

Design Strategy for Robust Organic Semiconductor Laser Dyes

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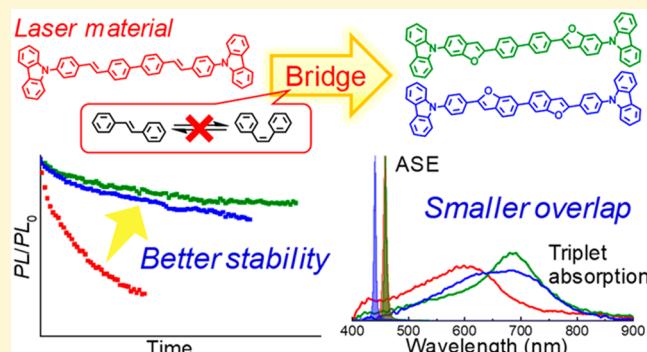
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ABSTRACT: A new molecular design for organic semiconductor laser dyes showing excellent optical properties and high robustness is disclosed in this work. The suitability of a furan moiety for increasing the thermal and photostability in newly developed furan-based derivatives (BPBFCz) is demonstrated by comparing a well-known laser molecule (BSBCz) having a bis-stilbene unit. The new derivatives exhibited high photoluminescence quantum yields of nearly 100% and radiative rate constants of $\sim 10^9$ s $^{-1}$ in both solution and doped films, and their properties were also excellent in neat films. The amplified spontaneous emission (ASE) thresholds of the BPBFCz materials were found to be very low ($< 1 \mu\text{J cm}^{-2}$), and the excited-state absorption in the ASE oscillation region was negligible, which is preferable for laser applications. In addition to these excellent optical properties, which are comparable or superior to those of BSBCz, the decomposition temperatures of the BPBFCz emitters were much higher than that of BSBCz, resulting in the suppression of impurity formation during the thermal deposition. In addition, the photostability of the new materials was dramatically improved compared with that of BSBCz. This study serves as a very significant advancement toward the practical application of organic semiconductor laser diodes and provides molecular design guidelines for robust organic laser molecules.



Organic light-emitting diodes (OLEDs) have been extensively researched in recent decades, resulting in their use in commercial products and their efficiencies reaching the theoretical limit.^{1–4} On the contrary, organic semiconductor laser diodes (OSLDs), the likely successor to OLEDs, and the practical application of organic gain media in solid-state lasers have been a challenging research topic.^{5,6} OSLDs are expected to provide new opportunities for electronic devices because of their wavelength tunability, mechanical flexibility, and low-cost manufacturability. Following long-term efforts to improve resonator structures and charge-injection device configurations, the first demonstration of an electrically pumped OSLD⁷ was reported in 2019 by using the relatively long-established bis-stilbene derivative BSBCz (Figure 1) as the organic semiconducting laser dye.^{8–11} Among the wide variety of laser dyes that have been developed according to diverse molecular design strategies,^{5,12–22} BSBCz is currently one of the best molecules in terms of availability and fluorescence and lasing properties. However, the stability of the OSLD at high current densities was extremely low, presumably due to the degradation of BSBCz,^{23,24} making practical application and detailed investi-

tigation of the OSLD difficult. Therefore, robust organic laser dyes that can withstand even high exciton densities are highly desired.

An analysis of reported organic laser dyes shows that a high radiative rate constant (k_r), that is, a high photoluminescence (PL) quantum yield (QY) and a short fluorescence lifetime (τ_f), is the key to obtaining low thresholds for amplified spontaneous emission (ASE) and lasing ($E_{\text{th}}^{\text{ASE}}$ and $E_{\text{th}}^{\text{laser}}$, respectively). A small excited-state absorption cross-section is also important for low thresholds and high stability because it decreases exciton losses in population inversion. In addition, materials that have facile and scalable synthetic routes, good processability, and high reproducibility are favorable. Moreover, good semiconducting properties and optical characteristics under neat conditions, that is, without a host/guest

