横浜国立大学　理工学部

化学･生命系学科　化学 EP　機能性色素化学研究室

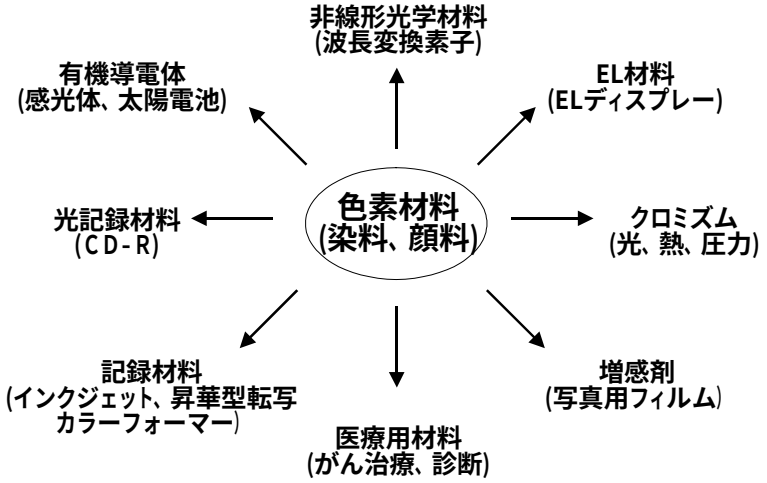
(大学院　環境情報学府　生命環境学専攻)

･研究テーマ

機能性色素の固体構造と電子構造に関する研究

当研究室では、以下に述べる機能性色素の研究から、例えば有機太陽電池などの環境技術への貢献を目指している。

近年の目覚ましい電子技術の発展に伴って、古くから染色や顔料などの着色材として用いられてきた色素が、下図で示すように様々な分野で応用されるようになっている。このような着色用途以外で用いられる色素は機能性色素(functional dye)呼ばれており、最近では、レーザープリンター用感光体、インクジェットプリンター用インク、有機 EL ディスプレーなど、私たちの身近なところで活躍している。そして、色素の応用範囲が着色用途以外の巾広い範囲に拡がるのに伴い、様々な用途に応じた色、すなわち目的とされる物性に適合した電子状態の分子が所望されるようになってきた。



分子とその色の関係については古くから多くの研究があり、現在では量子力学を基本とした種々の分子軌道計算を用いる事で、定性的あるいは半定量的に分子の色、すなわち電子状態を予測･検討できるようになった。単分子分散状態で色素を使用する染色などの用途には、このような手法での分子設計が可能である。一方で、結晶性薄膜や結晶性の微粒子などの固体状態において、溶液や分子分散状態と大きく異なる色調や物性を示す色素が多く知られている。しかし、分子と固体構造及び電子状態の関連性について十分に議論されていないため、現在のところ、固体における電子状態まで見通した分子設計は不可能である。そのため、固体状態で用いる機能性色素の材料

開発においては、試行錯誤的な手法や、極端な場合偶然に頼っているのが実情である。分子の状態と結晶などの集合体の状態を踏まえて色素材料を開発するためには、次の二つの点について考える必要がある。一つ目は、分子が集合してできる結晶における、分子構造と結晶構造の関連性である。この点については、多くの結晶学の研究者により、結晶構造予測の研究が活発に進められている。二つ目は、結晶状態での分子間相互作用についてである。結晶における分子配列とその電子状態については、特異な吸収バンドを示す J 会合体のように、固体構造と電子構造の関連性について比較的詳細に検討されている例もあるが、色素全体を見渡した場合、まだ十分に検討されているとは言い難い。これからの有機材料の開発においては、分子の結晶化と、結晶構造と電子状態の相関性という双方の観点から、分子に立ち戻る材料設計指針を見出すことが非常に重要である。このような観点から、当研究室では機能性色素の結晶構造と分子間相互作用、固体物性の相関関係を解明し、機能性色素に代表される低分子系有機結晶性材料の分子設計指針の創出を最終目標とし、以下のテーマについて現在取組んでいる。

a) 有機色素の真空蒸着膜の構造物性相関
b) ピラジン色素の結晶多形の構造物性相関　>> 例 >>
c) 色素結晶の同形性と分子構造の相関
d) 会合体を形成するビスアゾメチン色素の結晶構造制御

