

Recent progress of electronic materials based on 2,1,3-benzothiadiazole and its derivatives: synthesis and their application in organic light-emitting diodes

Youming Zhang^{1,2}, Jun Song^{3*}, Junle Qu³, Cheng-Peng Qian^{4*} and Wai-Yeung

Wong^{1*}

¹ *Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University (PolyU), Hung Hom, Hong Kong, P. R. China and PolyU Shenzhen Research Institute, Shenzhen 518057, P. R. China*

² *College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China*

³ *Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, P. R. China*

⁴ *Key Laboratory of Environmental Functional Materials Technology and Application of Wenzhou City, Institute of New Materials & Industry, College of Chemistry & Materials Engineering, Wenzhou University, Wenzhou 325035, PR China*

*E-mail: wai-yeung.wong@polyu.edu.hk; songjun@szu.edu.cn; qpc@wzu.edu.cn

Abstract: 2,1,3-Benzothiadiazole (BT) and its derivatives are very important acceptor units used in the development of photoluminescent compounds and are applicable for the molecular construction of organic light-emitting diodes, organic solar cells and organic field effect transistors. Due to their strong electron-withdrawing ability, construction of molecules with the unit core of BT and its derivatives can usually improve the electronic properties of the resulting organic materials. In this contribution, we review the synthesis of various polymers, small molecules and metal complexes with BT and its derivatives and their applications in organic light-emitting diodes. Furthermore, the molecular design rules based on these cores are discussed.

Keywords: 2,1,3-Benzothiadiazole, organic light-emitting diodes, synthesis, electronic properties, photoluminescence

Dr. Youming Zhang



Dr Youming Zhang, born in 1989, received his Ph.D. degree from the College of Chemistry, Xiangtan University, in 2017. From 2017 to now, he is a postdoctoral research associate with Professor Junle Qu at Shenzhen University and a visiting scholar with Professor Wai-Yeung Wong at The Hong Kong Polytechnic University. His research mainly focuses on the design and synthesis of organic optoelectronic materials in organic light-emitting diodes and organic solar cells.

Prof. Jun Song



Professor Jun Song, received the B. Eng. degree in information engineering from Zhejiang University, Zhejiang, China in 2001. He was the recipient of two Ph.D. degrees. The first was achieved in 2006 in optical engineering from Zhejiang University, Hangzhou, China, and his second Ph.D. in 2008 in electrical engineering from the Royal Institute of Technology, Stockholm, Sweden. Since 2009, he has been an Associate Professor with Institute of Optoelectronics in Shenzhen University, China. He has authored/co-authored about 60 papers in refereed international journals. His research interests include nanophotonics and its applications in renewable energy, biomedicine, electronic information and environmental protection.

Prof. Junle Qu



Junle Qu was born in Shann'xi province, China in 1970. He received his Ph.D. degree from the Xi'an Institute of Optics and Precision Mechanics, Chinese Academy of Sciences in 1998. He is currently a Professor in the College of Optoelectronic Engineering at Shenzhen University. His research focuses on the cutting-edge biomedical optical imaging techniques including FLIM, super-resolution and non-linear optical techniques and their application in monitoring cell processes and cell-drug interactions.

Dr. Peng-Cheng Qian



Peng-Cheng Qian obtained his Ph.D. degree in 2015 from Hunan University. He worked in Wenzhou University as Associate Professor from 2016. As a visiting scholar, he worked in UC Santa Barbara from 2017 to 2018. He is currently the Executive Dean of Institute of New Materials and Industrial Technology, Wenzhou University. His research focuses on the development of novel methods for constructing some heterocyclic compounds, creating of carbon-carbon bonds in a highly atom-economical and environment-friendly manner.

Prof. Wai-Yeung Wong



Wai-Yeung Wong obtained his B.Sc.(Hons.) and Ph.D. degrees from the University of Hong Kong. After postdoctoral works at Texas A&M University and the University of Cambridge, he joined Hong Kong Baptist University from 1998 to 2016 and he now works at the Hong Kong Polytechnic University as Chair Professor of Chemical Technology and Associate Dean of Faculty of Applied Science and Textiles. He is currently Associate Editor of *Journal of Materials Chemistry C*, and Editor of *Journal of Organometallic Chemistry* and *Topics in Current Chemistry*. He was awarded the RSC Chemistry of the Transition Metals Award, FACS Distinguished Young Chemist Award and State Natural Science Award from China, etc. His research focuses on synthetic inorganic/organometallic chemistry, especially aiming at developing metal-

organic molecules and polymers for organic optoelectronics and metal-based nanomaterials.

1 Introduction

π -Conjugated compounds are important in organic optoelectronic molecules due to their ability to precisely tune optoelectric properties, such as conductivity, charge-carrier mobility, light absorption and light emission. As a consequence, scientists have made great efforts to design organic compounds with excellent electronic transport properties to meet military and commercial requirements. Among the developed organic optoelectronic π -conjugated molecules, the construction of donor (D)-acceptor (A) structures is one of the most effective strategies to regulate the optoelectric properties of these materials [1–5]. Their band gap levels and optoelectronic properties can be readily tuned through systematic variation between the D and A units [6]. Furthermore, hybridization of the energy levels between the D and A units can decrease the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels, which leads to an unusually small HOMO-LUMO energy separation [7]. Therefore, the selection of D and A units is particularly important to synthesize organic π -conjugated materials with excellent optoelectronic properties.

In the early stage, D-A organic compounds were often used with non-conjugated electron-accepting groups, such as cyano [8–12], nitro [13–16], or halogen groups [17, 18] as substituents on an aryl subunit or a vinylene unit in the organic backbone. In the last decade, aromatic heterocycles with high HOMO energy levels (E_{HOMO}) have received much attention as stronger and more synthetically accessible acceptors. A variety of heterocyclic acceptors have been studied and covered in a couple of reviews [19–29]. However, only some of them are often used, such as 2,1,3-benzothiadiazole

(BT) [30–34], 2*H*-benzo[*d*][1,2,3]triazole [35–37], 3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione [38–43] and (*E*)-3-(2-oxoindolin-3-ylidene)indolin-2-one [44–47]. Among those, BT and its derivatives are promising types of acceptor units, owing to their strong electron-withdrawing property, intense light absorption and good photochemical stability, and are often coupled with a variety of electron-rich groups to form low-bandgap polymers, small molecules and transition metal complexes [30, 33, 48–52]. According to the rules of chemical aromaticity, BT has five pairs of π electrons and possesses excellent aromaticity [30]. This phenomenon attracts the attention of many researchers. BT derivatives have been applied in various fields such as organic photovoltaics (OPVs), dye-sensitized solar cells (DSSCs), organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), and electrochromic devices (ECDs) and their physical and chemical properties have been studied intensively [1–5]. So far, chemists have developed a number of BT-based derivatives with electron-withdrawing units, as shown in Figure 1. These derivatives can enhance their electron-withdrawing properties or expand the π -conjugated structure and aromaticity, thus further improving their optoelectronic properties. Based on the advantages of BT and its derivatives, various optoelectronic functional materials have been developed, with most of them exhibiting excellent performance.

At present, there are some commercially available BT-based derivative units on the market. However, most of them can only be used in the laboratory for scientific research due to their exorbitant price. Therefore, compounds at lower costs are required to promote commercialization. Optimizing the reaction conditions and reducing the cost

of energy are necessary to reduce the price. Based on these considerations, this review summarizes the recent progress on the small molecules, polymers and phosphorescent metal complexes with BT-based units, including their synthesis and application in OLEDs. After a survey on the structural, physicochemical properties and reactivity, the recent advances in the use of BT and its derivatives in OLEDs are disclosed which is very rare in literature. We also discuss the challenges of designing and developing BT-based emitting materials for high-efficiency OLEDs will also be discussed.

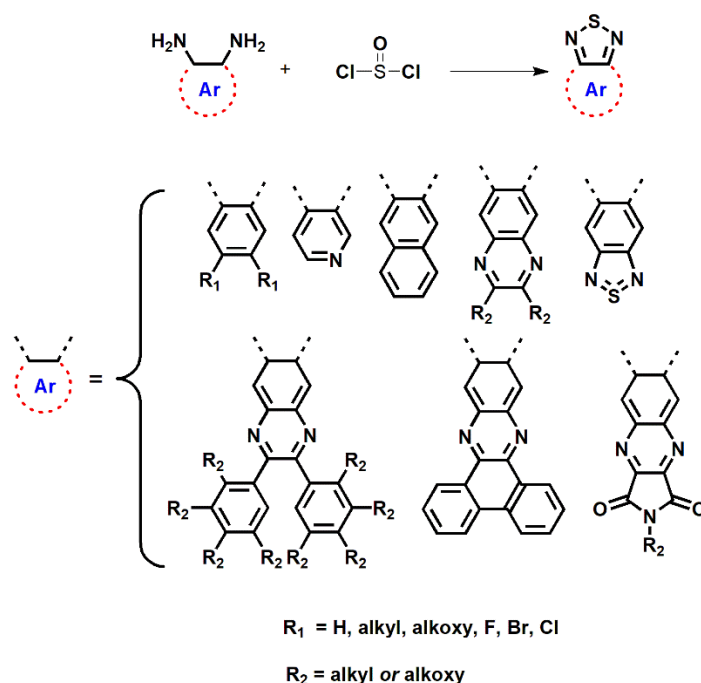


Figure 1. Chemical structures of 2,1,3-benzothiadiazole (BT), its derivatives as well as the classical synthetic route

2 Synthesis of BT acceptors and their derivatives

In order to combine BT and its derivatives with donor units, some functional groups must be introduced for the further synthesis of BT-containing π -extended

photoluminescent compounds. For example, halogen atom can be introduced for the Suzuki coupling reaction [53], tri-*n*-butyltin for the Stille coupling reaction [54] and zinc ion for the Negishi coupling reaction [55]. In these common metal-catalyzed coupling reactions, Suzuki coupling is generally employed as the first choice due to its advantages, including simplicity, mild reaction conditions, good yields and low cost. Hence, 4,7-dibromo-2,1,3-benzothiadiazole (**1**) is the most commonly used intermediate for the synthesis of BT-containing π -extended photoluminescent compounds. A large number of synthetic methods have been reported for this compound. The precursor **1** can be easily prepared in two steps from commercially available *ortho*-phenylenediamine in high yields on multigram and kilogram scales, and the intermediate can then be brominated by using liquid bromine and hydrogen bromide [56–60]. In addition, for regulating the optoelectronic properties of the desired final product, introduction of discrete electron-accepting or -donating substituent groups, such as nitro (**2**) [61], alkoxy (**3**) [62, 63], fluoro (**4**) [64] or cyano (**5**) [65] groups, which can weaken or enhance the electron-withdrawing property, into the BT block is considered to be an effective method. Their synthesis steps are generally complex but necessary for improving the performance. Figure 2 shows the synthetic routes of 4,7-dibromo-2,1,3-benzothiadiazole and its discrete substituted derivatives.

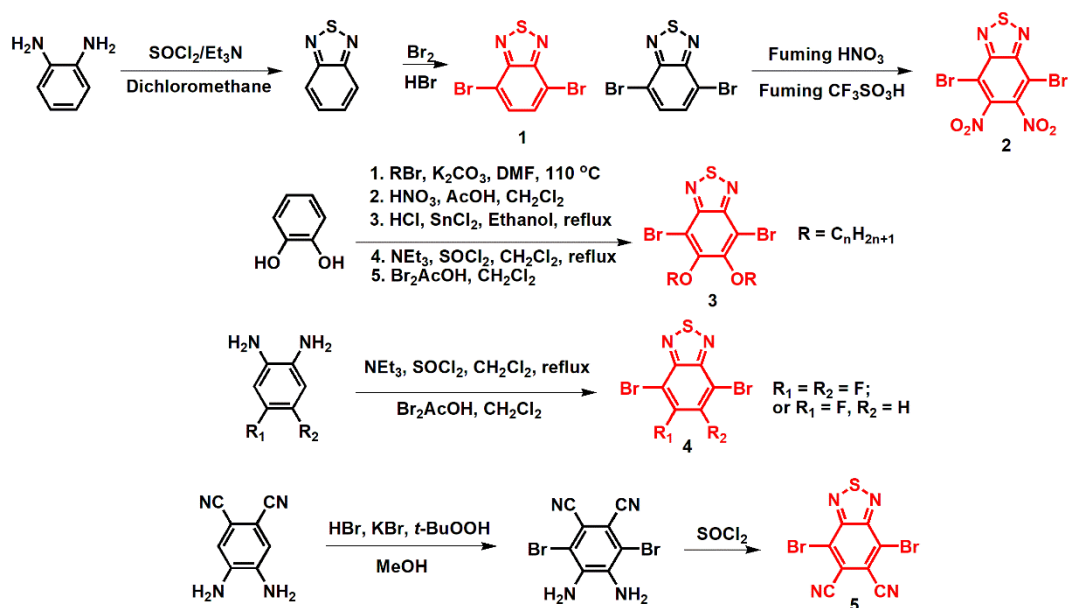


Figure 2. Synthetic routes of 4,7-dibromo-2,1,3-benzothiadiazole and its discrete substituted derivatives.

Except for the above, some heterocyclic or π -extended thiadiazole derivatives were also developed. For example, 4,7-dibromo-[1,2,5]thiadiazolo[3,4-*c*]pyridine (6, Figure 3), which has a strong electron-withdrawing property, can be synthesized by the similar process as 4,7-dibromo-2,1,3-benzothiadiazole when pyridine-3,4-diamine was used as the starting material [66]. Similarly, by further increasing the conjugation of the *o*-aryl diamines or introducing new hetero elements into the heteroaromatic ring, a series of BT-containing π -extended electron-deficient units were reported (7–11, Figure 3) [67–72]. These units exhibit a broader and stronger absorption ability than BT and have been widely used in the preparation of organic optoelectronic materials, especially for the design of NIR emitting molecules. Furthermore, the BT unit can be transformed into other acceptors, for example, the quinoxaline derivatives [5].

applications and have indeed been commercialized. As the core materials of electroluminescent devices, BT and its derivatives are usually used as the emissive-layer materials. Generally, these common organic electroluminescent materials can be in the forms of small molecules, polymers and transition metal complexes. In the following discussion, we summarize the development of these three types of electroluminescent materials containing BT and its derivatives.

