Color-Tunable Low-Threshold Amplified Spontaneous Emission from Yellow to Near-Infrared (NIR) Based on Donor–Spacer–Acceptor–Spacer–Donor Linear Dyes

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ABSTRACT: Organic lasing dyes possessing small energy gaps commonly suffer from high thresholds, because of energy-gap law, which induces detrimental nonradiative relaxation. Herein, molecules based on alternating donor (D) and acceptor (A) moieties are described. Those linear molecules are built with a spacer between D and A, with a general formula of D–spacer–A–spacer–D. Such modification of the A core allows one to obtain color-tunable lasing properties from yellow to near-infrared (NIR). Into more details, triphenylamine (TPA) is selected as the D moiety, while benzothiadiazole (BTd) and benzo[1,2-c:4,5-c']bis[1,2,5]thiadiazole (BBTD) with strong electron-withdrawing capability, are chosen as A cores for yellow ((TPA-F)₂BTd) and NIR ((TPA-F)₂BBTD) lasing dyes, respectively. Both dyes exhibit high photoluminescence quantum yields (PLQYs) and fast fluorescence radiative rate. The corresponding amplified spontaneous emission (ASE) thresholds of yellow and NIR

dyes are as low as 0.5 and 3.8 $\mu\text{J cm}^{-2}$ in the solution-processing blending films, with wavelength peaks at 550 and 811 nm, respectively. In those dyes, the long alkyl chains appended on the fluorene conjugated spacer guarantee the high solubility and prevent aggregation. Consequently, for ((TPA-F)₂BTd), the neat film allows one to reach PLQYs as high as 90%, with a low ASE threshold (1.9 $\mu\text{J cm}^{-2}$) and good stability. Therefore, such promising molecular design allows the realization of color-tunable ASE or lasing dyes with very low thresholds.

Organic dyes have been widely employed as light emitters for organic light-emitting diodes (OLEDs) and promising gain mediums for organic semiconductor lasers (OSLs) in the past few decades. This is due to the unique and outstanding merits, for instance, feasible chemical tunability for molecular designs, and being a lightweight thin film with flexibilities.^{1–4} In particular, with regard to the emerging organic lasing source, the potential applications in the fields of optical communication, high-sensitivity sensors, high-resolution spectroscopy, medical surgery and bio-integration, are beneficial from its exclusive characteristics, such as high intensity, mono-directionality, and large coherence length.⁵ Until now, careful chemical engineering of the energy gaps has allowed the preparation of small molecules, oligomers, and polymers that exhibiting stimulated emission from the deep-blue region to the near-infrared (NIR) region.^{6–11} Nevertheless, among those dyes, most of the candidates have high-lying energy levels, resulting in blue

emission. Those dyes show very low amplified spontaneous emission (ASE) and, therefore, low lasing thresholds ($<1 \mu\text{J cm}^{-2}$),¹² similar to the well-studied small molecule 4,4'-bis[(N-carbazole)styryl]biphenyl (BSBCz).^{7,13} BSBCz has realized quasi-continuous-wave (q-CW) optical lasing,^{14,15} and the indication of electrical-pumping organic semiconductor laser diodes (OSLDs) was described.¹⁶ By comparison, either for ASE or lasing thresholds, the progress of gain molecules spanning from the yellow region to the NIR region with smaller energy gaps largely still lags behind.¹⁷

Scheme 1. Synthesis Pathway of (TPA-F)₂BTD and (TPA-F)₂BBTD

Recently, π -conjugated oligomers, incorporating diverse donor (D) or acceptor (A) moieties, are widely exploited to accelerate the development of yellow to NIR lasing performance.^{5,18} For instance, chromophores including fluorene-based dendrimers,¹⁹ star-shaped macromolecules,²⁰ and boron difluoride curcuminoid-based thermally activated delayed fluorescence (TADF) derivatives,^{9,21,22} have been reported for their outstanding properties. Larger molecules could effectively circumvent the close packing-induced self-quenching and crystallization effect in small molecules. In addition, they also possess the same good solubility and optimal film morphology as polymers, to some extent.²³ However, promising ASE or lasing thresholds are rarely obtained, because of the energy-gap law effect, which is an intrinsic limit inducing a decrease in the fluorescence radiative process due to faster nonradiative processes. This phenomenon occurs because of the large vibrational overlap between a ground state and an excited state as the energy gap between the lowest excited state and the ground state becomes small.^{22,24–27} This energy-gap law decreases the fluorescence quantum yields, not only obstructing the output of high external quantum efficiency (EQE) in OLEDs, but also excluding the possibility to trigger ASE or lasing.^{28–30} Moreover, since the fast fluorescence radiative decay rate is one of the important parameters to realize ASE and lasing, the precise manipulation of D/A motifs, as well as the conjugated organic spacer, determines the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy and their overlap. Such HOMO/LUMO overlap, in contrast with charge transfer (CT) states, yields a hybrid locally excited charge transfer (HLCT) transition. Therefore, such HLCT induces large oscillator strength (f).^{31–33}