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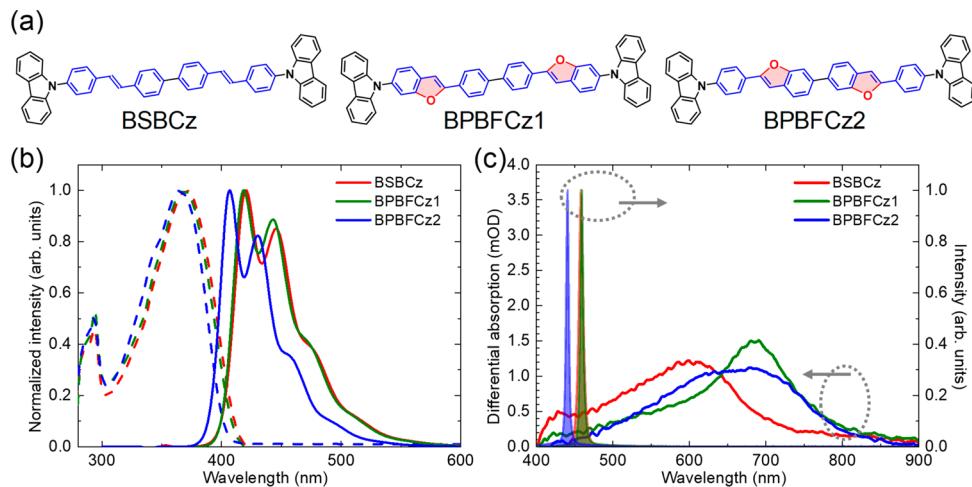


Figure 1. (a) Chemical structures of BSBCz and furan derivatives BPBFCz1 and BPBFCz2. (b) UV-vis absorption (dashed lines) and emission (solid lines) spectra of BSBCz, BPBFCz1, and BPBFCz2 in toluene. (c) ASE spectra in 6 wt % doped CBP films and triplet excited-state absorption spectra (at a time delay of 8 ns) in toluene of BSBCz, BPBFCz1, and BPBFCz2.

Table 1. Photophysical, Electrochemical, and ASE Properties of BSBCz, BPBFCz1, and BPBFCz2 in Solution, 6 wt % Doped CBP Films, and Neat Films

compd	condition	λ_{abs} (nm)	λ_{PL} (nm)	Φ_{PL} (-) ^a	τ (ns) ^b	$k_r/10^8$ (s^{-1})	HOMO (eV) ^c	LUMO (eV) ^c	$E_{\text{th}}^{\text{ASE}}$ ($\mu\text{J cm}^{-2}$)	λ_{ASE} (nm)
BSBCz	in solution ^d	370	420, 447	0.89	0.87	10	-5.53	-2.44		
BSBCz	in CBP film ^e	298, 331, 389	438, 462	0.98	1.3	7.5			0.49	458
BSBCz	in neat film	372	480	0.69	1.6	4.4	-5.92		1.2	481
BPBFCz1	in solution ^d	369	419, 443	0.96	0.97	9.9	-5.49	-2.40		
BPBFCz1	in CBP film ^e	298, 331, 380	441, 462	1.00	1.5	6.7			0.89	460
BPBFCz1	in neat film	370	484	0.89	2.2	4.1	-5.92		1.8	476
BPBFCz2	in solution ^d	365	407, 430	0.96	0.93	10.3	-5.48	-2.16		
BPBFCz2	in CBP film ^e	298, 331, 376	419, 445	1.00	1.3	7.6			0.45	442
BPBFCz2	in neat film	367	427, 452	0.87	1.8	4.8	-5.92		0.60	451

^aAbsolute PL quantum yield evaluated using an integrating sphere in N_2 . ^bIn N_2 . ^cEstimated versus the vacuum level from $E_{\text{HOMO}} = -4.80 - E_{\text{ox}}$ (vs Fc/Fc^+) or $E_{\text{LUMO}} = -4.80 - E_{\text{red}}$ (vs Fc/Fc^+) for DCM and ionization potential for neat films measured by photoelectron yield spectroscopy with a Riken Keiki AC-3 apparatus. ^dPhotophysical properties in toluene and HOMO–LUMO levels in DCM. ^eAbsorption maxima of a CBP neat film are at 297, 331, and 343 nm.

