

## Solution Processable Fluorene-Based Laser Dye for Organic Solid-State Lasers

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### Abstract

Fluorene-based laser dyes are well known to have low lasing thresholds in organic solid-state lasers. Here we report a fluorine based laser dye of 9,9'-(((1*E*,1'*E*)-(9,9,9',9'',9'',9''-hexahexyl-9*H*,9'*H*,9''*H*-[2,2':7',2''-terfluorene]-7,7''-diyl)bis(ethene-2,1-diyl)bis(4,1-phenylene))bis(9*H*-carbazole), (BSTFCz), which can be easily synthesized and solution processable. This laser dye emits photoluminescence in a blue region, with a high quantum yield of ~80%, a high radiative decay constant ( $k_r$ ) of  $\sim 1.1 \times 10^9 \text{ s}^{-1}$ , and a low amplified spontaneous emission (ASE) threshold of  $\sim 0.7 \mu\text{J cm}^{-2}$ . When this laser dye was combined with mixed-order distributed feedback gratings, we obtained a low lasing threshold of  $\sim 0.5 \mu\text{J cm}^{-2}$ .

### 1. Introduction

Organic lasers have many advantages, such as low cost, light weight, high mechanical flexibility, and high wavelength-tunability, compared to existing lasers and, therefore, can be used for many applications, such as sensors, optical communication, and spectroscopy. Recently, many remarkable performances have been reported from laser devices using a vacuum-deposited laser dye film of 4,4-bis[(*N*-carbazole)styryl]biphenyl (BSBCz) [1,2]. However, solution processable laser dyes are more advantageous than vacuum deposited laser dyes in terms of the fabrication cost. Therefore, new organic laser dye materials with enhanced laser properties and solution processability need to be developed. Since it is known that laser dyes with a fluorine unit exhibit low lasing thresholds [3], here we report a solution processable, easily synthesized, fluorene-based organic laser dye of 9,9'-(((1*E*,1'*E*)-(9,9,9',9'',9'',9''-hexahexyl-9*H*,9'*H*,9''*H*-[2,2':7',2''-terfluorene]-7,7''-diyl)bis(ethene-2,1-diyl)bis(4,1-phenylene))bis(9*H*-carbazole), (BSTFCz). The chemical structure of BSTFCz is shown in Fig. 1. BSTFCz was blended with a host material of tris(4-carbazoyl-9-ylphenyl)amine (TCTA), and this blend film was combined with mixed-order distributed feedback (DFB) gratings. These devices showed lasing under optical pumping, with a low threshold of  $\sim 0.5 \mu\text{J cm}^{-2}$ . Therefore, we believe that BSTFCz can be a potential candidate for future solution-processed electrically pumped organic semiconductor laser diodes (OSLDs).

### 2. Results and Discussion

The synthesis route of BSTFCz is shown in Fig. 1. First, a building block of vinylphenylcarbazole was synthesized in two steps, via a nucleophilic aromatic substitution reaction, followed by a Wittig reaction. To ensure high solubility of the chromophores in organic solvents for solution processing, two *n*-hexyl groups were incorporated into the central fluorene units. These solubilising groups were attached to the fluorene unit of SFCz via a nucleophilic substitution reaction to give precursors 3. Di-bromination of the commercially available hexahexyl terfluorene 4 at the C2 and C7' positions using bromine gave compound 5 in an excellent yield of 92%. Finally, the syntheses of BSTFCz were accomplished by palladium-catalysed Heck cross-coupling reactions of compounds 2 with 3 and 5 in moderate yields (39–55%).

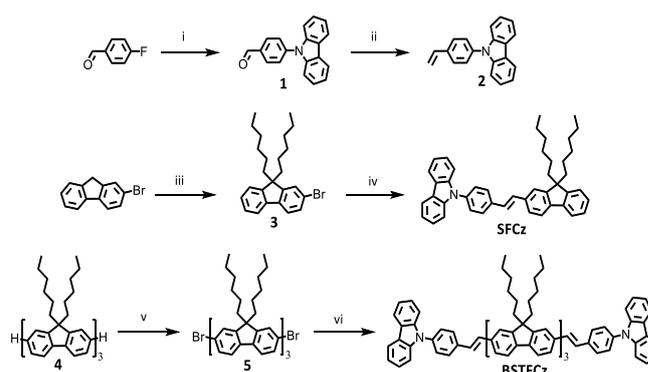


Fig. 1. Synthesis route of BSTFCz

Then absorption and photoluminescence (PL) studies were carried out on solutions, and neat and blend films of BSTFCz (Fig. 2). BSTFCz solutions showed blue emission with the distinctive vibronic structures. The peak of 0-0 transition for BSTFCz was at 421 nm. In neat films, a red-shift in absorption and PL was observed, indicating a strong intermolecular interaction in the solid state.