Herein, we designed and synthesized linear molecules where the skeleton can be described as D–spacer–A–spacer–D for promising lasing dyes. In more details, the donor moiety is chosen to be triphenylamine (TPA), while the fluorene-based spacers connect D units to the A core.³⁴ Benzothiadiazole (BTD) and benzo[1,2-c:4,5-c']bis[1,2,5]thiadiazole (BBTD) are selected as acceptors for yellow ((TPA-F)₂BTD) and NIR ((TPA-F)₂BBTD) lasing dyes, respectively. It is to be highlighted that long alkyl chains are appended on the fluorene units in order to provide high solubility to realize solution-process devices, as well as for suppressing intermo-

lecular aggregation.³⁵ The acceptor BBTD exhibits stronger electron-accepting capability than BTD, which is due to the extension of the heterocyclic core. Thus, the intensive D/A interplay further leads to a much smaller energy gap, thereby resulting in the large red-shift from yellow to NIR emission.³⁶ Benefiting from the reasonable HOMO/LUMO wavefunction distribution in the molecular skeleton, the noticeable wavefunction overlap guarantees the locally excited (LE) feature with large oscillator strength ($f \approx 0.5$). Such large absorption is accompanied by a fluorescence decay time of ~ 4 ns and high photoluminescence quantum yields (PLQYs). Thus, the optimal ASE thresholds for yellow and NIR emissions are 0.5 and 3.8 $\mu\text{J cm}^{-2}$, respectively, which are among the lowest ones in the corresponding spectral region, to the best of our knowledge. Here, it can be highlighted that the substitution of the fluorene unit with long alkyl chains allows solution process and effectively prevents the aggregation-caused quenching (ACQ) in the neat film, yielding the high PLQY of 90% in a neat film of (TPA-F)₂BTD, with an ASE threshold as low as 1.9 $\mu\text{J cm}^{-2}$. Moreover, the solution-processed OLEDs of (TPA-F)₂BTD and (TPA-F)₂BBTD are fabricated and show EQEs of 2.6% and 0.56% for yellow and NIR emission, respectively, with only slight efficiency rolloff under hundreds of current density injections.

RESULTS AND DISCUSSION

The two dyes were synthesized in a similar manner using divergent synthesis, as described in Scheme 1. A Suzuki cross-coupling reaction was realized on the 4,7-dibromo-2,1,3-benzothiadiazole (or 4,8-dibromobenzo[1,2-c:4,5-c']bis[1,2,5]thiadiazole) with the corresponding fluorene boronic ester (acid) counterpart in the presence of $\text{Pd}(\text{PPh}_3)_4$ yielding 1a and 1b with reasonable yields (ca. 75% and 48%, respectively). 1a (1b) was further brominated using bromine in chloroform to give 2a (2b). Subsequently, the dibromo derivatives 2a (2b) were capped by using a Suzuki cross-coupling reaction with 4-(diphenylamino)phenylboronic acid yielding (TPA-F)₂BTD, 3a ((TPA-F)₂BBTD, 3b). The specific molecular structures are presented in Figure 1a and 1b. It is noted that 3a and 3b are constructed on the same molecular structure, with 3b containing an extending heterocyclic core. The change from BTD to BBTD reinforces

Figure 1. (a, b) Molecular structures of yellow lasing dye (TPA-F)₂BTD (panel (a)) and near-infrared (NIR) lasing dye (TPA-F)₂BBTD (panel (b)); (c, d) the LUMO wavefunction distribution of (TPA-F)₂BTD with ethyl chain (panel (c)) and (TPA-F)₂BBTD with ethyl chain (panel (d)); and (e, f) the calculated HOMO wavefunction distribution of (TPA-F)₂BTD with ethyl chain (panel (e)) and (TPA-F)₂BBTD with ethyl chain (panel (f)).

the acceptor strength of the molecule for reducing the energy gap.

Cyclic voltammetry (CV) was performed to determine the HOMO and LUMO of the two dyes. Those two dyes show one-electron oxidation and reduction waves that can be attributed to the donor TPA end-group and BTD/BBTD acceptors, respectively. As shown in Figure S1 in the Supporting Information, the oxidation and reduction potentials were found to be +0.69 V and −1.62 V, respectively, for (TPA-F)₂BTD and +0.71 V and −0.89 V, respectively, for (TPA-

F)₂BBTD (vs. ferrocene/ferrocenium). Such values of oxidation and reduction yield HOMO and LUMO energies of ca. −5.71 eV (−5.72 eV) and −2.94 eV (−3.71 eV), respectively, providing an electrochemical gap value of 2.77 eV (2.01 eV). The value of the HOMO was in good agreement with the workfunction measurements (AC-3), yielding values of −5.79 and −5.82 eV in Figure S2 in the Supporting Information, for (TPA-F)₂BTD and (TPA-F)₂BBTD, respectively (see Table S1 in the Supporting Information).

