Synthesis and Macrocyclization-Induced Emission Enhancement of Benzothiadiazole-based Macrocycle

Chunju Li (✉ cjli@shu.edu.cn)

Tianjin Normal University <https://orcid.org/0000-0001-7450-4867>

Yue-Ling Bai

Shanghai University

Lei Cui

Shanghai University

Shuo Li

Shanghai University

Article

Keywords: macrocyclization-induced emission enhancement (MIEE), Benzothiadiazole-based macrocycle (BT-LC), fluorescence, OLEDs

Posted Date: September 21st, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-903498/v1>

License: This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Nature Communications on May 23rd, 2022. See the published version at <https://doi.org/10.1038/s41467-022-30121-0>.

Abstract

We presented a novel strategy for the improvement of luminophore's solid-state emission, i.e., macrocyclization-induced emission enhancement (MIEE), by linking luminophores through C(sp³) bridges to give a macrocycle. Benzothiadiazole-based macrocycle (BT-LC) has been synthesized by a one-step condensation of the monomer 4,7-bis(2,4-dimethoxyphenyl)-2,1,3-benzothiadiazole (BT-M) with paraformaldehyde, catalyzed by Lewis acid. BT-LC shows strong emission in both dilute solution and aggregated state. Moreover, in comparison with the monomer, macrocycle BT-LC produces much more intense fluorescence in the solid state ($\Phi_{\text{PL}}=99\%$) and exhibits better device performance in the application of OLEDs. The MIEE can be ascribed to the restriction of intramolecular motion and the alleviation of the concentration quenching by the macrocyclic topological structure.

Introduction

Organic luminescent materials with high quantum efficiencies have attracted intensive attention due to their extensive applications in sensors,¹⁻³ bioimaging,⁴⁻⁷ laser displays,⁸⁻¹⁰ light-emitting diodes,¹¹⁻¹⁴ and anti-counterfeiting.^{15,16} However, most of organic luminogens suffer from severe quenching effect in the aggregate state due to the formation of such detrimental aggregates as excimers and exciplexes,¹⁷⁻¹⁹ which greatly limits their applications in organic luminescent materials. To address aggregation-causing quenching (ACQ) issue, some effective methods have been built to improve emission efficiency, for example aggregation induced emission (AIE),²⁰⁻²⁶ crystallization induced emission (CIE)²⁷⁻²⁹ and supramolecular assembly induced emission enhancement.^{30,31} In these cases, it is highly dependent on the restriction of intramolecular motions and control of the twisted conformation of organic luminophores in the solid state.^{32,33} It is still urgent to develop new strategy for emission enhancement, which would be not only helpful to the construction of fantastic fluorophores and materials, but also significant to understand the relationship between luminescent mechanism and molecular structures.

In the past ten years, our group has focused on the synthesis and applications of new macrocycles, and has developed a versatile methodology for functional biphen[*n*]arenes.³⁴ We predicted that the macrocyclization of organic luminophore through sp³ methylene, i.e., the construction of luminophore-based macrocyclic arene, would efficiently enhance the emission. Such macrocyclization-induced emission enhancement (MIEE) is theoretically feasible considering the following two features: on one hand, it spatially separates chromophores in a single macrocycle to eliminate the concentration quenching to a certain degree;³⁵⁻³⁸ on the other hand, it restricts intramolecular motion by locking its skeleton into the rigid framework to suppress non-radiation relaxation.^{39,40} Herein, we report that benzothiadiazole-based macrocycle (BT-LC) produces interesting dual-state emission both in solution and aggregated state because of twisted intramolecular charge transfer (TICT) and AIE characteristics. In contrast, the corresponding monomer, BT-M, displays a typical ACQ phenomenon on molecular aggregation. Furthermore, fluorescence quantum yield of BT-LC macrocycle in the solid state, up to 99%, is much higher than that of BT-M. For the application of organic light-emitting diodes (OLEDs), the device

containing the macrocycle exhibits higher maximum brightness (B_{max}) and external quantum efficiency (EQE_{max}) than that for the monomer. MIEE reported here would be a general strategy for improving emission efficiency, and has the potential to be practically utilized in organic luminescent materials.

