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## Introduction

Recently, metal-free thermally activated delayed fluorescence (TADF) emitters have emerged as the most promising alternative to traditional phosphorescent organic light-emitting diodes (PHOLEDs), which can reach 100% internal quantum efficiency (IQE), due to their ability to harvest non-emissive triplet excitons through reverse inter-system crossing (RISC) by manipulating the singlet-triplet energy splitting ( $\Delta E_{ST}$ ).<sup>1,2</sup>

The small  $\Delta E_{\rm ST}$  and efficient RISC are the two important requirements for designing potential TADF emitters.<sup>1,2</sup> To achieve the small  $\Delta E_{\rm ST}$ , it is essential to minimize the spatial orbital overlap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).<sup>1-3</sup> In this regard, the development of donor–acceptor type bipolar molecular systems with or without  $\pi$ -conjugated linkers has been exemplified as the most promising approach to ensure the spatially separated HOMO and LUMO in the donor and acceptor units.<sup>1-3</sup> It has been demonstrated that the choice of donor and acceptor units plays an important role in achieving superior device performances.<sup>1-3</sup> So far, numerous

# 6*H*-Benzo[4,5]thieno[2,3-*b*]indole as a novel donor for efficient thermally activated delayed fluorescence emitters with EQEs over 20%<sup>+</sup>

Rajendra Kumar Konidena, Kyung Hyung Lee and Jun Yeob Lee 回 \*

In this report, we developed two novel indole-based electron donors, 6*H*-benzo[4,5]thieno[2,3-*b*]indole (**synBTI**) and 6*H*-benzofuro[2,3-*b*]indole (**synBFI**), for designing green thermally activated delayed fluorescence (TADF) emitters. Two TADF emitters, 2-(6*H*-benzo[4,5]thieno[2,3-*b*]indol-6-yl)-5-(4,6-diphenyl-1,3,5-triazin-2-yl)benzonitrile (**BTITrz**) and 2-(6*H*-benzofuro[2,3-*b*]indol-6-yl)-5-(4,6-diphenyl-1,3,5-triazin-2-yl)benzonitrile (**BTITrz**), were synthesized by integrating the two new donors with an aryltriazine acceptor. The effects of the heteroatoms in the donor units on the photophysical and electroluminescence properties of the TADF emitters were investigated in detail. The photophysical analysis revealed that **BTITrz** showed a relatively small singlet–triplet energy splitting, short delayed fluorescence lifetime and high photoluminescence quantum yield (PLQY) compared to its congener **BFITrz**. As a result, the organic light emitting diode fabricated using the **BTITrz** emitter exhibited superior device performance with a maximum external quantum efficiency (EQE) of 20.7% and current efficiency (CE) of 63.6 cd A<sup>-1</sup>. These results suggest that **synBTI** can function as a potential donor for designing efficient TADF emitters.

electron acceptors such as cyano, aryltriazine, sulfone, phosphine oxide, oxadiazole, benzophenone, pyrazine, arylborane, pyridine, and pyrimidine have been developed for the design of blue and green TADF emitters.<sup>1–3</sup> However, potential electron donors are mostly limited to carbazole and acridine derivatives.<sup>4</sup> Therefore, the development of efficient new electron donors for blue/green TADF emitters is highly desirable to expand the donor library.

Herein, we report two novel electron donors, viz., 6H-benzo-[4,5]thieno[2,3-b]indole (synBTI) and 6H-benzofuro[2,3-b]indole (synBFI), featuring different heteroatoms (O or S) to develop green TADF emitters. 2-(6H-Benzo[4,5]thieno[2,3-b]indol-6-yl)-5-(4,6-diphenyl-1,3,5-triazin-2-yl)benzonitrile (BTITrz) and 2-(6Hbenzofuro[2,3-b]indol-6-yl)-5-(4,6-diphenyl-1,3,5-triazin-2-yl)benzonitrile (BFITrz) were synthesized by combining the two donors synBTI and synBFI with an aryltriazine acceptor, respectively. The effects of the heteroatoms in the donor scaffolds on the photophysical and electroluminescence properties of the TADF emitters were studied in detail. The BTITrz material showed a small  $\Delta E_{ST}$ , a short delayed fluorescence lifetime ( $t_d$ ) and a high photoluminescence quantum yield (PLQY) compared to BFITrz due to the relatively strong donor character of the synBTI unit. The potential of these materials as TADF emitters was tested in multilayered OLED devices. The BTITrz-based device demonstrated excellent performance with a maximum EQE of 20.7% and CE of 63.6 cd  $A^{-1}$ .