The density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methods were performed to better clarify the geometrical difference and HOMO/LUMO wavefunction distribution of the molecules. As expected (see Figures 1c and 1d), the LUMO wavefunctions are mainly concentrated on the BTD and BBTD acceptor moieties, and partially extend to fluorene spacers; whereas HOMO wavefunctions are distributed along with the D-spacer (fluorene)—A molecular skeleton. Such HOMO/LUMO distribution is characteristic of a CT transition describing the S₁–S₀ transition. Herein, from Figure S3 in the Supporting Information, it is worth noting that the long alkyl chain does not participate in the orbital wavefunction distribution; thus, neither the influence of HOMO/LUMO distribution nor derivation of calculated values occurs within these two models. To some extent, either acceptor moieties or a fluorene bridge is involved in HOMO distribution for fulfilling the substantial HOMO/LUMO overlap, which leads to a large oscillator strength (*f*) for the CT state, promoting high S₁–S₀ transition dipole moment and, thus, the fast-radiative rate (*k_r*). Thus, the corresponding *f* for (TPA-F)₂BTD and (TPA-F)₂BBTD are 0.5521 and 0.4986, respectively, which is a prerequisite for triggering ASE or lasing activities. The calculated data are summarized in Table S2 in the Supporting Information.

Figure 2. (a) Absorption and photoluminescence (PL) spectra of (TPA-F)₂BTD in CBP with different doping ratios; (b) PLQY values of (TPA-F)₂BTD in CBP with different doping ratios; (c) time-dependent transient PL in nanosecond scale of blending films; (d) absorption and photoluminescence (PL) spectra of (TPA-F)₂BBTD with different doping ratios; (e) PLQY values of (TPA-F)₂BBTD with different doping ratios; and (f) time-dependent transient PL in nanosecond scale of blending films.

Table 1. Summary of Photophysical Properties and ASE Performance of (TPA-F)₂BTd and (TPA-F)₂BBTD

doping ratio (wt %)	Abs _{max} ^a (nm)	PL _{film} ^a (nm)	Φ _{PL, film} (%) ^a	τ (ns)	k _r (×10 ⁸ s ⁻¹)	ASE _{max} ^a (nm)	ASE threshold (μJ cm ⁻²)	ASE FWHM (nm)
(TPA-F) ₂ BTd								
3	467	548	99	3.7	2.7	550	0.50	11.2
6	443	560	95	3.8	2.5	555	0.72	10.4
15	444	570	94	3.8	2.4	557	1.56	10.0
40	440	562	90	3.9	2.3	567	1.62	11.0
60	440	565	91	4.1	2.2	568	2.80	7.6
100	441	568	89	4.5	2.0	573	2.67	7.8
(TPA-F) ₂ BBTD								
1	662	770	—	4.7	—	796	6.1	10.6
2	662	777	—	4.2	—	803	3.9	11.0
3	661	780	50	4.1	1.2	811	3.8	10.7
6	650	787	44	4.0	1.1	816	3.9	8.6
10	653	797	39	3.9	1.0	819	5.9	9.5
15	658	798	—	3.8	—	823	8.0	8.3

^aMeasured in doped film with different doping ratios in the CBP host.

To characterize the two dyes, photophysical studies were performed in solution. To that end, solvatochromism was recorded in eight different solvents with different polarities, which allowed us to have information on the excited-state dipole moment (the ground-state dipole moment was obtained from DFT calculation). As can be seen, while the absorption spectra do not move dramatically (Figure S4 in the Supporting Information), a red-shift of the emission of (TPA-F)₂BTd and (TPA-F)₂BBTD is observed when increasing the polarity of the solvent.

Such behavior is typical for CT state emission, revealing that the ground-state dipole moment is rather low, compared to the excited-state dipole moment, which is displayed in Figures S5 and S6 in the Supporting Information. In addition, the PLQYs were measured in those solutions, showing rather high values. The photophysical properties of (TPA-F)₂BTd and (TPA-F)₂BBTD were subsequently estimated at various doping ratios in a 4,4'-bis(*N*-carbazolyl)-1,10-biphenyl (CBP) matrix. Herein, CBP is employed as the host material, because of its relatively good solubility in chloroform, and the well-matched HOMO and LUMO wavefunctions with (TPA-F)₂BTd and (TPA-F)₂BBTD, according to the aforementioned estimated HOMO/LUMO values, which have been plotted in Figure S7 and Table S4 in the Supporting Information. Thus, effective host-guest energy transfer can be undertaken, as well as preventing the potential host-guest exciplex formation. Also, as shown in Figure S8 in the Supporting Information, the overlap between the fluorescence from CBP and the absorbance of the (TPA-F)₂BTd dye guarantees the very effective host-guest Förster energy transfer (FRET) characteristics. Note that a less efficient FRET is observed in the case of (TPA-F)₂BBTD, which is due to the red-shift of the absorption of the latter dye.