また最近、地球温暖化などの環境問題とこのような科学技術が具体的にどう関わっているかもっと幅広く知ってもらうため、高校や中学の学生を主な対象としたライフサイクルの考え方を取入れた環境教育プログラムの開発にも取組み始めた。

e) ライフサイクル思考に基づく携帯電話を題材とした環境教育プログラムの開発と実践

・メンバー

>>>>

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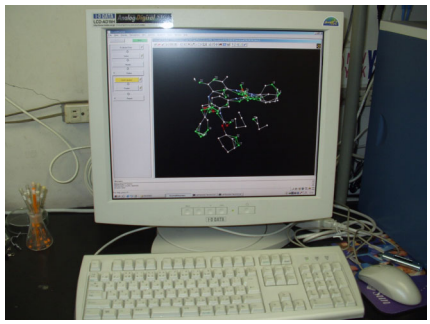
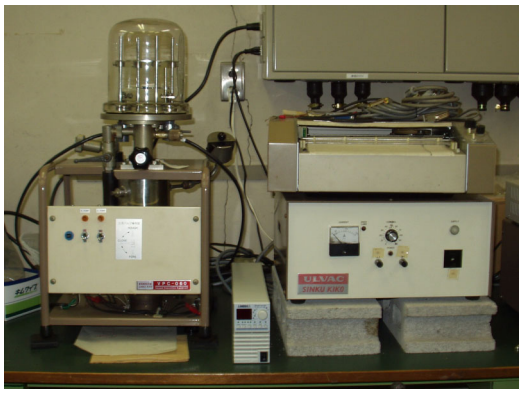
学部生：井上和哉　(4 年)、遠藤夏子　(4 年)、南貴也　(4 年)

・実験設備

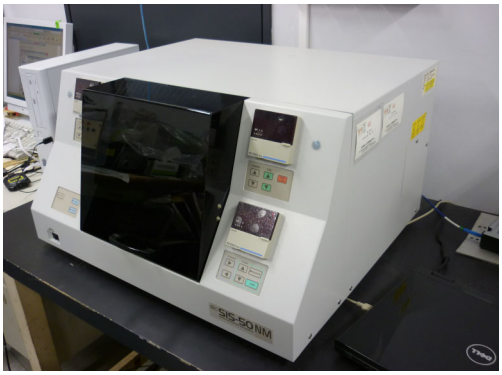
迅速型 X 線回折計 (Rigaku RAXIS-Rapid-F)：**単結晶構造解析**



真空蒸着装置 (Ulvac VPC-060 and VPC-200 with cooling unit)：**蒸着膜作製**



導波路分光装置 (SIS)：**固体の吸収スペクトル測定**



・研究業績 (2001 年以降)

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解説、書籍など

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6) **松本真哉、“携帯電話を題材とした環境教育プログラムの開発と実践 -その背景-”、**LCA **日本フォーラムニュース、**2010**、Vol 53**, 20-22
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8) **松本真哉、“産業技術をテーマとした環境教育の提案 -携帯電話を題材とした環境教育プログラム-”、日本** LCA **学会誌、**2009, **Vol. 5**, No. 3, 338-343.
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10) **松本真哉、"ディスプレイ用光学フィルムに求められる高機能・高性能化実現に役割担う機能性色素"、**WEB Journal**、**2007, **85**, 15-19.
11) **松本真哉(分担)、"携帯電話から環境問題を考える"、**in **環境教育 -基礎と実践-、横浜国立大学教育人間科学部環境教育研究会編、**2007**、共立出版、**151-153
12) **堀口-馬場本絵未、松本真哉、松居正樹、“非平面型ジシアノジアゼピン蛍光色素の合成と物性”、色材協会誌**, **79(12)**, 545-554(2006).
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・卒業生の進路

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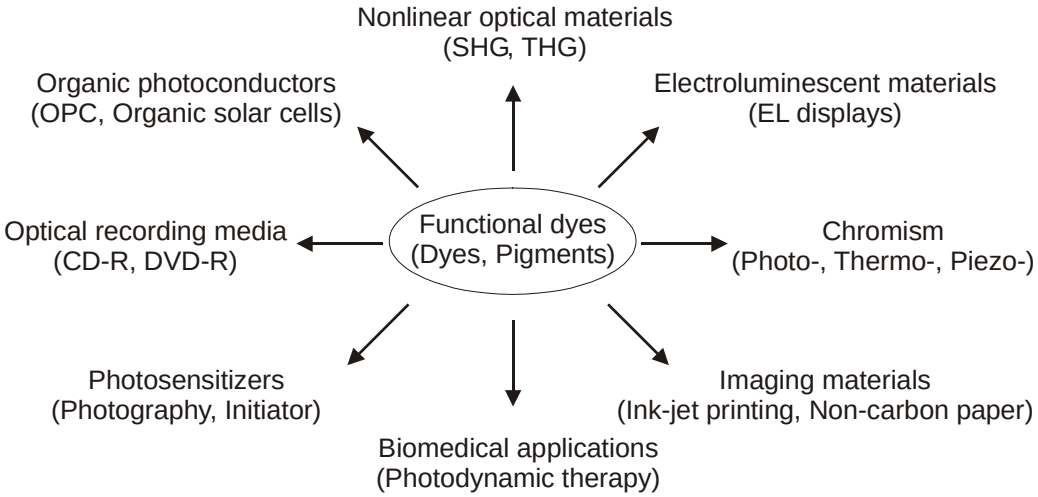
Department of Environment and Natural Sciences
Graduate School of Environment and Information Sciences
Yokohama National University
Matsumoto Lab.

