様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科学研究費助成事業　　研究成果報告書

令和　元 年　 ６ 月　 ３ 日現在

機関番号：１２６０８
研究種目：新学術領域研究（研究領域提案型）
研究期間：2014～2018
課題番号：２６１０７０１４

研究課題名（和文）分子集団の協同的光応答の分子レベル解明および動的制御

研究課題名（英文）Molecular-level study and control of cooperative photoresponse of molecular complexes

研究代表者
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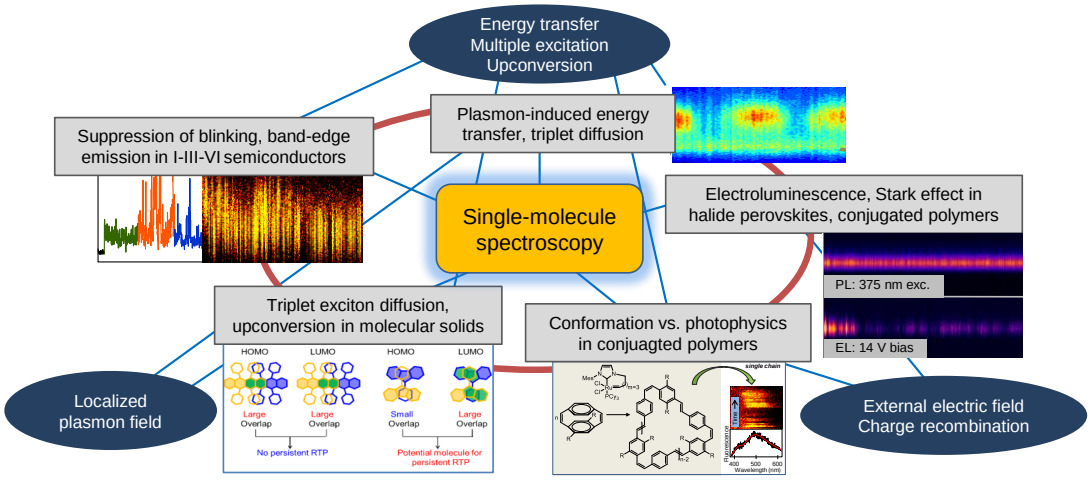
研究成果の概要（和文）：単一分子分光法を用いて、分子会合体、分子結晶、共役高分子等の分子集合体だけでなく、量子ドット、ペロブスカイトナノ結晶、分子と貴金属ナノ粒子からなるハイブリッドナノ粒子等の無機集合体の光励起応答の計測および制御を試みた。その結果、共役高分子の未解明な発光特性の起源の同定、I-III-IV属半導体ナノ粒子における欠陥やバンド端発光の起源の抽出、ペロブスカイトナノ粒子におけるブリンキングや発光収率を含む電界発光の制御、局在プラズモンによるハイブリッドナノ粒子における共鳴エネルギー移動の増強、そして固体材料のりん光や光アップコンバージョン特性に関する三重項励起子拡散の課題や役割の抽出に成功した。

研究成果の学術的意義や社会的意義
ポリフルオレンの緑発光の起源が凝集構造に由来することの発見は、従来考えられていたメカニズムを塗り替えるものである。また局在プラズモンによるエネルギー移動の増強や制御は、エネルギー移動距離の更なる向上を期待させるものである。さらに三重項励起子拡散に関する成果は、長寿命発光や低閾値光アップコンバージョンの特性向上に対して重要な知見をもたらすものとなる。
I-III-IV属半導体量子ドットにおける複数の欠陥サイトの発見やペロブスカイトナノ結晶のブリンキングの起源の発見は、既存の量子ドットディスプレイに使われているCd系量子ドット発光体の代替材料を見出していくための重要な知見であり社会的にも重要である。

研究成果の概要（英文）：Using single-molecule spectroscopy we studied and controlled the photoresponse of molecular complexes, such as aggregates, molecular crystals and conjugated polymers, as well as their semiconducting counterparts, such as quantum dots, and hybrid systems composed of noble metal nanoparticles and organic dyes. The results include conformational and spectroscopic characterization of poly(phenylene vinylene) and polyfluorene conjugated polymers, origin and suppression of defect emission and characterization of band-edge emission in I-III-IV semiconductor quantum dots, characterization of blinking, emission quantum efficiency and electroluminescence in halide perovskite nanocrystals, effect of enhancement of resonant energy transfer between organic dyes by localized plasmons and study of triplet exciton diffusion, phosphorescence and of triple-triplet annihilation and photon upconversion in molecular solids.