The solution-processed blended films were fabricated by spin-coating onto the fused silica substrates, and the corresponding film thickness is controlled to be ~150 nm. For yellow lasing dye (TPA-F)₂BTd, the doping ratios span values from 3 wt % to 100 wt % (in other words, the host-free neat film). From the absorbance in Figures 2a and 2d, the intensity of CT transition band between 400 nm and 500 nm of (TPA-F)₂BTd is gradually enhanced with an increase in the doping ratios. The consistent maximum absorption peak of the CT transition at ~444 nm, as well as no obvious broadening or shifting of this transition within such a large doping region,

implies that there might be little concentration-dependent quenching or intermolecular aggregation in those large molecules for (TPA-F)₂BTd. With an increase in the doping concentrations, the wavelength maximum exhibits a slight red-shift. Subsequently, the PLQYs are correspondingly estimated under the excitation of 340 nm radiation. Note that all PLQY values can almost exceed 90%. In detail, the unity PLQY values (close to 100%) can be achieved at low doping ratios; even in the neat film, there is only a slight reduction of the PLQY to 90%, which further confirms that a fluorene spacer with long alkyl chains in the D-spacer-A-spacer-D molecule not only reinforces the solubility, but also facilitates large steric hindrance to effectively reduce the intermolecular interaction and aggregation.

To gain further insights into those dyes, sub-nanosecond transient PL decay measurements were conducted for various doping ratios, and the fast fluorescence decay lifetime (τ) ranges from 3.7 ns to 4.5 ns, with respect to doping ratios.

According to the equation

$$k_f = \frac{\phi}{\tau}$$

where k_f denotes fluorescence radiative rate constant and ϕ is PLQY, all of the samples with various doping ratios possess high fluorescence radiative rate constants for blended films, indicating the potential to realize efficient ASE or lasing performance.

Alternatively, as a derivative of (TPA-F)₂BTd, (TPA-F)₂BBTD is distinguished by extending the heterocyclic core from BTd to BBTD to enhance the acceptor strength for realizing NIR emission. Thus, from Figure 2d, the PL emission of (TPA-F)₂BBTD showed a red-shift from the yellow region to the NIR regime at ~800 nm, and the fluorescence decay lifetime is also as fast as the same range as that of (TPA-F)₂BTd (from 3.8 ns to 4.7 ns). Nevertheless, because of the promoting nonradiative decay governed by the energy-gap law effect, the PLQYs decrease to 50% at a doping ratio of 3 wt %, but the corresponding k_f can maintain a value of 1×10^8 s⁻¹. All of the data are summarized in Table 1.

Both chromophores were further evaluated as emitting dyes in OLEDs. The specific device configuration is as follows: ITO (100 nm)/poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, 50 nm)/CBP:emitters (x wt %, Y nm)/2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1H-

Figure 3. OLED performance of (TPA-F)₂BTD-based yellow emission with different light-emitting layer thicknesses and (TPA-F)₂BBTD-based NIR emission with different doping ratios: (a, d) current density versus driving voltage ($J-V$) curve of (TPA-F)₂BTD (panel (a)) and (TPA-F)₂BBTD (panel (d)); (b, e) electroluminescence (EL) spectra of (TPA-F)₂BTD (panel (b)) and (TPA-F)₂BBTD (panel (e)); and (c, f) EQE versus current density characteristics of (TPA-F)₂BTD (panel (c)) and (TPA-F)₂BBTD (panel (f)).

Figure 4. ASE performance of (TPA-F)₂BTD-based solid-state films with different doping ratios in a CBP host matrix: (a) output waveguide emission intensity versus excitation power relationship; (b) ASE spectra of all of the films above the thresholds; (c) narrowing of FWHMs versus excitation power; and (d) relationship of fluorescence radiative rate constant with the ASE threshold, as a function of the doping ratios.

benzimidazole) (TPBi, 65 nm)/LiF (0.8 nm)/Al (100 nm), where hole-injection/transporting layer PEDOT:PSS and light-emitting layers are solution-processed, x represents the quantity of dye compared to the quantity of CBP, and Y is the thickness of the EML. In parallel, the electron-transporting layer (TPBi), electron-injection layer (LiF), and cathode (Al) are respectively thermally evaporated. The corresponding

energy-level alignment of device is schematically plotted in Figure S7 in the Supporting Information. For yellow emitter (TPA-F)₂BTD, the light-emitting layer based on CBP host matrix is doped with different concentrations from 3 wt % to 40 wt %, whose PLQYs of the corresponding solid-state films are close to unity (near or exceeding 95%). The device performance is presented in Figure S9 in the Supporting

Information. With respect to the PL spectra, the EL spectra undergo slight red-shift from 555 nm to 566 nm when increasing the doping concentrations. For the 3 wt % blend (PLQY = 99%), the thickness of the light-emitting layer is optimized from 60 nm to 150 nm by tuning the rotation rate during spin coating. As displayed in Figure 3a, it is evident that the turn-on voltage of OLEDs, Y1 (~150 nm), Y2 (~110 nm), Y3 (~80 nm) and Y4 (~60 nm) with different thickness, decreases from 7.5 V to 5.0 V by reducing the thickness of the light-emitting layers. Only a slight shift of the emission wavelength maximum is observed. The full-width at half-maximum (FWHM) of the EL spectrum is slightly narrowing, which might be ascribed to the cavity effect when tuning the thickness. As presented in the EQE to current density (EQE–J) curve in Figure 3c, the highest EQE values of yellow emission increase from 1.65% to 2.67% when decreasing the thickness. Note that all of the devices could tolerate high current injection, and there is slight efficiency rolloff within the variation of current density injection in several orders. For instance, the EQE of Y4 at 100 mA cm⁻² is maintained 1.70%, which is one of the inevitable prerequisites to further torch the terminal solution-processed electrical-pumping organic laser diodes.