system, are crucial to reducing exciton annihilation losses in devices.²⁵

In fact, BSBCz already satisfies all of these requirements, exhibiting a high k_r of $>10^8 \text{ s}^{-1}$ in neat films and a low $E_{\text{th}}^{\text{laser}}$ of $0.22 \mu\text{J cm}^{-2}$ when combined with a distributed feedback (DFB) structure. Furthermore, continuous-wave (CW) laser operation has been observed from it.^{23,24} Thus the π -conjugation system of the BSBCz structure provides a starting point for designing materials with excellent characteristics and improved stability.

In the chemical structure of BSBCz, the stilbene moiety is apparently a weak point, as cis–trans isomerization through triplet excited states might occur there.²⁶ Detailed mechanisms of isomerization at $\text{C}=\text{C}$ double bonds have been extensively examined for a wide variety of molecules.^{27–29} Such isomerization could worsen the semiconducting and photophysical characteristics,³⁰ thereby increasing the driving voltage required for lasing, and prevent coherent emission because of the mixing of isomers. In addition, a weakening of the double-bond nature in the excited state might also be playing a role in the degradation and decomposition of the molecule.

Bridged ring structures incorporating double bonds can be an effective way to suppress the isomerization. For example, carbon-bridged five-membered rings such as COPVs

(5,5,10,10-tetraalkyl-5,10-dihydroindeno[2,1-*a*]indene derivatives) do not significantly affect the π -conjugation system,^{19–22} so lasing properties similar to those of BSBCz could be expected. However, vacuum sublimation, which is favorable for fabricating OSLDs as well as obtaining better device performance, might become more difficult because of the increased molecular weight. On the contrary, nitrogen-, phosphorus-, and sulfur-bridged rings (pyrrole-, phosphole-, and thiophene-fused systems) such as BTBT ([1]benzothieno-[3,2-*b*][1]benzothiophene) are isoelectronic with chrysene and no longer resemble the electronic structure of stilbene, resulting in a significant decrease in the optoelectronics property.^{31–35} Although oxygen-bridging butadiene–furan with six π electrons—is considered to be isoelectronic with benzene-like pyrrole and thiophene, it more closely resembles a diene because of its small aromaticity.^{36,37} Therefore, we expected that a furan-fused system will yield excellent luminescence properties while improving the stability by suppressing cis isomerization.

Although [1]benzofuro[3,2-*b*][1]benzofuran (BFBF) has already been reported,^{38,39} we focused on a 2-phenylbenzofuran (PBF) unit in this work because it can be more easily synthesized. Thus we designed and synthesized two new

