

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

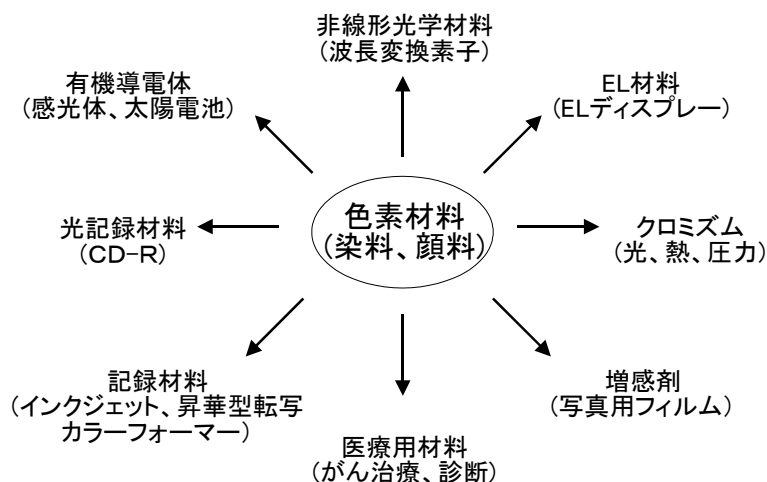
(大学院 環境情報学府 人工環境専攻)

・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きている。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幅広い範囲に広がるのに伴い、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

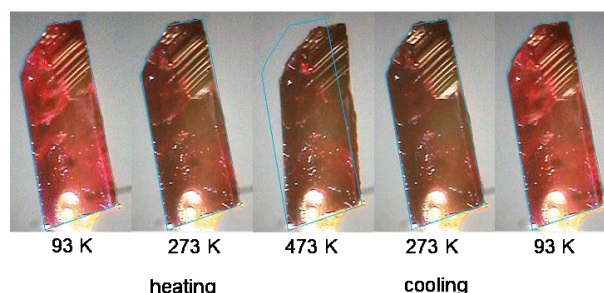
開発においては、試行錯誤的な手法や、極端な場合偶然に頼っているのが実情である。分子の状態と結晶などの集合体の状態を踏まえて色素材料を開発するためには、次の二つの点について考える必要がある。一つ目は、分子が集合してできる結晶における、分子構造と結晶構造の関連性である。この点については、多くの結晶学の研究者により、結晶構造予測の研究が活発に進められている。二つ目は、結晶状態での分子間相互作用についてである。結晶における分子配列とその電子状態については、特異な吸収バンドを示す J 会合体のように、固体構造と電子構造の関連性について比較的詳細に検討されている例もあるが、色素全体を見渡した場合、まだ十分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り組んでいる。



結晶①_2

- 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) **ビスアゾメチン色素の結晶構造制御や結晶の動的挙動 >> 例 >>**

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り組み始めた。



- 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

教員: 松本真哉 (教授)

>>>>

博士研究員: 権谷(佐藤)佐織、神藤拓実

院生(後期課程): 田高初奈 (4 年)、Lee Jae-Young (4 年)、Hwang Ji-Yong(3 年)、So Hee-Soo (3 年)、大嶋織江(2 年)

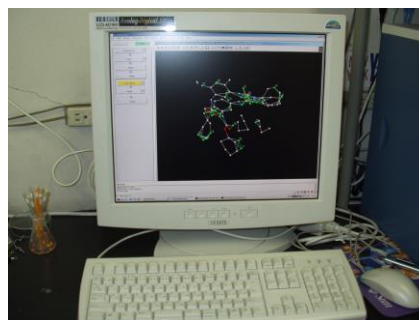


院生(前期課程): 大角茂登 (2 年)、川口純奈 (2 年)、菊地拓哉 (2 年)、岸優子 (2 年)

学部生: 大伴陽生 (4年)、菊池悠介 (4年)、袴田小春 (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 (2011 年以降)

