Academic Program [Oral A] | 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-：Oral A

Wed. Mar 26, 2025 3:55 PM - 4:45 PM JST | Wed. Mar 26, 2025 6:55 AM - 7:45 AM UTC
[F]2106(2106, Bldg. 2, Area 4 [1F])

[[F]2106-1vn] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Natsumi Fukaya, Tsuneaki Sakurai

Japanese
3:55 PM - 4:05 PM JST | 6:55 AM - 7:05 AM UTC
[[F]2106-1vn-01]
Detection of phosphonic acids and nucleotides using tetraphenylethylene-based diguanidine
○Kotone Yamada[1], Haruka Muroyama[1], Takahiro Kusukawa[1] (1. Kyoto Institute of Technology)

Japanese
4:05 PM - 4:15 PM JST | 7:05 AM - 7:15 AM UTC
[[F]2106-1vn-02]
Strong Emission of AIE-active Molecules Encapsulated by Aromatic Micelles in Water
○Ryuki Kitaura[1], Yuta Kikuchi[1], Lorenzo Catti[1], Michito Yoshizawa[1] (1. Institute of Science Tokyo)

Japanese
4:15 PM - 4:25 PM JST | 7:15 AM - 7:25 AM UTC
[[F]2106-1vn-03]
Aromatic Micelles and Tubes: Strong Emission of Doubly Encapsulated Dyes
○Daito Kidoh[1], Shinji Aoyama[1], Lorenzo Catti[1], Michito Yoshizawa[1] (1. Lab. for Chem. & Life Sci., Science Tokyo)

English
4:25 PM - 4:35 PM JST | 7:25 AM - 7:35 AM UTC
[[F]2106-1vn-04]
Aromatic Micelle-based Oligo(Amino Acid) Clusters with Broad Host Abilities
○Yunhan Ma[1], Lorenzo Catti[1], Tomohisa Sawada[1], Michito Yoshizawa[1] (1. Lab. for Chem. & Life Sci., Tokyo Tech)

English
4:35 PM - 4:45 PM JST | 7:35 AM - 7:45 AM UTC
[[F]2106-1vn-05]
Formation and Host Ability of Aromatic Micelles with Oligo(Amino Acid) Cavities in Water
○Lorenzo Catti[1], Yuta Kikuchi[1], Shinji Aoyama[1], Michito Yoshizawa[1] (1. Institute of Science Tokyo)

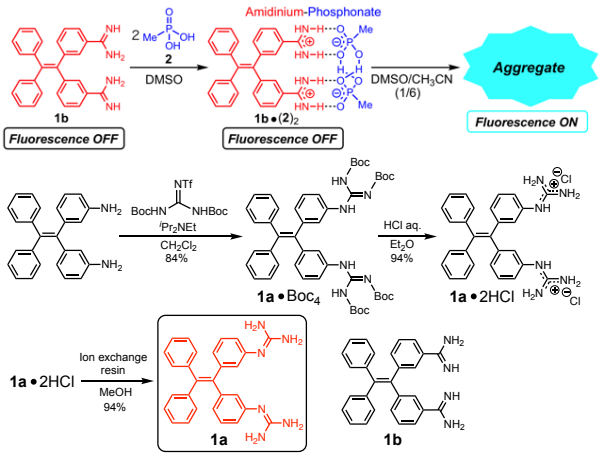
テトラフェニルエチレン骨格を有するジグアニジンによるホスホン酸およびヌクレオチドの検出

（京工繊大・工芸科学）○山田 琴音・室山 遥風・楠川 隆博
Detection of phosphonic acids and nucleotides using tetraphenylethylene-based diguanidine
(Kyoto Institute of Technology) Kotone Yamada, Haruka Muroyama, and Takahiro Kusukawa