For the NIR emitter (TPA-F)₂BBTD, the device configuration, similar to that of (TPA-F)₂BTD, is also applied in the solution-processed device, which is also blended in the CBP host with different concentration ratios from 1 wt % to 6 wt %.

More specifically, the turn-on voltage of NIR devices is ~8.0 V. In parallel, as displayed in Figure 3e, the corresponding EL spectra are located in the NIR regime, the spectral maximum shows red-shifting from 775 nm to 790 nm, with increasing the doping ratios (thickness of the emission layer is ~100 nm). Because of the limitations of the energy-gap law effect, the highest EQE is 0.56%, and all of the devices enable stable efficiency output with slight rolloff under large current density (over 100 mA cm⁻²).

According to the large oscillator strength, as well as relatively fast radiative decay rate (k_f) of (TPA-F)₂BTD and (TPA-F)₂BBTD, ASE of those dyes was performed with the hope to obtain an efficient threshold. In the context of the yellow lasing dye (TPA-F)₂BTD, concentration-dependent ASE properties from 3 wt % to 100 wt % were systematically evaluated in CBP blend films. The thickness for all of the prepared samples is >150 nm, which is thick enough to realize the edge waveguide. Figure 4a shows the output emission intensity from the edge at different excitation densities. It is evident that all of the studied samples (at different doping ratios) show ASE. ASE can be well-evidenced by changes in the intensity slope and a narrowing of the emission (i.e., decrease of the FWHM) up to a value of <10 nm. Also, from Figure 4b, the ASE peaks are adjustable from 549 nm to 573 nm (yellow) by changing the concentration ratios. All the detailed ASE characteristics are plotted in Figure S10 in the Supporting Information. By optimizing the thickness of the emission layer from 140 nm to 370 nm at 3 wt % (Figure S11 in the Supporting Information), the lowest threshold is obtained with a film 260 nm thick. Then, calculated from Figures 4a and 4d, the ASE thresholds increase from 0.5 $\mu\text{J cm}^{-2}$ to 2.7 $\mu\text{J cm}^{-2}$, when going from 3 wt % to 100 wt % in CBP. To the best of our knowledge, the yellow ASE threshold of ~0.5 $\mu\text{J cm}^{-2}$ is among the lowest values reported in the literature. The trend of ASE threshold change is almost consistent with the radiative rate ($k_f = 2.7 \times 10^8 \text{ s}^{-1}$ for 3 wt %, $2.0 \times 10^8 \text{ s}^{-1}$ for 100 wt %), because the

Einstein constant (B) is proportional to k_f , according to the following relationships:

$$B \propto \frac{c^3}{8\pi h \nu^3} k_f; \quad E_{\text{th}} \propto \frac{1}{B}$$

where c is the velocity of light, h represents Planck's constant, ν is the transition frequency, and E_{th} is the threshold. Herein, we notice that the host-free system also exhibits promising threshold values, which benefits from the effective limitation of intermolecular aggregation and reduced concentration quenching. The optimal threshold of only 1.9 $\mu\text{J cm}^{-2}$ is obtained in Figure 5, as well as Figure S12 in the Supporting

Figure 5. Optimization of thickness for ASE performance of (TPA-F)₂BTD-based solid-state neat films: (a) the relationship between ASE thresholds versus film thickness; (b) PL intensity and FWHMs versus excitation power of optimal thickness; and (c) ASE spectra of optimal sample with the change in excitation power.

Information. Moreover, because of the elimination of host (CBP), crystallization and degradation will be easier to prevent during the operation or preserving under the ambient conditions. Therefore, as presented in Figure S13 in the Supporting Information, the host-free system can tolerate moisture and oxygen under high nitrogen-lasing power excitation, and the ASE intensity can maintain almost 90% of the intensity of the original one after 1 h under ambient conditions, which is slightly more stable than the blend film.

For NIR emitter (TPA-F)₂BBTD, although the k_f ($\sim 1.0 \times 10^8 \text{ s}^{-1}$) is slightly lower than that of (TPA-F)₂BTD, which can be explained by the lower PLQYs, NIR ASE with low thresholds (going from 3.8 $\mu\text{J cm}^{-2}$ to 7.9 $\mu\text{J cm}^{-2}$ following the conditions) still occur under wide-range doping concentrations from 1 wt % to 40 wt % with decreasing slope efficiency in Figure 6, as well as Figure S15 in the Supporting Information (the corresponding thickness of samples is ~200 nm). The sharp narrowing FWHMs of NIR spectra at <10 nm are plotted in Figure 6b, with all of the ASE maxima exceeding 780 nm (passing by 796 to 847 nm). It is highlighted that the lowest NIR ASE threshold (3.8 $\mu\text{J cm}^{-2}$) is realized with a doping ratio of 3 wt % in CBP (Figure 6c).