School of Chemical Engineering, Sungkyunkwan University, 2066 Seobu-ro, Jangan-gu, Suwon, Gyeonggi 440-746, Korea. E-mail: leej17@skku.edu

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## **Results and discussion**

#### Molecular design and synthesis

Our molecular design was mainly intended to develop novel heterocycle fused indole-based donors (synBTI and synBFI) for blue/green TADF emitters. We focused on studying the effects of the heteroatoms (O or S) in the donor scaffolds on the photophysical and electroluminescence properties of the TADF emitters. The employed synthetic procedures to synthesize the target materials are schematized in Scheme 1. The synBTI and synBFI donors were synthesized in a two step synthetic protocol starting from the palladium-catalyzed Suzuki coupling reaction between boronic acids of 1a and 1b with 2-bromonitrobenzene to produce 2a and 2b, respectively.<sup>5</sup> Subsequently, Cadogan ring closing reactions were performed on intermediates 2a and 2b to yield novel donors of synBTI and synBFI, respectively.<sup>6</sup> Finally, the synBTI and synBFI donors were reacted with the acceptor scaffold 5-(4,6-diphenyl-1,3,5-triazin-2-yl)-2-fluorobenzonitrile under cesium carbonate mediated N-arylation reaction conditions to offer the target green TADF emitters BTITrz and BFITrz in excellent vields after column purifications and vacuum train sublimation procedures. The chemical structures of the compounds were analyzed by nuclear magnetic resonance spectroscopy (<sup>1</sup>H and <sup>13</sup>C NMR) and mass spectroscopy (MS) measurements.

#### Theoretical calculations

To estimate the frontier molecular orbital (FMO) distributions and singlet–triplet energy splittings ( $\Delta E_{ST}$ ) of these compounds, density functional theoretical (DFT) calculations were performed

on their model compounds using a B3LYP/6-31G(d,p) basis set. The optimized geometries and their frontier molecular orbital distributions (HOMO/LUMO) of the compounds are portrayed in Fig. 1 and 2. The compounds showed largely distorted structures between the donors and aryltrizine acceptor with a dihedral angle of above  $50^{\circ}$  due to the severe steric crowding between the donor and cyano acceptor on the phenyl linker. As a result, the HOMOs of the compounds were mainly localized on the synBTI or synBFI donor units, while the LUMOs were delocalized over the aryltriazine acceptor and cyanophenyl bridge. As expected from the FMO distribution, time dependent (TD)-DFT calculations were revealed that the compounds had a small  $\Delta E_{ST}$  of 0.16 eV with a singlet energy  $(S_1)$  of 2.56 eV and a triplet energy  $(T_1)$  of 2.40 eV for **BTITrz** and  $\Delta E_{ST}$  of 0.19 eV with S<sub>1</sub> of 2.58 eV and T<sub>1</sub> of 2.39 eV for BFITrz. These results indicate that the compounds would trigger effective reverse intersystem crossing for TADF emission.

#### Electrochemical and thermal properties

The redox behaviors of these compounds were investigated by using cyclic voltammetry measurements in a dilute dichloromethane solution with 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte. The oxidation potentials of the compounds were calibrated by using an  $Fc/Fc^+$  redox couple and the pertinent data are listed in Table 1. The electron donating strengths of the organic chromophores can be estimated based on their oxidation potentials. To understand the donor strengths of these new donors, their oxidation potentials were collected. Interestingly, **synBTI** showed a relatively small



Scheme 1 Synthetic approach of target materials.



Fig. 1 Optimized geometries of the compounds.



Fig. 2 FMO distributions of the compounds calculated employing the B3LYP/6-31G(d,p) basis set of the Gaussian 09 program.