Functional Dye Laboratory

Research area

Our major research topic is the elucidation of the relationship among the crystal structure, intermolecular interactions and solid-state optical and/or opto-electronical properties of functional dyes.

Recent remarkable developments in electronic technologies have opened up the novel applications of colorants (dyes and pigments) shown in the following figure. The name “functional dye” was given to dyes and pigments used in these new applications.



Many attempts to design the molecular structure of functional dyes using molecular orbital calculations have been successfully achieved in order to improve the characteristics of organic dyes or to create new functionalities of organic dyes. However, in the case of functional dyes used in the solid state, for example, for organic-photoconductors, electroluminescent devices and solid-state organic solar cells, we have many issues to be addressed with respect to the molecular design since the electronic states in the solid state are strongly influenced by unpredictable intermolecular interactions. The understanding of the relationship described above has been of great importance for the improvement of the solid-state properties of functional dyes as well as the design of organic dye solids.

Our final goal is to establish the strategy of molecular design of functional dyes for solid-state applications. The followings are our recent research projects.

Students from other countries are welcome to join our group!!

Research Projects

a) Study on structure-properties (optical, electronic etc.) relationship of vapor-deposited dye films.

b) Study on the electronic states of crystal polymorphs of dicyanopyrazine fluorescent dyes.

>>see example>>

c) Study on the relationship between molecular structure and isostructurality in a series of pyrazine dyes.

d) Crystal engineering of new bisazomethine dyes towards solid J-aggregates.

・Member

Professor

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Posdoc researcher

Saori SATO-GONTANI, Dr. Eng

Graduate student

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D2: Hyung-wook YU, Yoko AKUNE

D1: In-Sub SHIN, Hatsuna TADAKA, Jae-Young LEE

M2: Takuma SAKATA

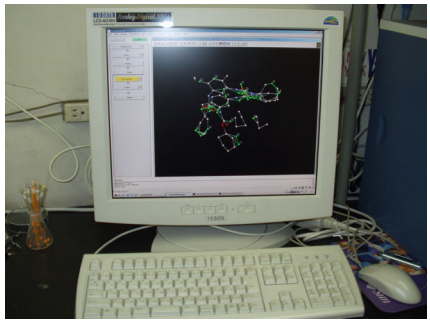
M1: Tetsuya UEHARA, Tatsuya OHASHI, Risa HIROSAWA, Takeru FUJISHIMA

Under graduate

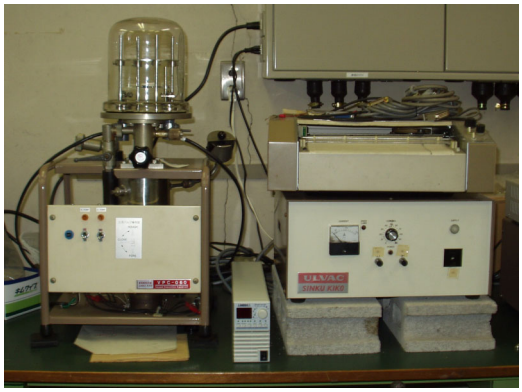
B4: Kazuya INOUE, Natsuko Endo, Takaya MINAMI

・Experimetal Equipments

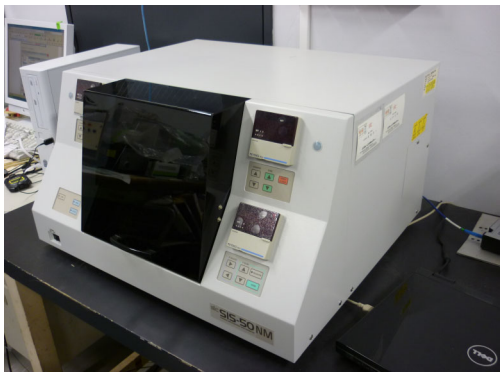
X-ray Diffractometer (Rigaku RAXIS-Rapid-F)