Recently, we reported the fluorescence detection of phosphonic acids using tetraphenylethylene-based diamidine **1b** in a DMSO/CH_3CN mixed solution. In this study, we performed fluorescence detection of phosphonic acids and nucleotides using tetraphenylethylene-based diguanidine **1a**, and selective detection of guanosine monophosphate (GMP) was observed.
Keywords: Guanidine; Fluorescence; Phosphonic acid; Nucleotide

当研究室では、テトラフェニルエチレン骨格を有するジアミジン **1b** が DMSO/CH_3CN 混合溶媒中でメチルホスホン酸 **2** と安定な 1：2 会合体を形成し、凝集誘起発光を示すことを明らかにしている。本研究では、テトラフェニルエチレンにグアニジル基が置換したジグアニジン **1a** を合成したところ、**1b** では検出できなかったヌクレオチドの選択的な検出に成功した。

ジグアニジン **1a** は Scheme 1 に従って Goodman 試薬によるグアニジル化、脱 Boc 化、イオン交換樹脂によるフリー化反応を利用して合成した。合成したジグアニジン **1a** に対して二当量のメチルホスホン酸 **2**、フェニルリン酸 **3** および種々のヌクレオチド(GMP, dAMP, CMP, dCMP)を DMSO /CH_3CN 混合溶媒中で混合したところ、グアノシン一リン酸(GMP)の場合にのみ強い蛍光発光が観測され、高い選択性が観測された(**Figure 1**)。発表では他の溶媒条件でのホスホン酸の検出についても併せて報告する予定である。



Scheme 1. Synthetic route of diguanidine **1a** and structure of **1b**•(**2**)$_2$.

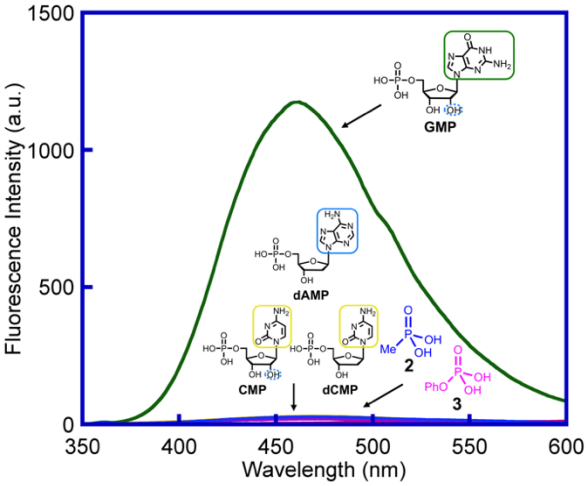


Figure 1. Fluorescence spectra of diguanidine **1a** upon the addition of phosphonic acids and nucleotides ([**1a**] = 50 μM, DMSO/MeCN = 1/1, λ_{ex}= 326 nm).

芳香環ミセルの内包による AIE 性分子の均一水溶液強発光

（東京科学大 化生研）○北浦立樹・菊地悠太・Lorenzo Catti・吉沢道人

Strong Emission of AIE-active Molecules Encapsulated by Aromatic Micelles in Water