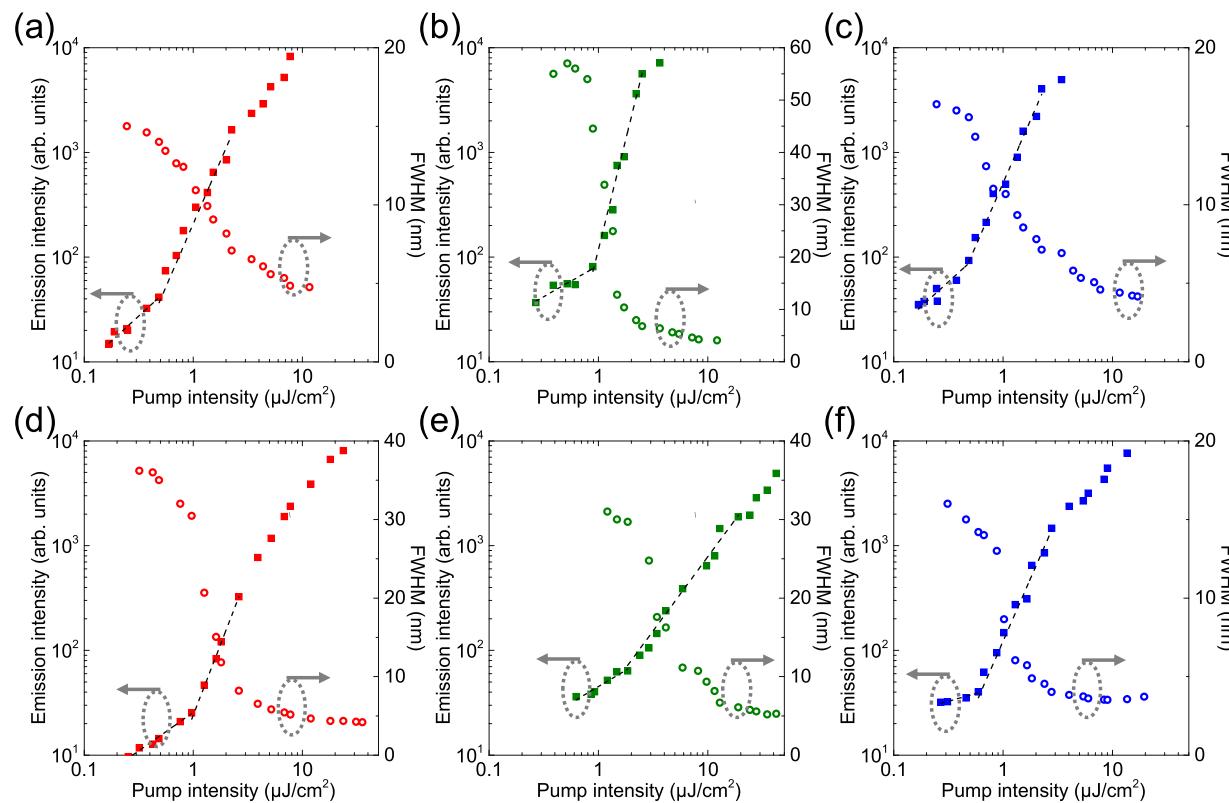


Figure 2. ASE characteristics of (a) BSBCz-doped, (b) BPBFCz1-doped, and (c) BPBFCz2-doped CBP films and (d) BSBCz, (e) BPBFCz1, and (f) BPBFCz2 neat films. Output PL intensity and FWHM as a function of the excitation energy.

laser dyes based on bisphenylbenzofuran (BPBF), namely, BPBFCz1 and BPBFCz2, as shown in Figure 1.

The synthesis methods are given in the *Supporting Information* (Method S1). Because the α -position of furan can easily be halogenated, the key intermediate is 6-bromobenzofuran, which was prepared according to the literature.^{40,41} Although a trace amount of 4-bromobenzofuran was also formed as an inseparable side product and the mixture of isomers was used for the next reaction, the final products can be isolated in pure form. As a result, BPBFCz1 and BPBFCz2 were successfully synthesized in relatively high yields in five steps. Although the solubilities of BPBFCz1 and BPBFCz2 are slightly higher than that of BSBCz in common organic solvents, they are not high enough for preparing thick films by solution process.

Figure 1b shows absorption and PL spectra in toluene. The spectra in other solvents and in vacuum-deposited films along with electrochemical and photoelectron yield spectroscopy measurements are detailed in the *Supporting Information* (Figures S1–S3 and Tables S1–S2) and summarized in Table 1. BPBFCz1 and BSBCz exhibited very similar spectra, indicating similar electronic structures for these compounds despite the introduction of the rigid furan rings. In fact, the HOMO–LUMO distributions (Method S2, Figure S4, and Table S3) and experimentally measured energy levels (Table 1) of BPBFCz1 and BSBCz are nearly identical. The HOMO of BPBFCz1 has a nodal surface on the furan ring and no coefficient on the oxygen atoms. Therefore, the effect of the furan ring on the HOMO is negligible. Although there are small orbital coefficients on oxygen in the LUMO of BPBFCz1, the overall distribution is also similar to that of BSBCz.