3.1 OLED materials based on BT-containing small molecules

Owing to their well-defined molecular structures, ease of purification, amenability to large-scale production and better batch-to-batch reproducibility, small molecule-based OLEDs have received an increasing interest. Early in 2008, Liu *et al.* reported a novel non-planar pentaphenylbenzene-functionalized BT derivative (**12**, Figure 4) and applied it in non-doped OLEDs as a red molecular emitter [75]. This device displayed a red emission with an emission peak at 621 nm, a maximum external quantum efficiency (EQE) of 1% and a maximum brightness of 1572 cd m⁻². Using a BT-based D- π -A bipolar structure as the branching part, three emitter molecules with single, double and triple branched units (**13–15**, Figure 4) were fabricated by Li *et al.* All of these small molecule-based devices showed red emission with an emission peak at 620 nm. Among them, the device based on **13** displayed a maximum luminance of 12192 cd m⁻² and a maximum current efficiency of 1.66 cd A⁻¹ [76]. By using benzothiadiazole-(4-hexyl)thiophene as arms, compounds **16** and **17** (Figure 4) with two arms and three arms, respectively, were further designed and synthesized by Li *et*

al. These two molecules showed red-shifted emission with peaks at 646 and 657 nm. The red-emissive OLED with **17** as the emitting layer and binary poly(*N*-vinylcarbazole) (PVK)/ poly-(*N,N'*-bis(4-butylphenyl)-*N,N'*-bis(phenyl)-benzidine) (poly-TPD) as the hole transporting layer (HTL) displayed a high maximum luminance of 7794 cd m⁻² and a maximum electroluminescence (EL) efficiency of 0.91 cd A⁻¹, which was among the highest values for the solution-processed red OLEDs at that time [77]. From their optical absorption and photoluminescence (PL) data, there is no or small luminescence peak shift after adding the absorption arms. Hence, the emission peaks mainly originated from the charge transfer between the donor (triphenylamine or thiophene) and the acceptor (BT).

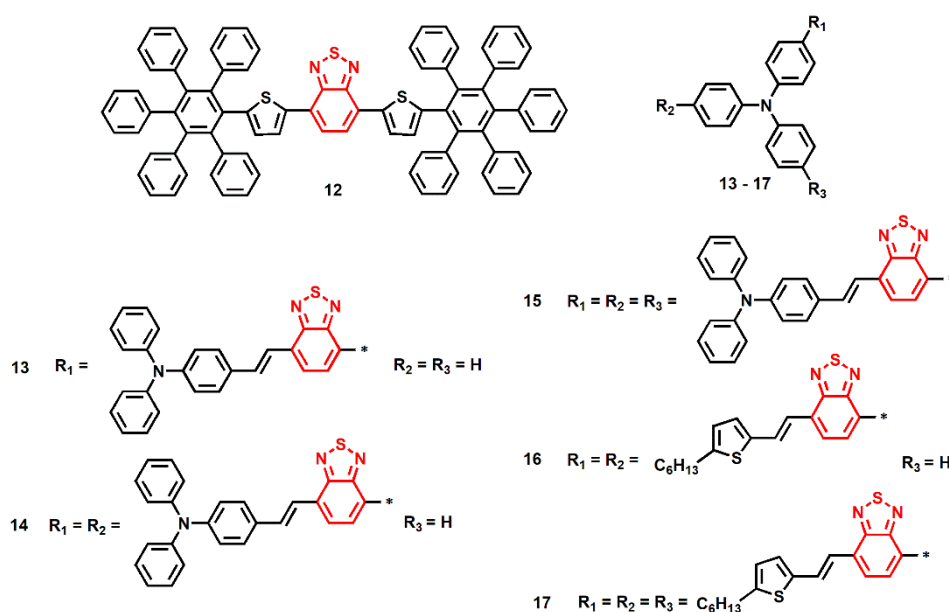


Figure 4. Chemical structures of **12**–**17**.

Tang *et al.* synthesized a series of BT-based small molecules for OLED materials. In 2011, they reported three BT and tetraphenylethene-based small molecules **18**–**20** (Figure 5) [78]. With the addition of BT and thiophene, the band gaps of these materials

were gradually narrowed (2.55 to 2.05 eV) and exhibited green to red emission (538 to 623 nm). An OLED fabricated using **19** as an emitter exhibited an orange-red EL with high luminance and efficiencies of 8330 cd m⁻², 6.1 cd A⁻¹ and 3.1%, respectively. In 2018, Tang's group synthesized three BT-based compounds with tetraphenylethene, phenanthro[9,10-*d*]imidazole and triphenylamine moieties which belong to aggregation-induced emission (AIE) emitters **21–23** (Figure 6) [79]. The AIE properties can be well modulated by functional groups and *tert*-butyl and diphenylamine moieties are further introduced to modulate the intermolecular interactions and electron donor-acceptor strength. Non-doped OLEDs were fabricated using these red molecules as the light-emitting layers, offering red EL at 650 nm and a high luminance and an EQE of up to 6277 cd m⁻² and 2.17%, respectively. Later in the same year, Tang's group further reported another series of BT-based deep red/near infrared (DR/NIR) AIE luminogens **24–28** (Figure 6) [80]. Their emission wavelengths could be tuned from the red to DR/NIR region by regulating the nature of the substituents. As a result, non-doped OLEDs based on AIEgen **27** showed an EL emission at 684 nm with a large radiance of 5772 mW Sr⁻¹ m⁻² and an impressive EQE of 1.73%. In order to fully exploit the properties of the material, Kwok *et al.* used **19** as a color conversion cap layer on top-emitting blue OLEDs and white OLEDs (WOLEDs) with Commission Internationale de L'Eclairage (CIE) coordinates of (0.34, 0.35), with high color stability over a wide range of driving voltages and peak efficiency of 17.7 cd A⁻¹ and 8.7 lm W⁻¹ [81].

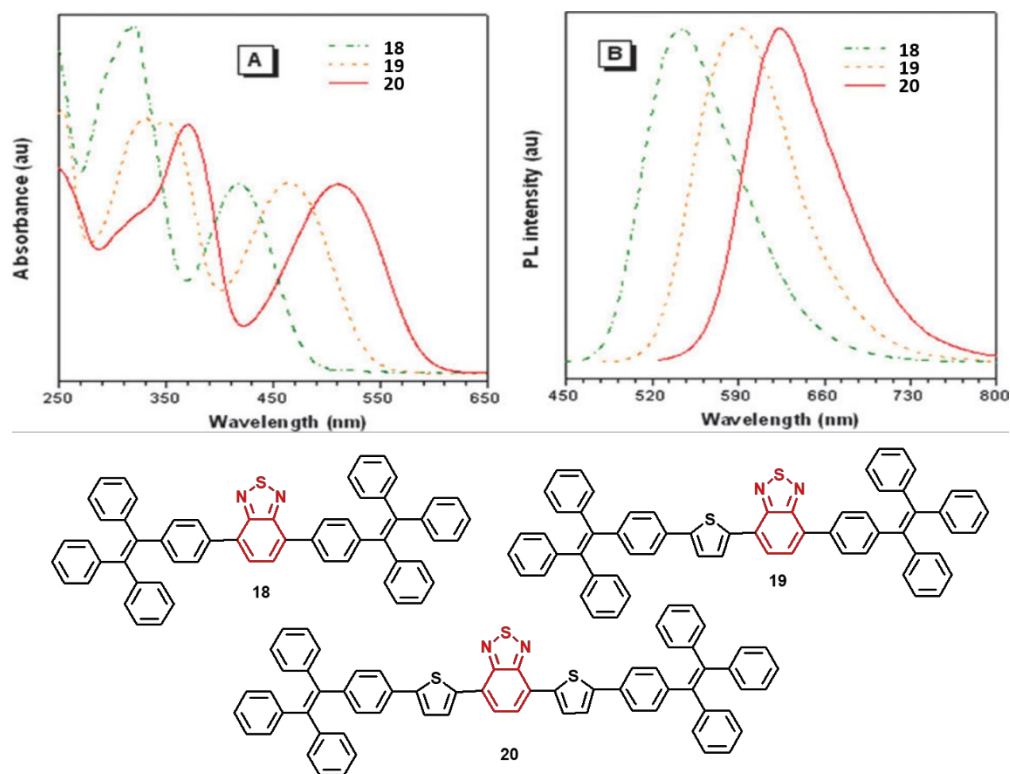


Figure 5. (A) Absorption, (B) PL spectra and chemical structures of **18–20**. Adapted with permission [78]. Copyright 2011, The Royal Society of Chemistry.

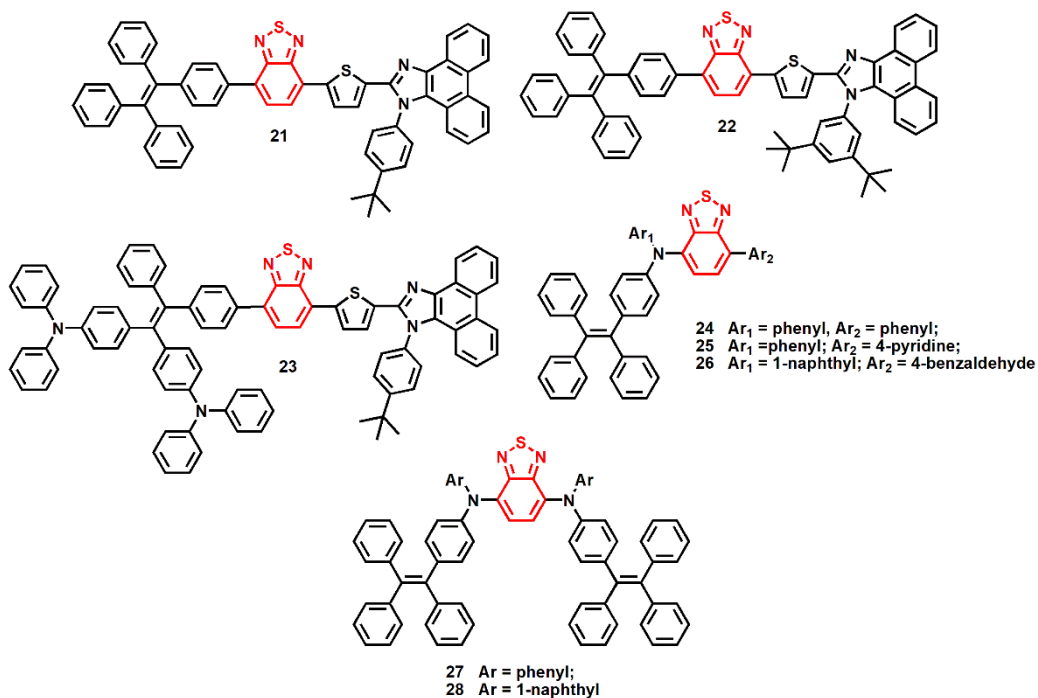


Figure 6. Chemical structures of **21–28**.

To further develop efficient luminescent materials, a number of BT-based small

molecules have been reported extensively by other research groups for the studies of their structure-property relationships. Promarak *et al.* designed and synthesized three dithienylbenzothiadiazole-derived hole-transporting red emitters **29–31** by increasing the number of electron-donating triphenylamine (TPA) functional groups [82]. The absorption and PL spectra of these emitters suggest that introduction of the electron-donating TPA at the donor part of **29** gives rise to more intense intramolecular charge transfer (ICT) interaction in **31** than that in **29**, while adding the electron-donating TPAs at the conjugated backbone of **29** yields less intense ICT interaction in **30** than that in **29** (Figure 7). A simple non-doped red OLED (indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS)/**29** (spin-coated)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP)/LiF-Al) with an efficiency of 6.25 cd A⁻¹ at 4.1 mA cm⁻², a low turn-on voltage (3.0 V) and a pure red emission ($\lambda_{\text{EL}} = 656$ nm, and CIE = (0.67, 0.33)) was attained. A very simple emitter of **32** based on a benzene-BT-benzene core (Figure 8) was synthesized by Skabara *et al.* and applied in a WOLED device [83]. This molecule possesses a combination of emissive states to give a white light with CIE coordinates of (0.38, 0.45) and a color temperature of 4500 K. Thomas *et al.* prepared four BT-based materials containing methyl substituents (**33–36**, Figure 8) [84]. The steric effect exerted by the methyl group is responsible for the non-planar arrangement of donor and acceptor, which inhibits the intramolecular charge transfer. The emitters exhibited absorption and emission at shorter wavelength when compared to non-methylated emitters. Solution-processed multi-layered OLED devices were fabricated by employing these compounds either as the host or dopant

emitter in a suitable host matrix and exhibited green/yellowish green EL with an EQE of 4.6%. With the above investigation, apart from the intramolecular donor-acceptor interaction, the spatial configuration of the molecules also has a great influence on the optical and electrical performance.