Table 1	Photophysical,	electrochemical	and thermal	data of the	compounds
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Compound	$\lambda_{ m abs}{}^{a}$ , nm ( $\epsilon_{ m max}$ , M <sup>-1</sup> cm <sup>-1</sup> × 10 <sup>3</sup> )	$\lambda_{\rm em}^{\ \ b}$ (nm), (film)	$E_{\rm S}/E_{\rm T}^{\ c}$ (eV)	$\Delta E_{\mathrm{ST}}^{d}$ (eV)	$HOMO/LUMO^{e}$ (eV)	$E_{g}^{f}(eV)$	$t_{\rm p}/t_{\rm d}^g ({\rm ns}/{\rm \mu s})$	${\Phi_{ m p}}^h/{\Phi_{ m d}}^i/{\Phi_{ m PL}}^j$	$T_{\mathrm{onset}}^{k}$ (°C)
BTITrz	381 (12.8), 271 (107.8)	526	2.79/2.76	0.03	5.79/3.48	2.31	13.1/4.3	0.20/0.46/0.66	441
BFITrz	379 (9.3), 270 (83.3)	518	2.82/2.75	0.07	5.84/3.47	2.37	14.6/26.6	0.16/0.34/0.50	419

<sup>*a*</sup> Collected in THF solution. <sup>*b*</sup> Collected for 10 wt% doped films in DPEPO. <sup>*c*</sup> Calculated from the onsets of fluorescence and phosphorescence spectra. <sup>*d*</sup> Calculated singlet-triplet energy gap. <sup>*e*</sup> HOMO and LUMO estimated from the cyclic voltammograms. <sup>*f*</sup> Electrochemical band gap. <sup>*g*</sup> Prompt ( $t_p$ ) and delayed ( $t_d$ ) fluorescence lifetimes. <sup>*h*</sup> Prompt fluorescence ( $\Phi_p$ ). <sup>*i*</sup> Delayed ( $\Phi_d$ ) PLQY determined from the total PLQY and the proportion of the integrated area of the individual components in the transient PL spectra to the total integrated area. <sup>*j*</sup> The absolute PLQY of the doped films in DPEPO measured using an integrating sphere in a nitrogen atmosphere at room temperature. <sup>*k*</sup> The temperature corresponds to 5% weight loss ( $T_{onset}$ ).

oxidation potential (+0.86 eV) compared to its analogue **synBFI** (+0.92 eV), indicating a strong donor character of the former. This could be attributed to the low electronegativity of the sulfur atom in **synBTI** compared to the oxygen atom in **synBFI**. Consequently, **BTITrz** revealed a high oxidation propensity when compared to **BFITrz**. The HOMO and LUMO energy levels of the compounds were calculated from their onset potentials of the oxidation and reduction waves with reference to ferrocene. The corresponding HOMO/LUMO energy levels of **BTITrz** and **BFITrz** were -5.79 eV/-3.48 eV and -5.84/-3.47, respectively.

The thermal stability of these compounds was investigated using thermogravimetric analysis (TGA) and the TGA traces are shown in Fig. 3 and the relevant data are listed in Table 1. Both **BTITrz** and **BFITrz** displayed excellent thermal stability, with marked thermal decomposition temperatures ( $T_{5d}$ ) corresponding to 5% weight loss of 441 °C and 419 °C, respectively. Therefore, the compounds exhibited desirable thermal stability for vapor deposited device fabrication.

#### Photophysical properties

The photophysical properties of these compounds were investigated by using ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) emission measurements. The electronic absorption spectra of the compounds recorded in tetrahydrofuran ( $10^{-5}$  M) and emission spectra of 10 wt% doped films in a DPEPO host are presented in Fig. 4 and the relevant data are listed in Table 1. The compounds mainly showed two independent absorption bands in the range of 250–400 nm. The short wavelength absorption peaks appearing below ~300 nm are assigned to the localized  $\pi$ - $\pi$ \* electronic transitions of the different aromatic conjugative units in the compounds. On the other hand, the long wavelength absorption peak that appeared above ~350 nm is attributed to the intramolecular charge Paper



transfer (ICT) transition from the synBTI or synBFI donor to the aryltriazine acceptor. Both compounds displayed a single emission peak, indicating that the fluorescence originated from the charge transfer (CT) states as expected from their FMO distribution. Furthermore, to understand the CT character of the singlet excited state, solvatochromism study was performed in different solvents by varying their Reichardt polarity index from non-polar cyclohexane (CH) to polar dichloromethane (MC). The compounds exhibited positive solvatochromism with large degrees of bathochromic shift ( $\Delta \lambda_{em}$ ) of 115 nm for **BTITrz** and 105 nm for BFITrz, confirming the CT nature of the excited singlet state.<sup>7</sup> Interestingly, the compounds showed vibrational features in non-polar CH and structureless spectra in the polar solvent. The phosphorescence spectra of the compounds were collected at low temperature in frozen THF matrix (Fig. 5). Both compounds showed featureless emission profiles, indicating that the triplet excited state has CT nature. The  $S_1/T_1$  energies of BTITrz and BFITrz estimated from their onset wavelengths of the fluorescence and phosphorescence spectra were found to be 2.79/2.76 eV and 2.82/2.75 eV, respectively. As a result, the





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corresponding  $\Delta E_{\rm ST}$ s of **BTITrz** and **BFITrz** were calculated to be 0.03 eV and 0.07 eV, respectively.