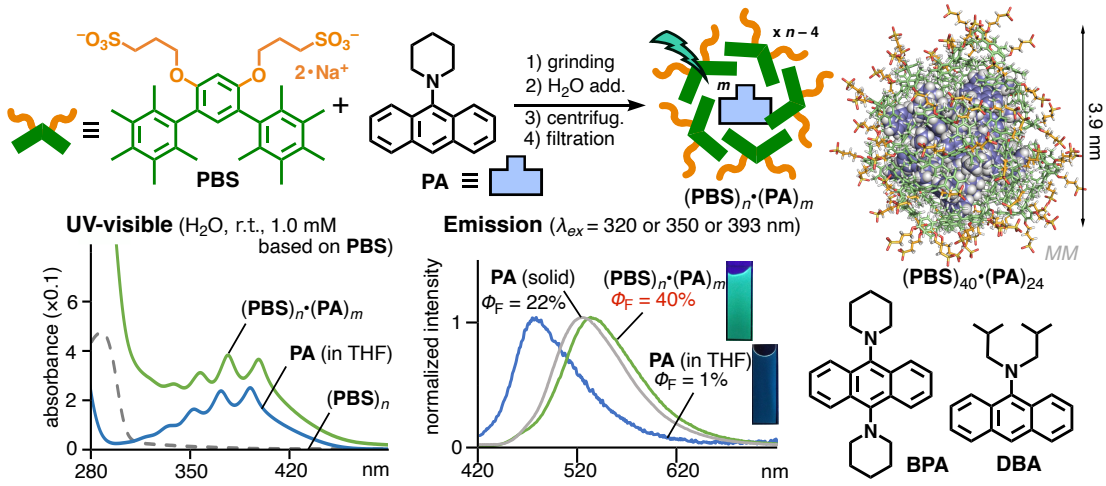
(*Lab. for Chem. & Life Sci., Science Tokyo*) ○Ryuki Kitaura, Yuta Kikuchi, Lorenzo Catti, Michito Yoshizawa

Aggregation-induced emission (AIE)-active molecules exhibit enhanced emission upon aggregation, while showing little to no emission in homogeneous solution states. Here we report strong AIE upon encapsulation of AIE-active dialkylamine-substituted anthracenes by aromatic micelles in homogeneous aqueous solution via a simple grinding protocol. The encapsulation-induced AIE effect for a cyclic alkylamine derivative was stronger than that for a branched one. The observed fluorescence quantum yield reached 40%, unlike that of only the derivative in the solid state (22%). The effects of other substituents on the AIE properties were also clarified.

Keywords: Aromatic micelle, Aggregation-induced emission, Encapsulation, Emission enhancement, Substituent effect

凝集することで強い発光を示す凝集誘起発光（AIE）性分子は、通常均一な溶液中では強い発光を示さない（*Chem. Rev.* **2015**, *115*, 11718-11940）。今回、芳香環ミセル (PBS)$_n$に通常の発光性分子と異なり（*Chem. Sci.* **2015**, *6*, 5059-5062）、AIE 性分子を内包することで、均一水溶液中で強発光を達成したので報告する。

アントラセンにピペリジンが結合した AIE 性分子 PA（G. Konishi *et al.*, *J. Mater. Chem. C* **2015**, *3*, 5940-5950）は PBS とのすり潰しと水の添加で水溶化できた（下図上）。内包体(PBS)$_n$･(PA)$_m$の構造は、UV-visible、DLS、NMR および分子モデリングで決定した。注目すべきことに、(PBS)$_n$･(PA)$_m$の蛍光量子収率は 40%で、有機溶媒中の PA と比べ 40 倍に、固体状態の PA と比べて 1.8 倍に向上した（下図中央）。さらに、２つのピペリジンを有する BPA とジイソブチルアミンを有する DBA から、それぞれ内包体を作成し、均一水溶液中の内包誘起 AIE に対する置換基効果を明らかにした（下図右）。