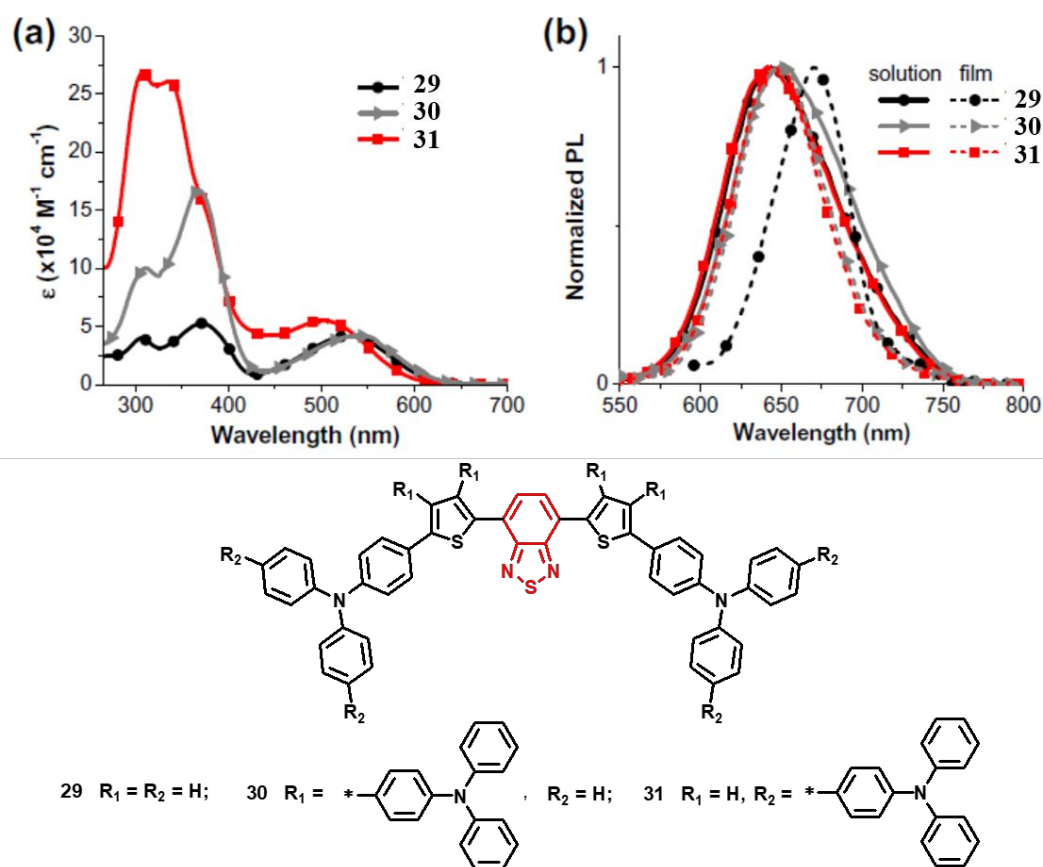


Figure 7. (a) Absorption, (b) PL spectra and chemical structures of **29–31**. Adapted with permission [82]. Copyright 2015, Elsevier.

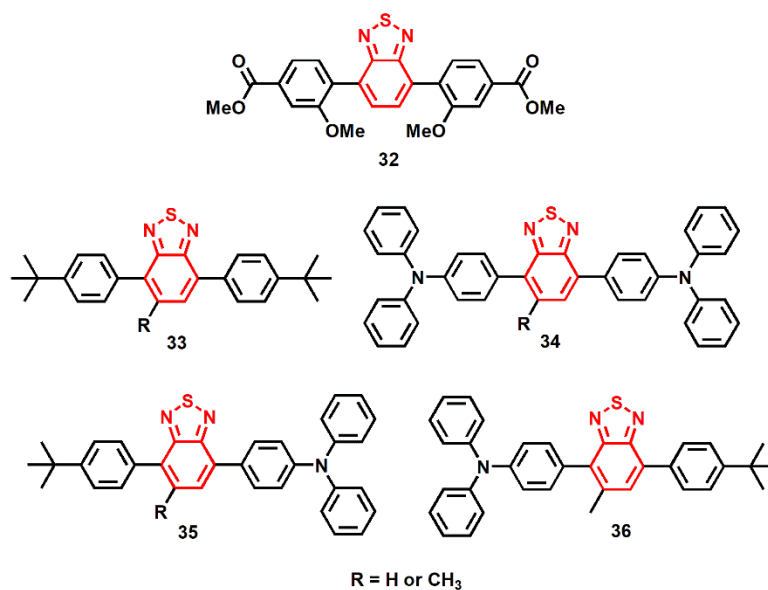


Figure 8. Chemical structures of **32–36**.

Recently, there are some new reports on OLEDs using BT-based small molecules. Lu *et al.* synthesized four D-A-D' type fluorescent materials by using BT as the acceptor, TPA as the donor, and monocarbaborane (**37**), phenyl (**38**), *p*-methoxyphenyl (**39**) or 4-pyridinyl (**40**) as the terminal donor groups (**Figure 9**) [85]. Interestingly, these luminescent materials can aggregate to form nanoparticles or nanocrystals upon adding water to their dilute THF solutions. Thus, they can also be applied as chemosensors in silver ion detection. Although the device performance is not good enough to compete with the reported ones, a series of electroluminescent devices with different properties were obtained when these emitters were used as the guest. Moreover, by doping **37** in PVK, a WOLED was obtained, which represented the first example of monocarbaborane-based materials for OLED applications. In order to develop red emitters, Skabara *et al.* also reported four red fluorescent materials based on the fluorene-thiophene-BT motif (**41–44**, **Figure 9**) [86]. By extending the molecular

conjugation through end-capping with additional fluorene units, or through incorporation of donor functionalities, compounds **42–44** exhibited improved OLED performance relative to the parent compound **41**. Although the device performance is not satisfactory, these molecules could also be considered as inexpensive fluorescent orange OLEDs for tandem white light devices.

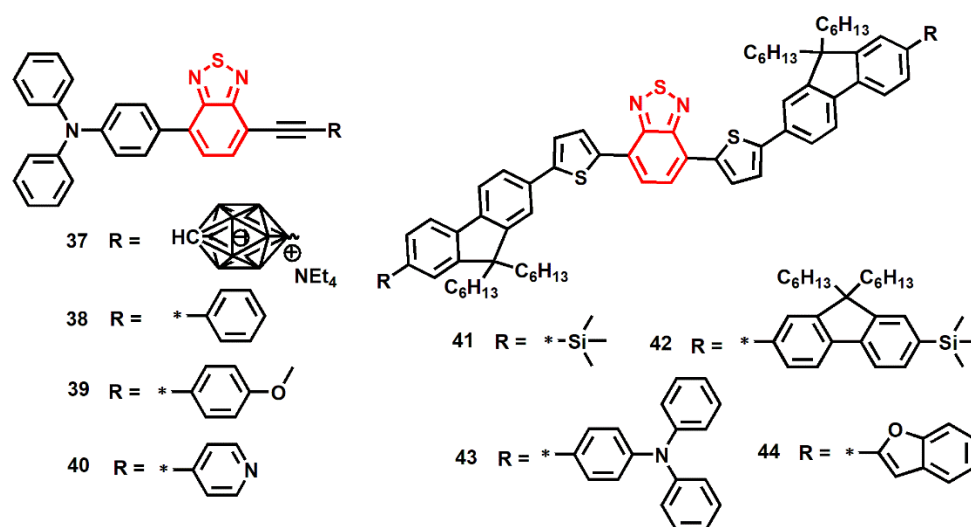


Figure 9. Chemical structures of **37–44**.

In recent years, to avoid environmental toxicity, high cost and improve the luminous efficiency, new thermally activated delayed fluorescence (TADF) and hybridized local and charge-transfer state (HLCT) materials have been proposed to harvest both singlet and triplet excitons and break the 5% EQE limit in OLED devices by controlling the excited state with both local excitation (LE) and charge transfer (CT) features and regulating the orbital separation between HOMO and LUMO [87–91]. For TADF, this kind of molecules can use the triplet excitons through RISC from the lowest triplet (T_1) to the lowest singlet states (S_1), resulting in a theoretical internal quantum efficiency of 100%. So, the value of S_1-T_1 energy gap (ΔE_{ST}) is the most important factor for the photophysical and EL properties. The smaller ΔE_{ST} is beneficial for harvesting the

triplet excitons via reverse intersystem crossing (RISC). For HLCT emission, the intersystem crossing of excitons between T_m and S_n with close energy levels can also occur in the excited state. This state combines both local excited (LE) and charge transfer (CT) states into a special one, possessing two combined and compatible characteristics: a large transition moment from the LE state (cold exciton) and a weakly bound exciton from the CT state (hot exciton). Based on these luminescence mechanisms, scientists have developed many highly efficient BT-based metal-free electrofluorescent emitters.

Yang *et al.* designed and synthesized three D-A-D structured fluorescent molecules by rationally employing BT as an acceptor (**45–47**, Figure 10) [92]. With an increase in the steric hindrance of the donor moieties (from diphenylamine to *9H*-carbazole and then to 9,9-dimethyl-9,10-dihydroacridine), the dihedral angles between the donor and acceptor moieties of **45**, **46** and **47** reveal an obvious increase (from 42° , 53° to 61° then to 86°). This spatial configuration can effectively regulate the distribution of HOMO and LUMO energy levels, and thus control the luminescence spectrum (Figure 10). Among them, emitter **47** showed an excellent TADF performance. It is worth mentioning that OLEDs containing the TADF emitter **47** achieved a maximum EQE of 8.8% with the emission peak at 636 nm. Ma *et al.* designed BT-based D-A-type chromophores in **48** (Figure 11) [93]. This emitter possesses a non-planar “butterfly-like” structure with a C-S-N-C dihedral angle (θ_N) of 142° and can break the spin statistics to utilize the triplet energy through HLCT. The EQE of the NIR OLED based on **48** was 1.54% with a low efficiency roll-off. The result suggests that fluorescent

molecule with “hot-exciton” mode and an HLCT state is an ideal strategy to design next-generation, high-efficiency and low-cost OLED materials and brings new hope for the development of organic small-molecule electroluminescent materials. Later, they further developed this concept with BT-based small organic molecules. Among them, the device of BT-based small organic molecule **49** (Figure 11) exhibited an EQE of 3.8% [94]. Chi *et al.* reported two BT-based red fluorophores (**50** and **51**, Figure 11) with HLCT properties. Compounds **50** and **51** enabled nondoped OLEDs with excellent EQE of 11.1% and 5.0%, attributed to the high exciton utilization efficiency of 82% and 46%. Furthermore, dyes **50** and **51** were utilized as complementary emitters with a sky-blue TADF material to fabricate two-color fluorescent WOLEDs in a fully nondoped emissive-layer configuration, and achieved high EQEs of 23.0% and 8.6%, respectively [95]. Su *et al.* prepared three D-A-type emitters with 5,6-difluorobenzo[*c*][1,2,5]thiadiazole as the acceptor, TPA as the donor, and thiophene as the π -bridge (**52–54**, Figure 11) [96]. These materials can emit orange-yellow to NIR emission due to the insertion of thiophene, and possess HLCT feature which may lead to an exciton utilization exceeding the limit of 25% of traditional fluorescent materials. As a result, the related devices exhibited relatively good performance with maximum EQE of 5.75%, 0.83%, and 1.44% for **52**, **53**, and **54** based OLEDs, respectively. In 2020, Wong’s group also reported two BT-based emitters by introducing one or two methyl groups between the donors and acceptor (**55–56**, Figure 11) [97]. Through the introduction of sterically hindered methyl groups, the spatial configuration of molecules have greatly changed, and thus the overlap of HOMO and LUMO has been

effectively regulated. As a result, emitter **55** showed an obvious HLCT feature with high PL quantum yield in organic solvents and solid state. Their corresponding devices showed excellent performances with maximum EQE of 8.47% and 7.29% for **55** and **56** doped OLEDs. Table 1 summarizes the photophysical and EL properties of various BT-containing small molecules.

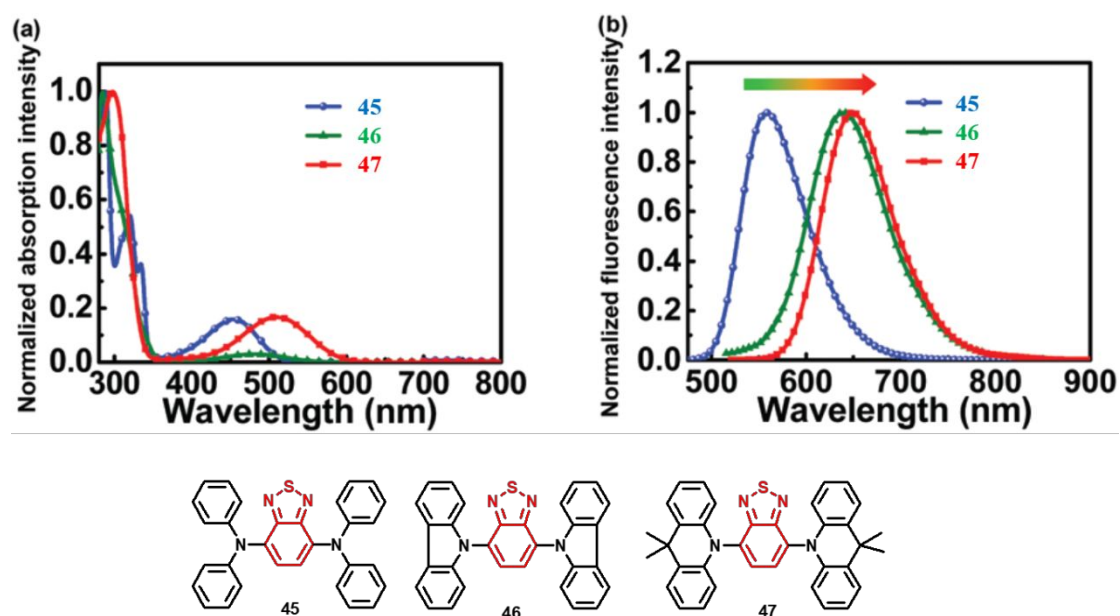


Figure 10. (a) Absorption, (b) PL spectra and chemical structures of **45–47**. Adapted with permission [92]. Copyright 2017, The Royal Society of Chemistry.