The TADF nature of these compounds was investigated by transient PL measurements using 10 wt% emitter doped DPEPO films at room temperature under vacuum and their decay profiles are shown in Fig. 6. The compounds displayed both prompt and delayed fluorescence components, confirming the presence of TADF character in these compounds. The prompt/delayed fluorescence lifetimes of BTITrz and BFITrz were 13.1 ns/4.3 µs and 14.6 ns/26.6 µs, respectively. BTITrz showed a short delayed fluorescence lifetime compared to **BFITrz** due to the relatively small  $\Delta E_{\rm ST}$  with the aid of the strong donor character of the synBTI unit. Moreover, the local triplet energy of the synBTI donor close to the CT triplet energy of BTITrz may assist the accelerated RISC (Fig. S2, ESI<sup>+</sup>). In the case of BFITrz, the energy difference between local triplet energy and CT triplet energy was relatively large, which could not improve the RISC. Furthermore, the absolute PLQYs of the doped films were analyzed by an integrating sphere method under a nitrogen atmosphere and the PLQY values of BTITrz and BFITrz were found to be 66% and 50%, respectively. The higher PLQY of



Fig. 4 Absorption and emission spectra of the compounds recorded in THF solution and 10 wt% doped DPEPO films, respectively



Transient PL decay profiles of the 10 wt% emitter doped DPEPO Fig. 6 films

**BTITrz** than that of **BFITrz** is ascribed to the efficient  $T_1$  to  $S_1$ RISC process of the former compound, judging from the high PLQY of the delayed component (46%) of **BTITrz** compared to **BFITrz** (34%). Further, the RISC rate constants of **BTITrz** and **BFITrz** estimated from their transient PL analysis and PLQY data were found to be  $4.92 \times 10^5$  s<sup>-1</sup> and  $3.20 \times 10^5$  s<sup>-1</sup>, respectively. These results suggest that **BTITrz** would work as an efficient TADF emitter in OLED devices.

#### **Electroluminescence properties**

The electroluminescence (EL) performance of these compounds was investigated in vacuum processed multilayer OLED devices by employing them as dopants in the DPEPO host. The adopted OLED device configuration is ITO (50 nm)/PEDOT:PSS (60 nm)/ TAPC (20 nm)/mCP (10 nm)/EML (25 nm: x wt%)/TSPO1 (5 nm)/ TPBi (20 nm)/LiF (1.5)/Al (200 nm). The doping concentration of the emitters was varied from 10% to 40% to verify the doping concentration effect. Diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1) and 1,3-bis(N-carbazolyl)benzene (mCP) served as electron transporting type and hole transporting type exciton blocking layers, respectively. Di-[4-(N,N-ditolyl-amino)phenyl]cyclohexane (TAPC) and LiF used as hole transport and electron injection layers, respectively. The emitting layers (EMLs) were BTITrz or BFTTrz (10, 20, 30, or 40 wt%) doped DPEPO layers. Here, high triplet energy DPEPO was used as the host to confine the excitons in the emitting layer. The device structure, energy level alignment diagram and chemical structures of the organic materials used in the device are presented in Fig. 7. The current voltage (J)-voltage (V)-luminance (L), and EQE versus L and EL spectra of the TADF devices according to the doping ratio are depicted in Fig. 8.

