

令和 5 年 6 月 10 日現在

機関番号：12608

研究種目：挑戦的研究(萌芽)

研究期間：2021～2022

課題番号：21K18927

研究課題名(和文) Study and control of long-range exciton transport in organic and hybrid nanostructures for future exciton-based electronics

研究課題名(英文) Study and control of long-range exciton transport in organic and hybrid nanostructures for future exciton-based electronics

研究代表者

VACHA Martin (Vacha, Martin)

東京工業大学・物質理工学院・教授

研究者番号：50361746

交付決定額(研究期間全体)：(直接経費) 5,000,000円

研究成果の概要(和文)：メゾスコピック有機構造における長距離励起子輸送の重要な要素を理解することを目的とし、超分子における励起子輸送を調べた。自己組織化超分子ナノファイバーとその束を蛍光顕微鏡と原子間力顕微鏡で同時測定したところ、3次元メソ構造が効率的な光導波路として機能することが分かった。一方、1次元ナノファイバーは数百nm程度の長い励起子拡散長を示した。このような大きな拡散長は、斜めの分子集合体の形成によって説明された。さらに、自己組織化超分子ナノリングを用い、励起子拡散に対するトポロジー効果を調べた。吸収と蛍光の偏光異方性と理論的シミュレーションにより、ナノリングに沿った励起子輸送が数nmであることが分かった。

研究成果の学術的意義や社会的意義

研究成果の科学的意義は、自己組織化超分子ナノファイバー内での長距離励起子輸送の発見にある。このような長距離での励起子拡散の報告は他に数件しかなく、本成果は、この現象が斜めの分子集合体の存在によって起こることを初めて解明した。また、本研究の社会的意義は、電流の代わりに励起子輸送によって駆動される励起子エレクトロニクス分野の基礎原理を探求することである。

研究成果の概要(英文)：Exciton transport in molecular and supramolecular structures was studied with the aim of understanding the key factors for long-range exciton transport in mesoscopic organic and hybrid systems. Simultaneous measurements by fluorescence and atomic force microscopy on self-assembled supramolecular nanofibers and their bundles showed that 3-dimensional mesostructures function as efficient light waveguides. On the other hand, 1-dimensional nanofibers exhibit long exciton diffusion lengths on the order of several hundreds of nanometers. Such large diffusion length values were explained by the formation of oblique molecular aggregates between individual monomers within the nanofibers. Further, the effect of topology on the exciton diffusion was studied using self-assembled supramolecular nanorings. Absorption and fluorescence polarization anisotropy together with theoretical simulations showed that the exciton transport along the nanorings is limited to several nanometers.

研究分野：Organic materials nanoscience

キーワード：exciton transport fluorescence microscopy

## 1. 研究開始当初の背景

Natural photosynthetic systems, as well as many organic molecules absorb the energy of light in the visible or UV spectral regions. Efficient transport of this excitation energy over long distances is crucial in the function of photosynthesis, and is also a key factor in synthetic light-harvesting systems such as solar cells. In the synthetic molecular systems, the transport of the excitation energy, so called excitons, is in most cases limited to distances on the order of nanometers to tens of nanometers. The efficiency of exciton transport is determined by electronic coupling between densely packed molecules and by the presence of electronic and structural disorder. Recently, there have been several reports of micrometer-length transport of singlet excitons measured in supramolecular systems, such as one-dimensional nanofibers of self-assembled H-aggregates of triarylamine, self-assembled nanotubes of J-aggregated amphiphilic cyanine dyes or crystalline conjugated polymer nanofibers. These results show the great potential for long-range exciton transport in synthetic organic systems and its engineering by molecular design, controlled self-assembly, and modification of coherent-incoherent interactions. Other potential key factors that can play a role in long-range exciton transport are topology and dimensionality of the building blocks of the nanostructures or of the structures themselves.

## 2. 研究の目的

The main objectives of the research are to study the exciton transport in a variety of synthetic molecular and supramolecular systems, with the aim of understanding the key design principles for long-range exciton transport in mesoscopic organic and hybrid structures, including the roles of topology and dimensionality, and to propose ways to actively control the key factors of the exciton transport efficiency for advanced applications.

