

ドナー・アクセプター性置換基を持つピレン誘導体の合成とその ソルバトフルオロクロミック特性の評価

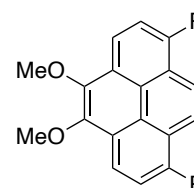
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Synthesis of Pyrene Derivatives with Donor-Acceptor Substituents and Evaluation of Their Solvatofluorochromic Properties (*Grad. Sch. Nat. Sci. Technol., Kanazawa Univ.*) ○Taisuke Shiina, Taniyuki Furuyama, Masahito Segi, Hajime Maeda

Pyrene has high fluorescence intensity and is widely used as a fluorescent material. However, the solvatofluorochromic molecules with pyrene core have been less investigated. In this study, 4,5-dimethoxypyrenes having various electron-withdrawing groups at 1,8-positions of pyrene were synthesized, and their solvent dependence of absorption and fluorescence spectra was investigated. When the fluorescence spectra of these compounds were measured using benzene, CH₂Cl₂, THF, MeCN, and DMF as solvents, the maximum fluorescence wavelength of each compound moved to the longer wavelength region as the polarity of the solvent increased. The higher amount of bathochromic shift was observed with increasing the electron-withdrawing ability of the substituents at 1,8-positions. It was also found that the fluorescence quantum yields increased by the introduction of triple bonds.

Keywords : Pyrene; Solvatofluorochromism; Donor-Acceptor; Fluorescence; Fluorescence quantum yield

ピレンは高い蛍光強度を有しており、蛍光材料として広く用いられている。しかしピレンを母骨格とするソルバトフルオロクロミック分子の開発はあまり進んでいない¹。本研究では、ピレンの4,5位にMeO基、1,8位に様々なアクセプター性置換基を導入した化合物**1-8**を合成し、それ



らの吸収・蛍光スペクトルにおける溶媒依存性を調べた。ベンゼン、CH₂Cl₂、THF、MeCN、DMFを溶媒としてそれらの化合物の蛍光スペクトルを測定したところ、いずれの化合物も溶媒の極性が上がるにつれて極大蛍光波長は長波長側に移動し、その移動量は1,8位の置換基の電子求引性が高いほど大きいことが分かった。また、蛍光量子収率は三重結合を導入することによって増加した。

Table1. Solvatofluorochromism of pyrene derivatives **1-8**.^{a)}

Compound	$\lambda_{em, max}$ (nm)		Φ_f	
	benzene	DMF	benzene	DMF
1 , R = CN	443	506	0.45	0.43
2 , R = COCH ₃	431	480	<0.01	0.04
3 , R = CHO	459	518	0.03	0.13
4 , R = C≡CCHO	460	511	0.37	0.41
5 , R = C=C(CN)C ₆ H ₅	508	523	0.02	<0.01
6 , R = C=C(CN)C ₆ H ₄ OMe- <i>p</i>	514	526	0.12	0.04
7 , R = C=C(CN)C ₆ H ₄ CF ₃ - <i>p</i>	520	539	<0.01	<0.01
8 , R = C≡C-C=C(CN)C ₆ H ₄ CF ₃ - <i>p</i>	528	557	0.36	0.18

^{a)} [**1-8**] = 1.0 × 10⁻⁵ M, λ_{ex} = 380 (**1**), 380 (**2**), 392 (**3**), 435 (**4**), 432 (**5**), 436 (**6**), 438 (**7**), 388 (**8**) nm.

1) a) Zöphel, L.; Enkelmann, V.; Müllen, K. *Org. Lett.* **2013**, *15*, 804-807.

b) Niko, Y.; Kawauchi, S.; Konishi, G. *Chem. Eur. J.* **2013**, *19*, 9760-9765.