On the contrary, BPBFCz2 has a slightly destabilized LUMO level, and its LUMO distribution slightly spreads to the nitrogen of the carbazole group, suggesting that the electron-accepting property of the central core is weakened because of the weak donor of benzofuran at the center of the molecule. Therefore, the intramolecular donor–acceptor interaction is decreased for BPBFCz2, whereas BSBCz and BPBFCz1 have weak donor–acceptor interactions between carbazole and the central biphenyl rings. This is also confirmed by the smaller shift of spectra for BPBFCz2 in polar solvents (Figure S1 and Table S1). As a result, BPBFCz2 exhibits spectra that are slightly blue-shifted to deep blue and a slightly larger HOMO–LUMO gap, although its electronic structure is still based on BSBCz. Interestingly, the PLQYs of BPBFCz1 and BPBFCz2 are higher than those of BSBCz under all of the conditions measured here. Although the PL decay lifetimes are slightly longer, the k_r values of BPBFCz1 and BPBFCz2 are very high (10^8 to 10^9 s⁻¹) and comparable to those of BSBCz, so low ASE and laser thresholds could be expected.

Film morphology is known to be important for the use of emitters in neat films.^{42–45} A smooth film surface owing to an amorphous morphology is crucial for the evaluation of ASE properties as well as the fabrication of OSLDs. The out-of-plane X-ray diffraction (XRD), atomic force microscopy (AFM), variable-angle spectroscopic ellipsometry, and uniaxial anisotropic models are shown in the *Supporting Information* (Figures S5–S7 and Table S4). Similar to BSBCz, vacuum-deposited BPBFCz1 and BPBFCz2 films were found to be amorphous, having a smooth surface with a high degree of horizontal orientation. The orientation order parameters were $S = -0.36$, -0.25 , and -0.47 for BSBCz, BPBFCz1, and BPBFCz2, respectively. The small difference in the molecular