## 3. 研究の方法

The principal method for the study of the exciton transport is fluorescence microscopy and nanoscale spectroscopy. The long-range transport is measured by exciting diffraction-limited size location of the molecular system (such as nanofiber) in confocal fluorescence mode, and observing the delocalization of fluorescence due to the exciton transport. For structures smaller than the diffraction limit of light, the transport is measured indirectly by, e.g., polarized absorption and fluorescence. To reveal the roles of topology and dimensionality, the fluorescence microscopy measurements are correlated with atomic force microscopy (AFM) imaging of the same samples. The simultaneous experiments are made possible by using a combined setup including an inverted fluorescence microscope with an AFM head placed on its top.

## 4. 研究成果

### *4.1. Simultaneous fluorescence and AFM microscopy of single conjugated polymer chains*

Conjugated polymer chains in compact conformations or in films exhibit spectral features that can be attributed to exciton transport along the main chain and emission from a low-energy site formed due to interactions between individual conjugated segments of the chain, including aggregates or excimers. We used atomic force microscopy (AFM) on single chains of the conjugated polymer polyfluorene (PFO) (Fig. 1a) to control the inter-segment interactions by mechanically unfolding the chain. Simultaneously with the force spectroscopy (Fig. 1b) we monitor fluorescence from the single PFO chains using a fluorescence microscope. We found that mechanical stretching of the chain causes disappearance of the green emission band which is populated by energy transfer from other parts of the chain (Fig. 1c, d). This observation provides evidence that the green emission originates from an intra-chain aggregated state on the self-folded chain which is decoupled by the stretching (Fig. 1e, f). In addition, the stretching upon laser irradiation leads to the appearance of additional features in the force spectra, small force peaks in

the initial stages of the unfolding (Fig. 1b, g). These features are attributed to a combination of excitonic and van der Waals coupling of a ground-state intra-chain aggregate.

