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学位論文題目	Metallophthalocyanine analogues fused with polycyclic aromatics and their optoelectronic functions (多環芳香族化合物縮環金属フタロシアニン類縁体の光・電子機能に関する研究)
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論文内容の要旨

The systematically exploring of molecular structures and control of molecular orientation generate superior molecular functions. In this thesis, the author has focused on molecular functions of two-dimensional (2D) π -conjugated molecular materials. The expansion of conjugation allows a delocalization of π electrons across all the adjacent aligned π -orbitals, and may lower the overall energy of the molecules. Recently, there is growing interest in developing conjugated molecules possessing two or three dimensional conjugation. The extension of π -electron delocalization showed various unique properties, including high mobility and variable band-gap, and can alter intermolecular interactions among molecules. The author developed several bottom-up synthetic routes for 2D conjugated molecules containing heteroatoms and metal ions, and investigated the structural effects of 2D molecules on their electronic and photonic properties.

In this thesis, the author has designed and synthesized thiophene-fused metallophthalocyanine analogues (**Chapter 2**), thiophene-fused zinc naphthalocyanine analogues (**Chapter 3**), and resorcin[4]-strapped zinc phthalocyanine (**Chapter 4**) for investigation of their optical and electronic functions in various states.

In **Chapter 2** thiophene-fused phthalocyanines **1–4** were synthesized through ring closing reactions from *o*-chloroethynylbenzene substructures. The self-organizing properties of thiophene-fused phthalocyanines were investigated in solution, at the air-water interface, and in the solid state. The attachment of *n*-hexylphenyl units at α -positions of the fused thiophene rings creates a network structure of nanoscopic fibrous assemblies with excellent long-range stacking through intermacrocycle interactions, which with the additional interaction between peripheral phenyl spacers. Cu-**1** and Cu-**2** acted as a soluble p-channel organic semiconductor, but the field-effect mobility was not high due to the low crystallinity in the solid state. Cu-**4** possessing thiophene spacers was polymerized into the electrochemically active films onto an

electrode by the connection of four thiophene terminals through an oxidative coupling reaction.

In **Chapter 3** two structural regioisomers of near-IR light absorbing **ZnTNc_{exo}** and **ZnTNc_{endo}** decorated with sixteen long alkyl chains were designed and synthesized. The author has elucidated the influence of the molecular structural differences between the two isomers on their self-organizing behavior and photoconductivity. Ring-expanded **ZnTNc_{exo}** and **ZnTNc_{endo}** assemble into one-dimensional columnar nanostructures over a wide temperature range from room temperature. TOF experiments have revealed that the organized **ZnTNc_{exo}** shows a well-balanced ambipolar carrier transport behavior, with carrier mobilities of the order of $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Spontaneous alignment of columnar assemblies on substrates is a key issue for improving the carrier mobilities.

In **Chapter 4** a resorcin[4]arene-strapped zinc phthalocyanine **1** was synthesized from two phthalonitriles **3** and **4**. Two benzene rings on one side of phthalocyanine ligand were strapped with resorcin[4]arene, while the other two benzene rings were decorated with four branched alkoxy chains. The introduction of resorcin[4]arene strongly affects the spectroscopic properties of the phthalocyanine. The shapes and positions of the absorption spectra of **1** depend strongly on the nature of the solvents. The Q band of **1** in CH_2Cl_2 is split into 694 and 740 nm due to the self-protonation of **1** on the *meso*-nitrogen of the phthalocyanine ligand. Bowl-shaped resorcin[4]arene can capture C_{60} through non-covalent interactions, and the complexation between **1** and C_{60} leads to an efficient electron transfer.