## Materials

## Polymorphous Luminescent Materials Based on 'T'-Shaped Molecules Bearing 4,7-Diphenylbenzo[c][1,2,5]thiadiazole Skeletons: Effect of Substituents on the Photophysical Properties

Gaowei Qian,<sup>[a]</sup> Xiangbing Wang,<sup>[a]</sup> Shengyue Wang,<sup>[a]</sup> Yanqiong Zheng,<sup>[c]</sup> Song Wang,<sup>[b]</sup> Weiguo Zhu,<sup>\*[a]</sup> and Yafei Wang<sup>\*[a]</sup>

**Abstract:** Polymorphism, the intrinsic character of one chemical compound with at least two distinct phase arrangements, plays a very key role in the photophysical properties. In this contribution, four 'T'-shaped molecules bearing the 2,1,3-benzothiadiazole (BTD) skeleton, named **5a–5d**, were prepared and characterized. All compounds exhibited excellent thermal stability and polymorphism in the solid state, evident from thermogravimetric analysis, differential scanning calorimetry, and polarized optical microscopy results. Intense emissions with high photoluminescent quantum yields were achieved both in solution (56–97%) and

neat films (33–98%). All compounds possessed clearly pHdependent luminescence properties in solution. Additionally, compound **5d** showed useful mechanochromic luminescence owing to the transformation between the crystal and amorphous state. Employing compounds **5a–5d** as the dopant, solution-processable organic light-emitting diodes (OLEDs) were fabricated and presented a highest external quantum efficiency of 6.15%, which is higher than the theoretical value of fluorescence-based OLEDs (~5%). This research provided a novel strategy for designing high-efficiency BTD-based polymorphic luminescent materials.

## Introduction

Over the past several decades, emissive materials, including both fluorescent and phosphorescent materials, have been widely applied in organic light-emitting diodes (OLEDs),<sup>[1-11]</sup> used in commercial products, such as car screens, mobile phone screens, and some solid-state lighting. Among these emissive materials, polymorphous luminescent materials have been pursued by researchers owing to their interesting emission properties, especially for the external-stimuli-responsive emission, which has potential application in sensors, fluores-

[a] G. Qian, X. Wang, Dr. S. Wang, Prof. W. Zhu, Prof. Y. Wang National Experimental Demonstration Center for Materials Science and Engineering Jiangsu Key Laboratory of Environmentally Friendly Polymeric Materials Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Jiangsu Engineering Laboratory of Light–Electricity–Heat Energy Converting Materials and Applications School of Materials Science & Engineering Changzhou University, Changzhou 213164 (P. R. China) E-mail: zhuwg18@126.com qiji830404@hotmail.com
[b] S. Wang Hubei University of Arts and Science, Xiangyang, 441053 (P. R. China)

[c] Dr. Y. Zheng
 Key Laboratory of Advanced Display and
 System Applications of Ministry of Education, Shanghai University
 149 Yanchang Rd., Shanghai 200072 (P. R. China)

 Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/chem.201904026.

Chem. Eur. J. 2019, 25, 1 – 11 Wiley Online Library

cent switches, and optical devices.<sup>[12–19]</sup> Polymorphism is actually the intrinsic character of one chemical compound with at least two phase arrangements, which plays a very key role in the photophysical properties. To date, considerable research focusing on polymorphous luminescent materials, such as mechanochromic and piezochromic luminescence, have been developed.<sup>[20–26]</sup>

2,1,3-Benzothiadiazole (BTD) as a star building block has received much attention in the optoelectronic field for liquidcrystalline, organic solar cells (OSCs), OLEDs, and organic fieldeffect transistors because of its planar structure, strong electron-withdrawing capacity, efficient fluorophores, and good intermolecular interactions.<sup>[27-32]</sup> With this in mind, some polymorphous luminescent materials based on the BTD moiety have been explored.<sup>[33-35]</sup> For example, introduction of an intramolecular B-N bond into the BTD group, Murata and his coworkers prepared the compound 4,7-bis[3-(dimesitylboryl)thien-2-yl]benzothiadiazole possessing reversible solvato-, thermo-, and mechanochromic luminescence.[36] Nagai et al. synthesized a series of highly emissive solid-state fluorophores (phenanthroimidazolylbenzothiadiazoles) with donor-acceptor (D-A) framework, which showed more versatile mechanochromic luminescence owing to the different morphology states.[37] Additionally, they found that the substituents on the phenyl group of the benzothiadiazole ring can effectively control the mechanochromic luminescence.[37] Recently, Hayashi and Yuan and their respective co-workers revealed the crystallizationinduced emission for commercially available 2,1,3-benzothiadiazole derivatives.<sup>[38, 39]</sup> As an alternative strategy, molecules



with liquid-crystalline properties can also show good polymorphous emission. Vieira and his colleagues synthesized a series of non-symmetric BTD-based liquid crystals and investigated the phase-dependent photoluminescence.<sup>[40]</sup> Sagara et al. reported an asymmetric cyclophane featuring the 4,7-bis(phenylethynyl)-2,1,3-benzothidadiazole group, which exhibited different emission properties in the liquidcrystalline and crystalline states.<sup>[41]</sup> To the best of our knowledge, most reported examples just focused on integrating donor groups/or alkyl chains into the 4 and 7 positions of BTD to achieve polymorphous luminescence. Few BTD-based polymorphous luminescent materials present satisfactory device performance in solution-processable OLEDs. Therefore, there is still space to explore the structure-property relationship of BTD-based polymorphous luminescent materials.

Herein, four novel BTD-based derivatives, 5a-5d, with 'T'-shaped geometry were designed and prepared. In these molecules, 4,7-diphenylbenzo[c]-[1,2,5]thiadiazole was used as the emissive core, whereas the 3,4,5-tris(dodecyloxy)benzamide was integrated into the 5 position of BTD to modify the solubility and phase state. This kind of 'T'-shaped ge-

ometry can control the emission property through the BTD skeleton and regulate the polymorphism through the side chains. To further explore the structure–property relationship, different substituents with electron-withdrawing and electron-donating properties were introduced into 4,7-diphenylbenzo[c] [1,2,5]thiadiazole. All compounds showed bright emission with very high emission quantum yield in solution (56–97%) and the solid state (33–98%). External-stimuli-responsive emission such as pH and mechanical grinding was observed for these novel compounds. Employing compounds 5a-5d as dopants, OLEDs fabricated by solution processing presented a maximum external quantum efficiency of >6%, which is among the highest reported for BTD-based fluorescent materials.