Results

Synthesis of BT-LC. The synthetic route of BT-LC is illustrated in Figure 1. The precursor 4,7-bis(2,4-dimethoxyphenyl)-2,1,3-benzothiadiazole (BT-M) was synthesized through Suzuki-Miyaura coupling reaction of 4,7-dibromo-2,1,3-benzothiadiazole and 2,4-dimethoxybenzeneboronic acid. 2,1,3-benzothiadiazole is a widely used building block in luminescent materials.^{41,42} BT-M is an ideal highly-emissive molecule, due to its D-A architecture with dimethoxyphenyl donor and 2,1,3-benzothiadiazole (BT) acceptor, where the push-pull system can improve the luminescence performance through the enhancement of intramolecular charge transfer (ICT).⁴³⁻⁴⁵ Subsequently, BT-LC was synthesized by a one-step condensation of BT-M with paraformaldehyde, catalyzed by Lewis acid of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (52% yield). All chemical structures were confirmed by ^1H and ^{13}C NMR spectroscopy, high resolution mass spectra (HRMS) as well as single crystal X-ray diffraction.

Table 1. Photophysical properties of BT-LC

	BT-LC		
	$\lambda_{\text{abs}}(\text{nm})$	$\lambda_{\text{em}}(\text{nm})$	$\Phi_{\text{PL}}(\%)$
TOL	401	529	86
THF	407	537	86
CHCl_3	406	545	83
DMF	410	561	89
Solid	-	562	99

λ_{abs} (nm): absorption maximum. λ_{em} (nm): fluorescence maximum. Φ_{PL} : absolute PL quantum yield ($\lambda_{\text{ex}} = 418$ nm).

Photophysical properties of BT-LC in solution. As depicted in Figure 2 and Table 1, its absorptions show negligible differences with λ_{abs} values of 401-410 nm. BT-LC exhibits high quantum yields values of 83-89%, and its emissions show remarkable bathochromic shift as the solvent polarity increases. Similar absorptions and emissions were observed for the monomer BT-M. This is due to intramolecular charge transfer (ICT) effect resulted by their distinguished D-A architectures.⁴⁶⁻⁴⁸ Particularly, both BT-LC and BT-M displayed large stokes shifts of 151 nm and 161 nm in DMF.

Macrocyclization-induced emission enhancement. From Figure 3a and Figure S10, the fluorescence intensity of BT-LC in THF/water mixtures becomes gradually reduced when the water fractions (f_w)

increase from 0 to 70%. Meanwhile, the emission peak shows a visible red-shift from 535 to 565 nm. This emissive phenomenon is attributed to the TICT effect.⁴⁹⁻⁵¹ As the water fractions (f_w) further increases from 70 to 95%, the fluorescence intensity sharply recovers, exhibiting a typical AIE property, and the emission peak blue-shifts to 547 nm. Such photo-physical behaviors demonstrate that BT-LC can be viewed as a dual-state emission (DSE) molecule.⁵²⁻⁵⁵ In sharp contrast, the emission intensity of the monomer BT-M swiftly decreases with increasing the f_w values, indicating a typical ACQ phenomenon (Figure 3b and S9). The quantum yield of BT-LC in the solid state is as high as 99%, which is much higher than that for BT-M (65%). The above results suggest that the macrocyclization through methylene bridges is an effective way to enhance emission efficiency in aggregated or solid state. The MIEE effect should be attributed to the rigidity induced by macrocyclization and spatial separation from macrocyclic topologic structure.

