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Article / Book Information

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Title(English)	Molecular-Geometry Approaches to Develop Functional Fluorophores Based on Classic Aromatic Hydrocarbons
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（博士課程）
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論 文 要 旨

THESIS SUMMARY

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Department of, Graduate major in 応用化学 コース

申請学位（専攻分野）： 博士 （ 工学 ）
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

This thesis entitled "Molecular-Geometry Approaches to Develop Functional Fluorophores Based on Classic Aromatic Hydrocarbons" consists of seven chapters.

Chapter 1 "Introduction" elucidates the relationship between electronic states and molecular geometries both from the fundamental and practical aspects. A substituted aromatic hydrocarbon features diversity in its electronic states, whose interactions can be controlled by its molecular geometry. This chapter insists that the structure-property relationship can be utilized to design functional fluorophores, exemplifying it with plenty of reports.

Chapter 2 "Fluorescence Solvatochromism and Dual-Mode Fluorescence Controlled by Torsional Restrictions at Donor-Acceptor Junctions" reveals that torsion at donor-acceptor junctions plays instrumental roles in control of fluorescence solvatochromism and manifestation of "Dual-mode fluorescence". In this chapter co-planarity of biphenyl analogs of PRODAN is modified by imposing various steric restrictions so that their fluorescence solvatochromism is controlled freely. In addition, severely twisted conformation of binaphthyl analog of PRODAN is utilized to develop the fluorophore that responds differently with different external stimuli, i.e. aggregation and glassification of media.

Chapter 3 "Directional Control of π-Conjugation Enabled by Distortion of the Donor Plane in Diarylaminoanthracene" proposes the novel strategy to extend π-conjugation. While the conventional design strategy for extension of π-conjugation is to construct rigid and coplanar π-systems, the novel strategy insists that π-conjugation can be extended by distortion of local structures of π-systems rather than their planarity. This chapter demonstrates the hypothetical design strategy to be valid by means of photophysical experiments and computational calculations of various *N*,*N*-diarylaminoanthracenes.

Chapter 4 "Steric-Environment Sensitivity of Fluorescence Activated by Twisted *N*,*N*-Dialkylamino Groups" reveals that strongly twisted *N*,*N*-dialkylamino groups activate aggregation-induced emission (AIE) and viscosity-sensitive fluorescence of polycyclic aromatic hydrocarbons (PAHs). Chapter 4-1 discusses effects of regioisomerism on the solution- and solid-state fluorescence of bis(piperidyl)anthracenes and finds that only 1,4- and 9,10-substitutions lead drastic AIE. Especially AIE of 9,10-bis(piperidyl)anthracene is prominent (its fluorescence quantum yields are 0.02, 0.79 and 0.86 in THF solution, colloidal suspension and polycrystalline solids, respectively.) among reported AIE luminogens in spite of its structural simplicity. Chapter 4-2 scrutinizes photophysical processes of these 9,10-bis(*N*,*N*-dialkylamino)anthracenes both from experimental and theoretical aspects and establishes the general design strategy of AIE luminogens and viscosity-sensitive fluorophores based on PAHs. As a result, *para*-substitution of donors is proved to be an effective strategy for designing AIE luminogens and viscosity-sensitive fluorophores. Donor moieties that face each other stabilize the S_1/S_0 minimum energy conical intersection (MECI) of anthracene and other PAHs, and thus internal conversion become fast in solution states but is suppressed in solid states or viscous media. This chapter applied the design strategy focusing on S_1/S_0 MECI to naphthalene and successfully developed the minimal fluorophore with drastic AIE and viscosity-sensitive fluorescence. Chapter 4-3 applies the design strategy to a pyrene chromophore. This chapter underscores the importance of Pyrene K-region from the standpoint of engineering S_1/S_0 MECI; substituents at both 4,5-position should be severely twisted due to their *peri*-hydrogens and it is known for deformation at K-region to lead more stable S_1/S_0 MECI. Therefore this chapter examined photophysical properties of pyrene derivatives with highly twisted *N*,*N*-dimethylamines at 1-, 1,6- or 4,5-positions. As a result, pyrene K-region, which has been utilized only for a key synthetic intermediate of e.g. annulative π-extension, is revealed to play the instrumental role in the design of AIE luminogens.

Chapter 5 "Terminal Functionalization of Highly Twisted Bis(*N*,*N*-dialkylamino)arenes and Its Application to Fluorescence Thermometers" proposes the facile synthetic methodologies for functionalization of the alkyl chains of highly twisted bis(*N*,*N*-dialkylamino)arenes, whose superior AIE and viscosity-sensitive fluorescence has been demonstrated in chapter 3. To examine the potential as a fluorescence probe, these functionalized bis(*N*,*N*-dialkylamino)arenes are further modified to methacrylate moieties and then co-polymerized with *N*-isopropylacrylamides. Obtained polymers and gels exhibited steep increase of fluorescence intensity and fluorescence quantum yields around 27−35 °C, around which poly(*N*-isopropylacrylamide) is subject to the coil-to-globule transition.

Chapter 6 "A Structurally Simple Bis(piperidyl)naphthalene Cross-linker Exhibiting Fluorescence Quenching and Photodegradation in Trichloromethyl-Containing Chloroalkanes" applied the design strategy of fluorophores focusing on their molecular geometry not only to operating fluorescence properties but also to leading mechanical functionality. In this chapter, 1,4-bis(piperidyl)naphthalene is employed as cross-linkers for poly(*n*-butyl methacrylate) gels to create the soft material that undergo fluorescence quenching and photodegradation selectively in 1,1,1-trichloromethyl-containing chroloalkanes. The obtained gels are highly fluorescent and stable in various organic solvents and chloroalkanes, but exhibits faint fluorescence and fast drop of the storage modulus upon UV irradiation when they are swollen by chloroform and 1,1,1-trichloroethane.

Chapter 7 "Conclusion" summarizes this thesis and describes the significance of the thesis in related disciplines and perspectives for future projects. This chapter summarizes what kind of molecular geometries lead superior fluorescence functionalities, which have been realized conventionally by means of development of novel π-skeleton and introduction of multiple substituents.

Since the molecular-geometry approaches simplified molecular structures of functional fluorophores much more than those developed in conventional strategies, the design strategy should facilitate further advancement of material science. Also the design strategy focusing on MECI is unprecedented and thus should bring about impacts on various disciplines.

備考 ： 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).