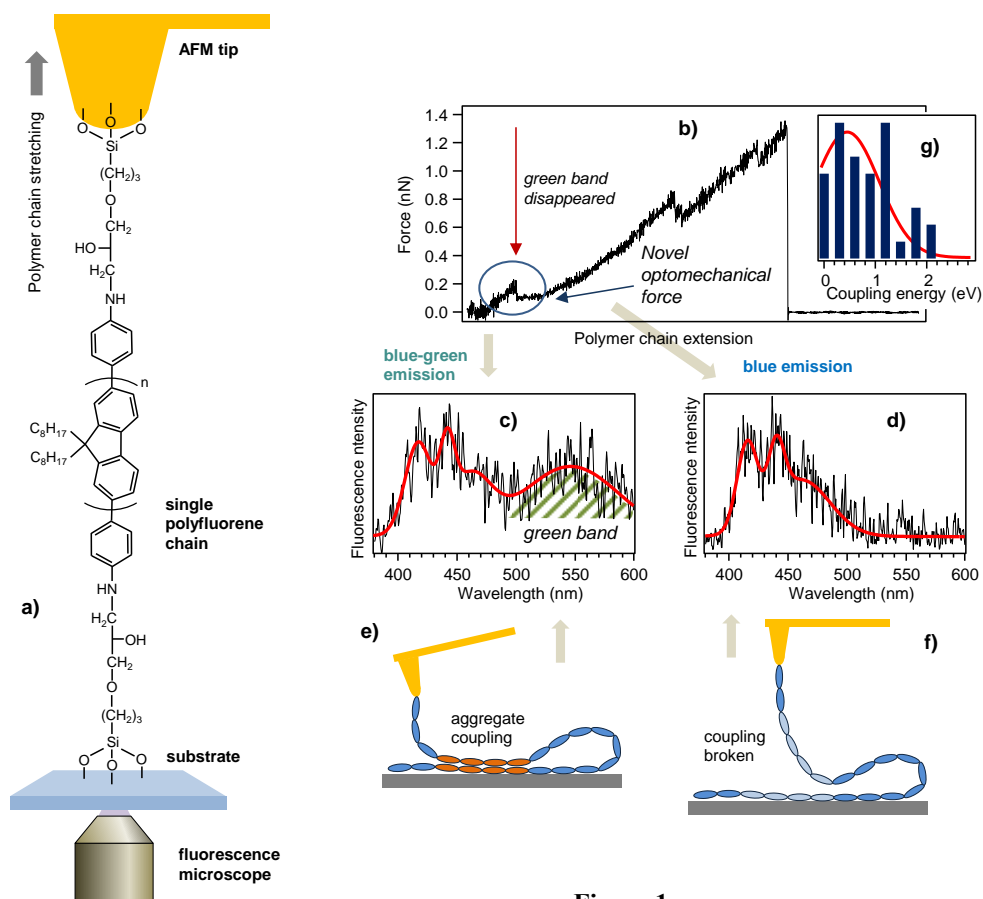


Figure 1

#### 4.2. Long-range exciton diffusion on self-assembled supramolecular nanofibers

The study of long-range exciton diffusion was realized on self-assembled supramolecular nanofibers of tris(phenylisoxazolyl)benzenes, as shown in the Fig. 2a, b. Single chirally assembled nanofibers can further aggregate into bundles with varying diameter. An example of such bundles is also shown in the AFM image in Fig. 2c.

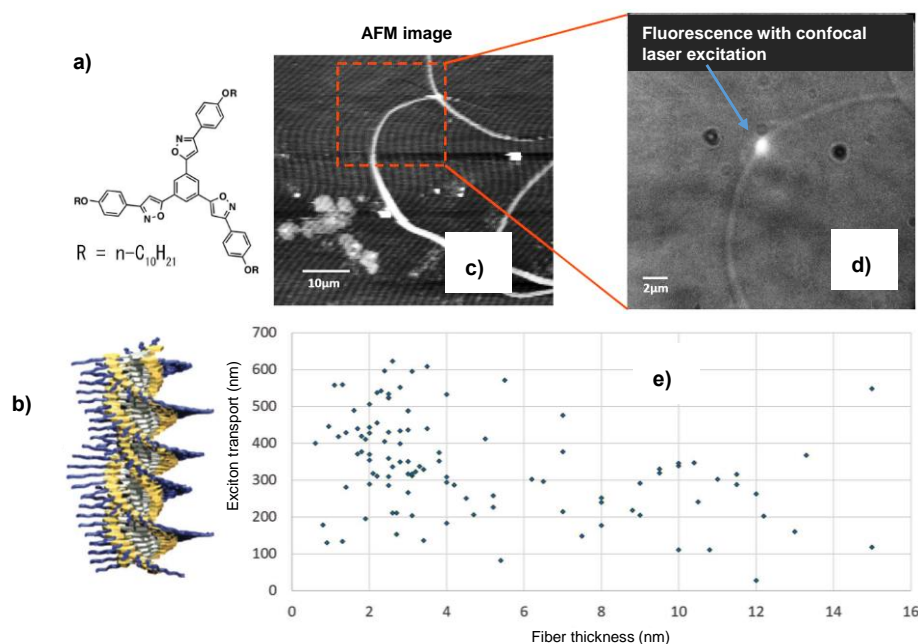
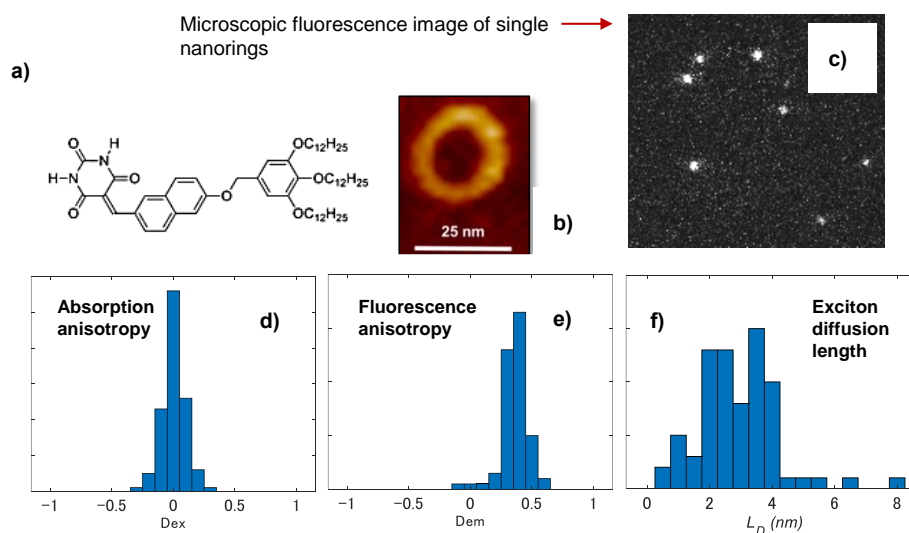