Mechanism study. Single crystal analysis was examined to understand macrocyclic effects. From Figure 4a and S14, BT-LC has a rigid triangular geometry with vertex angles of 112°, 114° and 115°. The C(sp³) bridges spatially separated three luminophores in a single macrocyclic molecule, leading to the alleviation of the concentration quenching to a certain degree. Three series of torsion angles between the central benzothiadiazole planes and their adjacent phenyl rings are 55.29°, 77.35°; 53.02°, 60.92°; and 56.40°, 69.05, respectively. In comparison, both torsion angles for the monomer BT-M are 63.70° (Figure S11). Macrocyclization of luminophores would efficiently reduce the space of their rotation, therefore preventing their rotation. Furthermore, the intramolecular hydrogen bonds (C-H...N 2.70 Å, and C-H...S 2.75 Å, Figure 4b) between benzothiadiazoles could further limit the intramolecular motion. It should be noted that BT-LC are racemes possessing a pair of enantiomers with double-included dimer geometry, where dimethoxyphenyl group of one enantiomer was encapsulated in the cavity of the other one through multiple intermolecular interactions (C-H...O 2.74 Å, 2.67 Å, and C-H...N 2.95 Å, Figure 4c). For the monomer, adjacent benzothiadiazole units were packed in an antiparallel stacking with a separation of about 4.98 Å (Figure S11b); no C-H...N/S hydrogen bonds were found. Obviously, the tight packing arrangement of BT-LC is more beneficial to fluorescence than that of BT-M. Thus, the above results suggest that MIEE effect should be due to the alleviation of quenching caused by spatial separation and the restriction of intramolecular motion by macrocyclic topologic structure and intra/intermolecular interactions.

The electronic structures of BT-M and BT-LC were calculated by the B3LYP/6-31G (d) method. As depicted in Figure S17, the electron density of the HOMO is well distributed over BT-M, while the LUMO are predominantly dominated by the central BT acceptor. Since the macrocycle is formed by linking the monomers with non-conjugated methylene groups, BT-LC exhibits HOMO and LUMO orbitals similar to BT-M. Separation of space between the HOMO and LUMO indicates the existence of effective ICT, which is consistent with the bathochromic shift of emission peak of BT-LC in solutions.

Table 2. Summary of the EL data of devices A and B

Device	Emitting layer	Dopant ratio (wt%)	V_{on} (V) ^a	B_{max} (cd/m ²) ^b	CE_{max} (cd/A) ^c	PE_{max} (lm/w ₂) ^d	EQE_{max} (%)	λ_{em} (nm) ^f	CIE (x, y) ^g
A	BT-M	5	3.98	2369	10.10	7.10	1.92	512	(0.29,0.53)
B	BT-LC	5	3.82	4355	9.93	8.25	2.82	534	(0.35,0.57)

^aTurn-on voltage. ^bMaximum brightness (B_{max}). ^cMaximum current efficiency (CE_{max}). ^dMaximum power efficiency (PE_{max}). ^eMaximum external quantum efficiency (EQE_{max}). ^fEL peak wavelength. ^gCommission International de l'Eclairage coordinates.

Electroluminescent (EL) properties. We then explore the possibility of applying BT-LC as OLED emitters. Thermogravimetric analysis (TGA) was first performed to assess its thermal stability. From Figure S24, the macrocycle has a higher decomposition temperature [Td (5 wt % loss) 423-426°C] than the monomer (286-291°C), demonstrating rigidity can increase the decomposition temperature. On the other hand, the spectral stabilities of BT-M and BT-LC were examined. The pristine BT-M displayed green fluorescence peaking at 491 nm. After grinding for 2 min, its maximum emission wavelength red-shifts to 505 nm and emits yellow-green fluorescence (Figure 3c). For BT-LC (Figure 3d), the emission wavelength and color of the pristine and ground sample were hardly affected by external stimuli, implying that macrocyclization can improve spectral stability.

High thermal decomposition temperatures suggested that the coevaporation technique is very suitable for purification of OLEDs. Subsequently, OLEDs were fabricated with a multilayer configuration: ITO (100nm)/HATCN (10 nm)/TAPC (40nm)/mCP:emitter (20nm)/TmPyPB (40nm)/LiQ (2 nm)/Al (100nm). The device A fabricated with monomer and the device B fabricated with macrocycle at 5% doping concentration were compared to reflect the performance of OLEDs. As shown in Figure 5 and Table 2, device B exhibited higher B_{max} and EQE_{max} than device A did. In other words, the macrocycle gives better device performance than the monomer which could be ascribed to improved quantum yield and rigidity caused by macrocyclization.