研究論文

- 1) T. Minami, H. Sato, S. Matsumoto, Macroscopic Crystalline Deformation in an Organic Dye during Reversible Phase Transition Caused by Alkyl Disorder, *CrystEngComm*, 2018, **20**, 2644-2647 DOI: 10.1039/C8CE00465J (selected as the back cover figure)
- 2) I.-S. Shin, Y. Shimada, E. Horiguchi-Babamoto, S. Matsumoto, Two polymorphs of 2,5-bis(dibenzylamino)-3,6-dichloro-p-hydroquinone with flexible dibenzylamino groups, *Acta Crystallographica*, 2018, **C74**, 437-441.
- 3) H. Abe, D. Hashikawa, T. Minami, K. Ohtani, K. Masuda, S. Matsumoto, M. Inouye, Hexaphenolic Rigid Cages Prepared by Self-Organization of C_{3v} Tridentates, *The Journal of Organic Chemistry*, 2018, **83**, 3132-3141 DOI: 10.1021/acs.joc.7b03111.
- 4) J.-C. Ribierre, T. Tanaka, L. Zhao, Y. Yokota, S. Matsumoto, D. Hashizume, K. Takaishi, T. Muto, B. Heinrich, S. Méry, F. Mathevet, T. Matsushima, M. Uchiyama, C. Adachi, T. Aoyama, Simultaneous edge-on to face-on reorientation and 1D alignment of small π -conjugated molecules using room temperature rubbing, *Advanced Functional Materials*, 2018, 1707038-1-12.
- 5) D. Suzuki, H. Abe, T. Minami, S. Matsumoto, M. Inouye, Preparation and higher-order structures of a 2,6-pyridylene and 2,6-pyrazylene alternating macrocycle with the inner nitrogen atoms in all the aromatic rings, *Chemistry Letters*, 2017, **46**, 1740-1742
- 6) R. Hirose, Y. Akune, N. Endo, S. Hatano, T. Hosokai, H. Sato, S. Matsumoto, A variety of solid-state fluorescence properties of pyrazine dyes depending on terminal substituent, *Dyes and Pigments*, 2017, **146**, 576-581.
- 7) 田高初奈, 平山世志衣, 高岡由紀子, 津田祥子, 水野建樹, 松本真哉, ライフサイクル思考を取り入れた環境教育が環境配慮意識及び行動に与える影響, *日本 LCA 学会誌*, 2017, **13(4)**, 349-359.
- 8) I.-S. Shin, Y. Shimada, S. Ishihara, E. Horiguchi-Babamoto, S. Matsumoto, Photo-Induced debenzoylation of 2,5-bis(dibenzylamino)-3,6-dichloro-p-benzoquinone, *Dyes and Pigments*, 2017, **144**, 110-118.
- 9) T. Ohashi, S. Gontani, K. Miyanaga, T. Kurata, Y. Akatani, S. Matsumoto, A novel black crystalline composite based on a fluoran dye and a bisphenol S derivative for high performance thermal papers, *Dyes and Pigments*, 2017, **142**, 198-200.
- 10) Y. Akune, R. Hirose, A. Koseki, S. Matsumoto, Role of halogen substituents in a series of polymorphic 2,5-diamino-3,6-dicyanopyrazine derivatives with highly flexible groups, *Zeitschrift für Kristallographie*, 2017, **232(5)**, 395-405.
- 11) Y. Akune, R. Hirose, N. Endo, S. Hatano, T. Hosokai, H. Sato, S. Matsumoto, Tuning of fluorescence efficiency via local modification of the crystal structure by benzyl groups in polymorphs of a pyrazine dye, *CrystEngComm*, 2017, **19**, 1947-1952.
- 12) S. Gontani, T. Ohashi, K. Miyanaga, T. Kurata, Y. Akatani, S. Matsumoto, Structural comparison of two Bisphenol S derivatives used as a color developer in high performance thermal paper, *Dyes and Pigments*, 2017, **139**, 549-555.
- 13) H.-W. Yu, B.-S. Kim, S. Matsumoto, Effect of alkoxy side chain length on the solid-state fluorescence behaviour of bisazomethine dyes possessing a dipropylamino terminal group, *Dyes and Pigments*, 2017, **136**, 131-139.

