APCE) of DSSCs for the electron injection from the excited orbital of Ru dye to the conduction band of TiO2 nano particles. Our final goal is to develop DSSCs with high performance and long lifetime by improving ABS and APCE mainly in the near infrared region.

#### 1. Feasibility Study on the Mass-Selected Velocity Map Imaging of Polyatomic Molecules and Fullerenes<sup>1)</sup>

A photoionization spectrometer for velocity map imaging (VMI) has been developed for measuring the scattering distribution of fragment ions from polyatomic molecules. The spectrometer contains a mass gate and an ion reflector which can discriminate ions with a particular mass-to-charge ratio m/z. The basic functions and feasibility of these devices were tested experimentally and theoretically. First, the photoions from Kr and C<sub>60</sub> were extracted into a time-of-flight (TOF) mass spectrometer by pulsed or continuous electrostatic fields. When the pulse-application timing on the mass gate was tuned to a specific m/z, the peak of the selected ions alone was present on a TOF spectrum. Second, the performance of the

34

mass gate in the VMI spectrometer was investigated by the computer simulations of the ion trajectories of fragments from  $C_{60}$ . The initial three-dimensional velocity distribution of  $C_{58}^+$ was projected onto the image plane with an energy resolution better than 10 meV. The  $C_{58}^+$  image was free from the contamination of other ions,  $e.g. C_{60}^+$  and  $C_{56}^+$ .

### 2. Mass-Analyzed Velocity Map Imaging of Thermal Photofragments from C<sub>60</sub><sup>2)</sup>

The velocity distributions of the fragments produced by dissociative photoionization of C<sub>60</sub> have been measured in the extreme UV region for the first time (see Figure 1), by using a flight-time resolved velocity map imaging technique combined with a high-temperature molecular beam and synchrotron radiation. Values of the average kinetic energy release were estimated at 6 different photon energies with respect to five reaction steps of sequential C\_2 ejection, starting from  ${C_{60}}^{2+} \rightarrow$  $C_{58}^{2+} + C_2$  to  $C_{52}^{2+} \rightarrow C_{50}^{2+} + C_2$ . The translational temperatures of the fragment ions were found to be lower than those obtained by laser multiphoton absorption of C<sub>60</sub>. The kinetic energies released in the first to fourth steps increase with increasing hv and reach 0.35–0.5 eV at hv = 102 eV, reflecting statistical redistribution of the excess energy in the transition state, whereas that in the fifth step leading to  $C_{50}^{2+}$  was exceptionally small.

### 3. Mass-Analyzed Velocity Map Imaging of Thermal Photofragments from C<sub>70</sub>

When C<sub>70</sub> fullerenes absorb extreme UV photons of synchrotron radiation, primary parent ions undergo stepwise C2 ejection to produce fragment ions containing even-numbered carbon atoms. We have measured (1) the yield curves of the  $C_{70-2n}^{2+}$  fragments (1  $\leq n \leq 6$ ) from C<sub>70</sub> by TOF mass spectrometry and (2) their translational temperatures by velocity



**Figure 1.** (a-c) y-t maps of the photoions from C<sub>60</sub> on which their counts are represented as a function of their arrival time *t* and the *y* coordinate of their incidence position on the PSD. The list-mode data at three hv positions are integrated over the whole *x* range. The *y* coordinate is proportional to the *y* component of the ion velocity. (d) TOF spectra of the photoions at hv = 102 eV obtained by integrating the signal counts of (c) over the whole *y* range.

map imaging technique. The yield curve and translational temperature showed marked anomalies at n = 5, which may arise from exceptional stability of the  $C_{60}^{2+}$  fragments that have an icosahedral structure similarly to isolated  $C_{60}$  fullerene.

# 4. Preparation and Evaluation of High Efficiency DSSCs<sup>3)</sup>

The high efficiency DSSCs were fabricated by using a screen-printing technique and a wet process. A TiO<sub>2</sub> anode was immersed for 3 days in the acetonitrile solution of Ru complex compound (N719). The mixture of I<sub>2</sub>, iodide salt, acetonitrile, *etc.* was used as a redox electrolyte. The counter electrode was covered with thin platinum film. The I–V characteristics of DSSCs were recorded under simulated sun light (power density = 100 mW cm<sup>-2</sup>). The highest overall energy conversion efficiency was *ca.* ~8%. The IPCE was calculated from the short current density and radiation power density as a function of the wavelength. The IPCE curve showed a peak of 0.73 at 535 nm. The performance and long-term stability of the DSSCs were studied by changing the thickness of the TiO<sub>2</sub> film, the deposition method of the Pt film, and the compositions of the redox electrolyte.

## 5. Azo Dyes as Photosensitizers for Organic Solar Cells<sup>4)</sup>

Fabrication and performance tests are reported on DSSCs containing azo dyes as photosensitizers. Fundamental properties of the DSSCs were obtained on the energy conversion



**Figure 2.** Correlation between the experimental data of the short current density of DSSCs and the theoretical energy levels of the LUMO of the solitary azo dyes.

efficiency  $\eta$ , short current and photoabsorbance in the wavelength range of 300 to 800 nm. Various azo dyes were synthesized in such a way that the positions and numbers of carboxylate and hydroxy groups differ from one dye to another. The carboxylate groups are considered to form strong linkages with the surface of TiO<sub>2</sub> nanoparticles to promote rapid electron injection from dye molecules to the conduction band of TiO<sub>2</sub>. We could demonstrate a remarkable correlation between the performance of the DSSCs and the energy level of the lowest unoccupied molecular orbital (LUMO) of the azo dye: no dye whose LUMO energy is lower than -1.5eV could allow us to make DSSCs with  $\eta > 0.1\%$  (see Figure 2). This finding is consistent with the necessary condition for the DSSC that the LUMO level should be higher than the lower bound of the conduction band of TiO<sub>2</sub>.

#### 6. Transient Fluorescence Spectroscopy of DSSCs Using Picosecond Laser

Observation was made on luminescence decay by timeresolved single photon counting using a picosecond laser ~470 nm or free electron laser of ~580 nm which operates at a repetition rate of 45 or 11.3 MHz, respectively. The apparent luminescence lifetime of the DSSC exposed to the air is longer than that preserved in vacuum, due to unwanted aggregation of the dye molecules at the surface of TiO<sub>2</sub> of the former DSSC. The kinetics of electron injection will be discussed on the basis of the luminescence lifetime of various DSSCs and photovoltaic electrodes

#### References

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