#### **Results and Discussion**

#### **Synthesis**

As depicted in Scheme 1, starting from the commercially available 4,7-dibromobenzo[c][1,2,5]thiadiazole, compound 1 was obtained by nitration reaction in the presence of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> at room temperature, then followed by the reduction reaction by using iron as a catalyst in CH<sub>3</sub>COOH. Typical Suzuki coupling reactions between compound 1 and phenylboronic acid derivatives were able to achieve compound 2 in 70% yield. 1-Bromododecane reacted with methyl 3,4,5-trihydroxybenzoate to yield compound 3 in the presence of K<sub>2</sub>CO<sub>3</sub> and acetone, which afforded compound 4 by hydrolysis. By employing oxalyl chloride and triphenylphosphine in acetonitrile at room temperature, condensation reaction of compound 2 with compound 4 yielded target compounds 5a-5d, which were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and TOF-MS analysis.



Scheme 1. Synthetic route for compounds 5a-5d. Reaction conditions: a) (1) H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, 0 °C, RT, 6 h; (2) Fe, CH<sub>3</sub>COOH, 0 °C, RT, 12 h; b) Pd(PPh<sub>3</sub>)<sub>4</sub>, 2 M K<sub>2</sub>CO<sub>3</sub>, toluene, CH<sub>3</sub>CH<sub>2</sub>OH, 80 °C, 24 h; c) K<sub>2</sub>CO<sub>3</sub>, Kl, acetone, 80 °C, 2 d; d) THF, CH<sub>3</sub>CH<sub>2</sub>OH, NaOH solution, 80 °C, 4 h; e) (COCl)<sub>2</sub>, Ph<sub>3</sub>P=O, CH<sub>3</sub>CN, RT, 30 min.

#### **Thermal properties**

To explore the thermal properties of these compounds, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out under N<sub>2</sub> atmosphere. As shown in Figure S1 (in the Supporting Information), all compounds exhibit good thermal stability with the decomposition temperatures above 380  $^\circ\text{C}$  at 5% weight loss, implying that introduction of different substituents into the emissive core has a negligible effect on the decomposition temperature. On the contrary, different DSC curves were detected for compounds 5 a-5 d (Figure 1). Compound 5a shows a clear phase transition at 38°C in the second heating circle, suggesting a crystal-crystal transition. Then, a very weak transition at about 48 °C is detected, followed by the clearing point at about 76°C. On the other hand, three exothermic peaks at 39, 32, and 18 °C are observed on the cooling process for compound 5a. The presence of multiple transition peaks implies that the compound has polymorphic behavior. When the fluorine atom is introduced, there are three endothermic peaks at 79, 103, and 109°C in the first heating cycle. However, only one endothermic peak (109°C) and one exothermic peak (80°C) were observed during the second heating and first cooling processes, indicating the presence of highly defective and imperfect crystals or solid mesophases that do not crystallize by cooling from the isotropic melt.<sup>[42]</sup> As for compound 5c, with tert-butyl substituents, the sample displays several endothermic peaks in the first and second heating scans owing to the complex polymorphic behavior, and then the compound becomes isotropic at 135 °C. Upon the cooling curve, three exothermic peaks are clearly observed at 95, 32, and 19°C. The DSC curves of compound 5d show sharp peaks at 234°C and 205°C, as well as very weak phase transition peaks at 44 °C and 42 °C upon heating and

Chem. Eur. J. 2019, 25, 1 – 11 W

www.chemeurj.org

2

© 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim





Figure 1. DSC thermograms of compounds 5 a-5 d.



Figure 2. POM images of compounds on cooling (5 a: 54°C; 5 b: 94°C; 5c:102°C; 5d: 190°C).

cooling scans, respectively. To further investigate the thermotropic behavior, polarized optical microscopy (POM) measurements were carried out for all compounds, which show distinct birefringence upon heating and cooling processes (Figure 2). Both DSC and POM results demonstrated that these BTD derivatives have polymorphous states.

#### **Photophysical properties**

As shown in Figure 3, all compounds show three absorption bands in dichloromethane ( $CH_2CI_2$ ,  $10^{-5}$  M) solution between





pound 5d presents a distinct redshifted and intense absorption spectrum compared with compounds 5a-5c, which is responsible for the carbazole group possessing good electrondonating properties, leading to strong ICT transition. Clearly, the different substituents have significant influence on the ground state.



Figure 3. Absorption spectra of all compounds in dichloromethane solution  $(10^{-5} \text{ M})$  at room temperature.

250 nm and 550 nm. The absorption bands in the range 250-

350 nm are attributed to the  $\pi$ - $\pi$ \* transitions in the aromatic ring, whereas the absorption bands between 350 nm and



CHEMISTRY A European Journal Full Paper

Under the excitation wavelength of 370 nm, all compounds display intense emission with evident ICT character both in  $CH_2CI_2$  solution and neat films at room temperature (Figure 4), and the photophysical data are summarized in Table 1. Com-



Figure 4. PL spectra of compounds 5a-5d in (a)  $CH_2CI_2$  solution and (b) neat film at room temperature.

pounds 5a-5d show maximum emission peaks at 484, 487, 502, and 545 nm in CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature. Compared with 5a and 5b, compounds 5c and 5d present clear redshifted emission profiles owing to the donor units of tertbutyl and carbazole. It is noted that the substituents in these molecules play a key role on the emission property caused by the ICT effect. To explore the ICT character of these molecules, solvent-dependent absorption and emission properties were examined. As depicted in Figure S2 (in the Supporting Information), all compounds exhibit almost the same absorption spectra in different solvents, which means that the solvent polarization has a negligible effect on the ground state. On the contrary, redshifted emissions are observed for these compounds with the increased solvent polarization, especially for compound 5d (Figure S3 in the Supporting Information), implying that the solvent polarization plays a positive effect on the excited state.