- 14) H.-W. Yu, B.-S. Kim, S. Matsumoto, Red to near-infrared fluorescence in the solid-state of alkoxy-substituted bisazomethine dyes possessing a dibutylamino terminal group, *Journal of the Japan Society of Colour Material(色材協会誌)*, 2016, **89(11)**, 380-388.
- 15) T. Jindo, B.-S. Kim, Y. Akune, E. Horiguchi-Babamoto, K.-P. Lee, K. Kinashi, Y. Ueda, S. Matsumoto, "Effects of terminal alkyl substituents on the low-dimensional arrangement of π -stacked molecules in the crystal structures of five bisazomethine dyes", *Zeitschrift für Kristallographie*, , 2016, **231(8)**, 487-498.
- 16) Y. Akune, R. Hirose, H. Takahashi, M. Shiro, S. Matsumoto, "Role of flexible bulky groups and weak interactions involving halogens in the vapoluminescence of a metal-free dye", *RSC Advances*, 2016, **6**, 74506 - 74509.
- 17) T. Tanaka, M. Ishitobi, T. Aoyama, S. Matsumoto, "Highly Oriented J-Aggregates of Nitroazo Dye and Remarkable Surface-Induced Chromism", *Langmuir*, 2016, **32**, 4710-4718
- 18) M. Inouye, A. Yoshizawa, M. Shibata, Y. Yonenaga, K. Fujimoto, T. Sakata, S. Matsumoto, M. Shiro, "Bulletproof Glass-Isolated Alkynylpyrenes as Extremely UV-Stable and Intensely Blue-Light-Emitting Molecules even in Condensed States", *Organic Letters*, 2016, **18**, 1960-1963
- 19) 中谷隼、田原聖隆、田中浩二、松本真哉、水野建樹、"選択型コンジョイント分析を用いた電力供給ビジョンに対する市民の選好評価"、*土木学会論文集 G(環境)* **71 (6)**, *環境システム研究論文集* 43, 2015, pp. 125-131.
- 20) 中原康敬、成田明沙美、松本真哉、中村栄子、"理科の学習に活用できるライフサイクル思考を取り入れた環境教育用教材の開発"、*LCA 学会誌*, 2015, **11(4)**, 359-365.
- 21) T. Jindo, B.-S. Kim, N. Sasaki, Y. Shinohara, Y.-A. Son, S.-H. Kim, S. Matsumoto, "The effect of terminal dimethyl and diethyl substituents on the J-aggregate-like molecular arrangements of bisazomethine dye molecules", *CrystEngComm*, 2015, **17**, 7213-7226.
- 22) Y. Akune, H. Gontani, R. Hirose, A. Koseki, S. Matsumoto, "The effects of molecular flexibility and substituents on conformational polymorphism in a series of 2,5-diamino-3,6-dicyanopyrazine dyes with highly flexible groups", *CrystEngComm*, 2015, **17**, 5789-5800.
- 23) H.-W. Yu, J.-Y. Lee, S. Angupillai, S. Wang, S. Feng, S. Matsumoto, Y.-A. Son, "A new dual fluorogenic and chromogenic "turn-on" chemosensor for Cu²⁺/F⁻ ions", *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2015, **151**, 48-55.
- 24) Y. Shimada, E. Horiguchi-Babamoto, S. Matsumoto, "Unexpected photochemical debenzoylation of 2,5-bis(dibenzylamino)-3,6-dichloro-p-benzoquinone", *Dyes and Pigments*, 2015, **121**, 336-341.
- 25) 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**, 716-72.
- 26) 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.
- 27) 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", *Chem. Commun.*, 2015, **51**, 5836-5839.
- 28) 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.
- 29) K. Kurumada, K. M. Ashraf, and S. Matsumoto, "Effects of heat treatment on various properties of organic-inorganic hybrid silica derived from phenyltriethoxysilane", Materials Chemistry and Physics, 2014, **144**, 132-138.
- 30) H. Abe, K. Ohtani, D. Suzuki, Y. Chida, Y. Shimada, S. Matsumoto, and M. Inouye, "Dipole-Driven Preparation of Alternating 2,6-/3,5-Substituted Pyridine-Acetylene Macrocycles and their Dipole-Driven π -Stacked Self-Assembled Structures", Organic Letters, 2014, **16**, 828-831.
- 31) X. Li, I. Y. Li, J. Zhang, Y.-A. Son, Y. Shimada, and S. Matsumoto, "Crystal structure of 2,3-bis(2,4-dimethylthiazole-3-yl)thiophene, C₁₄H₁₄N₂S₃", Zeitschrift fuer Kristallographie -New Crystal Structure-, 2013, **228**, 95-96.
- 32) 赤坂径高, 中原康敬, 田高初奈, 松本真哉, ライフサイクルの観点から水の利用を考える環境教育プログラムの開発、日本 LCA 学会誌, 2013, **9(1)**, 37-44.
- 33) T. Tanaka, M. Ishitobi, and S. Matsumoto, "Oriented Pyrazine Dye Films on Aligned Poly(tetrafluoroethylene) Layers", Chemistry Letters, 2013, **42(1)**, 34-36.
- 34) K. M. Ashraf, S. Matsumoto, and K. Kurumada, "Determination of heat-treatment temperature for completing the polycondensation of vinyl-substituted silica particles prepared by sol-gel method", Chemical Engineering & Technology, 2012, **35(12)**, 2155-2160.
- 35) 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.
- 36) S. Matsumoto, E. Horiguchi-Babamoto, R. Eto, S. Sato, T. Kobayashi, H. Naito, M. Shiro and H. Takahashi, "J-aggregate structure in a chloroform solvate of a 2,3-dicyanopyrazine dye", Dyes and Pigments, 2012, **95**, 431-435.
- 37) 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.
- 38) 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.
- 39) T. Tanaka, S. Matsumoto, T. Kobayashi, M. Sato, and T. Aoyama, "Highly Oriented J-aggregates of Bisazomethine Dye on Aligned Poly(tetrafluoroethylene) Surfaces", J. Phys. Chem. C, 2011, **115**, 19598-19605.
- 40) 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.
- 41) 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.
- 42) B.-S. Kim, T. Jindo, R. Eto, Y. Shinohara, Y.-A. Son, S.-H. Kim and S. Matsumoto, "Effects of alkoxy substitution on crystal structure of 2,3-bis[(E)-4-(diethylamino)-2-alkoxybenzylideneamino]fumaronitrile derivatives", CrystEngComm 2011, **13**, 5374-5383, selected as a hot article.