研究分野：有機材料ナノスケール特性

キーワード：1分子科学


Energy transfer
Multiple excitation
Upconversion
Plasmon-induced energy transfer, triplet diffusion
Suppression of blinking, band-edge emission in I-III-VI semiconductors
Single-molecule spectroscopy
Electroluminescence, Stark effect in halide perovskites, conjugated polymers
PL: 375 nm exc.
EL: 14 V bias
Triplet exciton diffusion, upconversion in molecular solids
HOMO
LUMO
Large Overlap
Small Overlap
No persistent RTP
Potential molecule for persistent RTP
Conformation vs. photophysics in conjuagted polymers
single chain
Localized plasmon field
External electric field
Charge recombination

I-III-IV b/[6• $(AgIn)_xZn_{2(1-x)}S_2$ b(ÂKZc@
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1. S. Ghimire, V. C. Nair, C. Muthu, K. Yuyama, M. Vacha and V. Biju: Photoinduced photoluminescence enhancement in self-assembled clusters of formamidinium lead bromide perovskite nanocrystals. *Nanoscale* **2019**, DOI: 10.1039/C8NR10082A 1w
2. S. Hirata: Roles of localized electronic structures caused by π degeneracy due to highly symmetric heavy atom-free conjugated molecular crystals leading to efficient persistent room-temperature phosphorescence. *Advanced Science* **2019**, DOI: 10.1002/advs.201900410 1w
3. D. K. Sharma, S. Hirata, V. Biju and M. Vacha: Stark effect and environment induced modulation of emission in single halide perovskite nanocrystals. *ACS Nano* **2019**, *13*, 624-632 1w
4. K. Narushima, Y. Kiyota, T. Mori, S. Hirata and M. Vacha: Suppressed triplet exciton diffusion due to small orbital overlap as a key design factor for ultralong-lived room temperature phosphorescence in molecular crystals. *Adv. Mater.* **2019**, *31*, 1807268 1w
5. T. Kameyama, M. Kishi, C. Miyamae, D. K. Sharma, S. Hirata, T. Yamamoto, T. Uematsu, M. Vacha, S. Kuwabata, and T. Torimoto: Wavelength-Tunable Band-Edge Photoluminescence of Non-stoichiometric Ag-In-S Nanoparticles via Ga^{3+} Doping. *ACS Appl. Mater. Interfaces* **2018**, *10*, 42844-42855 1w
6. S. Hatazaki, D. K. Sharma, S. Hirata, K. Nose, T. Iyoda, A. Kölsch, H. Lokstein and M. Vacha: Identification of short- and long-wavelength emitting chlorophylls in cyanobacterial photosystem I by plasmon-enhanced single-particle spectroscopy at room temperature. *J. Phys. Chem. Lett.* **2018**, *9*, 6669-6675 1w
7. T. Uematsu, K. Wajima, D. K. Sharma, S. Hirata, T. Yamamoto, T. Kameyama, M. Vacha, T. Torimoto, S. Kuwabata: Narrow Band-Edge Photoluminescence from $AgInS_2$ Semiconductor Nanoparticles by the Formation of Amorphous III-VI Semiconductor Shells. *NPG Asia Mater.* **2018**, *10*, 713-726 1w
8. T. Nakamura, D. K. Sharma, S. Hirata, M. Vacha: Intra-Chain Aggregates as the Origin of Green Emission in Polyfluorene Studied on Ensemble and Single Chain Level. *J. Phys. Chem. C* **2018**, *122*, 8137-8146 1w
9. B. Yu, J. I. Tracey, Z. Cheng, M. Vacha and D. M. O'Carroll: Plasmonic sphere-on-plane systems with semiconducting polymer spacer layers. *Phys. Chem. Chem. Phys.* **2018**, *20*, 11749-11757 1w
10. M. Liu, S. Hirata, T. Iyoda, M. Vacha and P. Piotrowiak: Excited State Behavior of Single Strand and Bulk P3HT in Contact with a Au-Nanowire Array. *J. Phys. Chem. C* **2018**, *122*, **7925-7933** 1w
11. B. J. Lidster, S. Hirata, S. Matsuda, T. Yamamoto, V. Komanduri, Y. Tezuka, M. Vacha, M. L. Turner: Macrocyclic Poly(p-phenylenevinylene)s by Ring Expansion Metathesis Polymerization and their Characterization by Single-Molecule Spectroscopy. *Chem. Sci.* **2018**, *9*, 2934-2941 1w
12. M. Vacha, D. K. Sharma, S. Hirata: Single-molecule studies beyond optical imaging: Multi-parameter single-molecule spectroscopy (Invited Review Article). *J. Photochem. Photobiol. C: Photochem. Rev.* **2018**, *34*, 121-136 1w
13. S. Hirata: Ultralong-lived room temperature triplet excitons: molecular persistent room temperature phosphorescence and nonlinear optical characteristics with continuous irradiation. *J. Mater. Chem. C* **2018**, *6*, 11785-11794 1w
14. S. Hirata: Intrinsic Analysis of Radiative and Room-Temperature Nonradiative Processes Based on Triplet State Intramolecular Vibrations of Heavy Atom-Free Conjugated Molecules toward Efficient Persistent Room-Temperature Phosphorescence. *J. Phys. Chem. Lett.* **2018**, *9*, 4251-4259 1w
15. L. Bujak, K. Narushima, D. K. Sharma, S. Hirata, M. Vacha: Plasmon enhancement of triplet exciton diffusion revealed by nanoscale imaging of photochemical fluorescence upconversion. *J. Phys. Chem. C* **2017**, *121*, 25479-25486 1w
16. S. Hirata, M. Vacha: Large Reverse Saturable Absorption at the Sunlight Power Level Using the Ultralong Lifetime of Triplet Excitons. *J. Phys. Chem. Lett.* **2017**, *8*, 3683-3689 1w
17. K. Narushima, S. Hirata, M. Vacha: Nanoscale triplet exciton diffusion via imaging of upconversion