Compared with the photoluminescence (PL) in solution, clearly hypsochromic emissions are observed for 5a-5d in neat film (Figure 3b and Table 1). Compounds 5a-5c show almost the same emission profiles with the maximum emission peaks at about 478 nm, whereas a maximum peak at 511 nm

was detected for compound 5d in neat film. To further explore their photophysical properties, the photoluminescent quantum yield (PLQY,  $\Phi_{\rm PL}$ ) and lifetime were investigated. Satisfactory PLQY values of 0.56, 0.69, 0.97, and 0.95 were obtained for compounds 5a, 5b, 5c, and 5d in CH<sub>2</sub>Cl<sub>2</sub> solution, respectively. Introduction of electron-donating moieties (tert-butyl and carbazole) has a positive effect on the emission efficiency. The 10 wt % doped poly(methyl methacrylate) (PMMA) films, except compound **5** $\mathbf{c}$ , exhibit decreased  $\Phi_{PL}$  values of 0.46 for 5a, 0.33 for 5b, and 0.70 for 5d owing to the concentration quenching. Compound **5**c still shows a high  $\Phi_{PL}$  in the doped film, which could be ascribed to the sterically challenging tertbutyl moiety effectively suppressing intermolecular interactions. Transient PL decay curves (Figure 5) present single exponential decay with the lifetimes in the nanosecond region (Table 1), suggesting that these emissions are from the singlet excitons. Based on  $\Phi_{PL}$  and lifetime, the radiative ( $K_r$ ) and nonradiative ( $K_{nr}$ ) rate constants were evaluated according to Equations (1) and (2), and the data are listed in Table 1.

$$K_{\rm r} = \Phi /_{\tau} \tag{1}$$

$$K_{\rm nr} = \frac{1}{\tau} - K_{\rm r} \tag{2}$$

Clearly, the compounds with donor units have higher emission efficiency because of the very small  $K_{nr}$ .



Figure 5. Transient photoluminescent decay curves of compounds 5a-5d in  $CH_2Cl_2$  at room temperature.

| Table 1. Photophysical data for compounds 5 a-5 d. |                              |  |   |  |                      |  |   |                            |                         |                        |                        |
|--|------------------------------|--|---|--|----------------------|--|---|----------------------------|-------------------------|------------------------|------------------------|
|  | $\lambda_{abs}{}^{[a]}$ [nm] | $\lambda_{_{em}}$ [nm]                   | <i>T</i> <sub>d</sub> <sup>[c]</sup> [°C] | $\Phi_{ m PL}$ [%]                     | $\tau^{[e]} \; [ns]$ | $K_{\rm r}^{\rm [f]}  [	imes 10^7  { m s}^{-1}]$ | $K_{\rm nr}^{\rm [f]}  [	imes 10^7  { m s}^{-1}]$ | $E_{\rm ox}^{\rm [g]}$ [V] | $E_{\rm red}^{[g]}$ [V] | E <sub>HOMO</sub> [eV] | E <sub>LUMO</sub> [eV] |
| 5 a  | 273, 326, 336, 383           | 484 <sup>[a]</sup><br>478 <sup>[b]</sup> | 392                                       | 56 <sup>[a]</sup><br>46 <sup>[d]</sup> | 8.54                 | 6.54   | 5.16  | 1.16                       | -1.32                   | -5.96                  | -3.48                  |
| 5 b  | 271, 326, 335, 381           | 487 <sup>[a]</sup><br>477 <sup>[b]</sup> | 383                                       | 69 <sup>[a]</sup><br>33 <sup>[d]</sup> | 7.93                 | 8.70   | 3.90  | 1.26                       | -1.34                   | -6.06                  | -3.46                  |
| 5c   | 276, 329, 338, 388           | 502 <sup>[a]</sup><br>479 <sup>[b]</sup> | 393                                       | 97 <sup>[a]</sup><br>98 <sup>[d]</sup> | 6.36                 | 15.3   | 0.40  | 1.23                       | -1.28                   | -6.03                  | -3.52                  |
| 5 d  | 292, 326, 340, 403           | 545 <sup>[a]</sup><br>510 <sup>[b]</sup> | 384                                       | 95 <sup>[a]</sup><br>70 <sup>[d]</sup> | 5.11                 | 18.6   | 1.0   | 0.80                       | -1.31                   | -5.6                   | -3.49                  |

[a] In dichloromethane solution. [b] In neat film. [c] Under N<sub>2</sub> with 20 °C min<sup>-1</sup>. [d] 10 wt% compound doped PMMA films. [e] In dichloromethane. [f] Radiative decay rate  $k_r = \Phi_{PL}/\tau$ ; nonradiative decay rate  $k_{nr} = 1/\tau - k_r$  [g] The neat film of the compounds in CH<sub>3</sub>CN,  $E_{\alpha}^{FCFc+} = 0.48$  V.

Chem. Eur. J. **2019**, 25, 1 – 11

www.chemeurj.org

© 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



#### **DFT calculations**

To investigate the relationship between molecular structure and electronic property, DFT was performed by using the Gaussian 09 program based on the B3LYP functional with 6-31G basis set. The DFT results reveal that the 4,7-diphenylbenzo[c][1,2,5]thiadiazole moiety and amide group make the major contributions to the highest occupied molecular orbitals (HOMO) for compounds **5a**, **5b**, and **5c**, whilst their lowest unoccupied molecular orbitals (LUMO) mainly localize at benzo[c]-[1,2,5]thiadiazole (Figure 6). In the case of **5d**, the LUMO shows the contribution from both the benzo[c] [1,2,5]thiadiazole and amide moieties, whereas the HOMO is mainly spread over the phenylcarbazole fragment. Notedly, the substituents have a significant effect on the electronic properties, which also explains the different absorption and emission properties of compounds 5a-5d.

#### pH-Dependent luminescence

Generally speaking, an amido bond in a molecule can play an important role for the emissive property through intermolecular interactions.<sup>[43,44]</sup> Therefore, in this context, pH-dependence fluorescence measurements were carried out for all compounds in  $CH_2CI_2$ . As shown in Figure 7, significant changes are observed for all compounds with different pH values. For compounds **5a** and **5b**, their emission intensities decrease sharply with increasing pH values, whereas the emissive shape and



Figure 6. Frontier orbitals of compounds 5a-5d in the ground state from DFT calculations.



Figure 7. Emission profiles of compounds 5a-5d as a function of the pH at the excitation wavelength of 370 nm.

Chem. Eur. J. 2019, 25, 1 – 11

www.chemeurj.org

© 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim





wavelength exhibit negligible change. This phenomenon could be explained by the physical quenching processes such as collisional deactivation and intermolecular interactions between the emissive unit and acid solvent. On the contrary, compounds **5c** and **5d** have different pH-dependent luminescence compared with compounds **5a** and **5b**, in which the emission intensity increases with the pH values at first and then decreases. In addition, the emission spectra of compounds **5a** and **5d** display a clear blueshift (ca. 13 nm for **5c** and 20 nm for **5d**) with increased pH values.