- 43) B.-S. Kim, S. Matsumoto and Y.-A. Son, "Crystal Structure of Crystal structure of (Z)-2-amino-3-[(E)-4-(dimethylamino)-2-ethoxybenzylideneamino]-2-butenedinitrile, C₁₅H₁₇N₅O", Zeitschrift fuer Kristallographie -New Crystal Structure-, 2011, **226**, 385-386.
- 44) T. Tanaka, T. Ashida and S. Matsumoto, " Highly Dichroic and Luminescent Triphenodioxazine Dyes ", Chemistry Letters, 2011, **40(6)**, 573-575.
- 45) 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.
- 46) D. Takaki, T. Okayama, H. Shuto, Y. Yamaguchi and S. Matsumoto, " Indenyl-Functionalized Triethylborane Adduct of N-Heterocyclic Carbene: Stepwise Coordination of Indenyl and NHC Ligands toward Molybdenum Fragment ", Dalton Trans., 2011, **40(7)**, 1445-1447.
- 47) B.-S. Kim, D. Kashibuchi, Y.-A. Son, S.-H. Kim and S. Matsumoto, " Effect of phenyl ring substitution on J-aggregate formation ability of novel bisazomethine dyes in vapour-deposited films ", Dyes and Pigments, 2011, **90**, 56-64.

解説、書籍など

- 1) 松本真哉、"機能性色素の基礎講座 14"、加工技術、2018, Vol. 53(No.3), 143-148
- 2) 松本真哉、"機能性色素の基礎講座 13"、加工技術、2017, Vol. 52(No.11), 555-559
- 3) 松本真哉、"機能性色素の基礎講座 12"、加工技術、2017, Vol. 52(No.8), 414-420
- 4) 松本真哉、"機能性色素の基礎講座 11"、加工技術、2017, Vol. 52(No.7), 366-370
- 5) 松本真哉、"機能性色素の基礎講座 10"、加工技術、2017, Vol. 52(No.5), 250-256
- 6) 松本真哉、"機能性色素の基礎講座 9"、加工技術、2017, Vol. 52(No.3), 147-151.
- 7) 松本真哉、"機能性色素の基礎講座 8"、加工技術、2017, Vol. 52(No.2), 96-100
- 8) 松本真哉、"機能性色素の基礎講座 7"、加工技術、2016, Vol. 51(No.12), 654-658.
- 9) 松本真哉、"機能性色素の基礎講座 6"、加工技術、2016, Vol. 51(No.9), 489-494.
- 10) 松本真哉、"機能性色素の基礎講座 5"、加工技術、2016, Vol. 51(No.5), 276-280.
- 11) 松本真哉、"機能性色素の基礎講座 4"、加工技術、2016, Vol. 51(No.4), 209-214.
- 12) 松本真哉、"機能性色素の基礎講座 3"、加工技術、2016, Vol. 51(No.3), 150-152.
- 13) 松本真哉(分担)、"機能性色素の構造・物性の評価と設計"、in 機能性色素の新規合成・実用化動向、CMC 出版、2016、12-22
- 14) 松本真哉、"機能性色素の基礎講座 2"、加工技術、2015, Vol. 50(No.12), 696-701.
- 15) 松本真哉、"機能性色素の基礎講座 1"、加工技術、2015, Vol. 50(No.10), 519-523.
- 16) 権谷(佐藤)佐織、松本真哉、"感熱記録用顕色剤の研究動向"、色材協会誌、2015, **88(11)**, 378-382.
- 17) 青山哲也、松本真哉、田島右副、Jean-Charles Ribierre、"有機トランジスタおよび有機発光材料における分子パッキング制御"、色材協会誌、2015, **88(10)**, 348-352.
- 18) 松本真哉、"もっと環境コミュニケーションを"、エコマテリアルマガジン、2015、**Vol. 8**, No. 1, 2-3.
- 19) 松本真哉(分担)、"色素結晶の色に影響する分子間相互作用"、in 日本の結晶学(Ⅱ) -その輝かしい発展-、2014、日本結晶学会、212-213

・卒業生の進路

・学部卒: 本学大学院環境情報学府、富山医科薬科大学大学院薬学研究科、株式会社リコー、東日本電信電話株式会社、富士電機システムズ株式会社、三菱電機株式会社、中学校教員(理科)など