Discussion

In summary, we have developed a novel strategy named “macrocyclization-induced emission enhancement (MIEE)” to improve luminous efficiency of chromophores by linking chromophores into macrocycle through C(sp³) bridges. The developed macrocycle without AIE units exhibited TICT and AIE characteristics, leading to intense fluorescence both in solution (eg, Φ_{PL} =89% in chloroform) and in the solid state (Φ_{PL} =99%). In contrast, the monomer showed typical ACQ phenomenon. Certainly, the macrocycle BT-LC exhibited higher maximum brightness and external quantum efficiency than the monomer in the application of OLEDs. MIEE is a new and effective approach to improve the luminophore's emission and would be helpful to developing organic luminescent materials.

Methods

General. All reagents were purchased commercially and used without further purification unless otherwise noted. ^1H NMR and ^{13}C NMR spectra were recorded using a Bruker Avance 500 MHz spectrometer. High-resolution mass spectra (HRMS) was determined on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument. UV-vis spectra were taken on a UV-2501PC UV-vis recording spectrophotometer (Shimadzu). Quantum efficiency were measured on HAMAMATSU C9920-02. Melting points were obtained on an X-4 digital melting point apparatus without correction. Single crystal X-ray diffraction data of BT-M were collected on a Bruker APXE II CCD detector using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Single crystal X-ray diffraction data of BT-LC were determined on Bruker D8 Venture using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Thermogravimetric Analysis (TGA) was recorded using a TA Instrument TA-Q500 and the samples were heated under nitrogen gas at a rate of $10 \text{ }^\circ\text{C}/\text{min}$. The current density-voltage-luminance characteristics, electroluminescent (EL) spectra, CIE $_{x,y}$ coordinates of devices are measured and recorded by computer-controlled PR655 spectrometer and Keithley 2400 digital power.

Synthesis and characterization. Synthesis and relevant characterization details are provided in the Supplementary Information.

Data availability. The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary Information. All data are available from the authors on reasonable request.

Declarations

Acknowledgements

The authors gratefully acknowledge the National Natural Science Foundation of China (21971192, 21772118, and 21571126) and the Natural Science Foundation of Tianjin City (20JCZDJC00200).

Author contributions

S.L., C.L., Y.B. and L.C. conceived this project and designed the experiments. S.L. contributed to most of the experimental work.

Additional information

Supplementary Information accompanies this paper at <http://www.nature.com/naturecommunications>

Competing interests: The authors declare no competing interests.

References

1. Kim, H. N., Guo, Z., Zhu, W., Yoon, J., Tian, H. Recent progress on polymer-based fluorescent and colorimetric chemosensors. *Chem. Soc. Rev.*, **40**, 79–93 (2011).