In summary, donor–spacer–acceptor–spacer–donor molecules have been successfully synthesized and characterized as a promising lasing candidate. The HOMO/LUMO wavefunction distribution was changed by tuning the acceptor character of the dye. Large oscillator strength, was obtained by tuning the relative D/A interplay strength to realize color-tunable organic lasing properties. Herein, triphenylamine (TPA) was selected as the donor moiety located at the end sites of molecules, benzothiadiazole (BTD) and benzo[1,2-c:4,5c']bis[1,2,5]thiadiazole (BBTD) with stronger electron-affinity capability, were chosen as acceptors for yellow ((TPA-F)₂BTD) and NIR ((TPA-F)₂BBTD) lasing dyes, respectively. In particular, the spacer bridge connected between donor and acceptor moieties was composed of a fluorene core, and the long alkyl chains were involved to guarantee the good

Figure 6. ASE performance of (TPA-F)₂BBTD-based solid-state films with different doping ratios in a CBP host matrix: (a) output waveguide emission intensity versus excitation power relationship; (b) ASE spectra of all the films above the thresholds; and (c) evolution of the ASE thresholds with different doping ratios under a thickness of ~ 200 nm.

solubility and prevention of intermolecular aggregation caused quenching in the case of (TPA-F)₂BTD. Therefore, the large radiative rates promoted the ASE properties over a large range of doping concentrations. Among them, very low ASE thresholds of $0.5 \mu\text{J cm}^{-2}$ for yellow emission ($\lambda_{\text{peak}} \approx 550$ nm) and $3.8 \mu\text{J cm}^{-2}$ for NIR emission ($\lambda_{\text{peak}} \approx 811$ nm) were achieved, which are among the lowest ASE thresholds in the corresponding emission region to the best of our knowledge. Meanwhile, benefiting from a suppressed ACQ effect, low ASE threshold of $1.9 \mu\text{J cm}^{-2}$ for pure (TPA-F)₂BTD films with good stability under ambient conditions has been realized. Overall, the insights from our molecular design provide a promising strategy to realize large-range color-tunable organic lasing properties for dyes with small energy gaps.

ASSOCIATED CONTENT

Supporting Information

Materials, general techniques, materials synthesis and characterization, ¹H NMR and ¹³C NMR spectra, cyclic voltammetry (CV), photoelectron spectra measured by AC-3, DFT calculation, dipole moments, photophysical properties in different solvents, thermogravimetric analysis, device performance, ASE threshold optimization of (TPA-F)₂BTD and (TPA-F)₂BBTD (PDF)

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Notes

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REFERENCES

- (1) Samuel, I. D. W.; Turnbull, G. A. Organic Semiconductor Lasers. *Chem. Rev.* 2007, 107, 1272–1295.
- (2) Kozlov, V. G.; Bulovic, V.; Burrows, P. E.; Forrest, S. R. Laser Action in Organic Semiconductor Waveguide and Double-Heterostructure Devices. *Nature* 1997, 389, 362–364.
- (3) Yap, B. K.; Xia, R. D.; Campoy-Quiles, M.; Stavrinou, P. N.; Bradley, D. D. C. Simultaneous Optimization of Charge-Carrier Mobility and Optical Gain in Semiconducting Polymer Films. *Nat. Mater.* 2008, 7, 376–380.
- (4) Jiang, Y.; Liu, Y. Y.; Liu, X.; Lin, H.; Gao, K.; Lai, W. Y.; Huang, W. Organic Solid-State Lasers: A Materials View and Future Development. *Chem. Soc. Rev.* 2020, 49, 5885–5944.
- (5) Kuehne, A. J.; Gather, M. C. Organic Lasers: Recent Developments on Materials, Device Geometries, and Fabrication Techniques. *Chem. Rev.* 2016, 116, 12823–12864.
- (6) Xia, R.; Lai, W.-Y.; Levermore, P. A.; Huang, W.; Bradley, D. D. C. Low-Threshold Distributed-Feedback Lasers Based on Pyrene-Cored Starburst Molecules with 1,3,6,8-Attached Oligo(9,9-Dialkyl-fluorene) Arms. *Adv. Funct. Mater.* 2009, 19, 2844–2850.
- (7) Aimono, T.; Kawamura, Y.; Goushi, K.; Yamamoto, H.; Sasabe, H.; Adachi, C. 100% Fluorescence Efficiency of 4,4'-Bis[(N-Carbazole)Styryl]Biphenyl in a Solid Film and the Very Low Amplified Spontaneous Emission Threshold. *Appl. Phys. Lett.* 2005, 86, 071110.
- (8) Xia, R.; Heliotis, G.; Hou, Y.; Bradley, D. D. C. Fluorene-Based Conjugated Polymer Optical Gain Media. *Org. Electron.* 2003, 4, 165–177.