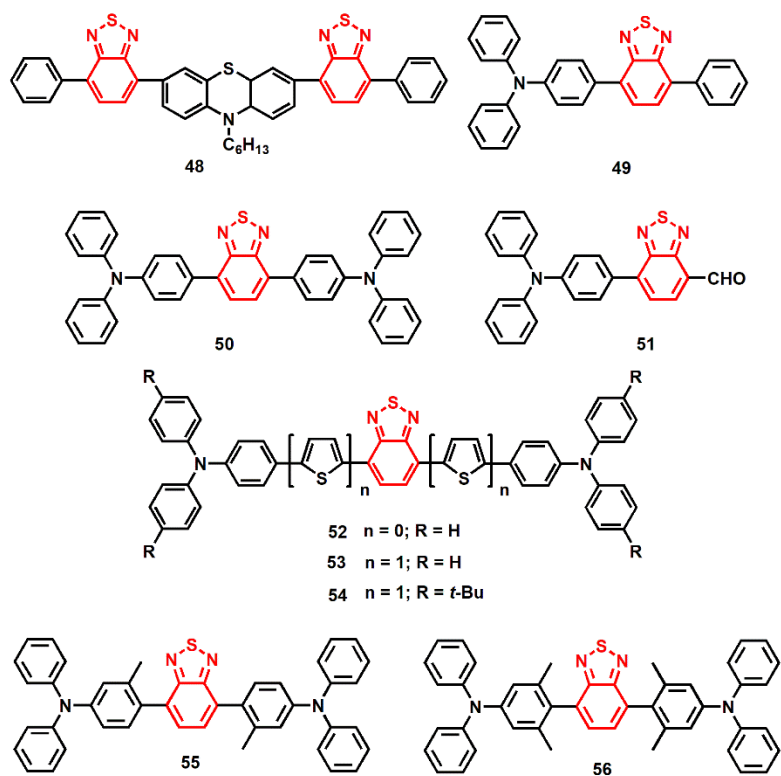


Figure 11. Chemical structures of **48–56**.

Table 1. Photophysical and EL properties of BT-containing small molecules.

	λ_{PL} (nm)	λ_{EL} (nm)	CE (cd A^{-1})	PE (lm W^{-1})	EQE_{max} (%)	Ref.
12	609	621	1.37	-	1.0	75
13	643	620	4.76	-	-	76
14	643	620	5.39	-	-	76
15	643	620	4.69	-	-	76
16	646	642	0.53	-	-	77
17	657	649	0.91	-	-	77
18	538	540	5.2	3.0	1.5	78
19	592	592	6.4	2.9	3.1	78/81

20	623	668	0.4	0.5	1.0	78
21	600	650	1.31	1.59	2.17	79
22	611	638	1.41	1.70	2.03	79
23	642	638	2.19	1.61	2.09	79
24	620	-	-	-	-	80
25	615	-	-	-	-	80
26	625	-	-	-	-	80
27	666	684	-	-	1.73	80
28	658	682	-	-	1.43	80
29	643	675	1.79	1.60	-	82
30	641	656	6.25	5.17	-	82
31	650	662	4.22	3.16	-	82
32	487	580	6.5	2.60	2.39	83
33	489/512	-	-	-	-	84
34	577/639	560	6.2	11.6	4.5	84
35	575/630	548	15.7	12.2	4.6	84
36	571	540	15.2	10.9	4.8	84
37	564	400/576	0.32	0.20	0.18	85
38	593	390/585	0.88	0.64	0.40	85
39	581	396/590	0.68	0.51	0.32	85
40	603	399/581	0.28	0.15	0.15	85
41	620	-	0.30	-	0.28	86

42	623	-	0.51	-	0.77	86
43	626	-	0.30	-	0.46	86
44	623	-	0.16	-	0.25	86
45	559	-	-	-	-	92
46	638	-	-	-	-	92
47	648	636	11.0	10.8	8.0	92
48	722	692	-	-	1.54	93
49	578/567	588	8.84	7.18	3.8	94
50	612	608	17.7	12.4	11.1	95
51	638	640	4.7	2.5	5.0	95
52	563	-	-	-	-	96
53	630	630	5.15	4.27	5.75	96
54	645	642	2.98	2.60	4.94	96
55	546-710	560	30.40	23.67	8.47	97
56	528-670	554	35.02	20.37	7.29	97

3.2 OLED materials based on BT-containing polymers

Due to their advantages of better film-forming properties, mechanical strength and thermal stability, as well as being able to fabricate large area electroluminescent devices by spin-coating, conjugated polymers have attracted tremendous attention in the field of flexible and large area optoelectronic devices based on low-cost solution processing techniques. In recent decades, remarkable progress has been realized in the

development of new π -conjugated materials for various applications, especially in terms of white light emission in OLEDs. For their simple chemical structures and excellent device performances, polymer electroluminescent materials based on BT acceptor units show great potential. In 2008, Yang *et al.* reported a ternary fluorene-based copolymer (**57**, Figure 12) with the fluorene segment as a blue emitter and the side chain iridium complex as a red emitter that can realize efficient white light emission [98]. By introducing a fluorescent green BT unit into the polyfluorene backbone, the efficiency and color purity of the ternary copolymers were improved compared to their binary fluorene-based copolymer without the BT acceptor. Furthermore, the efficiency can be increased by increasing the concentration of the iridium complex, which resulted from its efficient phosphorescence emission and the weak phosphorescent quenching due to its lower triplet energy level than that of polyfluorene. Soon afterwards, the same group synthesized another copolymer (**58**, Figure 12) by incorporating BT and iridium complex units into the polyfluorene backbone by the Suzuki polycondensation [99]. This main-chain polymer showed a similar white emission compared to **57** with a maximum luminous efficiency of 5.3 cd A⁻¹ and a maximum luminance of 9900 cd m⁻². By doping a concentration of 0.05 mol% 4,7-bithienyl-2,1,3-benzothiadiazole molecule into the polyfluorene chain as an orange-emitting unit, a type of polyfluorene copolymer (**59**, Figure 12) used for WOLEDs was synthesized by Wang *et al.* in 2013 [100]. The Förster energy transfer in an inter-chain was investigated through the change of performance caused by the different annealing temperature. In addition, by regulating the ratio of the BT-based

red-emitting monomer in conjugated polymers, Somanathan *et al.* reported a copolymer (**60**, Figure 12) that can emit a white emission in a single layer device [101]. Analyzed from the above case, the white light emission of the polymer is mostly obtained through the charge transfer within the polymer repeating unit, and the emission is usually originated from the single molecule luminescence.

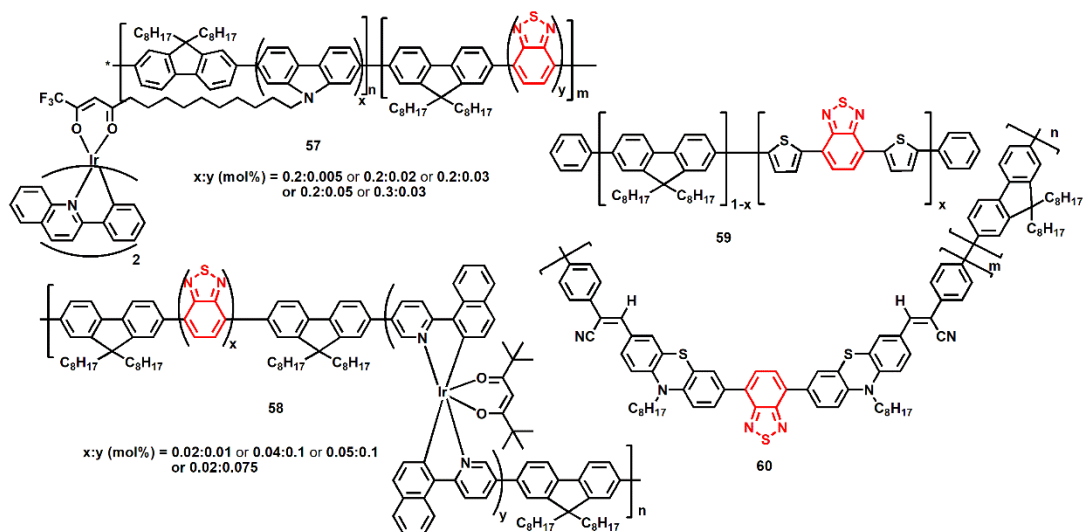


Figure 12. Chemical structures of **57–60**.

Benefiting from the conjugated push-pull branching unit, multi-arm shaped molecules always exhibit broader and stronger absorption/emission. Chromophores with different colors, such as red, green and blue, can be fused in the same molecule to realize white emission in a single-polymer system. Lai and coworkers reported a series of three, four and six-armed star-shaped polymers (**61–64**, Figure 13) with white light emission based on the BT moiety [102–104]. Using these star-shaped polymers as single dopants, most of their single-emissive-layer OLEDs demonstrated high-efficiency white light emission. For example, the three-armed star-shaped polymer **64** (Figure 13) exhibited high color quality saturated white EL with a current efficiency of 2.09 cd A⁻¹ and CIE coordinates of (0.34, 0.33), which matched well with the values of

standard saturated white emission at (0.33, 0.33). Considering their excellent EL performance, star-shaped polymers could be an important direction for the development of white light emissive materials.

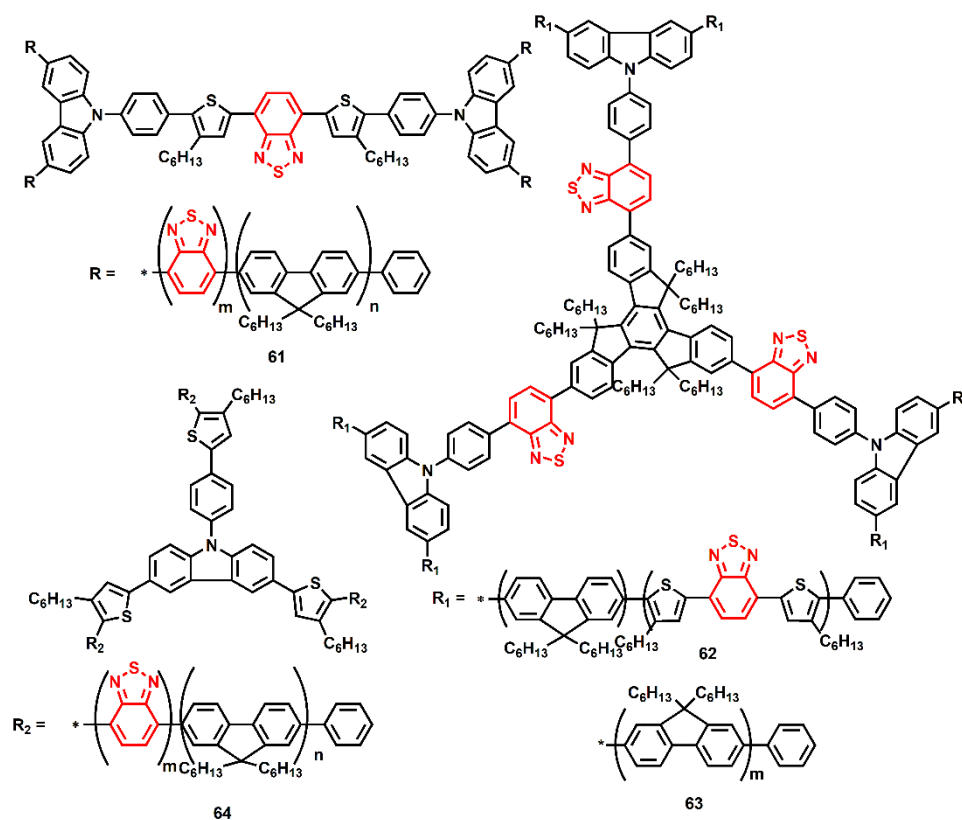


Figure 13. Chemical structures of **61–64**.

Due to their strong electron-withdrawing property, the BT-based polymers typically exhibit a narrow band gap and can usually emit DR and even NIR emission. For example, Gao *et al.* reported two conjugated polymers (**65** and **66**, Figure 14) by using 5,6-dialkoxy-derived benzothiadiazole derivatives as the dopant. By incorporating another BT unit in the main chain, the highest EQE and luminous efficiency were improved by two orders of magnitude for the new polymer **66** [105]. In addition, Patri *et al.* synthesized a series of low band gap π -conjugated BT-based polymers (**67–69**,

Figure 14) [106]. Because of the D-A interactions within the repeating units, an absorption band in the range of 687–663 nm with a band gap in the range of 1.35–1.43 eV and a PL emission between 755 and 773 nm were observed. Qu *et al.* reported another terpolymer (**70**, Figure 14) containing 9,9-dioctylfluorene, thiophene and BT units. A NIR emission device using this polymer as an emitter with an emission peak at 708 nm and luminance of 226 cd m⁻² were obtained [107].