芳香環ミセルとチューブ：二重内包による色素分子の強発光

（東京科学大 化生研）○木藤大翔・青山慎治・Lorenzo Catti・吉沢道人

Aromatic Micelles and Tubes: Strong Emission of Doubly Encapsulated Dyes

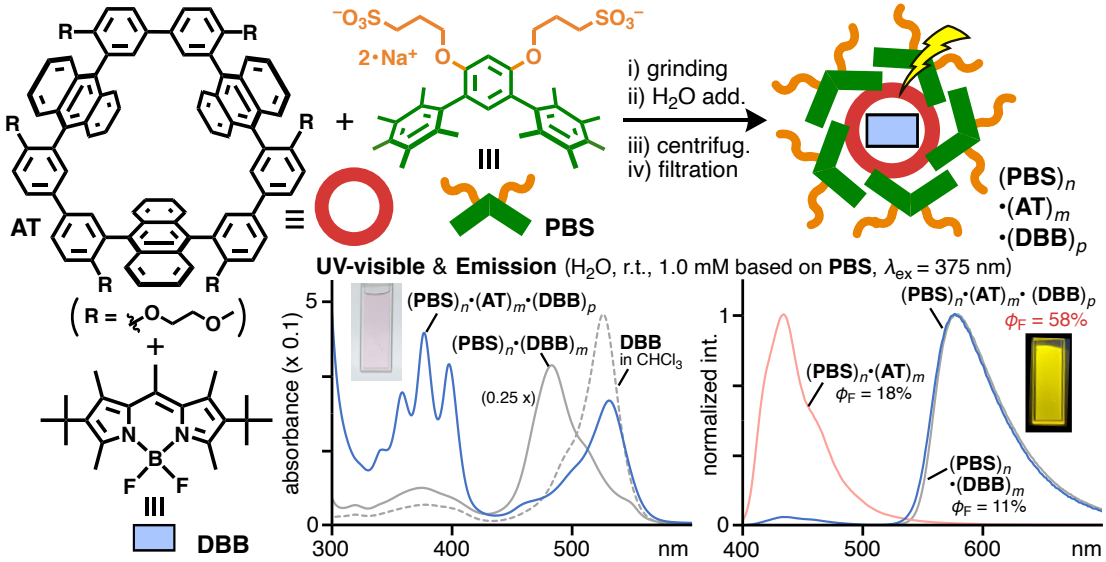
(*Lab. for Chem. & Life Sci., Science Tokyo*) ○Daito Kidoh, Shinji Aoyama, Lorenzo Catti, Michito Yoshizawa

Here we report new host functions via the hybridization of an aromatic micelle, formed from bent aromatic amphiphiles in water, and an aromatic tube, providing covalently linked three aromatic panels. The aromatic tubes and BODIPY derivatives are efficiently co-encapsulated by the aromatic micelle in water using a grinding protocol. The resultant hybrid host-guest composite shows new absorption bands derived from the three components and a strong emission band at 577 nm, derived from the BODIPY derivative, with a quantum yield of ~60%.

Keywords: Aromatic micelle, Aromatic tube, Hybrid, Double encapsulation, Strong emission

V型両親媒性分子 **PBS** からなる芳香環ミセルは水中で、複数の色素分子を内包できるがその発光性は凝集で低下する（*Chem. Sci.* **2015**, *6,* 5059）。共有結合性の芳香環チューブ **AT** は固体状態でのみ、色素を単分子内包して、強発光できる（*Chem. Asian J.* **2018**, *13,* 515）。今回、芳香環ミセルとチューブのハイブリッド化によって、新たなホスト能を開拓したので報告する。

AT と **PBS** と **DBB** のすり潰し法により、芳香環ミセルで芳香環チューブとBODIPY 誘導体を捕捉した二重内包体(**PBS**)$_n$·(**AT**)$_m$·(**DBB**)$_p$ が水中で効率良く生成することを、UV-visible スペクトルと DLS 測定で確認した（下図）。得られた桃色溶液の発光スペクトルでは、(**PBS**)$_n$·(**AT**)$_m$ の発光と異なり、577 nm に内包された **DBB** に由来する黄色強発光を観測した。その蛍光量子収率（Φ_F）は 58%で、(**PBS**)$_n$·(**DBB**)$_p$の約６倍、有機溶媒中の **DBB** と同等であった。以上のように、水中でのハイブリッドホストによる孤立化で、色素分子からの強発光を達成した。