2. Baek, P., Voorhaar, L., Barker, D., Travas-Sejdic, J. Molecular Approach to Conjugated Polymers with Biomimetic Properties. *Acc. Chem. Res.* **51**, 1581–1589 (2018).
3. Cao, S., Zhou, L., Liu, C., Zhang, H., Zhao, Y., Zhao, Y., Pil-lararene-based self-assemblies for electrochemical biosensors. *Bio-sensors and Bioelectronics.* **181**, 113164 (2021).
4. Feng, G., Liu, B. Aggregation-Induced Emission (AIE) Dots: Emerging Theranostic Nanolights. *Acc. Chem. Res.* **51**, 1404–1414 (2018).
5. Yu, H. J., Zhou, Q., Dai, X., Shen, F. F., Zhang, Y. M., Xu, X., Liu, Y., Photooxidation-Driven Purely Organic Room-Temperature Phosphorescent Lysosome-Targeted Imaging. *J. Am. Chem. Soc.* **143**, 13887–13894 (2021).
6. Chen, C., Ni, X., Tian, H. W., Liu, Q., Guo, D. S., Ding, D. Ca-lixarene-Based Supramolecular AIE Dots with Highly Inhibited Nonradiative Decay and Intersystem Crossing for Ultrasensitive Fluorescence Image-Guided Cancer Surgery. *Angew. Chem. Int. Ed.* **59**, 1–6 (2020).
7. Ni, F., Li, N., Zhan, L., Yang, C. Organic Thermally Activated Delayed Fluorescence Materials for Time-Resolved Luminescence Imaging and Sensing. *Adv. Opt. Mater*, **8**, 1902187 (2020).
8. Zhao, J., Yan, Y., Gao, Z., Du, Y., Dong, H., Yao, J., Zhao, Y. S. Full-color laser displays based on organic printed microlaser arrays, *Nature Communications* **10**, 870 (2019).
9. Zhou, Z., Zhao, J., Du, Y., Wang, K., Liang, J., Yan, Y., Zhao, Y. S. Organic Printed Core-Shell Heterostructure Arrays: A Universal Approach to All-Color Laser Display Panels. *Angew. Chem. Int. Ed.* **59**, 11814–11818 (2020).
10. Han, S., Zhang, W., Qiu, B., Dong, H., Chen, W., Chu, M., Liu Y., Yang, X., Hu, F., Zhao, Y. S. Controlled Assembly of Organic Composite Microdisk/Microwire Heterostructures for Output Cou-pling of Dual-Color Lasers. *Adv. Opt. Mater*, **6**, 1701077 (2018).
11. Jiang, H., Tao, Y., Jin, J., Dai, Y., Xian, L., Wang, J., Wang, S., Chen, R., Zheng, C., Huang, W. Resonance-driven dynamically bipolar organic semiconductors for high-performance optoelectronic applications. *Mater. Horiz.*, **7**, 3298–3304 (2020).
12. Matsuoka, K., Albrecht, K., Yamamoto, K., Fujita, K. Multi-functional Dendritic Emitter: Aggregation-Induced Emission En-hanced, Thermally Activated Delayed Fluorescent Material for Solu-tion-Processed Multilayered Organic Light-Emitting Diodes. *Sci. Rep.* **7**, 41780–41788 (2017).
13. Zhang, G. H., Xie, F. M., Wu, K., Li, Y. Q., Xie, G., Zou, S. J., Shen, Y., Zhao, X., Yang, C., Tang, J. X. High-efficiency white or-ganic light-emitting diodes based on all nondoped thermally activated delayed fluorescence emitters. *Adv. Mater. Interfaces.* **7**, 1901758 (2020).
14. Ding, H., Li, J., Xie, G., Lin, G., Chen, R., Peng, Z., Yang, C., Wang, B., Sun, J., Wang, C. An AIEgen-based 3D covalent organic framework for white light-emitting diodes. *Nat. Commun.*, **9**, 5234–5240 (2018).
15. Liang, X., Liu, T. T., Yan, Z. P., Zhou, Y., Su, J., Luo, X. F., Wu, Z. G., Wang, Y., Zheng, Y. X., Zuo, J. L. Organic Room-Temperature Phosphorescence with Strong Circularly Polarized Luminescence Based on Paracyclophanes. *Angew.Chem. Int. Ed.* **58**, 17220–17225 (2019).
16. Zhao, W., Liu, Z., Yu, J., Lu, X., Lam, J. W. Y., Sun, J., He, Z., Ma, H., Tang, B. Z. Turning on Solid-State Luminescence by Phototriggered Subtle Molecular Conformation Variations. *Adv. Mater.* **33**, 2006844