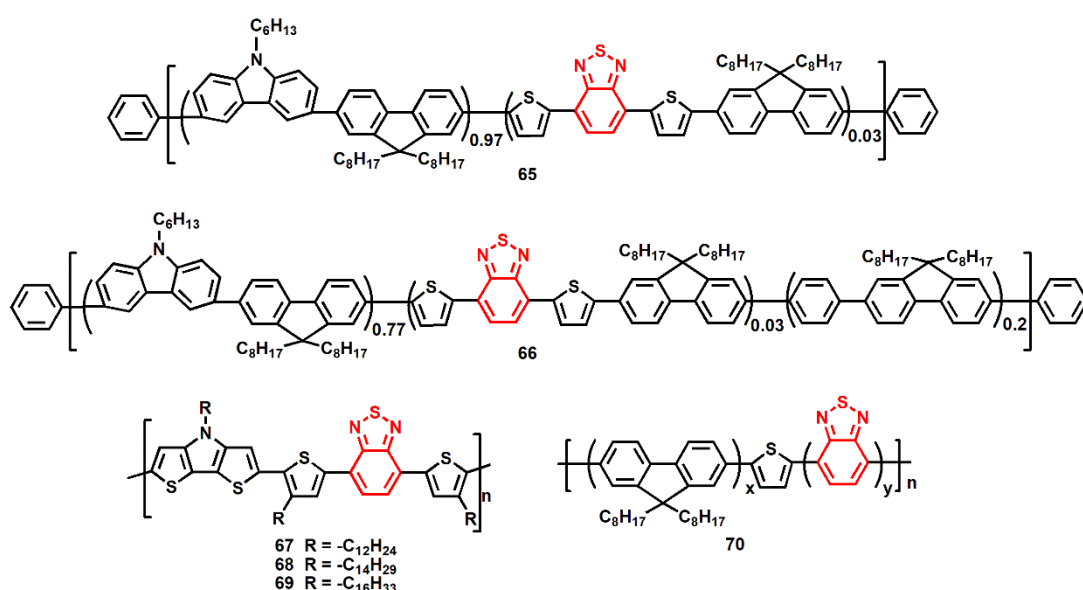


Figure 14. Chemical structures of **65–70**.

The luminescence efficiency of quantum dots can be improved by doping organic polymers into the device. Varlikli *et al.* reported a hybrid polymer light-emitting diode (PLED) containing a BT-based yellow-emitting polymer (**71**, Figure 15) and copper indium disulfide/zinc sulfide as the active layer. This device showed yellow EL with a maximum brightness of 56834 cd m⁻², a maximum current efficiency of 4.7 cd A⁻¹ and a maximum power efficiency of 2.3 lm W⁻¹ [108]. BT-based polymers also performed well when they were used as the electron/hole transport materials. Woo and coworkers designed and synthesized a BT-based alcohol-soluble conjugated polymer **72** (Figure

15) [109]. The resulting device using this polymer as an electron transport material exhibited improved performance compared to an Al cathode-based device and was comparable to the performance of the device with a Ca cathode. For hole transport materials, Grigalevicius *et al.* reported two polyethers containing electroactive pendant 4-(carbazol-2-yl)-7-arylbenzo[*c*]-1,2,5-thiadiazole moieties (**73** and **74**, Figure 15) [110]. These two polyethers showed very high thermal stability with initial thermal degradation and glass transition temperatures. The hole-transporting properties of the polymeric materials were tested in OLEDs with tris(8-hydroxyquinolato)aluminium (Alq₃) as the green emitter and electron transport material. The device exhibited a turn-on voltage of 6.2 V, a maximum current efficiency of 2.5 cd A⁻¹ and a maximum brightness exceeding 300 cd m⁻², which is ~30–90% higher than that of the device containing the widely used hole-transporting layers of poly(9-vinylcarbazole). Table 2 summarizes the photophysical and EL properties of BT-containing polymers.

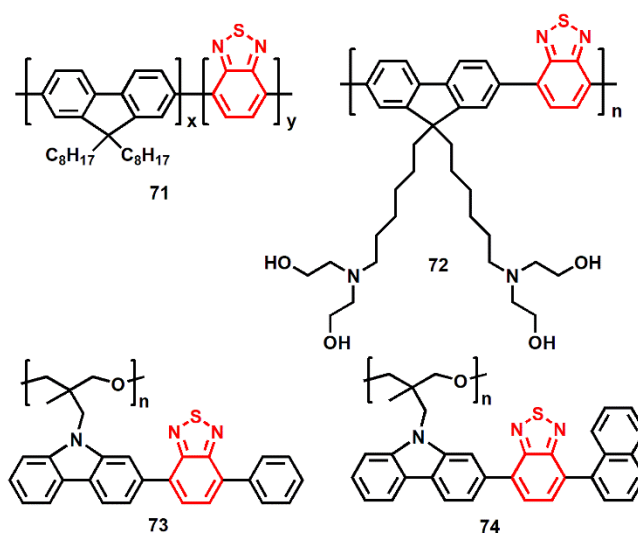


Figure 15. Chemical structures of **71–74**.

Table 2. Photophysical and EL properties of BT-containing polymers.

	λ_{PL} (nm)	λ_{EL} (nm)	CE (cd A^{-1})	PE (lm W^{-1})	EQE_{max} (%)	Ref.
57	440/580	400–700	6.1	-	-	98
58	440/530	420/520/625	5.3	-	2.7	99
59	423/446	440/635	3.51	-	-	100
60	415/637	/	4.5	4.2	-	101
61	-	425/426/517/566	2.74	-	1.1	102
62	-	-	1.71	0.68	1.45	103
63	-	-	1.60	0.77	1.51	103
64	-	430/450/512/600	2.09	-	1.01	104
65	579	616	0.006		0.008	105
66	575	616	1.26	-	1.04	105
67	758	795	-	-	-	106
68	763	780	-	-	-	106
69	773	814	-	-	-	106
70	628	708	0.039	-	-	107
71	550	-	2.26	1.18	-	108
72	539	-	2.40	-	-	109
73	-	-	2.5	-	-	110
74	-	-	1.5	-	-	110

3.3 OLED materials based on BT-containing transition metal complexes

In comparison to the small molecule- or polymer-based pure organic OLED materials, transition metal complexes can exhibit higher emission efficiency due to their strong spin-orbit coupling in the presence of heavy metals, which leads to an internal quantum efficiency theoretically as high as 100%. In order to investigate the D-A interaction of transition metal complexes and obtain a NIR phosphor, as well as electroluminescent devices, Zhu and co-workers reported a series of platinum(II) complexes (**75–79**, Figure 16) with NIR phosphorescent emission based on BT- containing ligands [111–113]. Using these complexes as single dopants, all of their single-emissive-layer OLEDs exhibited high-efficiency NIR emission. Their work strongly proved that appending a D-A framework into a complex is a useful strategy to obtain high-performance NIR emission.

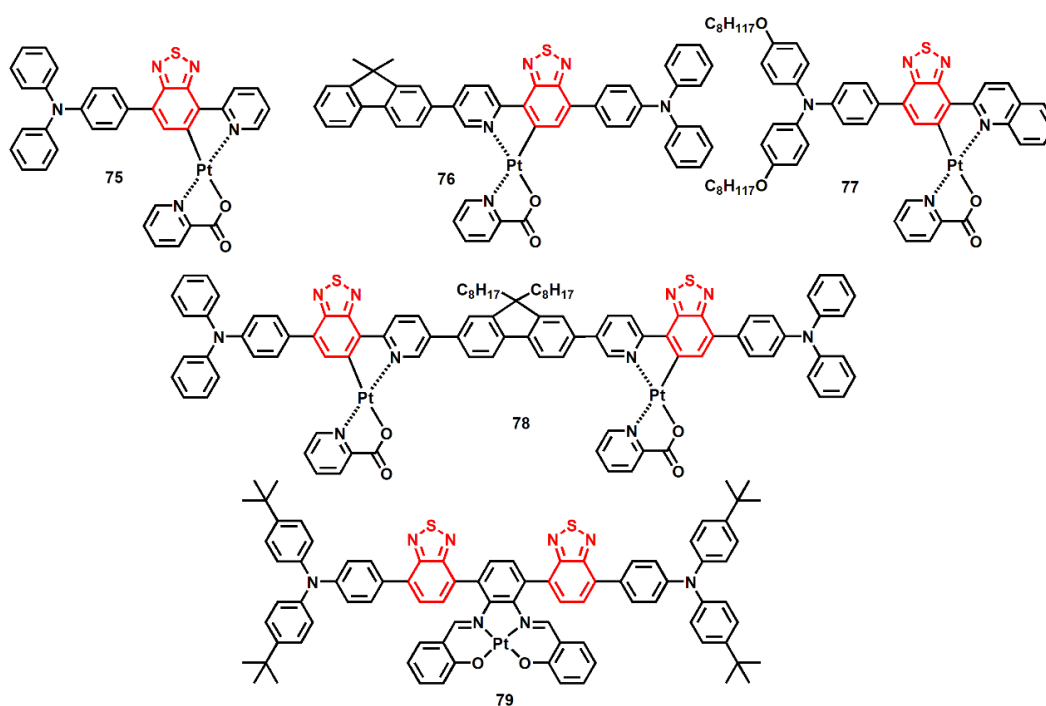


Figure 16. Chemical structures of **75–79**.

In addition, to further study the structure-property relationships of platinum(II) phosphors, particularly the effect of D-A structure on their photophysical and electronic

properties, Wong's group also reported a series of platinum(II) complexes **80–83** with an isomeric D-A conjugated BT-based ligand framework (Figure 17) [114]. The BT derivative of [1,2,5]thiadiazolo[3,4-*c*]pyridine was used as acceptor and coordination unit due to its stronger electron-withdrawing property. These isomeric complexes exhibit PL emissions ranging from 590 to 800 nm with band gaps of 1.7–2.0 eV. OLEDs using these complexes as single emissive layers display EL peaks at 626, 645, 826 and 571 nm, affording maximum EQEs of 0.13%, 0.04%, 0.49% and 0.22% for **80–83** doped devices, respectively. These results indicate that adjusting the coordination position with the isomeric conjugated ligand framework is an appropriate strategy to tune the light-emitting properties of platinum complexes in OLEDs. Table 3 summarizes the photophysical and EL properties of BT-containing transition metal complexes.

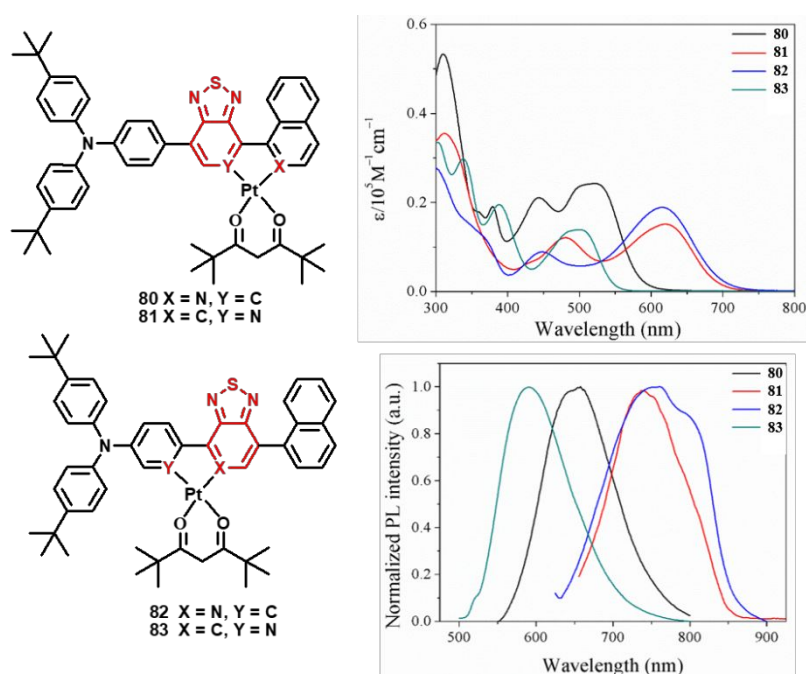


Figure 17. Chemical structures, absorption and PL spectra of **80–83**. Adapted with permission [114]. Copyright 2018, American Chemical Society.

Table 3. Photophysical and EL properties of BT-containing transition metal complexes.

	λ_{PL} (nm)	λ_{EL} (nm)	CE (cd A ⁻¹)	PE (lm W ⁻¹)	EQE_{max} (%)	Ref.
75	643	-	-	-	-	111
76	643	-	-	-	-	111
77	759	432/625/759	-	-	0.16	112
78	643	780	-	-	0.02	111
79	697	703	-	-	0.88	113
80	657	626/766	0.16	0.05	0.13	114
81	739	645/761	0.04	0.01	0.04	114
82	761	560/826	0.51	0.22	0.49	114
83	590	571	0.62	0.22	0.22	114

3.4 OLED materials based on π -extended BT derivatives

Generally, π -extended BT derivatives have a higher degree of conjugation and stronger electron-deficient ability. The resulting molecules usually exhibit absorptions at long wavelengths and narrower energy band gaps, making them potentially good candidates for NIR-OLEDs. There are many π -extended BT derivative-based small molecules and polymer materials that have been developed for NIR-OLEDs. Early in 2008, Wang and coworkers reported a series of D- π -A- π -D-type NIR fluorescent compounds based on benzobis(thiadiazole) and its selenium analogues (**84–94**, Figure 18) [115]. The PL wavelength of these chromophores ranges from 900 to 1600 nm and

their band gaps are between 1.19 and 0.56 eV. Interestingly, replacing the sulfur by selenium can lead to a red shift in emission and reduce the band gap further. Using these organic materials as single emissive layers, NIR emissions above 1 μm with an EQE of 0.05% and maximum radiance of 60 $\text{mW Sr}^{-1} \text{m}^{-2}$ were observed. Subsequently, through modification of the degree of conjugation and electron-deficient ability of the π -extended BT derivatives, as well as the use of other donor groups, more organic NIR EL materials were designed and synthesized by Wang *et al.* For example, in 2009, NIR fluorescent chromophores based on [1,2,5]thiadiazolo[3,4-*g*]quinoxaline as an electron acceptor and triphenylamine as an electron donor were synthesized and characterized (**95–97**, Figure 19) [71]. Their absorption and PL spectra were found to show an obvious red-shift when the π -conjugation of the acceptor unit was increased. The EL spectra of the devices based on these chromophores covered a range in wavelength from 748 to 870 nm and these device exhibited an EQE of over 1%. In the same year, by choosing benzo(1,2-*c*:4, 5-*c'*) bis((1,2,5)thiadiazole) as an electron acceptor, and slightly modified diphenylamino units as an electron donor, three new NIR organic materials (**98–100**, Figure 20) were prepared [70]. Non-doped OLEDs with NIR emission exclusively at 1080 nm with EQE of 0.28% have been achieved, which represented the best performance at that time. Later, in 2012, they designed and synthesized a family of D-A-D-type NIR fluorophores (**101** and **102**, Figure 20) using [1,2,5]thiadiazolo[3,4-*g*]quinoxaline or benzo[1,2-*c*:4,5-*c'*]bis[1,2,5]thiadiazole) as acceptors, and tetraphenylethene as the donor [116]. These emitters exhibited NIR emission in the wavelength range of 600–1100 nm. Non-doped OLEDs based on these

fluorophores were made which exhibited EL spectra peaking from 706 to 864 nm with EQE ranging from 0.89% to 0.20%. Their work in designing organic NIR materials based on π -extended BT derivatives has attracted great attention and considerable further investigation by other research groups.