Figure 2

The nanofiber and bundle thickness as measured by AFM vary from a few nanometers (individual nanofibers) to hundreds of nanometers (bundles). The nanostructures of various thickness were studied using fluorescence microscopy and spectroscopy. Briefly, in a confocal microscopic mode the excitation laser of 375 nm is focused into a diffraction limited spot on a location on the nanofiber/bundle (Fig. 2d). The excitons created in the excitation spot then diffuse along the nanofiber and cause spatial spread of the fluorescence signal. Analysis of the excitation laser profile together with the extended fluorescence profile provides an estimate of the exciton diffusion length. For thick nanofiber bundles (on the order of hundreds of nm) it was found that the bundles function as nanoscale organic waveguides. The light emitted around the excitation spot is efficiently coupled into the nanofiber bundle, propagates along the bundle length of several micrometers and is reemitted at the bundle ends. To exclude the effect of waveguiding, the exciton diffusion was studied on thin nanofibers with thickness below 20 nm. The diffusion length was studied at a statistical sample of different locations on tens of different nanofibers in simultaneous fluorescence and AFM imaging experiments. The AFM was used to confirm the correct thickness of the nanofiber at and around the excitation location. The exciton diffusion length plotted against the nanofiber thickness (Fig. 2e) shows large distribution of values, with an average diffusion length of 340 nm. The correlation of the diffusion length with the nanofiber thickness indicates that the average length is larger for individual nanofibers (thickness below ~ 6 nm, 1-dimensional structures) compared to small nanofiber bundles (thickness between 8 and 20 nm, 3-dimensional structures), pointing to the effect of dimensionality in the exciton transport. Further, it was found that there is no effect of the fiber curvature on the diffusion length within the range of curvatures observed in the samples. The unexpectedly long exciton diffusion length was tentatively interpreted in terms of the existence of oblique molecular aggregates which form between individual monomer units during the nanofiber self-assembly.

#### 4.3. Exciton diffusion in hierarchical supramolecular nanorings

To study the effect of topology on the exciton diffusion process, self-assembled supramolecular nanorings of naphthalene barbiturate (Fig. 3a, b) were studied by polarization fluorescence microscopy. Nanorings of the size of 20 – 30 nm cannot be resolved using optical microscopy, and in fluorescence images the individual nanorings appear as diffraction limited emission spots (Fig. 3c). Within this limitation on resolution, the shape of the nanorings was confirmed by measuring the absorption anisotropy. As expected for rotationally symmetric structures, the anisotropy values  $D_{ex}$  are narrowly distributed around 0 values (Fig. 3d), confirming the circular shape of the rings. The exciton diffusion is measured by fluorescence anisotropy. Theoretically, in the absence of exciton transport the fluorescence anisotropy  $D_{em}$  has a value of 0.5. The results measured on a statistical sample of nanorings show a distribution of  $D_{em}$  values, with a peak between 0.3 and 0.4 (Fig. 3e), indicating a partial exciton transport along the nanorings. The extent of the transport was estimated using a model in which the nanoring is formed by individual light-absorbing and emitting segments, and by assuming random walk diffusion of excitons created on the individual segments. The results in Fig. 3f show that on most of the rings the exciton diffusion length is limited to 2 – 4 nm, even though in some rings the diffusion length can reach up to 8 nm.



**Figure 3**

#### *4.4. Conclusions*

Exciton transport in molecular and supramolecular structures was studied with the aim of understanding the key factors for long-range exciton transport in mesoscopic organic and hybrid systems. Simultaneous measurements by fluorescence and atomic force microscopy on self-assembled supramolecular nanofibers and their bundles showed that 3-dimensional mesostructures function as efficient light waveguides. On the other hand, 1-dimensional nanofibers exhibit long exciton diffusion lengths on the order of several hundreds of nanometers. Such large diffusion length values were explained by the formation of oblique molecular aggregates between individual monomers within the nanofibers. Further, the effect of topology on the exciton diffusion was studied using self-assembled supramolecular nanorings. Absorption and fluorescence polarization anisotropy together with theoretical simulations showed that the exciton transport along the nanorings is limited to several nanometers.