- (2021).
17. Friend, R. H., Gymer, R. W., Holmes, A. B., Burroughes, J. H., Marks, R. N., Taliani, C., Bradley, D. D. C., Dos Santos, D. A., Brédas, J. L., Löfgren, M., Salaneck, W. R. Electroluminescence in conjugated polymers. *Nature*, **397**, 121 (1999).
 18. Saleesh Kumar, N. S., Gujrati, M. D., Wilson, James N. Evidence of preferential π -stacking: a study of intermolecular and intra-molecular charge transfer complexes. *Chem. Commun.* **46**, 5464–5466 (2010).
 19. Mei, J., Leung, N. L., Kwok, R. T., Lam, J. W., Tang, B. Z. Aggregation-Induced Emission: Together We Shine, United We Soar! *Chem. Rev.* **115**, 11718–11940 (2015).
 20. Luo, J., Xie, Z., Lam, J. W. Y., Cheng, L., Chen, H., Qiu, C., Kwok, H. S., Zhan, X., Liu, Y., Zhu, D., Tang, B. Z. Aggregation-induced emission of 1-methyl-1,2,3,4,5-pentaphenylsilole. *Chem. Commun.* 1740–1741 (2001).
 21. Hong, Y., Lam, J. W. Y., Tang, B. Z. Aggregation-induced emission. *Chem. Soc. Rev.*, **40**, 5361–5388 (2011).
 22. Li, B., He, T., Shen X., Tanga, D., Yin, S., Fluorescent supra-molecular polymers with aggregation induced emission properties. *Polym. Chem.*, 2019, 10, 796–818.
 23. Feng, H. T., Yuan, Y. X., Xiong, J. B., Zheng, Y. S., Tang, B. Z. Macrocycles and cages based on tetraphenylethylene with aggregation-induced emission effect. *Chem. Soc. Rev.*, **47**, 7452–7476 (2018).
 24. Lou, X. Y., Yang, Y. W. Manipulating Aggregation-Induced Emission with Supramolecular Macrocycles. *Adv. Opt. Mater.* **6**, 1800668 (2018).
 25. Lei, S. N., Xiao, H., Zeng, Y., Tung, C. H., Wu, L. Z., Cong, H. BowtieArene: A Dual Macrocycle Exhibiting Stimuli-Responsive Fluorescence. *Angew. Chem. Int. Ed.* **59**, 10059–10065 (2020).
 26. Chen, L., Chen, C., Sun, Y., Lu, S., Huo, H., Tan, T., Li, A., Li, X., Ungar, G., Liu, F., Zhang, M. Luminescent Metallacycle-Cored Liquid Crystals Induced by Metal Coordination. *Angew. Chem. Int. Ed.* **59**, 10143–10150 (2020).
 27. Zhang, H., Lin, D. Q., Li, B., Liu, H. F., Wang, S. S., Wang, Y. X., Sun, M. L., Lin, Z. Q., Yan, Y., Yu, M. N., Xie, L. H., Huang, W. Organic Micro-/Nanocrystals of SFX-Based Attractor-Repulsor Molecules with the Feature of Crystal-Induced Luminescence Enhancement. *J. Phys. Chem. C* **125**, 6249–6259 (2021).
 28. Yang, S., Yin, P. A., Li, L., Peng, Q., Gu, X., Gao, G., You J., Tang, B. Z., Crystallization-Induced Reversal from Dark to Bright Excited States for Construction of Solid-Emission-Tunable Squaraines. *Angew. Chem. Int. Ed.* **59**, 10136–10142 (2020).
 29. Zheng, C., Zhang, Q., Nie, H., Huang, W., Zhao, Z., Qin, A., Hu, R., Tang, B. Z. Fluorescence visualization of crystal formation and transformation processes of organic luminogens with crystallization-induced emission characteristics. *Mater. Chem. Front.*, **2**, 180–188 (2018).
 30. Wang, J., Yao, X., Liu, Y., Zhou, H., Chen, W., Sun, G., Su, J., Ma, X., Tian, H. Tunable Photoluminescence Including White-Light Emission Based on Noncovalent Interaction-Locked N,N'-

