様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

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研究課題名（和文）Investigation of donor/acceptor interactions toward high-performance organic near-infrared (NIR) lasers beyond 900 nm

研究課題名（英文）Investigation of donor/acceptor interactions toward high-performance organic near-infrared (NIR) lasers beyond 900 nm

研究代表者
ＴＡＮＧ　ＸＵＮ（TANG, XUN）

九州大学・工学研究院・学術研究員

研究者番号：７０９６１７５４

交付決定額（研究期間全体）：（直接経費）　　2,200,000円

研究成果の概要（和文）：本研究ではドナー(D)-アクセプター（A）間の相互作用の解明および制御による有機レーザー色素の長波長化を目的とした。分子骨格に強いドナーとアクセプターを導入することで発光を近赤外領域にシフトさせ、D-A間に機能性スペーサーを挿入することで大きな利得係数を実現できる。この戦略に基づき、低レーザー閾値と三重項-三重項アップコンバージョン特性を有する多重共鳴型の安定な分子骨格を提案した。また、設計した分子において、波長が900nmを超える高性能な分布帰還型（DFB）有機レーザーを実現した。本研究については3報の論文を発表し、国際学会にて口頭発表3件（招待発表1件を含む）、ポスター発表1件を行った。

研究成果の学術的意義や社会的意義
The research achievement clarifies the underlying mechanism of electron donating and accepting interactions to achieve high efficiency and radiative rate. Thus, potential strategies are proposed to realize high performance organic light emitting devices and near-infrared organic lasers.

研究成果の概要（英文）：This research is focusing on the understanding and manipulating the electronic donor (D) and acceptor (A) interactions for realizing organic lasers with longer wavelength. By incorporating strong donor and acceptor moieties, the emission can be shifted to near-infrared (NIR) region. Furthermore, after rationally inserting the functional spacers between D and A moieties, the molecules can obtain large gain coefficient. In general, this research proposes stable organic laser cores with multiple-resonance effect, which has a low lasing threshold and the triplet upconversion property. Furthermore, this research achieved high performance organic distributed feedback lasers with the wavelength exceeding 900 nm. During this research, three papers have been published on Angew. Chem., Adv. Mater., and Nat. Commun., also, three oral (including one invited presentation) and one poster presentation have been taken in the international conferences.

研究分野：Organic electronics

キーワード：Organic electronics　Organic lasers　D/A interactions

様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９（共通）

１．研究開始当初の背景

Organic semiconductor lasers have obtained considerate attention since their first demonstration in the 1960s. Specifically, long wavelength, such as near-infrared, organic lasers hold distinct promise in applications such as optical communication, optical storage, healthcare surgery, and biological sensing. Currently, the recorded lasing wavelength limit remains around ~850 nm, which was obtained by excited state intramolecular proton transfer. A primary challenge hindering the red-shifting of lasing wavelengths is the intrinsic nonradiative decay rate governed by the "energy-gap law" in narrow band-gap NIR emitters. Additionally, organic NIR gain materials face difficulties in harnessing triplets efficiently. Therefore, achieving organic NIR lasers with low thresholds is both crucial and demanding.

２．研究の目的

Electronic donor (D) and acceptor (A) interaction is the fundamental to induce the charge transfer (CT) state. The emissive wavelength can be feasibly tuned by adjusting the strength of D and A moieties. However, a distinct D/A separation would largely decrease the oscillator strength and suppress the radiation process. Thus, the understanding and manipulation of D/A interaction is the key to simultaneously realize the significant red-shifting and high radiative rate, leading to NIR organic lasers. Also, the CT state has been convinced to utilize the triplets by decreasing the singlet-triplet splitting, therefore, manipulating CT state is also potential to harvest triplets in organic laser system.