#### Mechanochromic luminescence

To further explore the relationship between molecular structure and emission, stimulus-dependent emission studies, such as grinding and fuming, were performed. Unfortunately, the pristine samples of compounds **5a–5c** present almost the same emissive profiles as those in the ground and fumed state (Figure S4 in the Supporting Information), implying no mechanochromic luminescence. Interestingly, distinct mechanochromic luminescence was observed for compound **5d** (Figure 8). The pristine sample of compound **5d** exhibits a maximum emissive peak at 562 nm, whereas a markedly hypsochromic



**Figure 8.** (a) PL spectra and photographs of compound **5 d** in response to external stimuli. Photographs were taken under UV irradiation with 365 nm. P: pristine; G: grinding; F: fuming. (b) Powder X-ray diffraction curves of compound **5 d** at room temperature.

Chem. Eur. J. **2019**, 25, 1 – 11

www.chemeurj.org

6

emission peak at 530 nm is observed after grinding the sample, implying destroyed  $\pi$ - $\pi$  interactions. When fuming the ground sample in dichloromethane vapor for 15 min, the emissive color can recover back to 554 nm, which is consistent with the emission in the pristine state. The photographs under UV light (Figure 8, inset) also demonstrate that the mechanochromic luminescence varies from yellow to green after grinding the sample, followed by turning back to yellow by fuming. Powder X-ray diffraction (PXRD) was then carried out to further explore the mechanism of the mechanochromic luminescence. Definitely, the PXRD patterns display almost identical diffraction peaks for compounds 5a-5c in different states, as shown in Figure S5 (in the Supporting Information, taking 5b and 5c as the examples). As for compound 5d, the PXRD patterns of the pristine sample show some sharp and intense diffraction peaks in the range 5–45°, implying that compound 5d has micro-crystalline structure in the pristine state.<sup>[45,46]</sup> After grinding the sample, broad diffraction peaks replaced the sharp and intense ones observed, suggesting compound 5d transforms from the crystal to amorphous phase after grinding. When the ground sample was fumed by the solvent, the diffraction peaks clearly reverted to the pattern of the pristine samples. Therefore, the mechanochromic luminescence behavior of compound 5 d is attributed to the transition between different phase states. It is noted that the mechanochromic luminescence in this molecular system is concerned not only with the intermolecular amido bond but also with the substituents.

#### **Electrochemical properties**

The electrochemical properties of the neat films of all compounds were investigated in CH<sub>3</sub>CN solution. The cyclic voltammetry (CV) curves are shown in Figure S6 (in the Supporting Information) and the data are listed in Table 1. All compounds exhibit irreversible redox potentials between -1.5-2.0 V. Owing to the same acceptor skeleton, all compounds show similar reduction potentials at about -1.30 V (vs. Fc/Fc<sup>+</sup>, the same below). The oxidation potentials are evaluated to be 1.16 V (vs. Fc/Fc<sup>+</sup>, the same below) for **5a**, 1.26 V for **5b**, 1.23 V for 5c, and 0.80 V for 5d. It is noted that compound 5d appears at a significantly lower oxidation potential than that of compounds 5a-5c, which can be explained by the strong electron-donating property of the carbazole moiety. Using the formula of  $E_{HOMO} = -(E_{ox} + 4.8) \text{ eV}$  and  $E_{LUMO} = -(E_{red} + 4.8) \text{ eV}$ , the HOMO and LUMO energy levels are estimated to be -5.96/-3.48 eV for **5a**, -6.06/-3.46 eV for **5b**, -6.03/ -3.52 eV for 5 c, and -5.6/-3.49 eV for 5 d (Table 1). The introduction of stronger donor substituents into the molecule is thus seen to decrease the electrochemical energy gap, which is consistent with the trends in the absorption and emission profiles.

#### **Electroluminescent properties**

To further explore the effect of the substituents on the electroluminescent (EL) properties, OLEDs were fabricated by solution processing with the configuration of ITO/PEDOT:PSS (40 nm)/

© 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



CzAcSF:dyes (10 wt %, 50 nm)/DPEPO (9 nm)/TmPyPB (40 nm)/ CsF (1.2 nm)/Al (120 nm) (see the Experimental Section for full details). In the devices, PEDOT:PSS acts as the hole injection layer. The emitter layer is a mixture of host CzAcSF and the dopant dyes. DPEPO and TmPyPB are the hole-blocking and electron-transport layers, respectively. Similar to the PL emission, the devices exhibit bluish-green emissions with the maximum emissive peaks at 490 nm for 5a, 490 nm for 5b, 492 nm for 5 c, and 498 nm for 5 d, which demonstrates that the exciton recombination occurs in the emissive layer (Figure 9a). Similar to the PL profiles, it is noted that introduction of the electron-donating group (tert-butyl and carbazole) has a clear effect on the redshifted EL spectra (Figure 9a and Table S1 in the Supporting Information). The Commission Internationale de L'Eclairage (CIE) coordinates are (0.18, 0.34), (0.18, 0.35), (0.18, 0.35), and (0.20, 0.41) for the 5a, 5b, 5c, and 5d-based devices, respectively (Figure S7 in the Supporting Information). On the other hand, the absence of host emission implies that a complete energy transfer is realized between host and guest in these devices.

The current density–voltage–luminance (*J–V–L*) characteristics of the devices are shown in Figure 9d, and the relative parameters are listed in Table S1 (in the Supporting Information). All the devices possess low turn-on voltages ( $V_{onr}$ , 1 cd m<sup>-2</sup>) of 3.6 V, and maximum brightness in the range 1012–1717 cd m<sup>-2</sup>. Owing to the superior emission properties, the devices based on **5c** and **5d** present better performances with the maximum current efficiencies (CE) of 13.88 and 15.94 cd A<sup>-1</sup> and external quantum efficiencies (EQE) of 6.07 and 6.15%, respectively, which is higher than the theoretical value of the fluorescence materials (ca. 5%).

## Conclusion

Four novel BTD-based polymorphous luminescent materials were synthesized and characterized. All compounds showed very bright emission with excellent emissive efficiency in solution and the solid state. Different substituents resulted in the compounds possessing distinct phase transitions. Increasing with electron-donating intensity, the emissive spectra exhibited a redshift. pH-dependent and mechanochromic luminescence were observed for these BTD derivatives owing to the different intermolecular interactions. By employing compounds 5a-5d as dopants, OLEDs fabricated by solution processing showed a maximum external quantum efficiency of >6%, which is among the highest reported for BTD-based fluorescent materials. This research proved that elaborate molecular engineering can provide polymorphic luminescent materials with satisfactory emission properties.