- Disubstituted Dihydrodibenzo[a,c]phenazines. *Adv. Opt. Mater.*, **6**, 1800074 (2018).
31. Huang, Z., Jiang, T., Wang, J., Ma, X., Tian, H., Real-Time Visual Monitoring of Kinetically Controlled Self-Assembly. *Angew. Chem. Int. Ed.* **60**, 2855–2860 (2021).
 32. Zhang, J., Zhang, H., LAM, J. W. Y., Tang, B. Z. Restriction of Intramolecular Motion (RIM): Investigating AIE Mechanism from Experimental and Theoretical Studies. *Chem. Res. Chinese Universi-ties*, **37**(1), 1–15 (2021).
 33. Viglianti, L., Leung, N. L. C., Xie, N., Gu, X., Sung, H. H. Y., Miao, Q., Williams, Ian D., Licandroe, E., Tang, B. Z. Aggregation-induced emission: mechanistic study of the clusteroluminescence of tetrathienylethene. *Chem. Sci.*, **8**, 2629–2639 (2017).
 34. Xu, K., Zhang, Z., Yu, C., Wang, B., Dong, M., Zeng, X., Gou, R., Cui, L., Li, C. J. A Modular Synthetic Strategy for Functional Macrocycles. *Angew. Chem. Int. Ed.* **59**, 7214–7218 (2020).
 35. Hua, B., Zhou, W., Yang, Z., Zhang, Z., Shao, L., Zhu, H., Huang, F., Supramolecular Solid-State Microlaser Constructed from Pillar[5]arene-Based Host – Guest Complex Microcrystals. *J. Am. Chem. Soc.* **140**, 15651–15654 (2018).
 36. Wu, H., Chen, Z., Chi, W., Bindra, A. K., Gu, L., Qian, C., Wu, B., Yue, B., Liu, G., Yang, G., Zhu, L., Zhao, Y. Structural Engineering of Luminogens with High Emission Efficiency Both in Solution and in the Solid State. *Angew. Chem. Int. Ed.* **58**, 11419–11423 (2019).
 37. Dong, H., Zhang, C., Zhao, Y. S. Host – Guest Composite Or-ganic Microlasers. *J. Mater. Chem. C* **5**, 5600–5609 (2017).
 38. Liang, G., Lam, J. W. Y., Qin, W., Li, J., Xie, N., Tang, B. Z. Molecular luminogens based on restriction of intramolecular motions through host–guest inclusion for cell imaging. *Chem. Commun.*, **50**, 1725–1727 (2014).
 39. Leung, N. L. C., Xie, N., Yuan, W., Liu, Y., Wu, Q., Peng, Q., Miao, Q., Lam, J. W. Y., Tang, B. Z. Restriction of Intramolecular Motions: The General Mechanism behind Aggregation-Induced Emission. *Chem. Eur. J.* **20**, 15349–15353 (2014).
 40. Yang, J., Guo, Q. X., Wen, X. D., Gao, X. M., Peng, Q., Li, Q. Q., Ma, D. G., Li, Z. Pyrene-based blue AIEgens: tunable intramolecular conjugation, good hole mobility and reversible mechanochromism. *J. Mater. Chem. C*, **4**, 8506–8513 (2016).
 41. Zhang, Y., Song, J., Qu, J., Qian, P. C., Wong, W. Y. Recent progress of electronic materials based on 2,1,3-benzothiadiazole and its derivatives: synthesis and their application in organic light-emitting diodes. *Sci China Chem*, **64**, 3 (2021).
 42. Wang, Y., Michinobu, T., Benzothiadiazole and its p-extended, heteroannulated derivatives: useful acceptor building blocks for high-performance donor-acceptor polymers in organic electronics. *J. Mater. Chem. C*, **4**, 6200–6214 (2016).
 43. Sun, Y., Wu, T., Zhang, F., Zhang, R., Wu, M., Wu, Y., Liang, X., Guo, K., Li, J. Rational design of slightly twisted coumarin mole-cules with remarkable solution and solid dual efficient luminescence. *Dyes and Pigments* **149**, 73–81 (2018).

