

科学研究費助成事業 研究成果報告書

令和元年6月24日現在

機関番号：14301

研究種目：研究活動スタート支援

研究期間：2017～2018

課題番号：17H06791

研究課題名(和文) Fundamental Studies of Excitons and Charge-Carriers in Organic Materials Relevant to Organic Electronics

研究課題名(英文) Fundamental Studies of Excitons and Charge-Carriers in Organic Materials Relevant to Organic Electronics

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交付決定額(研究期間全体)：(直接経費) 2,100,000円

研究成果の概要(和文)：本研究では、有機半導体材料の固相に存在する有機物質の結晶相と有機半導体材料の光物理・化学的特性の相関関係を理解し目的である。このため、共役系高分子を用いて無定形相形成を抑制し、決定相が優勢粒子を溶液状態で作成する方法を開発した。この粒子を固相でも溶液のような光学的性質を示した。

また、化学組成的に同一である形態的には、異なる二つの有機金属構造体(MOFs)を使用して、有機物質で形と光物理的性質の関係を研究した。本研究では、励起状態の局在化程度(局在化・非局在化)が化学組成の変化なしにトポロジだけで調整が可能であることを示した。

研究成果の学術的意義や社会的意義

無機太陽電池とは異なり、有機太陽電池では、まだ光エネルギーが電気エネルギーに変換される過程で未知の領域が多く、そのため、有機太陽電池の商業化は、無機太陽電池よりも遅い状況である。本研究課題で開発された高分子結晶相の粒子は、有機太陽電池で光エネルギーを電気エネルギーに変換させる結晶相でのメカニズムを研究を可能にした。また、有機半導体材料で分子の積層による構造の重要性和分子と光との相互作用を調節することができる方法を提示することができた。これは、今後の固相有機半導体材料を設計する基礎知識となる。

研究成果の概要(英文)：In this research program, the researcher aims to elucidate the correlations between crystalline domains that exist in organic semiconductors and their photophysical/photochemical properties. Toward this goal, we developed a novel method to synthesize conjugated polymer particles in solution-phase, which reveal the dominant formation of crystalline domains with the suppressed formation of amorphous domains. These polymer particles exhibit consistent optical properties either in dispersion or thin-film.

The researcher, in addition, investigated the correlations between organic semiconductor topology and photophysical properties utilizing chemically identical while topologically distinguished metal-organic frameworks (MOFs). These MOF samples show that the degree of the excited-state localization (localized vs delocalized) can be controlled only by modulating semiconductor topology without changing chemical composition.

研究分野：光物理学

キーワード：有機半導体 高分子自己組織化 光物理学

様式 C-19、F-19-1、Z-19、CK-19 (共通)

1. 研究開始当初の背景

Organic semiconducting materials have shown a potential for ultra-thin, mechanically flexible, lightweight, mass-producible, and low-cost optoelectronic devices. With this advantage, organic semiconductors have been introduced in modern molecular electronics such as photovoltaics (PVs), field-effect transistors (FETs), and light emitting diode (LEDs). These organic semiconductor-based optoelectronic devices utilize nano/molecular architectures. For example, polymer photovoltaics adopt bulk heterojunction structures, where complex four distinguished domains, namely, polymer crystalline, polymer amorphous, mixed amorphous polymer/fullerene, and pure fullerene can exist. In contrast to individual molecules of which the photophysical properties are intrinsic, polymer crystalline domains exhibit their optical and/or electrical characteristics governed by inevitable intermolecular interaction. (Fig. 1) Additionally, although it is now generally accepted that polymer crystalline domains play a major role over its amorphous counterpart in photon-to-charge conversion processes such as exciton dissociation (Fig. 2. Feier, H. et al. *Adv. Energy Mater.* (2015)), the detailed mobile-charge generation mechanisms are still yet to be elusive. Therefore, probing photophysics of conjugated polymer-based self-assemblies that feature mesoscopic ordering is necessary to understand the role of polymer morphological and structural factors on exciton/carrier dynamics.