・修士卒: 千葉大学大学院自然科学研究科博士課程、本学大学院環境情報学府博士課程、セイコーインスツル株式会社、TDK 株式会社、東洋インキ製造株式会社、イビデン株式会社、関西ペイント株式会社、凸版印刷株式会社、塩野義製薬株式会社、日本電子計算株式会社、大塚製薬株式会社、コニカミノルタ株式会社、太陽誘電株式会社、DIC 株式会社、地方公務員、中学校教員(理科)、株式会社竹中工務店、日本電気硝子、日本パーカライジング、島津製作所、ジェイテクト、東洋ゴム工業株式会社、日産化学工業株式会社、ヤマハ株式会社、ニチアス株式会社、明成化学工業株式会社、アサヒインテック株式会社、積水化学株式会社、東洋エンジニアリング株式会社など

・連絡先

住所: 〒240-8501 横浜市保土ヶ谷区常盤台 79-7

電話/FAX: 045-339-3366/3345

E-mail: matsumoto-shinya-py@ynu.ac.jp

・共同研究先など

- ・理化学研究所 先進機能元素化学研究チーム
(http://www.riken.jp/genso_kagaku/index.html)
- ・大阪府立大学工学部電子物理工学科 内藤研究室
(<http://www.pe.osakafu-u.ac.jp/pe3/pe3.html>)
- ・岐阜大学工学部機能材料工学科 松居研究室
(<http://mast.gifu-u.ac.jp/~ms1/>)
- ・富山大学薬学部 薬化学研究室
(<http://www.toyama-u.ac.jp/ph/yakka/index-j.html>)
- ・Prof. Sung-Hoon Kim, Department of Textile System Engineering, Kyungpook National University, (<http://dyeing.knu.ac.kr/>)
- ・Prof. Young-A Son, Department of Organic Materials and Textile System Engineering, Chungnam National University, (<http://textile.cnu.ac.kr/>)
- ・Prof. Jekaterina Erenpreisa, Biomedical Research and Study Centre, Latvia, (<http://www.lza.lv/scientists/ERENPR.HTM>)

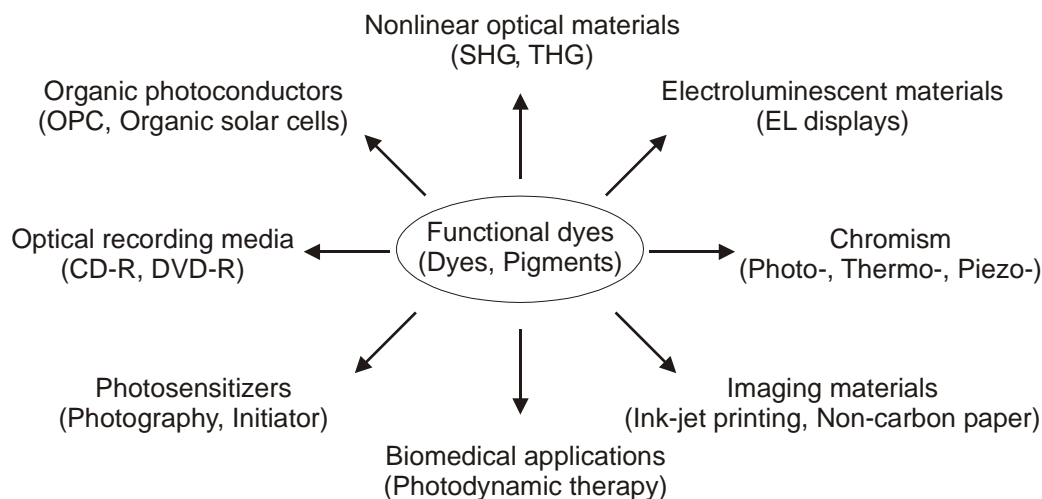
Graduate School of Environment and Information Sciences
Yokohama National University
Matsumoto Lab.

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. >>

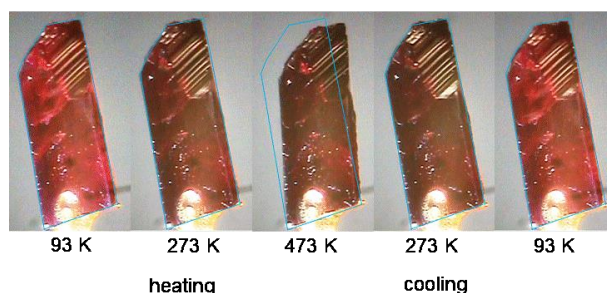
c) Study on the relationship between molecular structure and isostructurality in a series of pyrazine dyes.

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

e) Thermo-dynamical behavior of single crystals of a bisazomethine dye. >>



結晶①_2



Member

Professor
Shinya MATSUMOTO, Dr.Eng.