As shown in Fig. 8, the *J* and *L* of the devices increased gradually upon increasing the doping concentration from 10 wt% to 40 wt%. This can be explained by the dopant assisted charge injection and hopping mechanisms in the devices. Owing to the low-lying LUMO and shallow HOMO of these

materials compared to the DPEPO host, the direct charge trapping in the dopant would be the dominating EL mechanism in these devices. In particular, the large HOMO gap between the mCP and DPEPO interrupted the hole injection and transport, which is evident from the energy level diagram (Fig. 7). Therefore, the dopants would play a key role of hole trapping and transporting medium in the devices.<sup>8</sup> As a result, the I and L of the compounds increased with increasing doping concentration. The EQE vs. L plots of the compounds at different doping concentrations are shown in Fig. 8. The optimized device with a doping concentration of 20 wt% showed a maximum EQE of 20.7% and 12.0% for BTITrz and BFITrz, respectively. Interestingly, both compounds did not show any significant decrease in EQE according to the increase of the doping concentration from 20 wt% to 40 wt%, indicating that the concentration quenching effect is not evident in these materials. In general, the concentration quenching effect is mostly induced by the distance between emitters because the probability of exciton collision and quenching is increased at high doping concentration. However, it was not serious in the two emitters due to the introduction of the two new donors, relieving strong intermolecular interaction. This can also be indirectly confirmed by the small red-shift of the EL spectrum according to the doping concentration. As shown in the EL spectra, the TADF emitters showed green emission with CIE color coordinates in the range of 0.27 < x < 0.33 and 0.50 < y < 0.57 for **BTITrz** and 0.29 < x < 0.35 and 0.51 < y < 0.56 for **BFITrz**, depending on their doping concentration. The EL peak wavelengths of the compounds showed slight bathochromic shifts ( $\sim 10-12$  nm) by increasing the doping concentration from 10 wt% to 40 wt%. The EL spectra of both the compounds displayed slight bathochromic shifts according to the doping concentration due to the intermolecular interaction at the high doping concentration by the shortened intermolecular distance. However, the degree of red shift was quite small compared to other TADF emitters. The EL spectra were measured at 1000 cd m<sup>-2</sup>. Overall, BTITrz



Fig. 7 Device structure and energy level alignment of the materials.



Fig. 8 /-V-L plots of BTITrz (a) and BFITrz (d), EQE vs. luminance plots of BTITrz (b) and BFITrz (f), and EL spectra of BTITrz (c) and BFITrz (g).

	Concentration (wt%)	Voltage (V)	EQE (%)		Current efficiency (cd A <sup>-1</sup> )		Power efficiency ( $\text{lm W}^{-1}$ )		
Dopant			Max.	$(a)100 \text{ cd } \text{m}^{-2}$	Max.	(a)100 cd m <sup>-2</sup>	Max	(a) 100 cd m <sup>-2</sup>	CIE $(x, y)$
BTITrz	10	4.2	18.8	8.2	54.8	23.4	40.3	7.8	0.27, 0.50
	20	3.6	20.7	15.7	63.6	47.5	51.0	23.5	0.30, 0.54
	30	3.6	20.3	16.8	63.6	52.2	57.0	30.3	0.32, 0.56
	40	3.5	19.0	17.3	59.8	54.4	50.3	33.0	0.33, 0.57
BFITrz	10	4.5	11.3	2.8	33.4	8.0	24.9	2.1	0.29, 0.51
	20	3.6	12.0	7.3	36.8	22.2	29.9	9.7	0.32, 0.55
	30	3.6	10.7	7.6	33.3	23.5	27.4	12.0	0.33, 0.56
	40	3.5	10.3	8.1	32.1	25.1	26.4	13.4	0.35, 0.56

Table 2	2 EL	properties	of the	compounds
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exhibited superior device performance with a maximum EQE of 20.7%, current efficiency (CE) of 63.6 cd  $A^{-1}$  and power efficiency (PE) of 51.0 lm W<sup>-1</sup> compared with the **BFITrz**, which showed a maximum EQE of 12.0%, CE of 36.8 cd  $A^{-1}$  and PE of 29.9 lm W<sup>-1</sup>. This is attributed to the high PLQY, short  $t_d$  and efficient RISC of **BTITrz** compared to **BFITrz**. Although both compounds showed efficiency roll-off at a high luminance of 1000 cd m<sup>-2</sup>, the **BTITrz** device displayed a relatively small efficiency roll-off (26%) compared to the **BFITrz** device (40%), which is ascribed to its short  $t_d$ . These results indicate that **synBTI** 

can function as the potential donor for developing efficient TADF emitters. The device performances are summarized in Table 2 and are compared with other TADF devices in the ESI.<sup>†</sup>