- (9) D'Aleó A.; Sazzad, M. H.; Kim, D. H.; Choi, E. Y.; Wu, J. W.; Canard, G.; Fages, F.; Ribierre, J. C.; Adachi, C. Boron Difluoride Hemircurcuminoid as an Efficient Far Red to Near-Infrared Emitter: Toward OLEDs and Laser Dyes. *Chem. Commun.* 2017, 53, 7003–7006.
- (10) Rabbani-Haghighi, H.; Forget, S.; Chenais, S.; Siove, A.; Castex, M. C.; Ishow, E. Laser Operation in Nondoped Thin Films Made of a Small-Molecule Organic Red-Emitter. *Appl. Phys. Lett.* 2009, 95, 033305.
- (11) Wang, X.; Li, Z.-Z.; Zhuo, M.-P.; Wu, Y.; Chen, S.; Yao, J.; Fu, H. Tunable Near-Infrared Organic Nanowire Nanolasers. *Adv. Funct. Mater.* 2017, 27, 1703470.
- (12) Mamada, M.; Fukunaga, T.; Bencheikh, F.; Sandanayaka, A. S. D.; Adachi, C. Low Amplified Spontaneous Emission Threshold from Organic Dyes Based on Bis-stilbene. *Adv. Funct. Mater.* 2018, 28, 1802130.
- (13) Matsushima, T.; Yoshida, S.; Inada, K.; Esaki, Y.; Fukunaga, T.; Mieno, H.; Nakamura, N.; Bencheikh, F.; Leyden, M. R.; Komatsu, R.; Qin, C.; Sandanayaka, A. S. D.; Adachi, C. Degradation Mechanism and Stability Improvement Strategy for an Organic Laser Gain Material 4,4'-Bis[(N-carbazole)styryl]biphenyl (BSBCz). *Adv. Funct. Mater.* 2019, 29, 1807148.
- (14) Sandanayaka, A. S. D.; Yoshida, K.; Inoue, M.; Qin, C.; Goushi, K.; Ribierre, J.-C.; Matsushima, T.; Adachi, C. Quasi-Continuous-Wave Organic Thin-Film Distributed Feedback Laser. *Adv. Opt. Mater.* 2016, 4, 834–839.
- (15) Sandanayaka, A. S. D.; Matsushima, T.; Bencheikh, F.; Yoshida, K.; Inoue, M.; Fujihara, T.; Goushi, K.; Ribierre, J. C.; Adachi, C. Towards Continuous-Wave Operation of Organic Semiconductor Lasers. *Sci. Adv.* 2017, 3, No. e1602570.
- (16) Sandanayaka, A. S. D.; Matsushima, T.; Bencheikh, F.; Terakawa, S.; Potscavage, W. J.; Qin, C.; Fujihara, T.; Goushi, K.; Ribierre, J.-C.; Adachi, C. Indication of Current-Injection Lasing from an Organic Semiconductor. *Appl. Phys. Express* 2019, 12, 061010.
- (17) Chang, S.-J.; Liu, X.; Lu, T.-T.; Liu, Y.-Y.; Pan, J.-Q.; Jiang, Y.; Chu, S.-Q.; Lai, W.-Y.; Huang, W. Ladder-Type Poly(Indenofluorene-Co-Benzothiadiazole)s as Efficient Gain Media for Organic Lasers: Design, Synthesis, Optical Gain Properties, and Stabilized Lasing Properties. *J. Mater. Chem. C* 2017, 5, 6629–6639.
- (18) Mamada, M.; Komatsu, R.; Adachi, C. F8BT Oligomers for Organic Solid-State Lasers. *ACS Appl. Mater. Interfaces* 2020, 12, 28383–28391.
- (19) Kaniabolotsky, A. L.; Perepichka, I. F.; Skabara, P. J. Star-Shaped Pi-Conjugated Oligomers and Their Applications in Organic Electronics and Photonics. *Chem. Soc. Rev.* 2010, 39, 2695–2728.
- (20) Lai, W.-Y.; Xia, R.; He, Q.-Y.; Levermore, P. A.; Huang, W.; Bradley, D. D. C. Enhanced Solid-State Luminescence and Low-Threshold Lasing from Starburst Macromolecular Materials. *Adv. Mater.* 2009, 21, 355–360.
- (21) Kim, D.-H.; D'Aleó A.; Chen, X.-K.; Sandanayaka, A. S. D.; Yao, D.; Zhao, L.; Komino, T.; Zaborova, E.; Canard, G.; Tsuchiya, Y.; Choi, E.; Wu, J. W.; Fages, F.; Bredas, J.-L.; Ribierre, J.-C.; Adachi, C. High-Efficiency Electroluminescence and Amplified Spontaneous Emission from a Thermally Activated Delayed Fluorescent Near-Infrared Emitter. *Nat. Photon.* 2018, 12, 98–104.
- (22) Ye, H.; Kim, D. H.; Chen, X.; Sandanayaka, A. S. D.; Kim, J. U.; Zaborova, E.; Canard, G.; Tsuchiya, Y.; Choi, E. Y.; Wu, J. W.; Fages, F.; Bredas, J.-L.; D'Aleó A.; Ribierre, J.-C.; Adachi, C. Near-Infrared Electroluminescence and Low Threshold Amplified Spontaneous Emission above 800 nm from a Thermally Activated Delayed Fluorescent Emitter. *Chem. Mater.* 2018, 30, 6702–6710.