## **Experimental Section**

#### Materials and measurements

1,4-Dibromo-2,5-diiodobenzene, 4-(diphenylamine)phenylboronic acid, and diphenyl disulfide were commercially sourced from Energy Chemical Company Ltd. Other reagents were purchased from J&K Chemical and Aladdin. All reactions were carried out under N<sub>2</sub> atmosphere. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were acquired by using a Bruker Dex-300/400 NMR instrument with CDCl<sub>3</sub> as solvent. Mass spectra (MS) were recorded with a Bruker Autoflex MALDI-TOF instrument using dithranol as a matrix. UV/Vis absorption spectra were recorded by using a SHIMADZU UV-1650PC. Steady-state photoluminescence (PL) spectra were obtained with a PTI QuantaMaster 40 spectrofluorometer at room temperature and absolute PL quantum yields (PLQY) were recorded with a HAMA-



Figure 9. Electroluminescent (EL) characteristics of the devices based on 5 a-5 d. a) EL spectra; b) EQE-current density curves; c) current efficiency-current density characteristics; d) current density-voltage-luminance curves.

7

Chem. Eur. J. 2019, 25, 1 – 11

www.chemeurj.org



MASTU C9920-02G. Photoluminescence decay traces were obtained through the time-correlated single photon counting (TCSPC) technique by using a FLS980 instrument. A 377 nm pulsed laser was used as an excitation source and data analyses were performed by using exponential fitting models with FluoFit software. Thermogravimetric analysis (TGA) was carried out with a NETZSCH STA449 from 25 °C to 600 °C at a 20 °C min<sup>-1</sup> heating rate under N<sub>2</sub> atmosphere. Polarized optical microscopy was recorded with a Linkam Thms600/Nikon 50I. Cyclic voltammetry measurements were performed by using a 273A (Princeton Applied Research). Electrochemical properties were evaluated by cyclic voltammetry with three typical electrodes in degassed CH<sub>3</sub>CN solution with a rate of 100 mV s<sup>-1</sup>. The CV system employed Bu<sub>4</sub>NPF<sub>6</sub> as the electrolyte. A platinum disk was used as the working electrode, platinum wire was used as the counter electrode, and silver wire was used as the reference electrode. Ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) was used as the external standard compound. Each oxidation potential was calibrated by using ferrocene as a reference. DFT calculations were performed in the gas phase by using the Gaussian 09 quantum-chemical package. The geometry optimization for ground state derivatives was carried out by using B3LYP functionals with the 6-31G (d,p) basis set for all atoms. X-ray polycrystal diffraction was measured by D/MAX-2500/PC (40 kV, 300 mA) using CuK<sub>a</sub> radiation ( $\lambda = 1.5418$  Å). The scan rate is  $10^{\circ}$  min<sup>-1</sup> and the angle range is from 5 to 90°.

#### Device fabrication and measurement

The patterned ITO substrates were rinsed with acetone and isopropyl alcohol by using sonication for 15 min, followed by 15 min UVozone treatment. Organic layers,  $MOO_3$ , and Al were thermally evaporated at a deposition rate of 0.6-1 Å s<sup>-1</sup> for organic layers, 0.2 Å s<sup>-1</sup> for  $MOO_3$ , and 4-5 Å s<sup>-1</sup> for Al electrode. The emitter was dissolved in chlorobenzene and spin-coated onto the PEDOT:PSS layer. The current-voltage–luminance (*I–V–L*) characteristics of the devices were measured with a Keithley-236 source-measure unit, a Keithley-2000 multimeter unit, and a calibrated Si photodiode (Hamamatsu S5227-1010BQ). The luminance and efficiencies were calculated from the photocurrent measurement data obtained with the Si photodiode. The electroluminescence spectra were obtained by using a spectroradiometer (PR735).

In the devices, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) serves as the hole-injection layer, whereas bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO) and 1,3,5tri(*m*-pyrid-3-yl-phenyl)benzene (TmPyPB) act as the hole-blocking and electron-transport layers, respectively.

#### 4,7-Dibromobenzo[c][1,2,5]thiadiazol-5-amine

A mixture of 4,7-dibromobenzo[c][1,2,5]thiadiazole (6.0 g, 20.5 mmol) and H<sub>2</sub>SO<sub>4</sub> (12 mL) were stirred at 0 °C and then HNO<sub>3</sub> (24 mL) was added dropwise. The reaction mixture was stirred at room temperature for 6 h. After the mixture was poured into ice water, the yellow precipitate (5.12 g, 73 %) was collected. The solid was used in the next step without any further purification. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.28$  ppm (s, 1 H).

After that, a mixture of 4,7-dibromo-5-nitrobenzo[*c*][1,2,5]thiadiazole (5.0 g, 14.7 mmol)and acetic acid (120 mL) were stirred at 0 °C, then iron powder (4.2 g, 73.7 mmol) was added in batches to the mixture. After stirring at room temperature for 6 h, the mixture was poured into ice water, and the brownish yellow precipitate was collected (4.3 g, 95%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.47 (s, 1 H), 4.64 ppm (s, 2 H).

#### 4,7-Diphenylbenzo[c][1,2,5]thiadiazol-5-amine (2 a)

A mixture of 4,7-dibromobenzo[c][1,2,5]thiadiazol-5-amine (1.0 g, 3.24 mmol), phenylboronic acid (0.94 g, 8.20 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (187 mg, 0.162 mmol), ethanol (10 mL), 2 m K<sub>2</sub>CO<sub>3</sub> (10 mL), and toluene (30 mL) was stirred at 80 °C for 24 h under a nitrogen atmosphere. After cooling to room temperature, the mixture was poured into water (50 mL) and extracted with dichloromethane (3×30 mL). The combined organic layers were washed with water, dried over anhydrous MgSO<sub>4</sub>, and evaporated to dryness. The residue was purified by chromatography on a silica gel column eluting with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (v/v = 1:1) and recrystallized from *n*-hexane solution to afford a yellow solid (420 mg, 43 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.94–7.90 (m, 2H), 7.63–7.58 (m, 3H), 7.58–7.51 (m, 3H), 7.45 (dd, *J*=13.2, 7.3 Hz, 2H), 7.30 (s, 1H), 4.24 ppm (s, 2H).

#### 4,7-Bis(4-fluorophenyl)benzo[c][1,2,5]thiadiazol-5-amine (2b)

Compound **2b** was prepared by using the same synthetic process as for compound **2a**. The yield of the yellow product was 39%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.89$  (s, 2H), 7.62–7.55 (m, 2H), 7.29 (s, 1H), 7.26–7.20 (m, 4H), 4.21 ppm (s, 2H).