Posdoc researcher
Saori SATO-GONTANI, Dr. Eng
Takumi JINDO, Dr. Eng

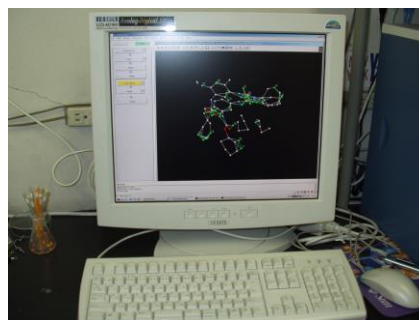
Graduate student
D3: Hatsuna TADAKA, Jae-Young LEE, Ji-Yong HWANG, Hee-Soo SO
D2:., Orié Oshima
M2: Shigeto OSUMI, Jyun-na KAWAGUCHI, Takuya KIKUCHI, Yuko KISHI

Under graduate

B4: Yousei OHTOMO, Yusuke KIKUCHI, Koharu HAKAMADA

Experimental 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 2011)

- 1) T. Minami, H. Sato, S. Matsumoto, Macroscopic Crystalline Deformation in an Organic Dye during Reversible Phase Transition Caused by Alkyl Disorder, *CrystEngComm*, 2018, 20, 2644-2647 DOI: 10.1039/C8CE00465J (selected as the back cover figure)
- 2) I.-S. Shin, Y. Shimada, E. Horiguchi-Babamoto, S. Matsumoto, Two polymorphs of 2,5-bis(dibenzylamino)-3,6-dichloro-p-hydroquinone with flexible dibenzylamino groups, *Acta Crystallographica*, 2018, C74, 437-441.
- 3) H. Abe, D. Hashikawa, T. Minami, K. Ohtani, K. Masuda, S. Matsumoto, M. Inouye, Hexaphenolic Rigid Cages Prepared by Self-Organization of C_{3v} Tridentates, *The Journal of Organic Chemistry*, 2018, 83, 3132-3141 DOI: 10.1021/acs.joc.7b03111.
- 4) J.-C. Ribierre, T. Tanaka, L. Zhao, Y. Yokota, S. Matsumoto, D. Hashizume, K. Takaishi, T. Muto, B. Heinrich, S. M[?]ry, F. Mathevet, T. Matsushima, M. Uchiyama, C. Adachi, T. Aoyama, Simultaneous edge-on to face-on reorientation and 1D alignment of small -conjugated molecules using room temperature rubbing, *Advanced Functional Materials*, 2018, 1707038-1-12.
- 5) D. Suzuki, H. Abe, T. Minami, S. Matsumoto, M. Inouye, Preparation and higher-order structures of a 2,6-pyridylene and 2,6-pyrazylene alternating macrocycle with the inner nitrogen atoms in all the aromatic rings, *Chemistry Letters*, 2017, 46, 1740-1742
- 6) R. Hirosawa, Y. Akune, N. Endo, S. Hatano, T. Hosokai, H. Sato, S. Matsumoto, A variety of solid-state fluorescence properties of pyrazine dyes depending on terminal substituent, *Dyes and Pigments*, 2017, 146, 576-581.
- 7) 田高初奈, 平山世志衣, 高岡由紀子, 津田祥子, 水野建樹, 松本真哉, ライフサイクル思考を取り入れた環境教育が環境配慮意識及び行動に与える影響, *日本 LCA 学会誌*, 2017, 13(4), 349-359.
- 8) I.-S. Shin, Y. Shimada, S. Ishihara, E. Horiguchi-Babamoto, S. Matsumoto, Photo-Induced debenzylation of 2,5-bis(dibenzylamino)-3,6-dichloro-p-benzoquinone, *Dyes and Pigments*, 2017, 144, 110-118.
- 9) T. Ohashi, S. Gontani, K. Miyanaga, T. Kurata, Y. Akatani, S. Matsumoto, A novel black crystalline composite based on a fluoran dye and a bisphenol S derivative for high performance thermal papers, *Dyes and Pigments*, 2017, 142, 198-200.
- 10) Y. Akune, R. Hirosawa, A. Koseki, S. Matsumoto, Role of halogen substituents in a series of polymorphic 2,5-diamino-3,6-dicyanopyrazine derivatives with highly flexible groups, *Zeitschrift für Kristallographie*, 2017, 232(5), 395-405.
- 11) Y. Akune, R. Hirosawa, N. Endo, S. Hatano, T. Hosokai, H. Sato, S. Matsumoto, Tuning of fluorescence efficiency via local modification of the crystal structure by benzyl groups in polymorphs of a pyrazine dye, *CrystEngComm*, 2017, 19, 1947-1952.
- 12) S. Gontani, T. Ohashi, K. Miyanaga, T. Kurata, Y. Akatani, S. Matsumoto, Structural comparison of two Bisphenol S derivatives used as a color developer in high performance

thermal paper, *Dyes and Pigments*, 2017, 139, 549-555.