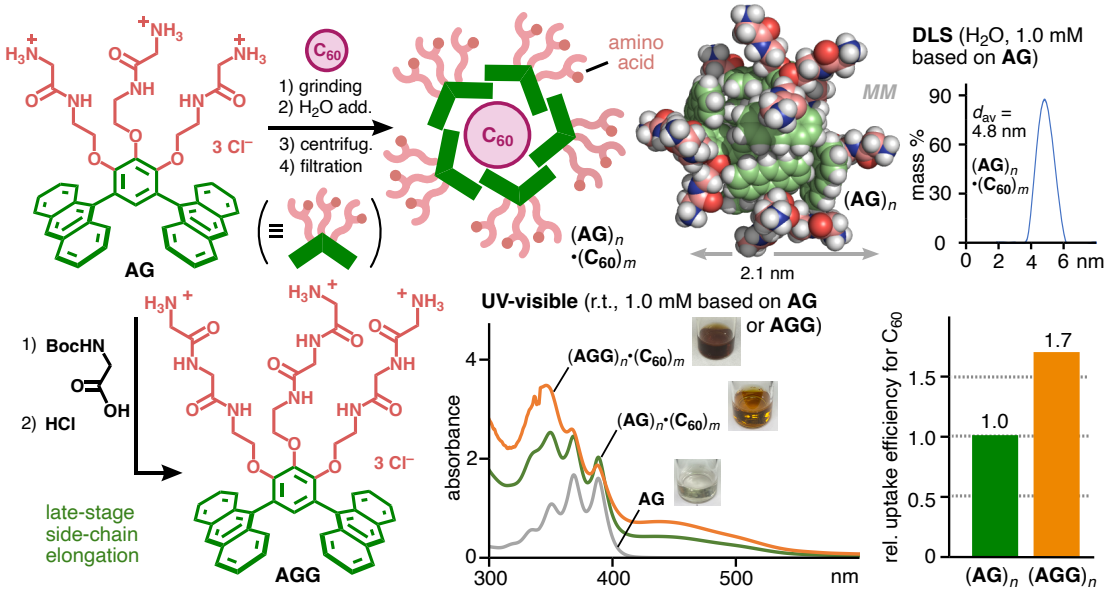
Aromatic Micelle-based Oligo(Amino Acid) Clusters with Broad Host Abilities

(*Lab. for Chem. & Life Sci., Science Tokyo*) Yunhan Ma, Lorenzo Catti, Tomohisa Sawada, Michito Yoshizawa

Keywords: Aromatic Micelle; Oligo(Amino Acid) Cluster; Encapsulation; Dye; Nanocarbon

Artificial peptide clusters have been developed inspired by sophisticated natural protein structures and functions. However, the majority of the clusters provide no or limited host functions.[1,2] To develop functional oligo(amino acid) clusters, here we report the synthesis and assembly of new bent bisanthracene amphiphiles,[3] featuring short hydrophilic oligo(amino acid)-based side-chains, and demonstrate their efficient uptake abilities toward hydrophobic dyes and nanocarbons in the cavities.

Bent amphiphile **AG** with three glycine-based side-chains is synthesized in 7 steps starting from 1,2,3-trimethoxybenzene (Figure top left). In water, amphiphile **AG** spontaneously assembles into aromatic micelle $(\mathbf{AG})_n$ in a quantitative fashion. The formation of small multi-glycine-coated clusters with ~2 nm average core diameter is indicated by NMR and DLS analyses. The resultant clusters display efficient host abilities toward dyes and nanocarbons (e.g., dye DCM and fullerene C_{60}) in water (Figure right). Unlike previous peptide-based amphiphiles, the late-stage elongation of the side-chains is achieved via simple peptide coupling to give glycylglycine-based amphiphile **AGG** and its aromatic micelle $(\mathbf{AGG})_n$ (Figure bottom left).



[1] M. Fujita *et al.*, *Chem. Sci.* **2010**, *1*, 68–71. [2] S. I. Stupp *et al.*, *J. Am. Chem. Soc.* **2014**, *136*, 12461–12468. [3] M. Yoshizawa, L. Catti, *Acc. Chem. Res.* **2019**, *52*, 2392–2404.