# 4,7-Bis(4-(*tert*-butyl)phenyl)benzo[c][1,2,5]thiadiazol-5-amine (2 c)

Compound **2c** was prepared by using the same synthetic process as for compound **2a**. The yield of the yellow product was 39%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.86 (d, *J* = 8.4 Hz, 2 H), 7.61–7.53 (m, 6 H), 7.28 (s, 1 H), 4.25 (s, 2 H), 1.40 ppm (s, 18 H).

#### 4,7-Bis(4-(9*H*-carbazol-9-yl)phenyl)benzo[*c*][1,2,5]thiadiazol-5-amine (2 d)

Compound **2d** was prepared by using the same synthetic process as for compound **2a**. The yield of the yellow product was 79%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.21 (dd, *J* = 13.7, 8.0 Hz, 6 H), 7.94 (d, *J* = 8.4 Hz, 2 H), 7.81 (dd, *J* = 12.0, 8.4 Hz, 4 H), 7.60 (dd, *J* = 11.8, 8.1 Hz, 4 H), 7.50–7.43 (m, 5 H), 7.33 (t, *J* = 7.4 Hz, 4 H), 4.46 ppm (s, 2 H).

#### Methyl 3,4,5-tris(dodecyloxy)benzoate (3)

A mixture of methyl 3,4,5-trihydroxybenzoate (10.0 g, 54.3 mmol), 1-bromododecane (80.0 g, 320 mmol), K<sub>2</sub>CO<sub>3</sub> (75.0 g, 0.54 mol), Kl (1.8 g, 10.8 mmol), and acetone (250 mL) was stirred at 80 °C for 2 days under a nitrogen atmosphere. After cooling to room temperature, the mixture was evaporated to dryness, poured into water (200 mL), and extracted with dichloromethane (3×150 mL). The combined organic layers were washed with water, dried over anhydrous MgSO<sub>4</sub>, and evaporated to dryness. The residue was purified by chromatography on a silica gel column eluting with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (v/v=1:2) and a white solid was achieved (18.5 g, 49%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =6.94 (s, 2H), 3.78 (s, 2H), 3.64 (s, 4H), 3.27 (s, 3H), 1.66 (s, 2H), 1.45 (d, *J*=32.8 Hz, 6H), 1.26 (s, 52H), 0.88 ppm (t, *J*=6.8 Hz, 9H).

#### 3,4,5-Tris(dodecyloxy)benzoic acid (4)

A mixture of methyl 3,4,5-tris(dodecyloxy)benzoate (10.0 g, 14.5 mmol), THF (90 mL), ethanol (30 mL), and aqueous solution of NaOH (30 mL) was stirred at  $80 \,^{\circ}$ C for 6 h. After cooling to room temperature, the mixture was poured into water (300 mL) and adjusted to pH 2 with hydrochloric acid (1 N). After that, the precipitate was collected and recrystallized from methanol solution to

Chem. Eur. J. **2019**, 25, 1 – 11

www.chemeurj.org

8

© 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



afford a white solid (8.5 g, 87%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.98 (s, 2H), 3.80 (t, *J* = 6.2 Hz, 2H), 3.68 (s, 4H), 1.67 (dt, *J* = 14.5, 7.2 Hz, 2H), 1.47 (d, *J* = 31.6 Hz, 6H), 1.25 (d, *J* = 2.9 Hz, 52H), 0.87 ppm (t, *J* = 6.7 Hz, 9H).

#### *N*-(4,7-Diphenylbenzo[*c*][1,2,5]thiadiazol-5-yl)-3,4,5-tris(dodecyloxy)benzamide (5 a)

A mixture of Ph<sub>3</sub>P=O (423 mg, 1.524 mmol) and acetonitrile (5 mL) was added to a 50 mL round-bottom flask, oxalyl chloride (252 mg, 1.89 mmol) was then added dropwise to the heterogeneous mixture. When the mixture was homogeneous after stirring at room temperature for 10 min, 3,4,5-tris(dodecyloxy)benzoic acid (1.03 g, 1.524 mmol) and the acetonitrile solution of 2a (600 mg, 1.89 mmol) was added slowly in order. The mixture was stirred at room temperature for 30 min. The reaction product was diluted with dichloromethane (30 mL), washed with saturated sodium bicarbonate (3×50 mL), dried over anhydrous MgSO<sub>4</sub>, and evaporated to dryness. The residue was purified by chromatography on a silica gel column eluting with petroleum ether/ $CH_2CI_2$  (v/v=2:1) and recrystallized from methanol solution to afford a yellow-green solid (135 mg, 9%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.22 (s, 1 H), 8.22 (s, 1H), 8.11-8.05 (m, 2H), 7.70-7.61 (m, 4H), 7.61-7.52 (m, 3H), 7.51–7.44 (m, 1 H), 6.80 (s, 2 H), 3.98 (t, J = 6.5 Hz, 2 H), 3.87 (t, J =6.5 Hz, 4 H), 1.86–1.66 (m, 6 H), 1.45 (dd, J=14.0, 6.3 Hz, 6 H), 1.30 (d, J=17.1 Hz, 48 H), 0.89 ppm (d, J=6.4 Hz, 9 H); <sup>13</sup>C NMR (75 MHz,  $CDCl_3$ ):  $\delta = 164.09$ , 153.30, 153.21, 150.82, 141.59, 137.07, 133.71, 130.48, 129.62, 129.48, 129.06, 128.66, 123.25, 120.02, 105.20, 73.58, 69.17, 31.95, 29.68, 29.39, 26.06, 22.71, 14.14 ppm; (MALDI-TOF MS): *m*/*z* calcd for C<sub>61</sub>H<sub>89</sub>N<sub>3</sub>O<sub>4</sub>S: 959.66; found: 960.77.

#### *N*-(4,7-Bis(4-fluorophenyl)benzo[*c*][1,2,5]thiadiazol-5-yl)-3,4,5-tris(dodecyloxy)benzamide (5 b)

Compound **5b** was prepared by using the same synthetic process as for compound **5a**. The yield of the light-yellow product was 17%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.13 (s, 1H), 8.10 (s, 1H), 8.09–8.04 (m, 2H), 7.65–7.60 (m, 2H), 7.35 (t, *J*=8.5 Hz, 2H), 7.27 (s, 1H), 7.23 (s, 1H), 6.81 (s, 2H), 3.99 (t, *J*=6.6 Hz, 2H), 3.89 (t, *J*=6.4 Hz, 4H), 1.85–1.76 (m, 4H), 1.72 (dd, *J*=14.8, 6.9 Hz, 2H), 1.51–1.41 (m, 6H), 1.36–1.21 (m, 48H), 0.88 ppm (t, *J*=6.6 Hz, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ =165.07, 153.28, 150.69, 141.80, 132.72, 132.50, 131.15, 128.51, 123.20, 119.16, 116.88, 116.59, 115.81, 115.53, 105.21, 73.61, 69.25, 31.94, 29.64, 29.38, 26.04, 22.70, 14.13 ppm; (MALDI-TOF MS): *m/z* calcd for C<sub>61</sub>H<sub>87</sub>F<sub>2</sub>N<sub>3</sub>O<sub>4</sub>S: 996.44; found: 996.55.