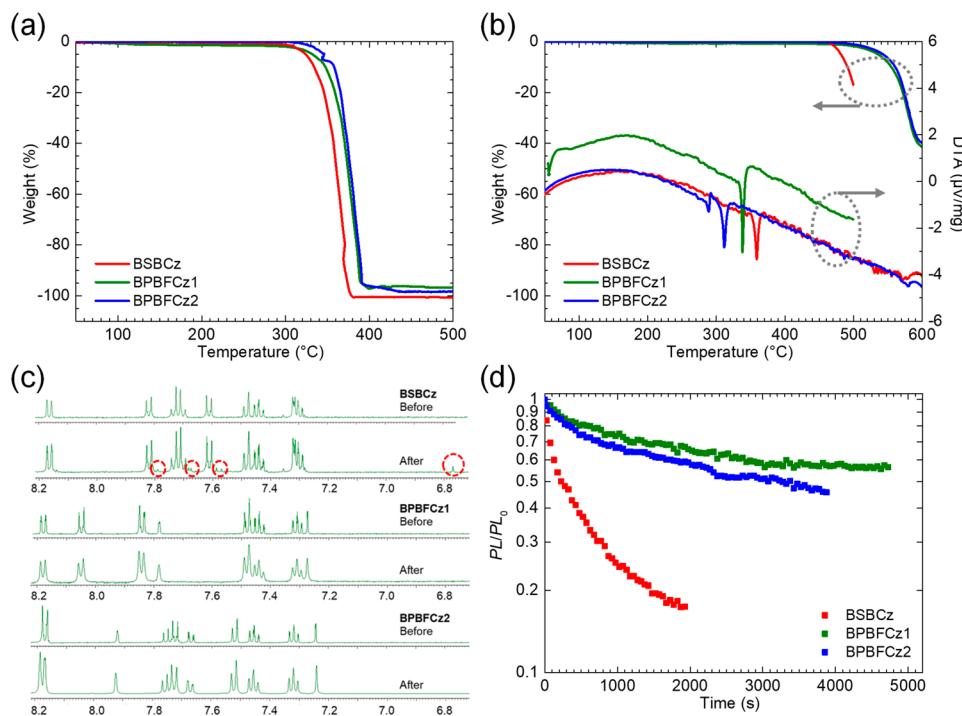


Figure 3. Thermal and photostability of BSBCz, BPBFCz1, and BPBFCz2. (a) TG at 1 Pa. The 5% weight loss temperatures indicate the sublimation temperature (324, 332, and 343 °C for BSBCz, BPBFCz1, and BPBFCz2, respectively). Note that noise exists in the BPBFCz2 signal at 345 °C because of the fluctuation of the monitoring temperature during the endothermic process. (b) TG-DTA at ambient pressure. The 5% weight loss temperature indicates the decomposition temperature (478, 539, and 543 °C for BSBCz, BPBFCz1, and BPBFCz2, respectively). (c) NMR spectra of BSBCz, BPBFCz1, and BPBFCz2 before (upper) and after (under) vacuum deposition. (d) PL intensity normalized to the initial PL intensity for BSBCz, BPBFCz1, and BPBFCz2 as a function of time irradiated by continuous-wave laser light at 355 nm (excitation power 3.3 mW).

orientation is due to the different molecular shapes of these three molecules. Overall, the excellent optical properties including high PLQYs under the neat conditions suggest a high potential for the application of the derivatives to single-layer OSLDs.

Figure 1c shows excited-state absorption spectra of BSBCz, BPBFCz1, and BPBFCz2, along with the ASE spectra of 6 wt % doped 4,4'-*N,N'*-dicarbazole-biphenyl (CBP) films (vide infra). (See Figures S8–S10 for details.) For the excited-state absorption measurements, the emitter concentration was adjusted to give the same absorbance at the excitation wavelength of 370 nm for all emitters. Because triplet excited states are sensitive to oxygen quenching, transient absorption spectroscopy (TAS) was performed under ambient and deoxygenated conditions to confirm the presence of a triplet excited state. In general, long-lived triplet excited states lead to significant losses, especially under CW operation and electrical excitation. A small overlap between the excited-state absorption and the ASE and lasing spectra is an important feature to avoid these losses.⁴⁶ Although the lifetimes of the triplet excited states are slightly longer for BPBFCz1 and BPBFCz2, all compounds have very short decays faster than 1 μ s. It is noteworthy that the triplet excited-state absorption spectra of BPBFCz1 and BPBFCz2 are red-shifted compared with that of BSBCz, resulting in a decrease in the overlap at the ASE wavelength. In addition, the calculation of absorption, stimulated emission, and triplet excited-state absorption cross sections (σ_{abs} , σ_{em} , and σ_{TT} , respectively) confirmed the condition of $\sigma_{\text{em}} > \sigma_{\text{TT}}$ (Method S3 and Figure S11), which is preferable for laser applications.

Figure 2 shows emission properties as a function of pump intensity and $E_{\text{th}}^{\text{ASE}}$ of BSBCz, BPBFCz1, and BPBFCz2 in 6 wt % doped CBP films and neat films for the optimized film thicknesses. The $E_{\text{th}}^{\text{ASE}}$ value was determined from a nonlinear increase in the emission intensities plotted against the excitation light intensity and is summarized in Table 1. The neat film of BPBFCz1 has an $E_{\text{th}}^{\text{ASE}}$ value of $1.8 \mu\text{J cm}^{-2}$, which is slightly higher than that of $1.2 \mu\text{J cm}^{-2}$ for BSBCz. In contrast, $E_{\text{th}}^{\text{ASE}}$ for the neat film of BPBFCz2 was the lowest at only $0.60 \mu\text{J cm}^{-2}$. These results are consistent with the overall k_r values, although we expected a lower $E_{\text{th}}^{\text{ASE}}$ for BPBFCz1 based on its faster k_r . Therefore, there may be room to improve the threshold through further optimization. Note that these results might be related to the degree of molecular orientation. The $E_{\text{th}}^{\text{ASE}}$ values for CBP films doped with BPBFCz1, BPBFCz2, and BSBCz were 0.90 , 0.45 , and $0.49 \mu\text{J cm}^{-2}$, respectively. Overall, these values are very low compared with those reported so far, with thresholds of $<1 \mu\text{J cm}^{-2}$ still very limited,^{5,10} confirming that the new derivatives are excellent lasing materials and are highly promising for use in OSLDs.