emission from single hybrid nanoparticles in molecular crystals. *Nanoscale* **201**7, *9*, 10653-10661 1
w

18. S. Hirata, M. Vacha: White Afterglow Room-Temperature Emission from an Isolated Single Aromatic Unit under Ambient Condition. *Adv. Opt. Mater.* **2017**, *5*, 1600996 1w
19. D. K. Sharma, S. Hirata, L. Bujak, V. Biju, T. Kameyama, M. Kishi, T. Torimoto, M. Vacha: Influence of Zn on the Photoluminescence of Colloidal $(AgIn)_xZn_{2(1-x)}S_2$ Nanocrystals. *Phys. Chem. Chem. Phys.* **2017**, ***19,*** 3963-3969 1w
20. L. Bujak, T. Ishii, D. K. Sharma, S. Hirata, M. Vacha: Selective turn-on and modulation of resonant energy transfer in single plasmonic hybrid nanostructures. *Nanoscale* **2017**, *9*, 1511-1519 1w
21. K. Kamada, Y. Sakagami, T. Mizokuro, Y. Fujiwara, K. Kobayashi, K. Narushima, S. Hirata, M. Vacha: Efficient triplet-triplet annihilation upconversion in binary crystalline solids fabricated by solution casting and operated in air. *Materials Horizons* **2017**, *4*, 83-87 1w
22. D. K. Sharma, S. Hirata, L. Bujak, V. Biju, T. Kameyama, M. Kishi, T. Torimoto, M. Vacha: Single-particle spectroscopy of I-III-VI semiconductor nanocrystals: spectral diffusion and suppression of blinking by two-color excitation. *Nanoscale* **2016**, *8*, 13687-13694 1w
23. S. Hirata, M. Vacha: Circularly Polarized Persistent Room-Temperature Phosphorescence from Metal-Free Chiral Aromatics in Air. *J. Phys. Chem. Lett.* **2016**, *7*, 1539-1545 1w
24. S. Hirata, M. Vacha: Large Transmittance Change Induced by Exciton Accumulation under Weak Continuous Photoexcitation. *Adv. Opt. Mater.* **2016**, *4*, 297-305 1w
25. Y. Katsurada, S. Hirata, K. Totani, T. Watanabe, M. Vacha: Photoreversible On-Off Recording of Persistent Room-Temperature Phosphorescence. *Adv. Opt. Mater.* **2015**, *3*, 1726-1737 1w
26. T. Imagawa, S. Hirata, K. Totani, T. Watanabe and M. Vacha: Thermally activated delayed fluorescence with circularly polarized luminescence characteristics. *Chem. Commun*. **2015**, *51*, 13268-1327 1w
27. S. Lee, K. Noda, S. Hirata, M. Vacha: Position-Dependent Three-Dimensional Diffusion in Nematic Liquid Crystal Monitored by Single-Particle Fluorescence Localization and Tracking. *J. Phys. Chem. Lett*. **2015**, *6*, 1403-1407 1w
28. Y. Tsubomoto, S. Hirata, K. Totani, M. Vacha, T. Watanabe: Long-lived Triplet Excitons Allowed by Intermolecular Hydrogen Bonding in Amorphous Matrix. *J. Photopolym. Sci. Technol.* **2015**, *28*, 573-577 1w
29. S. Hirata, K. Totani, T. Yamashita, C. Adachi and M. Vacha: Large reverse saturable absorption under weak continuous incoherent light. *Nature Mater*. **2014**, *13*, 938-946 1w
30. Y. Honmou, S. Hirata, H. Komiyama, J. Hiyoshi, S. Kawauchi, T. Iyoda, M. Vacha: Single molecule electroluminescence and photoluminescence of polyfluorene unveils the photophysics behind the green emission band. *Nature Commun*. **2014**, *5*, 4666 1w