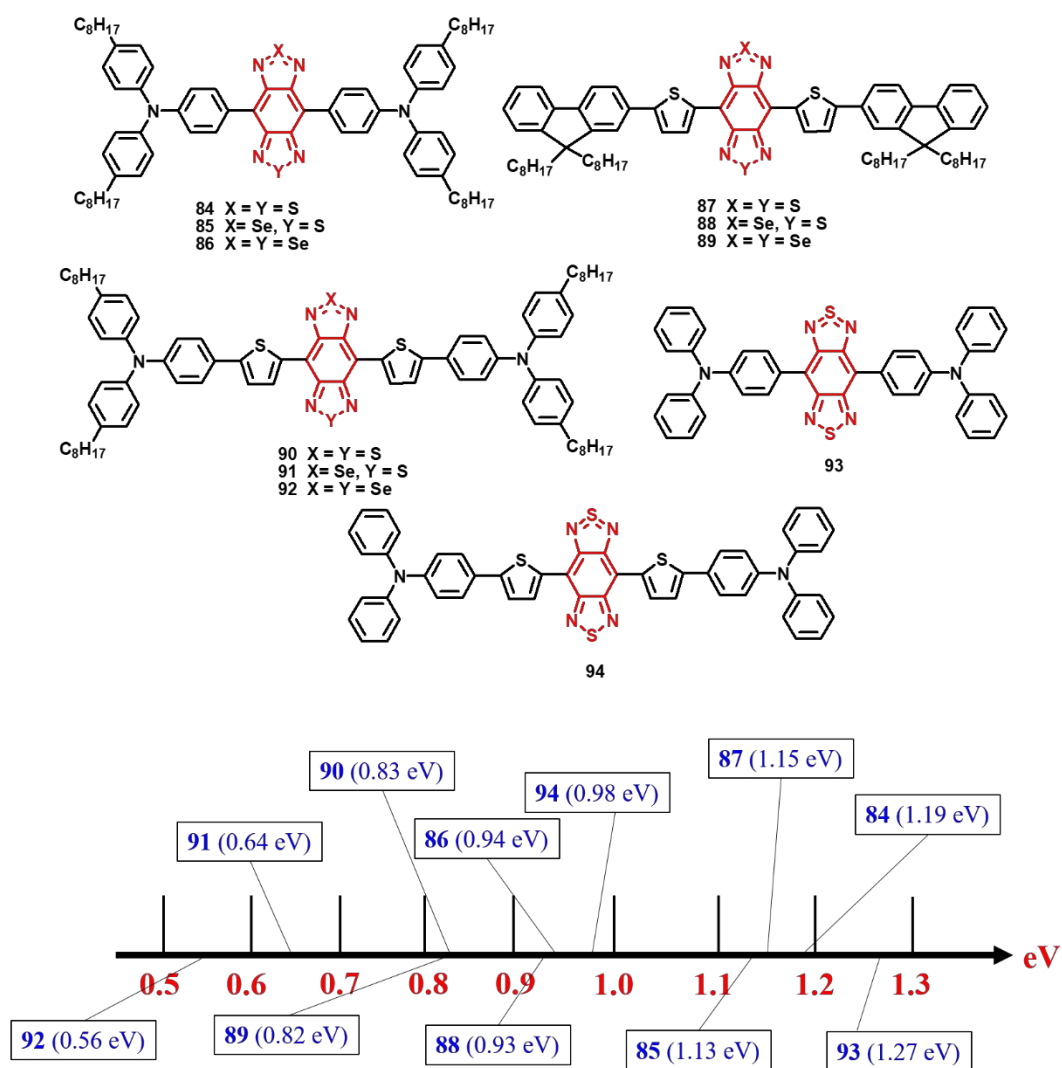


Figure 18. Chemical structures and a wide spectrum of energy gap values (in eV) for 84–94.

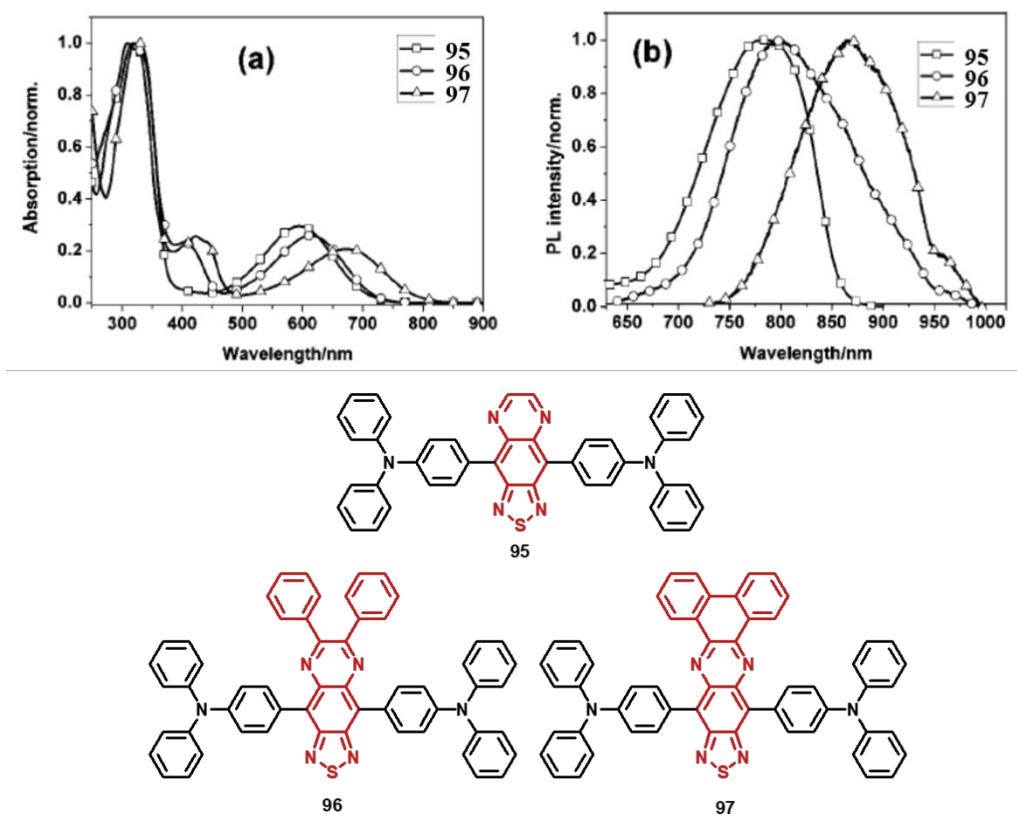


Figure 19. Chemical structures, absorption and PL spectra of **95**–**97**. Adapted with permission [71]. Copyright 2009, American Chemical Society.

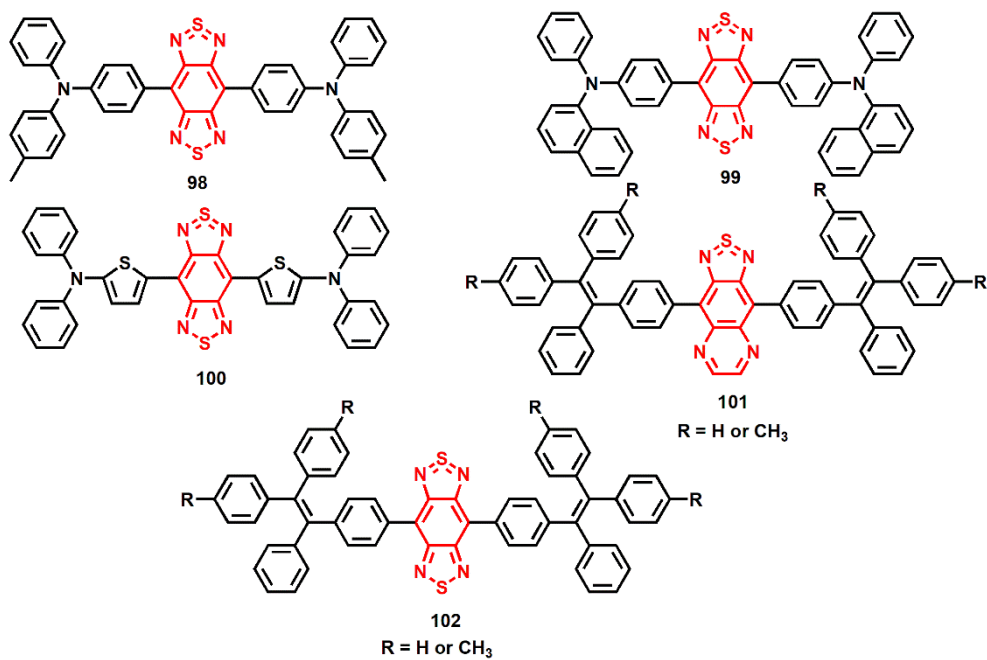


Figure 20. Chemical structures of **98**–**102**.

Xue *et al.* synthesized two π -extended BT derivative-based oligomers (**103** and **104**, Figure 21) [117]. The energies of the HOMO and LUMO of these oligomers are controlled by the D and A components. Using these oligomers as single emissive layers, EL wavelengths of 692 and 815 nm, as well as EQEs of 1.6 and 3.1% were obtained from their NIR OLEDs. Reynolds *et al.* also designed four π -extended BT-based oligomers (**105-108**, Figure 21) [118]. The relationship among the spectral, structural and electrochemical properties of these oligomers fully revealed the design rules for organic NIR luminescent materials based on BT or its derivatized heterocycles. Ma and coworkers reported NIR materials based on naphtho[2,3-*c*][1,2,5]thiadiazole as an electron acceptor and TPA as an electron donor (**109**, Figure 21) [119]. By incorporating another ancillary acceptor of cyanophenyl group, a red-shift was obtained as compared to its parent NIR emission peak at 710 nm. The non-doped OLED based on the emitter **109** exhibited an excellent NIR emission at 702 nm with a maximum EQE of 1.2%. Furthermore, by using this largely conjugated acceptor unit, they developed another three emitters of **110-112** with TPA as the donor group. All of these emitters can emit DR/NIR emission and exhibit HLCT properties. The related devices showed EL wavelengths of 664, 666 and 665 nm, as well as EQEs of 2.8%, 5.06% and 5.35%, respectively [94, 120]. In addition, Yang and coworkers also designed two NIR emissive materials (**113** and **114**, Figure 21) using naphtho[2,3-*c*][1,2,5]thiadiazole as an electron acceptor and TPA or di(*p*-tolyl)amine as the electron donor [121, 122]. The NIR OLEDs based on **113** and **114** emitters showed excellent EL performance with emission peaks at 696 and 786 nm, as well as EQE of 3.9% and 0.77%, respectively.