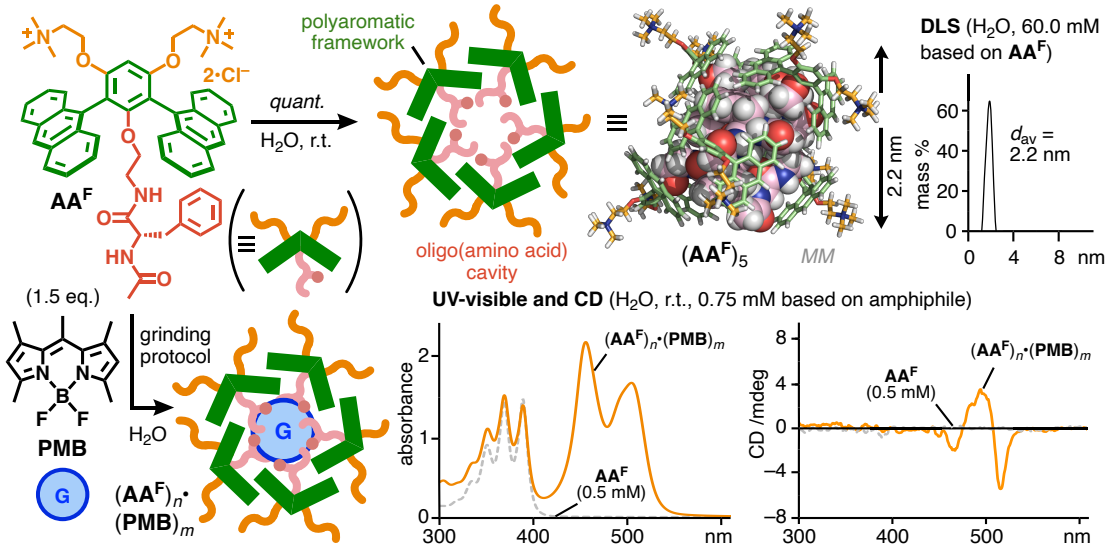
Formation and Host Ability of Aromatic Micelles with Oligo(Amino Acid) Cavities in Water

(*Lab. for Chem. & Life Sci., Science Tokyo*) Lorenzo Catti, Yuta Kikuchi, Shinji Aoyama, Michito Yoshizawa

Keywords: Aromatic Micelle; Internal Functionalization; Oligo(Amino Acid) Cavity; Encapsulation; Chirality Transfer

Mimicking natural protein cavities in water with molecular assemblies represents a challenge due to the weak interactions of amino acids. Most mimics rely on long amphiphilic peptides resulting in large/infinite assemblies with limited host functions and stabilities.[1] Aromatic micelles formed from bent amphiphiles possess strong host abilities and high stability, yet purely abiotic cavities.[2] We anticipated that the internal functionalization of aromatic micelles with amino acids or short peptides would provide discrete oligo(amino acid) cavities with unusual host functions in water.

We here report the synthesis of bent amphiphile **AA^F** featuring a phenylalanine-based group at the concave side, including Negishi and peptide couplings as the key steps (Figure, top left). The amphiphile quantitatively assembles in water into aromatic micelle (**AA^F**)$_n$, as indicated by NMR, fluorescence, and DLS analyses, providing a highly condensed oligo(amino acid) cavity with ~2 nm in diameter (Figure, top right). The resulting cavity efficiently encapsulates hydrophobic aromatic dyes (e.g., BODIPYs and coumarins) as well as aliphatic drugs. Notably, the CD spectrum shows a dye-derived Cotton effect, due to moderate chirality transfer from the chiral amino acid residues to the encapsulated achiral dyes. Furthermore, substituting the amino acids with tripeptides enables fine-tuning of the host properties of the aromatic micelle.



[1] Y. J. Jun, U. S. Toti, H. Y. Kim, J. Y. Yu, B. Jeong, M. J. Jun, Y. S. Sohn, *Angew. Chem. Int. Ed.* **2006**, *45*, 6173–6176. [2] M. Yoshizawa, L. Catti, *Acc. Chem. Res.* **2019**, *52*, 2392–2404.