- 13) H.-W. Yu, B.-S. Kim, S. Matsumoto, Effect of alkoxy side chain length on the solid-state fluorescence behaviour of bisazomethine dyes possessing a dipropylamino terminal group, *Dyes and Pigments*, 2017, 136, 131-139.
- 14) H.-W. Yu, B.-S. Kim, S. Matsumoto, Red to near-infrared fluorescence in the solid-state of alkoxy-substituted bisazomethine dyes possessing a dibutylamino terminal group, *Journal of the Japan Society of Colour Material(色材協会誌)*, 2016, 89(11), 380-388.
- 15) T. Jindo, B.-S. Kim, Y. Akune, E. Horiguchi-Babamoto, K.-P. Lee, K. Kinashi, Y. Ueda, S. Matsumoto, "Effects of terminal alkyl substituents on the low-dimensional arrangement of π -stacked molecules in the crystal structures of five bisazomethine dyes", *Zeitschrift für Kristallographie*, 2016, 231(8), 487-498.
- 16) Y. Akune, R. Hirosawa, H. Takahashi, M. Shiro, S. Matsumoto, "Role of flexible bulky groups and weak interactions involving halogens in the vapoluminescence of a metal-free dye", *RSC Advances*, 2016, 6, 74506 - 74509.
- 17) T. Tanaka, M. Ishitobi, T. Aoyama, S. Matsumoto, "Highly Oriented J-Aggregates of Nitroazo Dye and Remarkable Surface-Induced Chromism", *Langmuir*, 2016, 32, 4710-4718
- 18) M. Inouye, A. Yoshizawa, M. Shibata, Y. Yonenaga, K. Fujimoto, T. Sakata, S. Matsumoto, M. Shiro, "Bulletproof Glass-Isolated Alkynylpyrenes as Extremely UV-Stable and Intensely Blue-Light-Emitting Molecules even in Condensed States", *Organic Letters*, 2016, 18, 1960-1963
- 19) 中谷隼、田原聖隆、田中浩二、松本真哉、水野建樹、"選択型コンジョイント分析を用いた電力供給ビジョンに対する市民の選好評価"、*土木学会論文集 G(環境)71 (6), 環境システム研究論文集 43*, 2015, pp. 125-131.
- 20) 中原康敬、成田明沙美、松本真哉、中村栄子、"理科の学習に活用できるライフサイクル思考を取り入れた環境教育用教材の開発"、*LCA 学会誌*, 2015, 11(4), 359-365.
- 21) T. Jindo, B.-S. Kim, N. Sasaki, Y. Shinohara, Y.-A Son, S.-H. Kim, S. Matsumoto, "The effect of terminal dimethyl and diethyl substituents on the J-aggregate-like molecular arrangements of bisazomethine dye molecules", *CrystEngComm*, 2015, 17, 7213-7226.
- 22) Y. Akune, H. Gontani, R. Hirosawa, A. Koseki, S. Matsumoto, "The effects of molecular flexibility and substituents on conformational polymorphism in a series of 2,5-diamino-3,6-dicyanopyrazine dyes with highly flexible groups", *CrystEngComm*, 2015, 17, 5789-5800.
- 23) H.-W. Yu, J.-Y. Lee, S. Angupillai, S. Wang, S. Feng, S. Matsumoto, Y.-A Son, "A new dual fluorogenic and chromogenic "turn-on" chemosensor for Cu²⁺/F⁻ ions", *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2015, 151, 48-55.
- 24) Y. Shimada, E. Horiguchi-Babamoto, S. Matsumoto, "Unexpected photochemical debenzoylation of 2,5-bis(dibenzylamino)-3,6-dichloro-p-benzoquinone", *Dyes and Pigments*, 2015, 121, 336-341.

- 25) 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, 716-72.
- 26) 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.
- 27) J. C. Ribierre, L. Zhao, S. Furukawa, T. Kikitsu, D. Inoue, A. Muranaka, K. Takaishi, T. Muto, S. Matsumoto, D. Hashizume, M. Uchiyama, P. Andr?, C. Adachi, T. Aoyama, "Ambipolar organic field-effect transistors based on solution-processed single crystal microwires of a quinoidal oligothiophene derivative", *Chem. Commun.*, 2015, 51, 5836-5839.
- 28) 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.
- 29) K. Kurumada, K. M. Ashraf, and S. Matsumoto, "Effects of heat treatment on various properties of organic-inorganic hybride silica derived from phenyltriethoxysilane", *Materials Chemistry and Physics*, 2014, 144, 132-138.
- 30) H. Abe, K. Ohtani, D. Suzuki, Y. Chida, Y. Shimada, S. Matsumoto, and M. Inouye, "Dipole-Driven Preparation of Alternating 2,6-/3,5-Substituted Pyridine-Acetylene Macrocycles and their Dipole-Driven p-Stacked Self-Assembled Structures", *Organic Letters*, 2014, 16, 828-831.
- 31) X. Li, I. Y. Li, J. Zhang, Y.-A Son, Y. Shimada, and S. Matsumoto, "Crystal structure of 2,3-bis(2,4-dimethylthiazole-3-yl)thiophene, C₁₄H₁₄N₂S₃", *Zeitschrift fuer Kristallographie -New Crystal Structure-*, 2013, 228, 95-96.
- 32) 赤坂径高, 中原康敬, 田高初奈, 松本真哉, ライフサイクルの観点から水の利用を考える環境教育プログラムの開発、*日本 LCA 学会誌*, 2013, 9(1), 37-44.
- 33) T. Tanaka, M. Ishitobi, and S. Matsumoto, " Oriented Pyrazine Dye Films on Aligned Poly(tetrafluoroethylene) Layers", *Chemistry Letters*, 2013, 42(1), 34-36.
- 34) K. M. Ashraf, S. Matsumoto, and K. Kurumada, "Determination of heat-treatment temperature for completing the polycondensation of vinyl-substituted silica particles prepared by sol-gel method", *Chemical Engineering & Technology*, 2012, 35(12), 2155-2160.
- 35) 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.
- 36) S. Matsumoto, E. Horiguchi-Babamoto, R. Eto, S. Sato, T. Kobayashi, H. Naito, M. Shiro and H. Takahashi, "J-aggregate structure in a chloroform solvate of a 2,3-dicyanopyrazine dye", *Dyes and Pigments*, 2012, 95, 431-435.