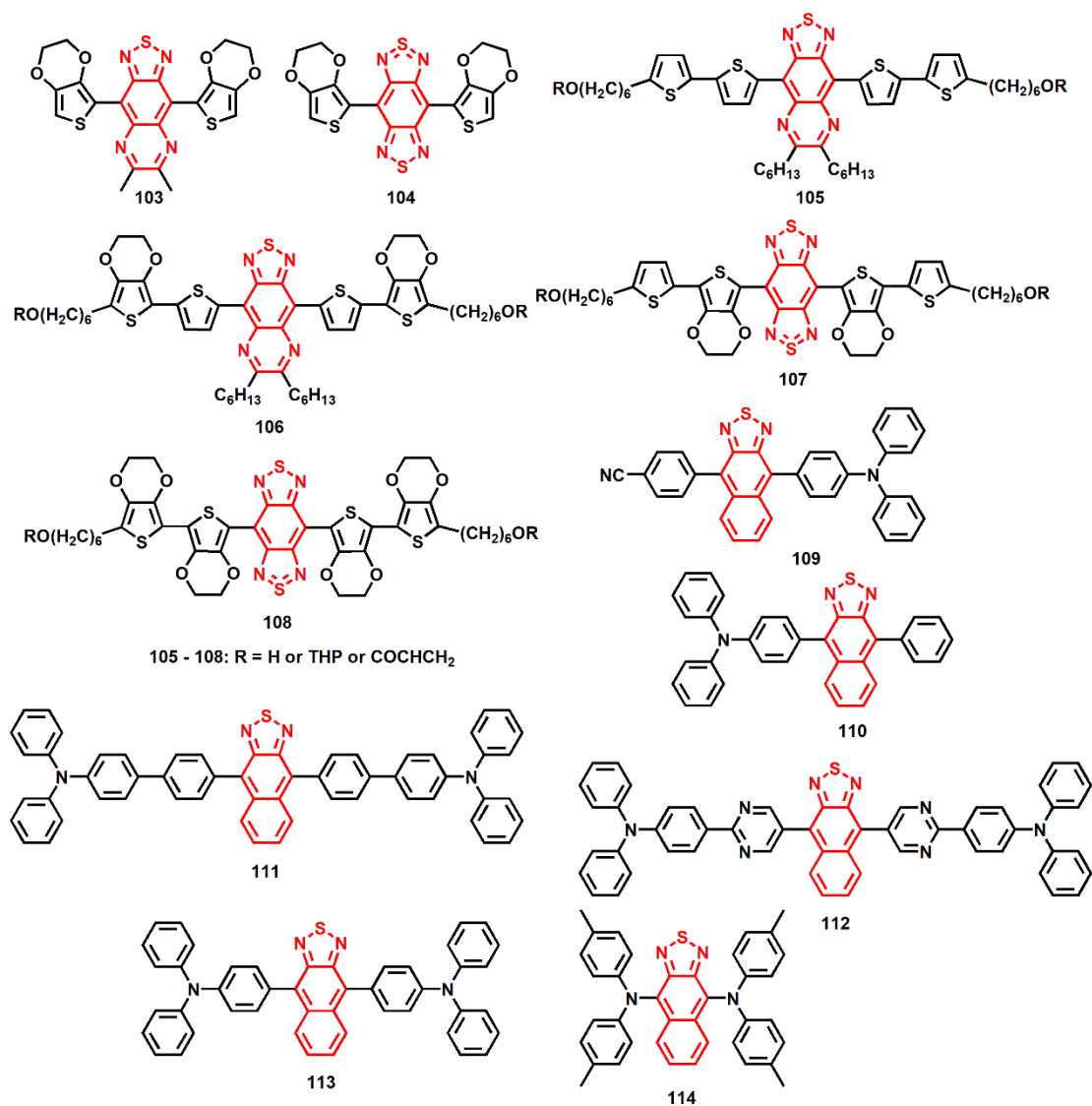


Figure 21. Chemical structures of **103-114**.

π -Extended BT derivative-based copolymers can also be applied as NIR EL materials. Wang and coworkers reported a series of NIR emitting copolymers (**115**, Figure 22), based on a low band gap fluorophore copolymerized with a high-band-gap host backbone [123]. By regulating the ratio of polymerizable monomers, the copolymers with different degrees of polymerization were obtained with different optoelectric performance. Using these copolymers as the emissive layers, NIR OLEDs emitted different EL emission peaks within 690–930 nm and EQEs of 0.04–0.36% were

obtained. Table 4 summarizes the photophysical and EL properties of π -extended BT derivatives.

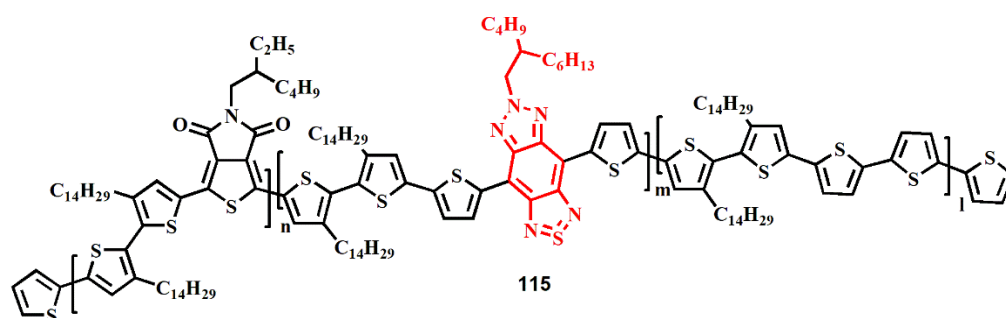


Figure 22. Chemical structure of **115**.

Table 4. Photophysical and EL properties of π -extended BT derivatives.

	λ_{PL} (nm)	λ_{EL} (nm)	EQE_{max} (%)	Ref.
84	1065	-	-	115
85	1120	-	-	115
86	1230	-	-	115
87	1055	-	-	115
88	1120	-	-	115
89	1285	-	-	115
90	1125	-	-	115
91	1295	-	-	115
92	1360	-	-	115
93	975	1050	0.05	115
94	1120	1115	-	115
95	784	752	1.12	71

96	800	748	1.20	71
97	768	823	0.27	71
98	1080	1080	0.73	70
99	1040	1050	0.33	70
100	1285	1220	-	70
101	700/780	706/749	0.89/0.29	116
102	787/857	802/864	0.43/0.20	116
103	698	692	3.1	117
104	805	815	1.5	117
105	900	-	-	118
106	974	-	-	118
107	1020	-	-	118
108	1088	-	-	118
109	710	702	1.2	119
110	687/668	664	2.8	94
111	675	665	5.35	120
112	676	666	5.06	120
113	683	696	3.9	121
114	785	786	0.77	122
115	700–900	680–930	0.004–0.49	123

4 Conclusion

Organic luminescent materials have attracted considerable interest because of their excellent potential in electronic devices, chemical detectors, fluorescent probes and so on. It is important to obtain fluorescent materials with high luminous efficiency through molecular design. More and more efficient EL molecules have been developed successively. However, many new challenges remain to be met for a variety of needs. For example, due to the complex molecular structure, most of the high-efficiency luminescent materials are still in the laboratory-scale research stage and cannot be mass produced.

This review summarizes the advances in EL materials based on BT acceptor unit and its derivatives, including the chemical preparation of materials and their EL performance. Due to their strong ability for electron withdrawal, construction of molecules with the unit core of BT and its derivatives can usually improve the resulting electronic properties. In addition, by modifying the structure of BT, such as by introducing electron-donating or electron-withdrawing groups, and expanding the conjugated structure of the unit, the electronic properties of the materials can be effectively regulated. Based on these methods, EL materials developed based on these units can emit light from visible to NIR, as well as white emission. However, there are also problems with those molecules based on BT derivatives. For example, due to their good planarity and strong electron-withdrawing property, the HOMO and LUMO of the resulting molecules are not well separated, which can always cause large ΔE_{ST} , and the utilization efficiency of triplet excitons is low. Furthermore, π -extended BT

derivatives typically have a higher degree of conjugation and largely planar structure, which would give rise to low solubility for the resulting molecules. Generally, introduction of long alkyl chains can increase the solubility, but it also increases the vibration factors and enhances the non-radiative transition, which reduces the internal quantum efficiency.

Except for the molecular structure, the configuration of the fabricated devices also has a great influence on the final performance. Therefore, the optimization of device process is particularly important. All in all, the excellent device performance requires the joint efforts of material chemists and device engineers.

5 Acknowledgements

This work was financially supported by the Science, Technology and Innovation Committee of Shenzhen Municipality (JCYJ20180507183413211), the National Natural Science Foundation of China (51873176, 51903157, 21828102), Hong Kong Research Grants Council (PolyU153058/19P and C6009-17G), Hong Kong Polytechnic University (1-ZE1C), the Endowed Professorship in Energy from Ms Clarea Au (847S) and China Postdoctoral Science Foundation Funded Project (2017M622748, 2019T120747). P. Qian also thanks the Foundation of Wenzhou Science & Technology Bureau (No. W20170003).

6 References

- 1 Wang ZY. Near-infrared organic materials and emerging applications. Taylor & Francis Group, LLC, Boca Raton 2013, ISBN-13: 978-1-4398-6194-3
- 2 Qian G, Wang ZY. *Chem Asian J*, 2010, 5: 1006–1029

- 3 Zhang YM, Wang YF, Song J, Qu JL, Li BH, Zhu WG, Wong WY. *Adv Optical Mater*, 2018, 6: 1800466
- 4 Xiang HF, Chen JH, Ma XF, Zhou XF, Chruma JJ. *Chem Soc Rev*, 2013, 42: 6128–6185
- 5 Wang E, Hou L, Wang Z, Hellström S, Mammo W, Zhang F, Inganäs O, Andersson MR, *Org Lett*, 2010, 20: 4470–4473
- 6 Zhang Y, Bao X, Xiao M, Tan H, Tao Q, Wang Y, Liu Y, Yang R, Zhu W. *J Mater Chem A*, 2015, 3: 886–893
- 7 Liu T, Zhu L, Gong S, Zhong C, Xie G, Mao E, Fang J, Ma D, Yang C. *Adv Optical Mater*, 2017, 5: 1700145
- 8 Wang S, Yan X, Cheng Z, Zhang H, Liu Y, Wang Y. *Angew Chem Int Ed*, 2015, 54: 13068–13072
- 9 Yuan Y, Hu Y, Zhang YX, Lin JD, Wang YK, Jiang ZQ, Liao LS, Lee ST. *Adv Funct Mater*, 2017, 27: 1700986
- 10 Wang B, Wang Y, Hua J, Jiang Y, Huang J, Qian S, Tian H. *Chem Eur J*, 2011, 17: 2647–2655
- 11 Bis JA, Vishweshwar P, Weyna D, Zaworotko MJ. *Mol Pharm*, 2007, 4: 401–416
- 12 Pond SJK, Rumi M, Levin MD, Parker TC, Beljonne D, Day MW, Brédas JL, Marder SR, Joseph W. Perry JW. *J Phys Chem A*, 2002, 106: 11470–11480
- 13 Melo CEA, Nandi LG, Domínguez M, Rezende MC, Machado VG. *J Phys Org Chem*, 2015, 28: 250–260
- 14 Albert IDL, Marks TJ, Ratner MA. *J Am Chem Soc*, 1997, 119: 6575–6582
- 15 Qian Y, Xiao G, Wang G, Lin B, Cui Y, Sun Y. *Dyes Pigm*, 2007, 75: 218–224
- 16 Liu G, Zhang B, Chen Y, Zhu CX, Zeng L, Chan DSH, Neoh KG, Chen J, Kang ET. *J Mater Chem*, 2011, 21: 6027
- 17 Kim HG, Kim M, Clement JA, Lee J, Shin J, Hwang H, Sin DH, Cho K. *Chem Mater*, 2015, 27: 6858–6868
- 18 Cui C, Wong WY. *Macromol Rapid Commun*, 2016, 37: 287–302
- 19 Dou C, Long X, Ding Z, Xie Z, Liu J, Wang L. *Angew Chem Int Ed*, 2016, 55: 1436–1440
- 20 Bürgi L, Turbiez M, Pfeiffer R, Bienewald F, Kirner HJ, Winnewisser C. *Adv Mater*, 2008, 20: 2217–2224
- 21 Allard S, Forster M, Souharce B, Thiem H, Scherf U. *Angew Chem Int Ed*, 2008, 120: 4138–4167

- 22 Lei T, Wang JY, Pei J. *Acc Chem Res*, 2014, 47: 1117–1126
- 23 Li YF. *Acc Chem Res*, 2011, 45: 723–733
- 24 Zhou P, Zhang ZG, Li Y, Chen X, Qin J. *Chem Mater*, 2014, 26: 3495–3501
- 25 Takimiya K, Osaka I, Nakano M. *Chem Mater*, 2013, 26: 587–593
- 26 Guo X, Facchetti A, Marks TJ. *Chem Rev*, 2014, 114: 8943–9021
- 27 Cheng YJ, Yang SH, Hsu CS. *Chem Rev*, 2009, 109: 5868–5923
- 28 Guo X, Xin H, Kim FS, Liyanage ADT, Jenekhe SA, Watson MD. *Macromolecules*, 2011, 44: 269–277

- 29 Wang M, Hu X, Liu P, Li W, Gong X, Huang F, Cao Y. *J Am Chem Soc*, 2011, 133: 9638–9641

- 30 Parker TC, Patel DG, Moudgil K, Barlow S, Risko C, Brédas JL, Reynolds JR, Marder SR. *Mater Horiz*, 2015, 2: 22–36

- 31 Zhang M, Tsao HN, Pisula W, Yang C, Mishra A, Müllen K. *J Am Chem Soc*, 2007, 129: 3472–3473

- 32 Zhou E, Cong J, Yamakawa S, Wei Q, Nakamura M, Tajima K, Yang C, Hashimoto K. *Macromolecules*, 2010, 43: 2873–2879

- 33 Neto BAD, Lapis AAM, da Silva Júnior EN, Dupont J. *Eur J Org Chem*, 2013, 2013: 228–255

- 34 Tan SE, Sarjadi MS. *Poly Sci Ser B*, 2017, 59: 479–496
- 35 Yu J, Tan H, Meng F, Lv K, Zhu W, Su S. *Dyes Pigm*, 2016, 131: 231–238
- 36 Xiao B, Tang A, Zhang J, Mahmood A, Wei Z, Zhou E. *Adv Energy Mater*. 2017, 7: 1602269

- 37 Tang A, Xiao B, Chen F, Zhang J, Wei Z, Zhou E. *Adv. Energy Mater*. 2018, 8: 1801582

- 38 Lee J, Park HJ, Joo JM, Hwang DH. *Macromol Res*, 2019, 27: 115–118
- 39 Data P, Kurowska A, Pluczyk S, Zassowski P, Pander P, Jedrysiak R, Czwartosz M, Otulakowski L, Suwinski J, Lapkowski M, Monkman AP. *J Phys Chem C*, 2016, 120: 2070–2078

- 40 Wu XF, Fu WF, Xu Z, Shi M, Liu F, Chen HZ, Wan JH, Russell TP. *Adv Funct Mater*, 2015, 25: 5954–5966

- 41 Tang A, Zhan C, Yao J, Zhou E. *Adv Mater*, 2017, 29: 1600013
- 42 Liu C, Dong S, Cai P, Liu P, Liu S, Chen J, Liu F, Ying L, Russell TP, Huang F, Cao Y. *ACS Appl Mater Interfaces*, 2015, 7: 9038–9051