Vacuum Deposition Equipment (Ulvac VPC-060 and VPC-200 with a cooling unit)



Optical Waveguide Spectrophotometer



・List of Recent Publications (from 2001)

1) N. Okada, R. Eto, E. Horiguchi-Babamoto, T. Kobayashi, H. Naito, M. Shiro, H. Takahashi, S. Matsumoto, “Optical properties of three differently colored crystal modifications of a

2,3-dicyanopyrazine dye", Bulletin of the Chemical Society of Japan, 2015, 88, 716-721.

2) T. Tanaka, M. Ishitobi, T. Aoyama, S. Matsumoto, "End group effect on aggregation in oriented bisazomethine dye films on aligned poly(tetrafluoroethylene) layers", Chemistry Letters, 2015, 44, 462-464.
3) J. C. Ribierre, L. Zhao, S. Furukawa, T. Kikitsu, D. Inoue, A. Muranaka, K. Takaishi, T. Muto, S. Matsumoto, D. Hashizume, M. Uchiyama, P. André, C. Adachi, T. Aoyama, "Ambipolar organic field-effect transistors based on solution-processed single crystal microwires of a quinoidal oligothiophene derivative", Chemical Communications, 2015, 51, 5836-5839.
4) J. C. Ribierre, Y. Yokota, M. Satoh, A. Ishizuka, T. Tanaka, S. Watanabe, M. Matsumoto, A. Muranaka, S. Matsumoto, M. Uchiyama, T. Aoyama, "Influence of the Grain Orientation on the Charge Transport Properties of Organic Field-effect Transistors", RSC Advances, 2014, 4, 36729-36737.
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10) J. Chiba, W. Shirato, Y. Yamade, B.-S. Kim, S. Matsumoto, and M. Inouye, "Furanose ring conformations in a 1'-alkynyl C-nucleoside and the dinucleotide", Tetrahedron, 2012, 68, 9045-9049.
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12) J. C. Ribierre, M. Satoh, A. Ishizuka, T. Tanaka, S. Watanabe, M. Matsumoto, S. Matsumoto, M. Uchiyama and T. Aoyama, "Organic Field-Effect Transistors Based on J-aggregate Thin Films of a Bisazomethine Dye", Organic Electronics, 2012, 13(6), 999-1003.

13) B.-S. Kim, S. Matsumoto and Y.-A, Son, "Crystal structure of (2Z)-2-amino-3-[(E)-4-(diethylamino)-2-methoxybenzylideneamino]-2-butenedinitrile, C16H19N5O", Zeitschrift fuer Kristallographie -New Crystal Structure-, 2012, 227, 19-20.
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15) T. Tanaka, M. Satoh, M. Ishitobi, T. Aoyama and S. Matsumoto, "Highly Dichroic Bisazomethine Dye Films on Friction-transferred Poly(tetrafluoroethylene) Layers", Chemistry Letters, 2011, 40(10), 1170-1172.
16) K. Kinashi, K.-P. Lee, S. Matsumoto, K. Ishida, Y. Ueda, "Alkyl substituent effects on J- or H-aggregate formation of bisazomethine dye", Dyes and Pigments, 2011, 92, 783-788.
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19) T. Tanaka, T. Ashida and S. Matsumoto, " Highly Dichroic and Luminescent Triphenodioxazine Dyes ", Chemistry Letters, 2011, 40(6), 573-575.
20) B.-S. Kim, S.-H. Kim, S. Matsumoto and Y.-A, Son, " Crystal Structure of 2-[4-(9H-carbazol-9-yl)benzylidene]- -2,3-dihydroinden-1-one, C28H19NO ", Zeitschrift fuer Kristallographie -New Crystal Structure-, 2011, 226, 177-178.
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25) K. Kurumada, Y. Kaminuma and S. Matsumoto, "Entrapment of organic liquid species in molecular scale in sol-gel derived silica glass matrix", Advanced Powder Technology, 2010, **21**, 23–27.

26) S. Matsumoto, S. Takeshima, S. Sato and K. Kabashima, “Crystal structure of two new developers for high-performance thermo-sensitive paper - Hydrogen-bond network in urea-urethane derivatives -”, Dyes and Pigments, 2010, **85**, 139-142.
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