３．研究の方法

Regarding to the dilemma, the research was inspired by the following transition rate and energy-gap law mechanisms:

Transition rate in D/A type molecules: $$k_r \propto CE_V H_{if}^2 r^2 \quad (1)$$

Energy-gap law: $$k_{nr} \propto exp\left\{-\frac{\Delta E}{\hbar\omega_M}\left[In\left(\frac{\Delta E}{l\lambda_M}\right)-1\right]\right\} \quad (2)$$

From equation 1, it is evident that k_r is proportional to the D/A electronic coupling and effective distance in the D/A type molecules. Therefore, the connection between D and A moieties would be significant to control the D-A distance and wavefunction overlap. For equation 2, the rigidity of molecular skeleton is crucial to reduce the reorganization energy, thus, suppress the nonradiative process. Additionally, CT-type emission commonly possesses broad spectrum with multiple vibronic transition modes. Under the identical energy gap, the utilization of the vibronic transition modes would also be crucial to realize the color tunable organic lasers.

４．研究成果

In this research, we focus on the comprehension of electronic D/A interactions to realize the organic lasers with longer wavelength. We have proposed three strategies to investigate the intrinsic properties: (1) tuning the electron-donating strength to tune the emission wavelength; (2) extending the conjugation length; (3) figuring out the function of spacers. As shown in Figure 1, we chose benzo[1,2-c:4,5c']bis[1,2,5]thiadiazole as the strong A moiety, and fluorene with alkyl chains as the spacer, and first designed and synthesized the S-A-S type molecule. However, this S-A-S molecule has high amplified spontaneous emission (ASE) thresholds (>15 µJ cm^{-2}) and relatively short wavelength (<800 nm). To improve the performance, incorporating the strong donor moiety (TPA) and its derivatives was proposed to establish the D-S-A-S-D type molecules. Consequently, the target molecule exhibited a reduced ASE thresholds (<5 µJ cm^{-2}) and a longer wavelength ASE peak (close to 830 nm). Additionally, the D-S-A-S-S-S-A-S-D type molecule with longer conjugation length could also red-shift the ASE wavelength with promising lasing performance. However, when further increasing the donor strength, the lasing performance became worse, indicating the stronger electron donating strength would significantly change the wavefunction distribution. The next research focused on understanding the functional spacers between D and A.

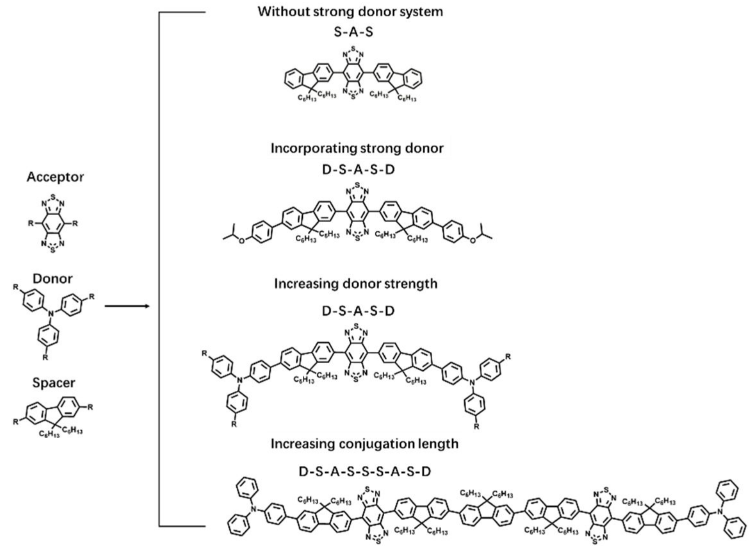

Figure 1. Molecular structures of the fragments of acceptor (BBTD), donor (TPA), and spacer (fluorene) in this research. Molecular design by incorporating D, A, and fluorene moieties with different donating strength and conjugation length.

To further understand the role of the functional spacer between D and A, spacers with different conjugation lengths were designed as shown in Figure 2. The distance between D and A moieties was increased from 5.73 to 18.31 Å. The density functional theory (DFT) calculation was conducted to indicate the change of wavefunction distributions. As can be seen, the lowest unoccupied molecular orbital (LUMO) was localized at the BBTD, while the highest occupied molecular orbital (HOMO) would be shifted to the end-capped D moiety as increasing the spacer length. Thus, when the spacer length is 18.31 Å, there is almost no wavefunction overlap between LUMO and HOMO, the oscillator strength and radiative rate also largely reduced. Resultantly, the molecule with the fluorene spacer has the better balance of CT and locally-excited (LE) state.