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1. M. Vacha: Electroluminescence and modulation of photophysics in single halide perovskite nanocrystals (*Invited*). 14th IUPAC International Conference on Novel Materials and their Synthesis, Guangzhou, China, October 21-25, 2018.
2. M. Vacha: Nanoscale Characterization of Functional Polymers and Hybrid Organic Materials by Single-molecule Spectroscopy (*Plenary*). 14th IUPAC International Conference on Novel Materials and their Synthesis, Guangzhou, China, October 21-25, 2018.
3. M. Vacha: Photophysics and electroluminescence of single nanocrystals of halide perovskites and related nanomaterials *(Invited*). 13th International Conference on Hole Burning, Single Molecule and Related Spectroscopies, Suzdal, Russia, August 6-12, 2018.
4. M. Vacha: Spectroscopy of single nanocrystals of doped I-III-IV semiconductors and organic-inorganic hybrid nanoparticles (*Invited*). 28th International Conference on Photochemistry, Strasbourg, France, July 16-21, 2017.
5. M. Vacha: Light-Harvesting from Single-Molecule Perspective: Selective Turn-on of Energy Transfer by Localized Plasmon and Role of Aggregation in Photophysics of Polyfluorenes (*Invited*). Interdisciplinary Conference on Light-Harvesting Phenomena and Related Topics LHP 2017, Banz Monastery, Germany, March 26-30, 2017.
6. M. Vacha: Nanoscale characterization of functional polymers and hybrid organic materials by single-molecule spectroscopy (*Invited*). Indo-Japan Joint Symposium on Polymeric Materials, Thiruvananthapuram, Kerala, India, January 31-February 1, 2017.
7. M. Vacha: Nanoscale characterization of functional polymers and hybrid organic materials by single-molecule spectroscopy (*Invited*). Asia Conference on Nanoscience and Nanotechnology AsiaNANO 2016, Sapporo, Japan, October 10-13, 2016.
8. M. Vacha: Nanoscale characterization of functional hybrid organic materials by single-molecule spectroscopy (*Invited*). 2016 International Symposium on Integrated Molecular/Materials Science & Engineering, Qingdao, China, October 14-15, 2016.
9. M. Vacha: Single-molecule study of conformation-related photophysics in conjugated molecular

complexes and organic dye-gold nanoparticle structures (*Invited*). 19th Conference on Dynamical Processes in Excited States of Solids, Chimie Paris Tech, Paris, France, July 17-22, 2016.

10. M. Vacha: Molecular-level study and control of conformation and photophysics in conjugated molecular complexes (*Invited*). The International Chemical Congress of Pacific Basin Societies 2015, Honolulu, Hawaii, USA, December 15-20, 2015.

11. M. Vacha: Single-molecule study and control of conformation-related photophysics in conjugated molecular complexes (*Invited*). 12th International Conference on Hole Burning, Single Molecule and Related Spectroscopies, Estonian Institute of Physics, Tartu, Estonia, August 24-27, 2015.

12. M. Vacha: Molecular-level study and control of conformation and photophysics in conjugated molecular complexes (*Invited*). 11th International Conference on Optical Probes of Conjugated Polymers and Organic Nanostructures, Hong Kong University of Science and Technology, Hong Kong, June 14-19, 2015.

13. M. Vacha: Spectroscopy of single conjugated polymer chains: electroluminescence, photoluminescence and mechanical control of photophysics (*Invited*). 8th Asian Photochemistry Conference APC 2014, Kerala, India, November 10-13, 2014

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