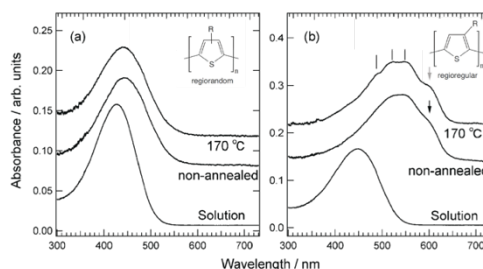


Fig. 1. Comparative UV-vis spectra of (a) rra-P3HT and (b) rr-P3HT in solution and in solid-phase. (Dang, M. T. et al., *Chem. Rev.* (2013))

In this regard, the applicant has shown that the raised valence band (VB) energy level of regioregular poly-3-hexylthiophene (rr-P3HT) featuring strong intermolecular interactions, with respect to that of regiorandom P3HT (rra-P3HT) results in the selective photoinduced carrier generation by increasing Gibbs energy driving force for rr-P3HT in photoinduced hole transfer dynamics (Park, J. et al. *J. Phys. Chem.* (2015)). The distinctive nature of intermolecular interactions can significantly modulate photoinduced processes such as dynamics of excitons and electron transfer.

In spite of this significance of polymer crystalline domains on their photophysics, it is challenging to investigate this due to aforementioned structural complexity in solid-state organic semiconductors (pure amorphous, pure crystalline, amorphous/crystalline interface, mixed polymer/electron acceptor domains). In this regard, it is desired to understand the photophysics at the pure polymer crystalline domains where photoexcitation will generate exciton and will serve as electron-donator.

2. 研究の目的

The current research program aimed:

- 1) to develop synthetic routes for polymer-based self-assemblies, featuring mesoscopic ordering,
- 2) to probe photophysics of conjugated polymer-based self-assemblies,
- 3) to elaborate how solid-state structures in condensed-phase organic semiconductors induced by molecular packing impact photophysical properties and excited-state dynamics.

3. 研究の方法

The applicant will focus on:

- 1) developing synthetic routes for polymer-based self-assemblies, featuring mesoscopic ordering,
- 2) characterizing the condensed-phase structures of polymer-based self-assemblies using methods such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD),

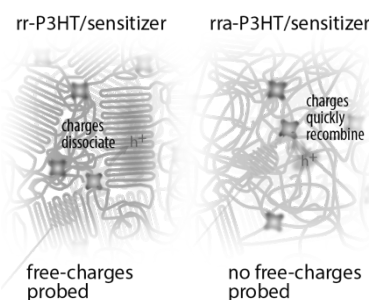


Fig. 2. The role of polymer crystalline domain on exciton dissociation.

3) probing photophysical and electrical properties, using optical spectroscopy.

Various polymer self-assembly structures, featuring dimensions of 100s nm – several μm and comparable to device dimensions have been reported, based on self-assembly engineering techniques such as thermal treatment, electrospinning, and solvent engineering. Our strategy utilizes solvent engineering and we will utilize centrifugation to purify crystalline polymer particles. This strategy will ensure to avoid morphological complications such as defects in solid-state structures to elaborate intrinsic intermolecular interactions of polymer structures.

4. 研究成果

1) Synthesis of poly-3-hexylthiophene polymer self-assemblies and the characterization.

With regioregular poly-3-hexylthiophene (rr-P3HT), polymer particles are produced using solvent engineering and following particle separation processes. These polymer particles were obtained in solution-phase as dispersion, and exhibit 100s of nanometer particle dimensions, as verified from SEM. In addition, the polymer particles exhibit highly crystalline structures probed by XRD and TEM (Fig 3.). Especially, XRD diffraction pattern results show 16 Å polymer backbone-to-backbone distance and TEM electron diffraction pattern results show ~ 5 Å polymer plane-to-plane distance, suggesting compact polymer packing. The dimension of these crystalline domains extends even to 100s of nanometer, which confirms highly suppressed amorphous domain formation. UV-vis spectroscopic results for the particle dispersion sample as well as the thin-film sample which is drop-casted from particle dispersion show that no additional molecular packing is introduced from solvent evaporation during thin-film formation, and enhanced polymer crystallinity is accomplished due to initial solvent engineering process. In addition, the lack of amorphous domains contrasts to reference drop-casted rr-P3HT samples. (*manuscript in preparation*)