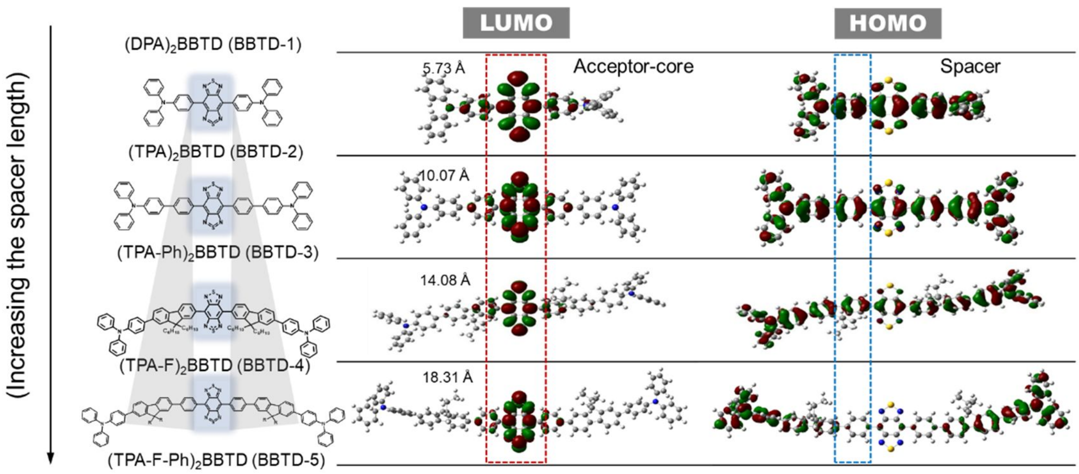

Figure 2. Molecules with different functional spacers between D and A fragments. Density functional theory calculation of LUMO and HOMO wavefunction distribution for molecules with difference spacer lengths.

Benefitting from the involvement of CT state, the molecule exhibited a broad spectrum with the full-width at half maximum (FWHM) around 100 nm, indicating multiple vibronic modes contribute to the radiation process. Therefore, distributed feedback resonators with different grating sizes were subsequently designed and fabricated to extract lasing output at a wide-range wavelength regime. As shown in Figure 3, by utilizing the wide-spread radiative modes, organic lasers can be achieved from around 800 nm to exceeding 900 nm, which is one of the organic solid-state lasers with the longest wavelength. The manuscript of this work is under preparing. Moreover, the potential use of triplets in organic lasers is important, organic molecules with multiple-resonance (MR) effects exhibited lasing and triplet upconversion properties. The preliminary research has proposed a robust MR-lasing core to convince the suppression of excited-state absorption. Strategies for red-shifting MR-lasing core would be further explored in the future research.

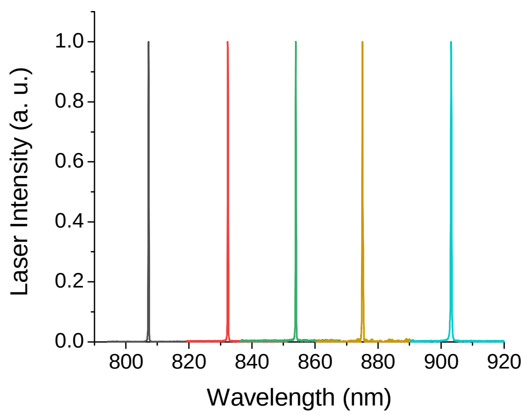

Figure 3. NIR organic lasers based on D-S-A-S-D molecules in this research.

Publications:

1. X. Tang,* M. Xie, Z. Lin, K. Mitrofanov, T. Tsagaantsooj, Y. T. Lee, R. Kabe, ASD Sandanayaka, T. Matsushima, T. Hatakeyama, C. Adachi, A Rigid Multiple Resonance Thermally Activated Delayed Fluorescence Core Toward Stable Electroluminescence and Lasing, *Angewandte Chemie International Edition*, 2024, 136, e202315210.