#### *N*-(4,7-Bis(4-(*tert*-butyl)phenyl)benzo[*c*][1,2,5]thiadiazol-5-yl)-3,4,5-tris(dodecyloxy)benzamide (5 c)

Compound **5**c was prepared by using the same synthetic process as for compound **5**a. The yield of the green product was 60%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.18 (s, 1H), 8.30 (s, 1H), 8.00 (d, *J* = 6.7 Hz, 2H), 7.66 (d, *J*=8.5 Hz, 2H), 7.58 (dd, *J*=8.6, 2.4 Hz, 4H), 6.89 (s, 2H), 3.99 (t, *J*=6.6 Hz, 2H), 3.93 (t, *J*=6.3 Hz, 4H), 1.77 (ddd, *J*=15.3, 12.5, 7.3 Hz, 6H), 1.47 (s, 6H), 1.41 (d, *J*=1.6 Hz, 18H), 1.26 (s, 48H), 0.88 ppm (t, *J*=6.6 Hz, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ =165.26, 153.21, 150.68, 147.65, 141.76, 136.65, 134.26, 130.40, 130.05, 129.10, 126.44, 125.63, 123.29, 119.83, 105.61, 73.61, 69.22, 50.89, 31.94, 31.35, 29.65, 29.38, 26.17, 22.70, 14.13 ppm; (MALDI-TOF MS): *m/z* calcd for C<sub>69</sub>H<sub>105</sub>N<sub>3</sub>O<sub>5</sub>S: 1071.78; found: 1073.11.

#### *N*-(4,7-Bis(4-(9*H*-carbazol-9-yl)phenyl)benzo[*c*][1,2,5]thiadiazol-5-yl)-3,4,5-tris(dodecyloxy)benzamide (5 d)

Compound **5 b** was prepared by using the same synthetic process as for compound **5 a**. The yield of the brown-yellow product was 26%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.37 (s, 1 H), 8.40–8.36 (m, 3 H), 8.19 (d, *J* = 7.8 Hz, 4 H), 7.98–7.92 (m, 4 H), 7.81 (d, *J* = 8.5 Hz, 2 H), 7.59 (d, *J* = 8.2 Hz, 4 H), 7.47 (q, *J* = 7.2 Hz, 4 H), 7.37–7.31 (m, 4 H), 6.93 (s, 2 H), 3.96 (t, *J* = 6.5 Hz, 2 H), 3.82 (t, *J* = 6.4 Hz, 4 H), 1.69 (dd, *J* = 14.6, 6.8 Hz, 2 H), 1.53–1.39 (m, 6 H), 1.33–1.07 (m, 52 H), 0.88 ppm (td, *J* = 6.8, 2.4 Hz, 9 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 165.22, 153.38, 140.75, 140.29, 132.71, 130.93, 127.53, 127.14, 126.26, 126.07, 123.80, 123.57, 120.59, 120.54, 120.39, 120.37, 120.15, 109.97, 109.66, 109.64, 105.41, 73.61, 69.39, 31.94, 29.69, 29.39, 25.93, 22.71, 14.14 ppm; (MALDI-TOF MS): *m/z* calcd for C<sub>85</sub>H<sub>103</sub>N<sub>5</sub>O<sub>4</sub>S: 1289.77; found: 1290.87.

## Acknowledgments

Financial support was provided by the National Natural Science Foundation of China (51773021, 51911530197, U1663229, 51473140), Six Talent Peaks Project in Jiangsu Province (XCL-102), the Talent Project of Jiangsu Specially Appointed Professor, Natural Science Fund for Colleges and Universities in Jiangsu Province (No. 19KJA430002), the Open Fund of Key Laboratory of Advanced Display and System Applications of Ministry of Education, Shanghai University, and Natural Science Foundation of Hunan Province (No. 2017JJ2245).

## **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** 2,1,3-benzothiadiazole derivatives • organic lightemitting diodes • photophysical properties • polymorphous luminescent materials • structure–property relationship

- [1] C. W. Tang, S. A. VanSlyke, Appl. Phys. Lett. 1987, 51, 913-915.
- [2] P. Tao, Y. Miao, H. Wang, B. Xu, Q. Zhao, Chem. Rec. 2019, 19, 1531– 1561.
- [3] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* **1998**, 395, 151–154.
- [4] H. Sasabe, J. Kido, Chem. Mater. 2011, 23, 621-630.
- [5] M. C. Gather, A. Köhnen, K. Meerholz, Adv. Mater. 2011, 23, 233-248.
- [6] H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature* 2012, 492, 234–238.
- [7] J.-H. Jou, S. Kumar, A. Agrawal, T.-H. Lia, S. Sahoo, J. Mater. Chem. C 2015, 3, 2974–3002.
- [8] L. Xiao, Z. Chen, B. Qu, J. Luo, S. Kong, Q. Gong, J. Kido, Adv. Mater. 2011, 23, 926–952.
- [9] M. S. Lowry, S. Bernhard, Chem. Eur. J. 2006, 12, 7970-7977.
- [10] S. P. Anthony, ChemPlusChem 2012, 77, 518-531.
- [11] S. C. Rasmussen, S. J. Evenson, C. B. McCausland, Chem. Commun. 2015, 51, 4528-4543.
- [12] Y. Sagara, S. Yamane, M. Mitani, C. Weder, T. Kato, Adv. Mater. 2016, 28, 1073-1095.
- [13] H. Sun, S. Liu, W. Lin, K. Y. Zhang, W. Lv, X. Huang, F. Huo, H. Yang, G. Jenkins, Q. Zhao, W. Huang, *Nat. Commun.* **2014**, *5*, 3601.
- [14] M.-K. Tsang, G. Bai, J. Hao, Chem. Soc. Rev. 2015, 44, 1585-1607.
- [15] Y. Sagara, T. Kato, Angew. Chem. Int. Ed. 2008, 47, 5175-5178; Angew. Chem. 2008, 120, 5253-5256.