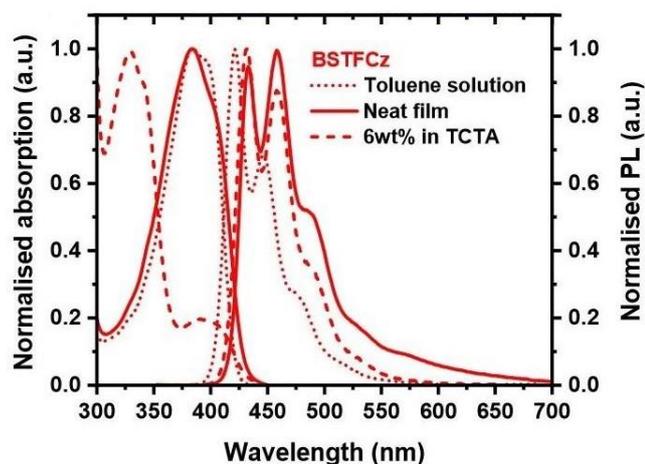


Fig. 2. Normalized UV-Vis absorption and PL spectra of BSTFCz

The absorption and PL spectra for blended films were found to be also red-shifted when compared with solutions, although their red-shift was smaller than that of neat films. The red-shift is proof of aggregation, which can often be circumvented by reducing the doping concentrations. The photophysical parameters of BSTFCz are summarized in Table I. Blend films had a high radiative decay constant ( $k_r$ ) value of  $\sim 1.1 \times 10^9 \text{ s}^{-1}$ , which is comparable to those of state-of-the-art organic laser dyes, such as BSBCz [1] and octafluorene [3]. Such high  $k_r$  can contribute to reduced thresholds of amplified spontaneous emission (ASE).

Table I. Photophysical parameters of BSTFCz

		$\lambda_{\text{abs}}$ (nm),	$\lambda_{\text{PL}}$	PLQY	PL lifetime	$k_r$
		[ $\epsilon, \text{dm}^2 \text{ mol}^{-1} \text{ cm}^{-1}$ ]	(nm)	(%)	(ns)	( $\times 10^9 \text{ s}^{-1}$ )
BSTFCz	Solution	385 [ $1.98 \times 10^5$ ]	421	81 $\pm$ 4	0.66	1.24
	Blend film	329	431	80 $\pm$ 6	0.73	1.10
	Neat film	383	459	45 $\pm$ 9	0.56	0.81

Next, we studied ASE properties of solution-processed blend films under 337-nm photoexcitation using a nitrogen laser (NL100), which has a frequency of 20 Hz and pulse width of 3.5 ns. We found that 6 wt.% doping of BSTFCz into TCTA led to the lowest ASE threshold of  $\sim 0.7 \mu\text{J cm}^{-2}$  as shown in Fig. 3. This value is very low among recently reported organic laser dyes, which can be attributed to the high molar extinction coefficient  $\epsilon$  and high  $k_r$  as shown in Table I. Moreover, BSTFCz exhibited the spectral narrowing at the 0-1 vibration in blended films which is common in reported organic laser dyes and can be explained by the presence of an efficient quasi-four energy level system for laser oscillation.

Then we studied the laser properties of a BSTFCz film embedded into a mixed-order DFB structure. In this DFB design, we placed twelve first-order periods and four second-order periods. Therefore, we were able to enhance both the feedback and the surface emission properties. Figure 4 displays laser emission profiles measured with the same condition mentioned above. BSTFCz devices thus fabricated had a low laser threshold of  $\sim 0.5 \mu\text{J cm}^{-2}$ .

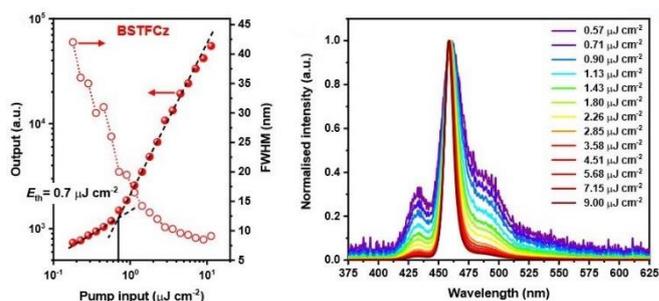


Fig. 3. ASE properties of 6 wt.% BSTFCz:TCTA films.

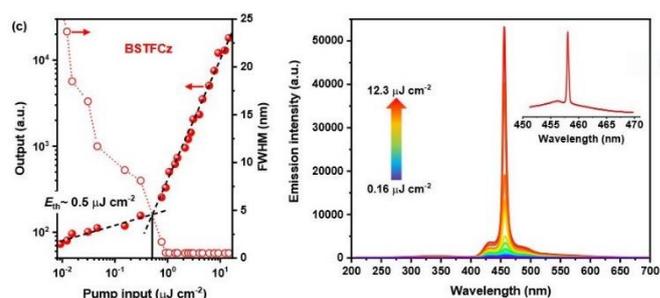


Fig. 4. Laser properties of 6 wt.% BSTFCz:TCTA films.

### 3. Conclusions

In summary, hybridization of trifluorenes and cabazolylstyryl structural motifs was successful in achieving a new solution processable semiconductor laser dye, BSTFCz, which exhibited a low ASE threshold of  $\sim 0.7 \mu\text{J cm}^{-2}$  and a low laser threshold of  $\sim 0.5 \mu\text{J cm}^{-2}$  when incorporated in a mixed-order DFB structure. The obtained low threshold values can be attributed to the high molar extinction coefficient and high radiative decay rate of BSTFCz.

### Acknowledgements

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### References

- [1] A. S. D. Sandanayaka *et al.* *Sci. Adv.* **3** (2017) e1602570.
- [2] A. S. D. Sandanayaka *et al.* *Appl. Phys. Express*, **12** (2019) 061010.
- [3] D.-H. Kim *et al.* *Appl. Phys. Lett.* **110** (2017) 023303.