2. X. Tang,* C.A.M. Senevirathne, T. Matsushima, ASD Sandanayaka, C. Adachi, Progress and Perspective toward Continuous-Wave Organic Solid-State Lasers, *Advanced Materials*, 2023, 2211873.
3. Y-C. Chen#, X. Tang#, K. Wang, X. Xiong, X. C. Fan, S. Luo, R. Walia, Y. Xie, T. Zhang, D. Zhang, J. Yu, X. K. Chen, C. Adachi, X. H. Zhang, Efficient, narrow-band, and stable electroluminescence from organoboron-nitrogen-carbonyl emitter, *Nature Communications*, 2024, 15, 731.

Conference (as invited speaker):

1. X. Tang and C. Adachi, Molecular Donor-Acceptor Interaction for Realizing Low Threshold Organic Lasers from Visible to Near-Infrared regime, The 12th Laser Display and Lighting Conference 2023 (LDC 2023), Yokohama, Japan. (Invited speaker)

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　1件）

1．著者名	4．巻
Tang Xun、Xie Mingchen、Lin Zesen、Mitrofanov Kirill、Tsagaantsooj Tuul、Lee Yi‐Ting、Kabe Ryota、Sandanayaka Atula S. D.、Matsushima Toshinori、Hatakeyama Takuji、Adachi Chihaya	136
2．論文標題	5．発行年
A Rigid Multiple Resonance Thermally Activated Delayed Fluorescence Core Toward Stable Electroluminescence and Lasing	2023年
3．雑誌名	6．最初と最後の頁
Angewandte Chemie	1-10
掲載論文のDOI（デジタルオブジェクト識別子）	査読の有無
10.1002/ange.202315210	有
オープンアクセス	国際共著
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	該当する

1．著者名	4．巻
Cheng Ying-Chun、Tang Xun、Wang Kai、Xiong Xin、Fan Xiao-Chun、Luo Shulin、Walia Rajat、Xie Yue、Zhang Tao、Zhang Dandan、Yu Jia、Chen Xian-Kai、Adachi Chihaya、Zhang Xiao-Hong	15
2．論文標題	5．発行年
Efficient, narrow-band, and stable electroluminescence from organoboron-nitrogen-carbonyl emitter	2024年
3．雑誌名	6．最初と最後の頁
Nature Communications	1-9
掲載論文のDOI（デジタルオブジェクト識別子）	査読の有無
10.1038/s41467-024-44981-1	有
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1．著者名	4．巻
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Progress and Perspective toward Continuous-Wave Organic Solid-State Lasers	2023年
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Advanced Materials	/
掲載論文のDOI（デジタルオブジェクト識別子）	査読の有無
10.1002/adma.202211873	有
オープンアクセス	国際共著
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2．論文標題	5．発行年
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3．雑誌名	6．最初と最後の頁
ACS Materials Letters	1450-1455
掲載論文のDOI（デジタルオブジェクト識別子）	査読の有無
10.1021/acsmaterialslett.3c00310	有
オープンアクセス	国際共著
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2．論文標題 Artificial p-n‐like Junction Based on Pure 2D Organic-Inorganic Halide Perovskite Structure Having Naphthalene Diimide Acceptor Moieties	5．発行年 2023年
3．雑誌名 Advanced Optical Materials	6．最初と最後の頁 1-8
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/adom.202202734	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4件（うち招待講演　1件／うち国際学会　2件）

1．発表者名 Xun Tang
2．発表標題 Molecular Donor-Acceptor Interaction for Realizing Low Threshold Organic Lasers from Visible to Near-Infrared regime
3．学会等名 The 12th Laser Display and Lighting Conference 2023 (LDC2023)（招待講演）（国際学会）
4．発表年 2023年

1．発表者名 Xun Tang
2．発表標題 A Multiple Resonance Thermally Activated Delayed Fluorescence Core Toward Stable Organic Electroluminescence and Lasing
3．学会等名 14th Japan-China Joint Symposium on Conduction and Photoconduction in Organic Solids and Related Phenomena（国際学会）
4．発表年 2023年

1．発表者名 Xun Tang
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4．発表年 2024年

１．発表者名 Xun Tang, Chihaya Adachi
２．発表標題 Molecular Interactions in Donor-Acceptor-Donor Skeletons Toward Near-Infrared Organic Lasers
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〔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