## Conclusions

In conclusion, we designed and synthesized two new green TADF emitters named **BTITrz** and **BFITrz**, which were derived from the **synBTI** and **synBFI** donor units. The effects of the heteroatoms in the donor units on the photophysical and EL properties of the TADF emitters were investigated in detail. **BTITrz** showed a relatively small  $\Delta E_{\rm ST}$ , high PLQY and short delayed fluorescence lifetime compared to **BFITrz**. Furthermore, **BTITrz** exhibited superior performance with a maximum EQE of 20.7% and CE of 63.6 cd A<sup>-1</sup> compared to **BFITrz**, which demonstrated a maximum EQE of 12.0% and CE of 36.8 cd A<sup>-1</sup>. We believe that **synBTI** can expand the donor library for designing efficient TADF emitters.

## Experimental

#### General methods

The chemicals and solvents purchased from commercial suppliers were used as received. The materials were purified by a column chromatography technique using 100-200 mesh silica as a stationary phase. All reactions were performed under an inert atmosphere. Freshly distilled solvents were used for the chemical reactions and analytical measurements. The <sup>1</sup>H and <sup>13</sup>C nuclear magnetic spectral data (NMR) were recorded on a 500 MHz NMR spectrometer. The chemical shift values are quoted against Me<sub>4</sub>Si (0.00 ppm). The absorption and emission measurements were recorded on a UV-vis spectrophotometer at room temperature. The absolute PLQYs of 10 wt% emitter doped films in a DPEPO host were measured using a calibrated integrating sphere connected to a spectrofluorimeter. Transient PL measurements were collected on the 10 wt% emitter doped DPEPO films. The thermal stability of the compounds was estimated using a thermogravimetric analyzer (TGA) under a N<sub>2</sub> atmosphere at a heating rate of 10 °C min<sup>-1</sup>. Electrochemical measurements were collected on a CHI electrochemical analyzer with a conventional three electrode configuration containing a glassy carbon working electrode, a platinum wire auxiliary electrode and a nonaqueous Ag/AgNO3 acetonitrile reference electrode. An Fc/Fc<sup>+</sup> internal standard was used to calibrate the peak potentials. Theoretical calculations were performed using DFT computational methods on the Gaussian 09 programme package.9

#### Synthesis

The starting materials such as benzo[b]thiophen-3-ylboronic acid (1a), benzofuran-3-ylboronic acid (1b), and 2-nitrobromobenzene were purchased from TCI Chemicals. The acceptor scaffold 5-(4,6-diphenyl-1,3,5-triazin-2-yl)-2-fluorobenzonitrile was synthesized as per the given procedure in the literature.<sup>10</sup>

**3-(2-Nitrophenyl)benzo[***b***]thiophene (2a).** A mixture of **1a** (5.0 g, 28.0 mmol), 2-nitrobromobenzene (8.4 g, 42.1 mmol), tetrakis(triphenylphosphine)palladium(0) (1.6 g, 1.4 mmol) and potassium carbonate (11.6 g, 84.0 mmol) was dissolved in a 1:3 mixture of THF and water. The reaction mixture was refluxed for 24 h and the progress of the reaction was examined by thin layer chromatography (TLC). The reaction mixture was washed with dichloromethane and water several times. The organic layer was dried over anhydrous MgSO<sub>4</sub> and the removal of the solvent under vacuum resulted in a colorless residue. The purification of

the crude product by column chromatography using dichloromethane (DCM): hexane (1:2) eluent yielded intermediate **2a** as a colorless solid, yield: 5.0 g, 80%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 7.99 (d, *J* = 8.0 Hz, 1H), 7.78 (s, 1H), 7.69–7.66 (m, 1H), 7.60–7.54 (m, 2H), 7.39–7.35 (m, 2H), 7.28–7.25 (m, 1H). MS (APCI) *m*/*z* 256.01 [(M + H)<sup>+</sup>].

**6H-Benzo**[4,5]thieno[2,3-*b*]indole (synBTI). A mixture of 2a (5.0 g, 22.2 mmol) and triphenylphosphine (17.2 g, 66 mmol) was suspended in 20 mL of *o*-dichloromethane and degassed for 15 min. The reaction mixture was kept at 150 °C for 6 h and the progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was extracted with DCM and the organic layer was dried over anhydrous MgSO<sub>4</sub>. The removal of the solvent under vacuum resulted in a black colored crude mixture. The purification of the crude mixture by column chromatography using DCM : hexane (1 : 1) eluent resulted in **synBTI** as a pale yellow solid, yield: 4.0 g, 81%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 8.23 (s, 1H), 7.88 (d, *J* = 10.0 Hz, 1H), 7.82 (d, *J* = 10.0 Hz, 1H), 7.33–7.30 (m, 1H), 7.28–7.22 (m, 2H). MS (APCI) *m*/z 224.01 [(M + H)<sup>+</sup>].