- 37) 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.
- 38) 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.
- 39) T. Tanaka, S. Matsumoto, T. Kobayashi, M. Sato, and T. Aoyama, "Highly Oriented J-aggregates of Bisazomethine Dye on Aligned Poly(tetrafluoroethylene) Surfaces", *J. Phys. Chem. C*, 2011, 115, 19598-19605.
- 40) 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.
- 41) 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.
- 42) B.-S. Kim, T. Jindo, R. Eto, Y. Shinohara, Y.-A. Son, S.-H. Kim and S. Matsumoto, "Effects of alkoxy substitution on crystal structure of 2,3-bis[(E)-4-(diethylamino)-2-alkoxybenzylideneamino]fumaronitrile derivatives", *CrystEngComm* 2011, 13, 5374-5383, selected as a hot article.
- 43) B.-S. Kim, S. Matsumoto and Y.-A. Son, "Crystal Structure of Crystal structure of (Z)-2-amino-3-[(E)-4-(dimethylamino)-2-ethoxybenzylideneamino]-2-butenedinitrile, C₁₅H₁₇N₅O", *Zeitschrift fuer Kristallographie -New Crystal Structure-*, 2011, 226, 385-386.
- 44) T. Tanaka, T. Ashida and S. Matsumoto, "Highly Dichroic and Luminescent Triphenodioxazine Dyes", *Chemistry Letters*, 2011, 40(6), 573-575.
- 45) 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.
- 46) D. Takaki, T. Okayama, H. Shuto, Y. Yamaguchi and S. Matsumoto, "Indenyl-Functionalized Triethylborane Adduct of N-Heterocyclic Carbene: Stepwise Coordination of Indenyl and NHC Ligands toward Molybdenum Fragment", *Dalton Trans.*, 2011, 40(7), 1445-1447.
- 47) B.-S. Kim, D. Kashibuchi, Y.-A. Son, S.-H. Kim and S. Matsumoto, "Effect of phenyl ring substitution on J-aggregate formation ability of novel bisazomethine dyes in vapour-deposited films", *Dyes and Pigments*, 2011, 90, 56-64.

-Address

79-7, Tokiwadai, Hodogaya-ku, Yokohama 240-8501, JAPAN

Phone/Fax:+81-45-339-3366/3345

E-mail: matsumoto-shinya-py@ynu.ac.jp

-Collaboration

- Dr. Tetsuya Aoyama, Advanced Elements Chemistry Research Team, RIKEN
(http://www.riken.jp/genso_kagaku/index.html)
- Dr. Takashi Kobayashi, Faculty of Engineering, Osaka Prefecture University
(<http://www.pe.osakafu-u.ac.jp/pe3/pe3.html>)
- Prof. Dr. Masaki Matsui, Faculty of Engineering, Gifu University
(<http://mast.gifu-u.ac.jp/~ms1/>)
- Prof. Dr. Masahiko Inoue, Faculty of Pharmaceutical Sciences, University of Toyama
(<http://www.toyama-mpu.ac.jp/ph/yakka/index-j.html>)
- Prof. Dr. Sung-Hoon Kim, Department of Textile System Engineering, Kyungpook National University (<http://dyeing.knu.ac.kr/>)
- Prof. Dr. Young-A Son, Department of Organic Materials and Textile System Engineering, Chungnam National University, (<http://textile.cnu.ac.kr/>)
- Prof. Dr. Jekaterina Erenpreisa, Biomedical Research and Study Centre, Latvia
(<http://www.lza.lv/scientists/ERENPR.HTM>)