Finally, we evaluated the stabilities of the materials using thermogravimetric–differential thermal analysis (TG-DTA) and photodegradation tests under CW laser irradiation (Figure 3). The TG measurements at 1 Pa revealed sublimation temperatures that are similar for the three materials, with final weights reaching close to -100% . At ambient pressure, the decomposition of BPBFCz1 and BPBFCz2 appeared at temperatures >500 °C, which is ca. 60 °C higher than that of BSBCz. These results indicate that the thermal stability of the stilbene unit was dramatically improved by crosslinking with oxygen atoms and forming a fused-furan ring. In addition,

the larger difference between sublimation and decomposition temperatures indicates that BPBFCz1 and BPBFCz2 are less likely to decompose when vacuum-deposited.

Here we confirmed that BSBCz is indeed not extremely stable at high temperatures, as seen in *Figure 3c*. The NMR spectra for a thin film of BSBCz prepared by vacuum deposition at a pressure of $<10^{-4}$ Pa exhibit small peaks at around 6.77, 7.58, 7.68, and 7.90 ppm, which were not observed before sublimation. The impurity formed during sublimation upon heating might be its *cis* isomer, according to the NMR of a *cis*-stilbene (*Figure S12*). This indicates that the films of BSBCz in previous works, including in an electrically pumped laser device, were, unfortunately, not highly pure, and these impurities may be difficult to avoid because the vacuum level in the deposition chamber used here is already very high. On the contrary, BPBFCz1 and BPBFCz2 showed identical NMR spectra before and after vacuum deposition, indicating that sublimation occurs without decomposition and isomerization. Therefore, these compounds could provide high-purity thin films, which is promising for improving OSLD performance.

Furan rings are known to undergo photooxidation reactions and are considered to have low photostability. Indeed, the emission color for the neat film of BPBFCz2 in ambient air rapidly changed upon irradiation with excitation light because of a growing emission band at 600–700 nm, although BPBFCz1 showed no such behavior (see *Figure S13*). However, this photoreaction could be completely suppressed with encapsulation in a glove box, after which emission at longer wavelengths was not observed even following strong excitation, suggesting that the material may still be useful because organic devices are generally fabricated without exposure to air.

Figure 3d shows the change of PL intensity as a function of the irradiation time for neat films of BSBCz, BPBFCz1, and BPBFCz2 under N_2 . The samples were excited using a CW laser with an excitation wavelength of 355 nm to include the effect of triplet excitons, and the exciton densities were controlled to be equal for all samples under the same excitation intensity by adjusting the film thickness. The emission intensity of BSBCz decreased more rapidly compared with those of BPBFCz1 and BPBFCz2, and the half-life times of the emission intensities for the furan derivatives were 20 times longer than that of BSBCz. The same trend was also observed under light amplification (*Figure S14*). These results indicate that the excited-state stability can be dramatically improved by a small modification of the double-bond structure.

In conclusion, we succeeded in designing and synthesizing new organic laser materials based on a fused furan ring. Despite the fact that BSBCz was used in many advanced organic laser devices owing to its low lasing thresholds, its poor stability could hinder further applications. In this work, we confirmed that the purity of vacuum-deposited films of BSBCz is low because of *cis* isomerization. On the contrary, BPBFCz1 and BPBFCz2 clearly demonstrate that there is a way to improve the stability without sacrificing optical and lasing properties. The BPBFCz emitters showed quite high PLQYs, small excited-state absorption cross-sections, and low ASE thresholds. In addition, both thermal and photostabilities were dramatically improved. These results suggest that BPBFCz1 and BPBFCz2 are very promising materials in terms of developing organic semiconductor laser diodes. Furthermore, this strategy of employing furan to improve the stability could

find wide application because stilbene moieties are already frequently used in organic fluorescent and laser dyes.^{47–56}

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmaterialslett.9b00536>.

Synthesis and characterization (Method S1), DFT calculations (Method S2), reagents (Table S5), instruments (Table S6), experimental details (Method S4) and NMR spectra (Data S1) ([PDF](#))

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Notes

The authors declare no competing financial interest.

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