44. Lei, Y. X., Dai, W. B., Liu, Z. Q., Guo, S., Cai, Z. X., Shi, J. B., Zheng, X. Y., Zhi, J. G., Tong, B., Dong, Y. P. A novel strategy for realizing dual state fluorescence and low-temperature phosphorescence. *Mater. Chem. Front.*, **3**, 284–291 (2019).
45. Li, M., Niu, Y., Zhu, X., Peng, Q., Lu, H. Y., Xia, A., Chen, C. F. Tetrahydro[5]helicene-based imide dyes with intense fluorescence in both solution and solid state. *Chem. Commun.*, **50**, 2993–2995 (2014).
46. Antaris, A. L., Chen, H., Cheng, K., Sun, Y., Hong, G. S., Qu, C. R., Diao, S., Deng, Z. X., Hu, X. M., Zhang, B., Zhang, X. D., Yaghi, O. K., Alamparambil, Z. R., Hong, X. H., Cheng, Z., Dai, H. J. A small-molecule dye for NIR-II imaging. *Nat. Mater.* **15**, 235 (2016).
47. Bhattacharyya, A., Chandra Makhal, S., Guchhait, N. Comparative Photophysical Study of Differently Substituted Cinnamaldehyde-Based Chalcones: From Intramolecular Charge Transfer to Fluorogenic Solvent Selectivity. *J. Phys. Chem. A* **123**, 6411–6419 (2019).
48. Gao, H., Gao, Y., Wang, C., Hu, D., Xie, Z., Liu, L., Yang, B., Ma, Y. Anomalous Effect of Intramolecular Charge Transfer on the Light Emitting Properties of BODIPY. *ACS Appl. Mater. Interfaces* **10**, 14956–14965 (2018).
49. Morozumi, T., Anada, T., Nakamura, H. New Fluorescent “Off-On” Behavior of 9-Anthryl Aromatic Amides through Controlling the Twisted Intramolecular Charge Transfer Relaxation Process by Complexation with Metal Ions. *J. Phys. Chem. B* **105**, 2923–2931 (2001).
50. Sasaki, S., Drummen, G. P. C., Konishi, G. i. Recent advances in twisted intramolecular charge transfer (TICT) fluorescence and related phenomena in materials chemistry. *J. Mater. Chem. C* **4**, 2731–2743 (2016).
51. Karmakar, S., Ambastha, A., Jha, A., Dharmadhikari, A., Dharmadhikari, J., Venkatramani, R., Dasgupta, J. Transient Raman Snapshots of the Twisted Intramolecular Charge Transfer State in a Stilbazolium Dye. *J. Phys. Chem. Lett.* **11**, 4842–4848 (2020).
52. Yan, X., Cook, T. R., Wang, P., Huang, F., Stang, P. J. Highly emissive platinum (II) metallacages. *Nat. Chem.* **7** (4), 342–348 (2015).
53. Zheng, X., Zhu, W., Zhang, C., Zhang, Y., Zhong, C., Li, H., Xie, G., Wang, X., Yang, C. Self-Assembly of a Highly Emissive Pure Organic Imine-Based Stack for Electroluminescence and Cell Imaging. *J. Am. Chem. Soc.* **141**, 4704–4710 (2019).
54. Chen, G., Li, W. B., Zhou, T. R., Peng, Q., Zhai, D., Li, H. X., Yuan, W. Z., Zhang, Y. M., Tang, B. Z. Conjugation-Induced Rigidity in Twisting Molecules: Filling the Gap Between Aggregation-Caused Quenching and Aggregation-Induced Emission. *Adv. Mater.* **27**, 4496–4501 (2015).
55. Xu, Y., Ren, L., Dang, D., Zhi, Y., Wang, X., Meng, L., A Strategy of “Self-Isolated Enhanced Emission” to Achieve Highly Emissive Dual-State Emission for Organic Luminescent Materials, *Chem. Eur. J.* **24**, 10383–10389 (2018).

Figures

Figure 1

The synthetic route of BT-LC.

Figure 2

Photophysical properties of BT-LC in solution. Normalized UV/Vis absorption spectra (solid lines) and fluorescence spectra (dashed lines) of BT-LC in different solvents (3.3×10^{-6} M; $\lambda_{\text{exc}} = 418$ nm). Insets: photographs of BT-LC in different solvents under 365 nm UV illuminations.

Figure 3

Photo-physical behaviors of BT-LC in aggregated state. a Fluorescence intensity of BT-LC and b Fluorescence intensity of BT-M in THF/water mixtures with different fractions of water (0-95%, v/v). Inset: photographs of the compounds with different fw taken under 365 UV illumination. c Normalized fluorescence spectra of BT-LC and d Normalized fluorescence spectra of BT-M before and after grinding. Insets: photographs in unground and ground states under 365 nm UV illuminations.

Figure 4

Single-crystal X-ray diffraction analysis. a Torsion angles of BT-BC. b intramolecular interactions of BT-LC: C-H...N (blue lines), C-H...S (green lines). c intermolecular interactions of BT-LC: C-H...O (red lines); C-H...N (blue lines). For clarity, some hydrogen atoms and solvents are omitted.

Figure 5

The performance of device A and B. a Current density-voltage-luminance (J-V-L) characteristics of A and B; b plots of current efficiency versus luminance.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [BTLCcheckcif.pdf](#)
- [BTLC.cif](#)
- [BTMcheckcif.pdf](#)
- [BTM.cif](#)

- [Sl.pdf](#)