## 5. 主な発表論文等

〔雑誌論文〕 計5件（うち査読付論文 5件/うち国際共著 5件/うちオープンアクセス 0件）

1. 著者名 Furuya Ryotaro, Omagari Shun, Tan Qiwen, Lokstein Heiko, Vacha Martin	4. 巻 143
2. 論文標題 Enhancement of the Photocurrent of a Single Photosystem I Complex by the Localized Plasmon of a Gold Nanorod	5. 発行年 2021年
3. 雑誌名 Journal of the American Chemical Society	6. 最初と最後の頁 13167 ~ 13174
掲載論文のDOI (デジタルオブジェクト識別子) 10.1021/jacs.1c04691	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する
1. 著者名 Yan Hao, Tseng Tzu-Wei, Omagari Shun, Hamilton Iain, Nakamura Tomonori, Vacha Martin, Kim Ji-Seon	4. 巻 156
2. 論文標題 Dynamic molecular conformational change leading to energy transfer in F8-5% BSP copolymer revealed by single-molecule spectroscopy	5. 発行年 2022年
3. 雑誌名 The Journal of Chemical Physics	6. 最初と最後の頁 074704 ~ 074704
掲載論文のDOI (デジタルオブジェクト識別子) 10.1063/5.0080406	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する
1. 著者名 Agarwal Anubha, Omagari Shun, Vacha Martin	4. 巻 7
2. 論文標題 Nanoscale Structural Heterogeneity and Efficient Intergrain Charge Diffusion in a Series of Mixed MA/FA Halide Perovskite Films	5. 発行年 2022年
3. 雑誌名 ACS Energy Letters	6. 最初と最後の頁 2443 ~ 2449
掲載論文のDOI (デジタルオブジェクト識別子) 10.1021/acsenerylett.2c01271	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する
1. 著者名 Nakamura Tomonori, Omagari Shun, Liang Xiaobin, Tan Qiwen, Nakajima Ken, Vacha Martin	4. 巻 17
2. 論文標題 Simultaneous Force and Fluorescence Spectroscopy on Single Chains of Polyfluorene: Effect of Intra-Chain Aggregate Coupling	5. 発行年 2023年
3. 雑誌名 ACS Nano	6. 最初と最後の頁 8074 ~ 8082
掲載論文のDOI (デジタルオブジェクト識別子) 10.1021/acsnano.2c09773	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1. 著者名 Agarwal Anubha, Omagari Shun, Vacha Martin	4. 巻 na
2. 論文標題 Air-stable mixed cation lead halide perovskite films and microscopic study of their degradation process	5. 発行年 2023年
3. 雑誌名 Nanoscale	6. 最初と最後の頁 na
掲載論文のDOI (デジタルオブジェクト識別子) 10.1039/D3NR02003G	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

〔学会発表〕 計5件 (うち招待講演 3件 / うち国際学会 4件)

1. 発表者名 Martin Vacha
2. 発表標題 Single-Molecule Spectroscopy in Physics and Chemistry of Materials: From Conjugated Polymers and Perovskite Nanocrystals to Photosynthetic Systems
3. 学会等名 RIES-Hokudai International Symposium (招待講演)
4. 発表年 2021年

1. 発表者名 Martin Vacha
2. 発表標題 Excitonic coupling phenomenon directly revealed on single chains of polyfluorene by combined force spectroscopy and fluorescence microscopy
3. 学会等名 30th International Conference on Photochemistry (国際学会)
4. 発表年 2021年

1. 発表者名 Martin Vacha, Ryotaro Furuya, Shun Omagari, Qiwen Tan, Heiko Lokstein
2. 発表標題 Plasmon enhanced photocurrent in a single Photosystem I complex
3. 学会等名 28th IUPAC Symposium on Photochemistry (国際学会)
4. 発表年 2022年

1. 発表者名 Martin Vacha
2. 発表標題 Real-time monitoring and control of photophysics of polyfluorenes and other nanoscale systems on single-molecule level
3. 学会等名 14th Hole Burning, Single Molecule and Related Spectroscopies Conference (招待講演) (国際学会)
4. 発表年 2022年

1. 発表者名 Martin Vacha
2. 発表標題 Electroluminescence at the nanoscale: Single-molecule and single-particle spectroscopy of conjugated polymers and perovskite nanocrystals
3. 学会等名 13th instalment of the International Conference of Electroluminescence and Optoelectronic Devices (招待講演) (国際学会)
4. 発表年 2022年

〔図書〕 計0件

〔産業財産権〕

〔その他〕

-

6. 研究組織

氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考
---------------------------	-----------------------	----

7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8. 本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関
---------	---------