2-(6H-Benzo[4,5]thieno[2,3-b]indol-6-yl)-5-(4,6-diphenyl-1,3,5triazin-2-yl)benzonitrile (BTITrz). A mixture of synBTI (1.0 g, 4.5 mmol), 5-(4,6-diphenyl-1,3,5-triazin-2-yl)-2-fluorobenzonitrile (1.5 g, 4.5 mmol) and cesium carbonate (4.3 g, 13.0 mmol) was suspended in 20 mL of dimethylformamide in a pressure tube. The reaction mixture was refluxed for 3 h. The progress of the reaction was monitored by TLC analysis. After completion of the reaction, extraction with DCM, drying over MgSO<sub>4</sub> and the evaporation of the solvent gave a yellow residue. The crude reaction mixture was purified on column chromatography using DCM: hexane (1:1) as an eluent to get BTITrz (2.0 g, 83% yield) as a yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 9.26 (s, 1H), 9.11-9.09 (m, 1H), 8.76 (d, J = 8.0 Hz, 4H), 8.15 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, J = 1H), 7.66–7.58 (m, 6H), 7.51 (d, J = 7.0 Hz, 1H), 7.42–7.30 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 172.30, 169.08, 143.81, 142.55, 141.91, 138.41, 136.91, 135.68, 134.80, 133.33, 132.70, 129.32, 129.05, 127.80, 125.65, 124.06, 123.37, 122.97, 122.41, 121.41, 120.68, 119.65, 116.16. MS (APCI) m/z 556.10 [(M + H)<sup>+</sup>].

**3-(2-Nitrophenyl)benzofuran (2b).** Intermediate **2b** was prepared from **1b** (5.0 g, 30.8 mmol), 2-nitrobromobenzene (9.2 g, 46.2 mmol), tetrakis(triphenylphosphine)palladium(0) (1.7 g, 1.54 mmol) and potassium carbonate (12.7 g, 92.4 mmol) using a similar procedure to that described above for **2a**. Yellow solid. Yield, 5.4 g, 75%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 8.00 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.88–7.65 (m, 1H), 7.64–7.54 (m, 1H), 7.42–7.32 (m, 4H). MS (APCI) *m*/*z* 240.01 [(M + H)<sup>+</sup>].

**6H-Benzofuro**[2,3-*b*]indole (synBFI). The donor synBFI was prepared from 2b (5.0 g, 20.9 mmol) and triphenylphosphine (16.4 g, 62.7 mmol) using a similar procedure to that described above for synBTI. Colorless solid. Yield, 3.5 g, 81%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ ppm): 8.28 (s, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.0 (s, 1H), 7.79 (d, *J* = 7.0 Hz, 1H), 7.48–7.45 (m, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.28–7.26 (m, 3H). MS (APCI) *m/z* 208.00 [(M + H)<sup>+</sup>].

2-(6H-Benzofuro[2,3-b]indol-6-yl)-5-(4,6-diphenyl-1,3,5-triazin-2-yl)benzonitrile (BFITrz). BFITrz was prepared from synBFI

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(1.0 g, 4.8 mmol), 5-(4,6-diphenyl-1,3,5-triazin-2-yl)-2-fluorobenzonitrile (1.7 g, 4.8 mmol) and cesium carbonate (4.6 g, 14.4 mmol) using a similar procedure to that described above for **BTITrz**. Yellow solid. Yield, 1.8 g, 75%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 9.41 (s, 1H), 9.19 (s, 1H), 8.80 (s, 1H), 7.94–7.88 (m, 3H), 7.64–7.48 (m, 7H), 7.41–7.35 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 172.37, 135.53, 134.16, 133.31, 129.83, 128.73, 128.23, 124.45, 122.57, 120.11, 119.32, 112.30, 111.82. MS (APCI) *m*/*z* 540.13 [(M + H)<sup>+</sup>].

## Conflicts of interest

There are no conflicts to declare.

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