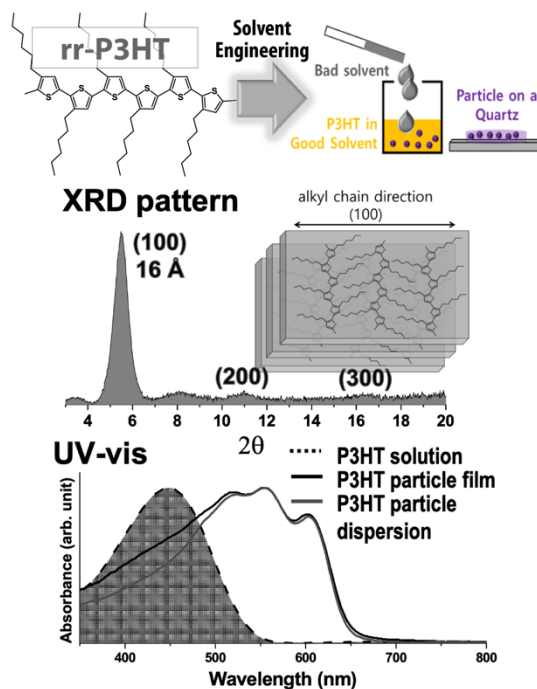


Fig. 3. Summary of rr-P3HT crystalline particle synthesis, particle characterization using XRD, electron microscopy, and optical spectroscopy

2) Photophysical dynamics of polymer self-assemblies.

We also examined the excited-state relaxation processes and optical properties of hybrid polymer nanoparticles using optical spectroscopy as well as femtosecond transient absorption spectroscopy. (Park, J. et al. *Polymer* (2019), Park, J. et al. *Sci. Rep.* (2018)) These studies

demonstrate the enhanced polymer structural ordering can accelerate nonradiative excited-state relaxation and therefore can induce heat release from polymer nanoparticles to surroundings, and this behavior of polymer self-assemblies can be utilized in photoacoustic imaging applications. (Fig. 4.)

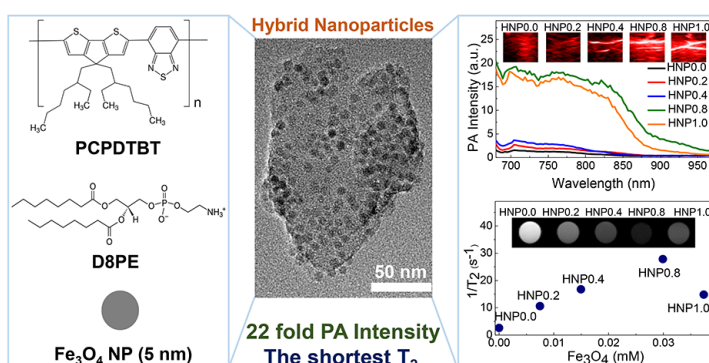


Fig. 4. Hybrid polymer nanoparticles and enhanced photoacoustic response in enhanced polymer-ordering

3) Photophysics in metal-organic frameworks (MOFs).

In addition to initial proposed studies utilizing conjugated polymer self-assemblies, we extended our studies, which investigate chemically identical but topologically distinguished metal-organic frameworks (MOFs):

$Zr_6(\mu_3-O)_4(\mu_3-OH)_4(-OH_2)_4(TBAPy)_2$, and explored the correlation between molecular packing and excited-state dynamics. (*J. Am. Chem. Soc.* (2018), 10488-10496, *J. Am. Chem. Soc.* (2018), 2756-2760) These MOFs (NU-901 and NU-1000, Fig. 5.) consist of pyrene entities as an organic unit and inert Zr metal clusters that serve as bridge units to modulate intermolecular (inter-pyrene) packing.

NU-901 MOFs feature pyrene-pyrene orientation favoring intermolecular interactions due to a short pyrene-pyrene center-to-center distance (9.52 Å) and a small pyrene-pyrene torsional angle (20°), contrasting counterpart NU-1000 MOFs (10.92 Å distance and 60° torsional angle). These structural features contribute to excited-state dynamics, where NU-901 exhibit delocalized excimer-like excited-state whereas NU-1000 show localized excited-state. These works show that the topological arrangement of the organic chromophores in condensed-phase materials critically controls the excited-state electronic structures.

