Graduate School of Science and Technology Doctoral Thesis Abstract

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Student ID	2121427	Submission date	2024 / 12 / 16 (yyyy/mm/dd)
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Title	Construction of novel organic supramolecular polymers and their integration with $CsPbBr_3$ perovskite quantum dots		

Supramolecular assembly driven via non-covalent interactions such as hydrogen bonding, π-π stacking, or/and van der Waals interactions allows the formation of complex structures with a high degree of functional diversity owing to their versatile design strategy and tunable inter/intramolecular interactions. One-dimensional (1D) supramolecular polymer (SP), possessing sequentially π-stacked nanostructures, is one of the key assemblies due to their dynamic and reversible nature in response to external stimuli. Cesium lead halide perovskite quantum dots ($CsPbX_3$ QDs, X = Cl/Br/I) are artificial semiconductor nanocrystals with unique photophysical properties such as tunable optical properties by size and composition, broad absorption, and sharp emission. Combining QDs with SPs yields a new generation of hybrid materials. Such synergistic approach boosts the functionality of QDs as well as SPs, facilitating superior electron and/or exciton transfers both within each component or between each other in the system.

$CsPbBr_3$ QDs are known to be excellent electron donors.[1] Thus, interacting them with π-conjugated organic molecules possessing deep LUMO like naphthalenediimide (NDI) can exhibit photoinduced electron transfer (PET). Although a PET system using monomeric NDI derivative as an electron acceptor has been reported, that using SPs of NDI is not yet realized. In Chapter 2, I developed a PET system composed of $CsPbBr_3$ QDs and SP of cholesterol functionalized NDI derivative **L5** (Fig. 1a). The SP(**L5**) was prepared in low polarity solvent and the fiber-like assembly formation was confirmed by spectroscopy and transmission electron microscopy (TEM). The photophysical interactions in the excited state were evaluated by photoluminescence (PL) and time-resolved measurements (Fig. 1b). Upon mixing QD with SP, the PL intensity of QDs significantly decreased. The coexistence of fibrous SP and QD was detected by TEM (Fig. 1c). Considering the energy

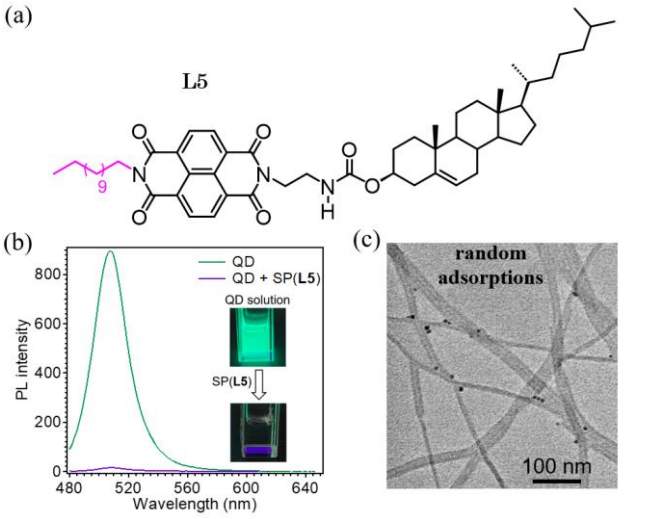

Figure 1 (a) Structure of **L5** (b) PL quenching on mixing QD with SP(**L5**) (c) TEM image of co-aggregate.

levels of QD and NDI, I concluded that the PL decrease was caused by a PET from QD (donor) to NDI (acceptor) core of SP due to the interdigitation between the alkyl chains of SP(**L5**) and QD surface ligands.

Recently, high-order assembled QDs have attracted attention because they offer superior properties such as long-range exciton diffusion and collective fluorescence (superfluorescence).[2] As a new strategy for the formation of assembled QDs, Yamauchi and group have reported the 1D-assembly of spherical QDs on organic SP template.[3] However, the methodology to form and control ordered 1D-arrays of QDs is not well established yet. In addition, 1D-arrangement of cubic QDs is still challenging.[4] In Chapter 3, I attempted to form high-order 1D-array of cubic $CsPbBr_3$ QDs on a new SP template composed of NDI derivative **L1'** with pyridyl adhesion site for QDs (Fig. 2a). The fiber-like SP(**L1'**) was prepared in low polarity solvent mixture. Upon mixing the SP(**L1'**) template with QDs, the ligand exchange of the weakly adsorbed surface ligands of QDs with the adhesion sites on the SP resulted in the formation of a short-range 1D array of QDs along the template as observed in the TEM image (Fig. 2b). Upon successive heat-cool process, longer-range ordered 1D-arrays of QDs were formed along the re-constructed longer SP(**L1'**) templates (Fig. 2c). Moreover, photo-excited state studies by PL spectra and time-resolved measurements revealed continuous fluorescence resonance energy transfer (FRET) between closely assembled QDs, namely exciton diffusion (Fig. 2d).

