Organic-Inorganic Hybrid Dendrimer with a CdS Nano-Core: The Liquid-Crystalline Structure-dependent Photoluminescence Behavior

Kiyoshi Kanie[1,*], Masaki Matsubara[1], Warren Stevenson[2], Jun Yabuki[1], Xiangbing Zeng[2], Haoliang Dong[2], Kazunobu Kojima[1], Shigehide F. Chichibu[1], Atsushi Muramatsu[1], and Goran Ungar[2,3]

[1]*Institute of Multidisciplinary Research for Advanced Material, Tohoku University, Sendai, Japan*
[2]*Department of Materials Science and Engineering, University of Sheffield, Sheffield, UK*
[3]*Department of Physics, Zhejiang Sci-Tech University, Hangzhou, China*

**kanie@tagen.tohoku.ac.jp*

Semiconductor quantum dots (QDs) have attracted a great deal of attention in material science due to their size-dependent and tuneable absorption and emission properties. In addition, periodic arrays of QDs have a considerable potential in applications in novel nano-electronic and optical devices. Recently, we developed liquid-crystalline (LC) organic-inorganic hybrid dendrimers,[1] where the dendrimer has a spherical gold nanoparticle (NP) at its core. Dense surface modification of spherical gold NPs with LC **G2** dendron molecules was found to result in a hybrid exhibiting a thermotropic LC phase with simple cubic structure. In the present study, we focus on imparting such ability to self-organize onto monodisperse QD nanospheres. As a result, dendron-modified QDs were obtained, displaying ordered superlattices. Such structures were found to exhibit unusual photoluminescence (PL) behaviour. CdS NPs **C1**-**C3** with different degrees of CO_2H modification were prepared as the core of the dendrimer. Surface modification of **C1**-**C3** by **G2** was carried out by amidation reaction. The average sizes of the core particles of **C1**, **C2**, and **C3** were calculated as 3.9, 3.9, and 3.8 nm, respectively. The numbers of **G2** molecules per one particle for **G2**/**C1**, **G2**/**C2**, and **G2**/**C3** were obtained as 69, 54, and 47, respectively, from TG analysis. SAXS and DSC measurements showed that **G2**/**C1** exhibited thermotropic LC phases. At 150 °C, **G2**/**C1** formed a new thermotropic cubic LC phase with $P2_13$ symmetry. The cubic structure was retained at room temperature after cooling. On the other hand, only random structure was seen for **G2**/**C2** and **G2**/**C3**. The **G2**/**C1** dendrimer as deposited on a glass substrate, also formed a disordered structure. In such a state, it showed strong PL when UV irradiated at 365 nm. However, the PL was quenched when the **G2**/**C1** dendrimer self-organized in the cubic phase after annealing at 150 °C followed by cooling. Such PL quenching behaviour was totally reversible, and appears to be derived from the periodic cubic structure of **G2**/**C1**. The unprecedented structure-dependent PL behaviour of the dendronized LC QDs is summarized in **Figure 1**. The detailed analysis on PL quenching behaviour by femto-second laser is now in progress. Such unusual PL behavior might be a powerful tool to develop future functional devices.

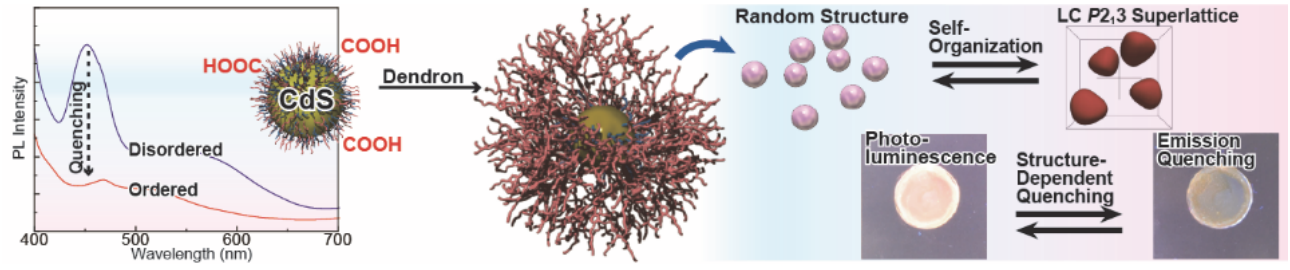

Figure 1. A Schematic Image of Structure-dependent Photoluminescence Behavior of Liquid-Crystalline "Organic-Inorganic Hybrid Dendrimer" with a CdS NP at Its Core.

Acknowledgements This work is supported by JSPS No. 24•9313 (MM), No. 22685019 (KK), No. 25288087 (KK), and Bilateral Joint Research Project (KK)), the Asahi Glass Foundation (KK), the NSF-EPSRC Pire program, project "RENEW" (EP-K034308), the Leverhulme Foundation (RPG-2012-804), and the 1000 Talents Program of P.R. China (GU).

[1] K. Kanie, M. Matsubara, X. Zeng, F. Liu, G. Ungar, H. Nakamura, A. Muramatsu, *J. Am. Chem. Soc.,* 2012, **134**, 808.