- (23) Qian, Y.; Wei, Q.; Del Pozo, G.; Mroz, M. M.; Lueer, L.; Casado, S.; Cabanillas-Gonzalez, J.; Zhang, Q.; Xie, L.; Xia, R.; Huang, W. H-Shaped Oligofluorenes for Highly Air-Stable and Low-Threshold Non-Doped Deep Blue Lasing. *Adv. Mater.* 2014, 26, 2937–2942.
- (24) Qian, G.; Zhong, Z.; Luo, M.; Yu, D.; Zhang, Z.; Wang, Z. Y.; Ma, D. Simple and Efficient Near-Infrared Organic Chromophores for Light-Emitting Diodes with Single Electroluminescent Emission above 1000 nm. *Adv. Mater.* 2009, 21, 111–116.
- (25) Yao, L.; Zhang, S.; Wang, R.; Li, W.; Shen, F.; Yang, B.; Ma, Y. Highly Efficient Near-Infrared Organic Light-Emitting Diode Based on a Butterfly-Shaped Donor-Acceptor Chromophore with Strong Solid-State Fluorescence and a Large Proportion of Radiative Excitons. *Angew. Chem., Int. Ed.* 2014, 53, 2119–2123.
- (26) Han, X.; Bai, Q.; Yao, L.; Liu, H.; Gao, Y.; Li, J.; Liu, L.; Liu, Y.; Li, X.; Lu, P.; Yang, B. Highly Efficient Solid-State Near-Infrared Emitting Material Based on Triphenylamine and Diphenylfumarionitrile with an EQE of 2.58% in Nondoped Organic Light-Emitting Diode. *Adv. Funct. Mater.* 2015, 25, 7521–7529.
- (27) Thompson, J.; Anni, M.; Lattante, S.; Pisignano, D.; Blyth, R. I. R.; Gigli, G.; Cingolani, R. Amplified Spontaneous Emission in the Near Infrared from a Dye-Doped Polymer Thin Film. *Synth. Met.* 2004, 143, 305–307.
- (28) Ho, C.-L.; Li, H.; Wong, W.-Y. Red to Near-Infrared Organometallic Phosphorescent Dyes for OLED Applications. *J. Organomet. Chem.* 2014, 751, 261–285.
- (29) Zampetti, A.; Minotto, A.; Cacialli, F. Near-Infrared (NIR) Organic Light-Emitting Diodes (OLEDs): Challenges and Opportunities. *Adv. Funct. Mater.* 2019, 29, 1807623.
- (30) Kim, J. H.; Yun, J. H.; Lee, J. Y. Recent Progress of Highly Efficient Red and Near-Infrared Thermally Activated Delayed Fluorescent Emitters. *Adv. Opt. Mater.* 2018, 6, 1800255.
- (31) Usta, H.; Alimli, D.; Ozdemir, R.; Tekin, E.; Alkan, F.; Kacar, R.; Altas, A. G.; Dabak, S.; Gürek, A. G.; Mutlugun, E.; Yazici, A. F.; Can, A. A Hybridized Local and Charge Transfer Excited State for Solution-Processed Non-Doped Green Electroluminescence Based on Oligo(P-Phenyleneethynylene). *J. Mater. Chem. C* 2020, 8, 8047–8060.
- (32) Li, W.; Pan, Y.; Xiao, R.; Peng, Q.; Zhang, S.; Ma, D.; Li, F.; Shen, F.; Wang, Y.; Yang, B.; Ma, Y. Employing ~100% Excitons in OLEDs by Utilizing a Fluorescent Molecule with Hybridized Local and Charge-Transfer Excited State. *Adv. Funct. Mater.* 2014, 24, 1609–1614.
- (33) Li, W.; Pan, Y.; Yao, L.; Liu, H.; Zhang, S.; Wang, C.; Shen, F.; Lu, P.; Yang, B.; Ma, Y. A Hybridized Local and Charge-Transfer Excited State for Highly Efficient Fluorescent OLEDs: Molecular Design, Spectral Character, and Full Exciton Utilization. *Adv. Opt. Mater.* 2014, 2, 892–901.
- (34) Zhen, C.-G.; Chen, Z.-K.; Liu, Q.-D.; Dai, Y.-F.; Shin, R. Y. C.; Chang, S.-Y.; Kieffer, J. Fluorene-Based Oligomers for Highly Efficient and Stable Organic Blue-Light-Emitting Diodes. *Adv. Mater.* 2009, 21, 2425–2429.
- (35) Amarasinghe, D.; Ruseckas, A.; Vasdekis, A. E.; Turnbull, G. A.; Samuel, I. D. W. High-Gain Broadband Solid-State Optical Amplifier Using a Semiconducting Copolymer. *Adv. Mater.* 2009, 21, 107–110.
- (36) Parker, T. C.; Patel, D. G.; Moudgil, K.; Barlow, S.; Risko, C.; Bredas, J.-L.; Reynolds, J. R.; Marder, S. R. Heteroannulated Acceptors Based on Benzothiadiazole. *Mater. Horiz.* 2015, 2, 22–36.