Chem. Eur. J. 2019, 25, 1–11 www.chemeurj.org

9

© 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



CHEMISTRY A European Journal Full Paper

- [16] Y. Dong, J. Zhang, X. Tan, L. Wang, J. Chen, B. Li, L. Ye, B. Xu, B. Zou, W. Tian, J. Mater. Chem. C 2013, 1, 7554–7559.
- [17] A. L. Balch, Angew. Chem. Int. Ed. 2009, 48, 2641–2644; Angew. Chem. 2009, 121, 2679–2682.
- [18] A. Pucci, G. Ruggeri, J. Mater. Chem. 2011, 21, 8282-8291.
- [19] M. Sase, S. Yamaguchi, Y. Sagara, I. Yoshikawa, T. Mutai, K. Araki, J. Mater. Chem. 2011, 21, 8347–8354.
- [20] Z. Chi, X. Zhang, B. Xu, X. Zhou, C. Ma, Y. Zhang, S. Liu, J. Xu, Chem. Soc. Rev. 2012, 41, 3878–3896.
- [21] R. Li, S. Xiao, Y. Li, Q. Lin, R. Zhang, J. Zhao, C. Yang, K. Zou, D. Li, T. Yi, *Chem. Sci.* 2014, *5*, 3922–3928.
- [22] Y. Sagara, T. Kato, Nat. Chem. 2009, 1, 605-610.
- [23] G. Zhang, J. Lu, M. Sabat, C. L. Fraser, J. Am. Chem. Soc. 2010, 132, 2160-2162.
- [24] Z. Zhang, D. Yao, T. Zhou, H. Zhang, Y. Wang, Chem. Commun. 2011, 47, 7782–7784.
- [25] Y. Zhang, Y. Ma, L. Kong, Y. Tian, J. Yang, Dyes Pigm. 2018, 159, 314– 321.
- [26] X. Huang, Y. Zhou, L. Qian, M. Liu, Y. Cheng, H. Wu, J. Mater. Chem. C 2018, 6, 5075-5096.
- [27] T. S. Sukhikh, D. S. Ogienko, D. A. Bashirov, S. N. Konchenkoa, *Russ. Chem. Bull.* 2019, 68, 651–661.
- [28] A. A. Vieira, R. Cristiano, A. J. Bortoluzzi, H. Gallardo, J. Mol. Struct. 2008, 875, 364–371.
- [29] F. Silvestri, A. Marrocchi, M. Seri, C. Kim, T. J. Marks, A. Facchetti, A. Taticchi, J. Am. Chem. Soc. 2010, 132, 6108–6123.
- [30] B. A. DaSilveira Neto, A. S. A. Lopes, G. Ebeling, R. S. Goncalves, V. E. U. Costa, F. H. Quina, J. Dupont, *Tetrahedron* 2005, *61*, 10975–10982.
- [31] S.-H. Kang, G. D. Tabi, J. Lee, G. Kim, Y.-Y. Noh, C. Yang, *Macromolecules* 2017, 50, 4649–4657.
- [32] F. Ni, Z. Wu, Z. Zhu, T. Chen, K. Wu, C. Zhong, K. An, D. Wei, D. Ma, C. Yang, J. Mater. Chem. C 2017, 5, 1363–1368.
- [33] S. Ito, T. Yamada, T. Taguchi, Y. Yamaguchi, M. Asami, Chem. Asian J. 2016, 11, 1963–1970.

- [34] B. Bardi, C. D. Agnese, M. Tassé, S. Ladeira, A. Painelli, K. I. M.-C. Ching, F. Terenziani, *ChemPhotoChem* **2018**, 2, 1027–1037.
- [35] X. Song, H. Yu, X. Yan, Y. Zhang, Y. Miao, K. Ye, Y. Wang, *Dalton Trans.* 2018, 47, 6146–6155.
- [36] H. Shimogawa, O. Yoshikawa, Y. Aramaki, M. Murata, A. Wakamiya, Y. Murata, Chem. Eur. J. 2017, 23, 3784-3791.
- [37] S. Nagai, M. Yamashita, T. Tachikawa, T. Ubukata, M. Asami, S. Ito, J. Mater. Chem. C 2019, 7, 4988–4998.
- [38] G. He, L. Du, Y. Gong, Y. Liu, C. Yu, C. Wei, W. Z. Yuan, ACS Omega 2019, 4, 344–351.
- [39] S. Hayashi, T. Koizumi, N. Kamiya, Cryst. Growth Des. 2017, 17, 6158–6162.
- [40] T. O. Benevides, E. Regis, C. R. Nicoleti, I. H. Bechtold, A. A. Vieira, *Dyes Pigm.* 2019, 163, 300-307.
- [41] Y. Sagara, A. Seki, Y. Kim, N. Tamaoki, J. Mater. Chem. C 2018, 6, 8453– 8459.
- [42] L. Veltri, V. Maltese, F. Auriemma, C. Santillo, S. Cospito, M. L. Deda, G. Chidichimo, B. Gabriele, C. D. Rosa, A. Beneduci, *Cryst. Growth Des.* 2016, 16, 5646-5656.
- [43] Y. Sagara, T. Mutai, I. Yoshikawa, K. Araki, J. Am. Chem. Soc. 2007, 129, 1520-1521.
- [44] S. Mo, Q. Meng, S. Wan, Z. Su, H. Yan, B. Z. Tang, M. Yin, Adv. Funct. Mater. 2017, 27, 1701210.
- [45] Y. Q. Dong, J. W. Y. Lam, B. Z. Tang, J. Phys. Chem. Lett. 2015, 6, 3429– 3436.
- [46] P. Z. Chen, J.-X. Wang, L.-Y. Niu, Y.-Z. Chen, Q.-Z. Yang, J. Mater. Chem. C 2017, 5, 12538–12546.

Manuscript received: September 3, 2019 Revised manuscript received: September 29, 2019 Version of record online:

© 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

10



# **FULL PAPER**

Four 'T'-shaped molecules bearing the 2,1,3-benzothiadiazole skeleton were prepared and characterized. All compounds exhibited excellent thermal stability and polymorphism in the solid state. The structure–property relationship of these compounds was systematically explored. A highest external quantum efficiency of 6.15%, beyond the theoretical value of fluorescence-based OLEDs (~5%), were achieved for the solution-processable OLEDs.



## Materials

G. Qian, X. Wang, S. Wang, Y. Zheng, S. Wang, W. Zhu,\* Y. Wang\*

#### 

Polymorphous Luminescent Materials Based on 'T'-Shaped Molecules Bearing 4,7-Diphenylbenzo[c] [1,2,5]thiadiazole Skeletons: Effect of Substituents on the Photophysical Properties