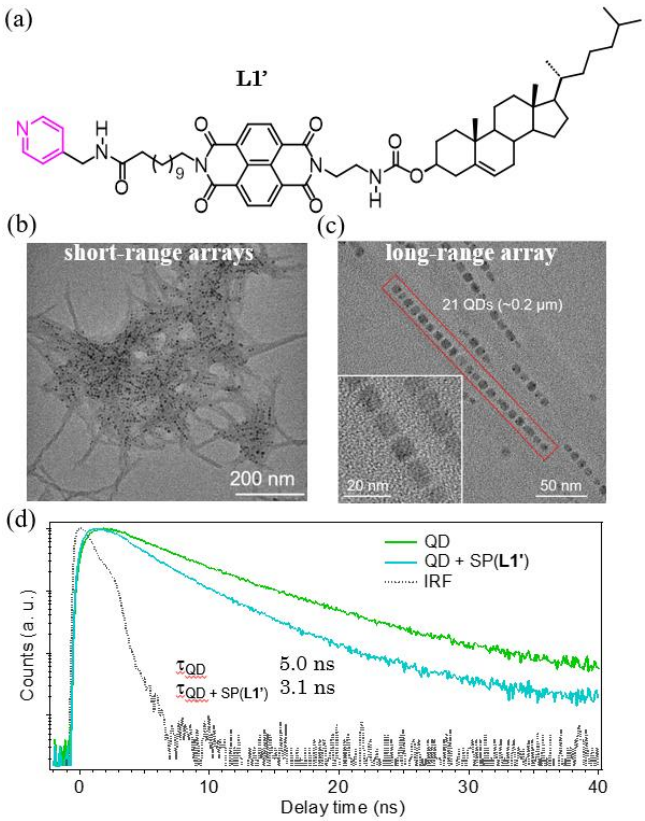

Figure 2 (a) Structure of **L1'**. (b-c) TEM images of short-and long-range array of QD on SP(**L1'**). (d) PL decay curves of QD and QD + SP(**L1'**) mixture.

To summarize, I developed certain SPs designed to interact with $CsPbBr_3$ QDs. The PET system realized between SP(**L5**) and QD reflects the non-covalent interactions between them. SP(**L1'**) serve as effective template for the precise 1D-arrangement of QDs, further demonstrating the occurrence of FRET between adjacent QDs. Furthermore, tuning of SP(**L1'**) morphology by heat-cool treatment led to the formation of longer-range well-organized 1D-array structures. These findings enable new opportunities towards the realization of advanced optoelectronic devices and energy-harvesting systems where the optimized integration of QDs with SPs enhances the effectiveness of light absorption or electron transfers.

[1] K. Wu, et al. *J. Am. Chem. Soc.* **2015**, *137*, 12792. [2] a) G. Rainò, et al. *Nature* **2018**, *563*, 671. b) E. Penzo, et al. *ACS Nano* **2020**, *14*, 6999. [3] M. Yamauchi, et al. *Angew. Chem. Int. Ed.* **2024**, *63*, e202314329. [4] a) Y. Ji, et al. *J. Mater. Chem. C* **2019**, 7, 8471. b) A. Pan, et al. *Nanoscale* **2017**, 9, 17688.

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（論文審査結果の要旨）

水素結合、πスタッキング、ファンデルワールス相互作用などの非共有結合相互作用によって駆動される超分子集合体は、その多彩な設計戦略と調整可能な分子間/分子内相互作用により、高度な機能多様性を有する複雑な構造の形成を可能にする。一次元（1D）超分子ポリマー（SP）は、外部刺激に応答して動的かつ可逆的な性質を持つため、重要な集合体の一つである。ハロゲン化セシウム鉛ペロブスカイト量子ドット（$CsPbX_3$ QDs, X = Cl/Br/I）は、サイズや組成によって光学特性を調整でき、幅広い吸収や鋭い発光など、ユニークな光物理特性を持つ人工半導体ナノ結晶である。QD と SP を組み合わせることで、新世代のハイブリッド材料が生まれる。

第 2 章では、$CsPbBr_3$ QD とコレステロール官能基化ナフタレンジイミド誘導体（NDI）の SP からなる光誘起電子移動システムを開発した。ファイバー状の集合体形成は分光法と透過型電子顕微鏡（TEM）で確認した。励起状態における挙動は、フォトルミネッセンス（PL）と時間分解測定によって評価した。QD と NDI のエネルギー準位を考慮すると、PL 強度の低下は、SP のアルキル鎖と QD の表面配位子との相互貫入により、QD（ドナー）から NDI（アクセプター）コアユニットへの光誘起電子移動に起因すると結論した。

第 3 章では、ピリジル接着部位を持つ NDI 誘導体からなる新しい SP 鋳型上に、QD の高次 1 次元配列形成を試みた。ファイバー状の SP は低極性混合溶媒中で調製した。SP 鋳型と QD を混合すると配位子交換が起こり、鋳型に沿って QD の短距離 1 次元アレイが形成することを TEM で確認した。加熱冷却を繰り返すと、再構築された長い SP 鋳型に沿って、より長距離に秩序化された QD の 1 次元アレイが形成した。さらに、PL スペクトルと時間分解測定による光励起状態の解析から、密接に会合した QD 間の連続的な蛍光共鳴エネルギー移動（FRET)、すなわち励起子拡散が明らかになった。

本研究では、異種ナノ材料を分子レベルで階層的に配列制御するための新手法を提供しており、その成果は新しい知見を見出し学術的に重要であると判断される。以上より、審査委員一同は，本論文が博士（理学）の学位論文として価値あるものと認めた。