

## Studies on photon energy utilization in chromophoric ionic liquids

久光, 翔太

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氏 名 : 久光 翔太

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(発色団含有イオン液体中における光エネルギー利用に関する研究)

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## 論 文 内 容 の 要 旨

In the thesis, researches on synergistic features of photo-functional species in ionic liquids (ILs) and ionic glasses are described, gazing forward to develop a new group of materials that have the environment where the interaction between photon and matter is maximized. As research subjects, TTA-UC functionalities were focused because those are exhibited by the collective behavior of molecular systems. The achievements in each study are summarized below.

In chapter 2, inspired by the continuous nanostructure of ILs, a new family of photo-functional ILs which show efficient TTA-UC were developed for the first time. A novel fluorescent IL, comprising an aromatic 9,10-diphenylanthracene 2-sulfonate anion and an alkylated phosphonium cation, showed pronounced interactions between chromophores, as revealed by its spectral properties. Upon dissolving a triplet sensitizer, the IL demonstrated photon upconversion based on triplet-triplet annihilation (TTA-UC). Interestingly, the TTA-UC process in the chromophoric IL was optimized at a much lower excitation intensity compared to the previous nonionic liquid TTA-UC system. The superior TTA-UC in this IL system is characterized by a relatively high triplet diffusion constant which is ascribed to the presence of ionic chromophore networks in the IL.

In chapter 3, a novel chromophoric ionic liquid (IL) with two-dimensional (2D) nanostructural order is developed, and its structure-property relationship is investigated by harnessing photon upconversion based on triplet energy migration. An ion pair of 9,10-diphenylanthracene-2-sulphonate (DPAS) and asymmetric quaternary phosphonium ion exhibited both ionic crystal (IC) and supercooled IL phases at room temperature. Single crystal X-ray analysis of the IC phase showed an alternate alignment of polar (ionic) and non-polar (non-ionic) layers, and this layered structure was basically maintained even in the IL phase. The diffusion length of triplet excitons in the IL phase, obtained by the analysis of upconverted emission in succession to triplet-triplet annihilation (TTA), is larger than the domain size estimated from powder X-ray analysis. This suggests that triplet excitons in chromophoric ILs can diffuse over the nanostructured domains.

In chapter 4, a newly synthesized P<sub>555</sub>DPAS showed 1D chain-like nanostructure, which was different from our previous IL P<sub>22214</sub>DPAS. The 1D chain-like P<sub>555</sub>DPAS showed improved

singlet and triplet excitonic characteristics. By successfully controlling the dimension of nanostructures in ILs, the TTA-UC performances are improved for the first time. This work will open the door to new worlds where the functions of ILs can be tuned proficiently by controlling the dimension of nanostructures of ILs.

In chapter 5, anthracene-modified ionic glass molecules were synthesized. The compounds showed PXRD and SAXS peaks in low angle region, which suggested the existence of ordered nanostructures in the ionic glasses and the nanostructures were considered to be classified two-dimensional structures. Inter-chromophore interactions of anthracenes were observed and TTA-UC was achieved in chromophoric ionic glass materials for the first time. The relatively high quantum yield 3.6% was observed in  $P_{\text{tphC14}}\text{DPAS}$  with doped 0.01% PtOEP.

In chapter 6, an ionic liquid (IL) composed of 9-anthracenecarboxylate anion and ammonium cation possessing three diethylene glycol chains shows phototriggered dimerization of anthracene chromophores. It causes segregation and crystallization of protonated 9-anthracenecarboxylic acid dimer, which is associated with the concurrent liberation of the free amine in the IL. This work provides a new molecular design for photoresponsive ILs, whose first application for site-selective photopatterning is demonstrated.

The behind objectives of this thesis were to understand and to control the arrangements of functional moieties of ILs in the segregated nanostructures as spaces where to exhibit and maximize the functionalities. The researches proceeded step by step toward the understanding of the relationship between the arrangements of functional species and synergistic features of them. The goal in this aspect, to lay the foundational of the principal theory for future researchers who will work on functional ILs, was succeeded by the researches in this thesis.