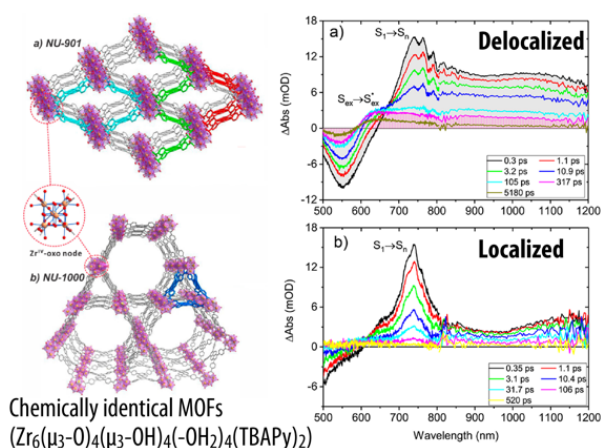


Fig. 5. Summary of photophysics of chemically identical but topologically distinguished metal-organic frameworks

5. 主な発表論文等

〔雑誌論文〕 (計 5 件)

- ① D. T.-T. Pham, D. Lee, E. Kang, J. Park, T. J. Shin, S. Kim, J. Park, "Ordered Assemblies of Fe_3O_4 and a Donor-Acceptor-Type π -Conjugated Polymer in Nanoparticles for Enhanced Photoacoustic and Magnetic Effects", *Polymer*, **2019**, *161*, 205-213, 査読有, doi.org/10.1016/j.polymer.2018.12.020.
- ② J. Yu, J. Park, A. Van Wyk, G. Rumbles, P. Deria, "Excited State Electronic Properties in MOFs as a Function of Topological Framework", *Journal of the American Chemical Society*, **2018**, *140*, 10488-10496. 査読有, DOI: 10.1021/jacs.8b04980
- ③ J. Noh, S. Jung, D. G. Koo, G. Kim, K. S. Choi, J. Park, T. J. Shin, C. Yang, J. Park, "Thienoisindigo-Based Semiconductor Nanowires Assembled with 2-Bromobenzaldehyde via Both Halogen and Chalcogen Bonding and Their Application to Organic Field-Effect Transistors", *Scientific Reports*, **2018**, *8*, 14448, 査読有, DOI:10.1038/s41598-018-32486-z.
- ④ A. Van Wyk, T. Smith, J. Park, P. Deria, "Charge-Transfer within Zr-Based Metal-Organic Framework: The Role of Polar Node", *Journal of the American Chemical Society*, **2018**, *140*, 2756-2760, 査読有, DOI: 10.1021/jacs.7b13211
- ⑤ J. Park, T.-H. Park, L. E. Sinks, P. Deria, J. Park, M.-H. Baik, M. J. Therien, "Unusual Solvent Polarity Dependent Excitation Relaxation Dynamics of a Bis[*p*-ethynylthiobenzoato]Pd-linked Bis[(porphinato)zinc] Complex", *Molecular Systems Design & Engineering*, **2018**, *3*, 275-284, 査読有, DOI: 10.1039/c8me00001h

〔学会発表〕 (計 5 件)

- ① Jaehong Park, "Excited-State Relaxation Dynamics of Porphyrin Array Modulated by Solvent Polarity", 日本化学会 第99春季年会, **2019**
- ② Jaehong Park, "Photoinduced mobile-carrier dynamics in semiconductors", 122nd General Meeting of the Korean Chemical Society (招待講演), **2018**
- ③ Jaehong Park, "Variation of excited-state dynamics in trifluoromethyl functionalized C60 fullerenes", フラールン・ナノチューブ・グラフェン学会, **2018**
- ④ Jaehong Park, "Solvent Polarity Dependent Excited-State Dynamics of Porphyrin Structures", International conference on porphyrins and phthalocyanines (招待講演), **2018**
- ⑤ Jaehong Park, "Photoinduced Intermolecular Electron Transfer of Electron

Donor/Acceptor Systems in a Low-Dielectric Medium”, *10th Asian Conference on Ultrafast Phenomena* (招待講演), 2018

[その他]

ホームページ等

<https://park-group.wixsite.com/park-group/publications>

6. 研究組織

該当なし

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