- 43 Lei T, Lai YC, Hong G, Wang H, Hayoz P, Weitz RT, Chen C, Dai H, Bao Z. *Small*, 2015, 11: 2946–2954

- 44 Ganguly A, Zhu J, Kelly TL. *J Phys Chem C*, 2017, 121: 9110–9119
- 45 Lu Q, Cai W, Zhang X, Yang C, Ge H, Chen Y, Niu H, Wang W. *Eur Poly J*, 2018, 108: 124–137
- 46 Jiang Y, Gao Y, Tian H, Ding J, Yan D, Geng Y, Wang F. *Macromolecules*, 2016, 49: 2135–2144
- 47 Wang JT, Takashima S, Wu HC, Chiu YC, Chen Y, Isono T, Kakuchi T, Satoh T, Chen WC. *Adv Funct Mater*, 2016, 26: 2695–2705
- 48 Liu J, Zhou QG, Cheng YX, Geng YH, Wang LX, Ma DG, Jing XB, Wang FS. *Adv Funct Mater*, 2006, 16: 957–965
- 49 Chen L, Li P, Cheng Y, Xie Z, Wang L, Jing X, Wang F. *Adv Mater*, 2011, 23: 2986–2990
- 50 Liu J, Chen L, Shao S, Xie Z, Cheng Y, Geng Y, Wang L, Jing X, Wang F. *J Mater Chem*, 2008, 18: 319–327
- 51 Ku SY, Chi LC, Hung WY, Yang SW, Tsai TC, Wong KT, Chen YH, Wu CI. *J Mater Chem*, 2009, 19: 773–780
- 52 Zhang J, Chen W, Rojas AJ, Jucov EV, Timofeeva TV, Parker TC, Barlow S, Marder SR. *J Am Chem Soc*, 2013, 135: 16376–16379
- 53 Sanzone A, Calascibetta A, Ghiglietti E, Ceriani C, Mattioli G, Mattiello S, Sassi M, Beverina L. *J Org Chem*, 2018, 83: 15029–15042
- 54 Wang X, Wang M. *Polym Chem*, 2014, 5: 5784–5792
- 55 Cao Q, Howard JL, Wheatley E, Browne DL. *Angew Chem Int Ed*, 2018, 57: 11339–11343
- 56 Heiskanen JP, Vivo P, Saari NM, Hukka TI, Kastinen T, Kaunisto K, Lemmetyinen HJ, Hormi OE. *J Org Chem*, 2016, 81: 1535–1546
- 57 Roy C, Bura T, Beaupré S, Légaré MA, Sun JP, Hill IG, Leclerc M. *Macromolecules*, 2017, 50: 4658–4667
- 58 Mancilha FS, DaSilveira Neto BA, Lopes AS, Moreira PF, Quina FH, Gonçalves RS, Dupont J. *Eur J Org Chem*, 2006: 4924–4933
- 59 Jin Y, Kim Y, Kim SH, Song S, Woo HY, Lee K, Suh H. *Macromolecules*, 2008, 41: 5548–5554
- 60 Speros JC, Paulsen BD, Slowinski BS, Frisbie CD, Hillmyer MA. *ACS Macro Lett*, 2012, 1: 986–990
- 61 Hassan Omar O, la Gatta S, Tangorra RR, Milano F, Ragni R, Operamolla A,

- Argazzi R, Chiorboli C, Agostiano A, Trotta M, Farinola GM. *Bioconjugate Chem*, 2016, 27: 1614–1623
- 62 Wang T, Scarratt NW, Yi H, Coleman IF, Zhang Y, Grant RT, Yao J, Skoda MWA, Dunbar ADF, Jones RAL, Iraqi A, Lidzey DG. *J Mater Chem C*, 2015, 3: 4007–4015
- 63 Lee J, Malekshahi Byranvand M, Kang G, Son SY, Song S, Kim GW, Park T. *J Am Chem Soc*, 2017, 139: 12175–12181
- 64 Livi F, Zawacka NK, Angmo D, Jørgensen M, Krebs FC, Bundgaard E. *Macromolecules*, 2015, 48: 3481–3492
- 65 Wudarczyk J, Papamokos G, Marszalek T, Nevolianis T, Schollmeyer D, Pisula W, Floudas G, Baumgarten M, Mullen K. *ACS Appl Mater Interfaces*, 2017, 9: 20527–20535
- 66 Oosterhout SD, Savikhin V, Zhang J, Zhang Y, Burgers MA, Marder SR, Bazan GC, Toney MF. *Chem Mater*, 2017, 29: 3062–3069
- 67 Hasegawa T, Ashizawa M, Aoyagi K, Masunaga H, Hikima T, Matsumoto H. *Org Lett*, 2017, 19: 3275–3278
- 68 Cai T, Zhou Y, Wang E, Hellström S, Zhang F, Xu S, Inganäs O, Andersson MR. *Sol Energy Mater Sol Cells*, 2010, 94: 1275–1281
- 69 Kavak E, Us CN, Yavuz E, Kivrak A, Özkut M. *Electrochim Acta*, 2015, 182: 537–543
- 70 Qian G, Zhong Z, Luo M, Yu D, Zhang Z, Wang ZY, Ma D. *Adv Mater*, 2009, 21: 111–116
- 71 Qian G, Zhong Z, Luo M, Yu D, Zhang Z, Ma D, Wang ZY. *J Phys Chem C*, 2009, 113: 1589–1595
- 72 Yen YS, Ni JS, Hung WI, Hsu CY, Chou HH, Lin JT. *ACS Appl Mater Interfaces*, 2016, 8: 6117–6126
- 73 Oliveira FF, Santos DC, Lapis AA, Correa JR, Gomes AF, Gozzo FC, Moreira PF, Jr., de Oliveira VC, Quina FH, Neto BA. *Bioorg Med Chem Lett*, 2010, 20: 6001–6007
- 74 Cruz EHG, Carvalho PPHR, Corrêa JR, Silva DAC, Diogo EBT, Souza Filho JD, Cavalcanti BC, Pessoa C, Oliveira HCB, Guido BC, Silva Filho DA, Neto BAD,

- da Silva Júnior EN. *New J Chem*, 2014, 38: 2569
- 75 Sun X, Xu X, Qiu W, Yu G, Zhang H, Gao X, Chen S, Song Y, Liu Y. *J Mater Chem*, 2008, 18: 2709
- 76 Yang Y, Zhou Y, He QG, He C, Yang CH, Bai FL, Li YF. *J Phys Chem B*, 2009, 113: 7745–7752
- 77 Zhang J, Yang Y, He C, Li Y. *Sci China Chem*, 2011, 54: 695–698
- 78 Zhao Z, Deng C, Chen S, Lam JW, Qin W, Lu P, Wang Z, Kwok HS, Ma Y, Qiu H, Tang BZ. *Chem Commun*, 2011, 47: 8847–8849
- 79 Li Y, Wang W, Zhuang Z, Wang Z, Lin G, Shen P, Chen S, Zhao Z, Tang BZ. *J Mater Chem C*, 2018, 6: 5900–5907
- 80 Lee WWH, Zhao Z, Cai Y, Xu Z, Yu Y, Xiong Y, Kwok RTK, Chen Y, Leung NLC, Ma D, Lam JWY, Qin A, Tang BZ. *Chem Sci*, 2018, 9: 6118–6125
- 81 Chen S, Kwok HS. *Org Electron*, 2011, 12: 677–681
- 82 Thangthong A, Prachumrak N, Sudyoasuk T, Namuangruk S, Keawin T, Jungstittiwong S, Kungwan N, Promarak V. *Org Electron*, 2015, 21: 117–125
- 83 Angioni E, Chapran M, Ivaniuk K, Kostiv N, Cherpak V, Stakhira P, Lazauskas A, Tamulevičius S, Volyniuk D, Findlay NJ, Tuttle T, Grazulevicius JV, Skabara PJ. *J Mater Chem C*, 2016, 4: 3851–3856
- 84 Pathak A, Justin Thomas KR, Singh M, Jou JH. *J Org Chem*, 2017, 82: 11512–11523
- 85 Peng Z, Zhang K, Huang Z, Wang Z, Duttwyler S, Wang Y, Lu P. *J Mater Chem C*, 2019, 7: 2430–2435
- 86 Fell VHK, Findlay NJ, Breig B, Forbes C, Inigo AR, Cameron J, Kanibolotsky AL, Skabara PJ. *J Mater Chem C*, 2019, 7: 3934–3944
- 87 Guo J, Li XL, Nie H, Luo W, Gan S, Hu S, Hu R, Qin A, Zhao Z, Su SJ, Tang BZ. *Adv Funct Mater* 2017, 27: 1606458
- 88 Wong MY and Eli ZC. *Adv. Mater.* 2017, 29: 1605444
- 89 Liu B, Yu ZW, He D, Zhu ZL, Zheng J, Yu YD, Xie WF, Tong QX, Lee CS. *J Mater Chem C*, 2017, 5: 5402–5410

- 90 Chen WC, Yuan Y, Ni SF, Tong QX, Wong FL, Lee CS. *Chem Sci*, 2017, 8: 3599–3608
- 91 Xue J, Liang Q, Zhang Y, Zhang R, Duan L, Qiao J. *Adv Funct Mater*. 2017, 27: 1703283
- 92 Ni F, Wu Z, Zhu Z, Chen T, Wu K, Zhong C, An K, Wei D, Ma D, Yang C. *J Mater Chem C*, 2017, 5: 1363–1368
- 93 Yao L, Zhang S, Wang R, Li W, Shen F, Yang B, Ma Y. *Angew Chem Int Ed*, 2014, 53: 2119–2123
- 94 Li W, Pan Y, Yao L, Liu H, Zhang S, Wang C, Shen FZ, Lu P, Yang B, Ma Y. *Adv Optical Mater*, 2014, 2: 892–901
- 95 Chen X, Yang Z, Li W, Mao Z, Zhao J, Zhang Y, Wu YC, Jiao S, Liu Y, Chi Z. *ACS Appl Mater Interfaces* 2019, 11: 39026–39034
- 96 Xie W, Li B, Cai X, Li M, Qiao Z, Tang X, Liu K, Gu C, Ma Y, Su SJ. *Front Chem*, 2019, 7: 276
- 97 Zhang Y, Zhou X, Zhou C, Su Q, Chen S, Song J, Wong WY. *J Mater Chem C*, 2020, 8: 6851–6860
- 98 Xu Y, Guan R, Jiang J, Yang W, Zhen H, Peng J, Cao Y. *J Polym Sci Polym Chem*, 2008, 46: 453–463
- 99 Chen Q, Liu N, Ying L, Yang W, Wu H, Xu W, Cao Y. *Polymer*, 2009, 50: 1430–1437
- 100 Wang H, Xu Y, Tsuboi T, Xu H, Wu Y, Zhang Z, Miao Y, Hao Y, Liu X, Xu B, Huang W. *Org Electron*, 2013, 14: 827–838
- 101 Nagaraju S, Ravindran E, Varathan E, Subramanian V, Somanathan N. *RSC Adv*, 2016, 6: 92778–92785
- 102 Jiu Y, Wang J, Liu C, Lai W, Zhao L, Li X, Jiang Y, Xu W, Zhang X, Huang W. *Chin J Chem*, 2015, 33: 873–880
- 103 Jiu YD, Liu CF, Wang JY, Lai WY, Jiang Y, Xu WD, Zhang XW, Huang W. *Polym Chem*, 2015, 6: 8019–8028
- 104 Jiu Y, Wang J, Yi J, Liu CF, Zhang XW, Lai WY, Huang W. *Polym Chem*, 2017, 8: 851–859
- 105 Liu Z, Fang C, Cai X, Gao X, Li P, Zhang Q, Tu G. *Dyes Pigm*, 2018, 156: 39–44

- 106 Mishra SP, Palai AK, Srivastava R, Kamalasanan MN, Patri M. *J Polym Sci Polym Chem*, 2009, 47: 6514–6525
- 107 Qu B, Feng L, Yang H, Gao Z, Gao C, Chen Z, Xiao L, Gong Q. *Synth Met*, 2012, 162: 1587–1593
- 108 Demir N, Oner I, Varlikli C, Ozsoy C, Zafer C. *Thin Solid Films*, 2015, 589: 153–160
- 109 Ahn HI, Moon JS, Kim WG, Uddin MA, Choi J, Kim C, Woo HY, Kim N, Oh JW. *Org Electron*, 2015, 25: 206–211
- 110 Krucaite G, Tavgeniene D, Xie Z, Lin X, Zhang B, Grigalevicius S. *Opt Mater*, 2018, 76: 63–68
- 111 Zhang YM, Meng F, Tang JH, Wang Y, You C, Tan H, Liu Y, Zhong YW, Su S, Zhu W. *Dalton Trans*, 2016, 45: 5071–5080
- 112 Yu J, He K, Li Y, Tan H, Zhu M, Wang Y, Liu Y, Zhu W, Wu H. *Dyes Pigm*, 2014, 107: 146–152
- 113 Zhang Y, Yin Z, Meng F, Yu J, You C, Yang S, Tan H, Zhu W, Su S. *Org Electron*, 2017, 50: 317–324
- 114 Zhang Y, Chen Z, Wang X, He J, Wu J, Liu H, Song J, Qu J, Chan WT, Wong WY. *Inorg Chem*, 2018, 57: 14208–14217
- 115 Qian G, Dai B, Luo M, Yu D, Zhan J, Zhang Z, Ma D, Wang ZY. *Chem Mater*, 2008, 20: 6208–6216
- 116 Du X, Qi J, Zhang Z, Ma D, Wang ZY. *Chem Mater*, 2012, 24: 2178–2185
- 117 Yang Y, Farley RT, Steckler TT, Eom SH, Reynolds JR, Schanze KS, Xue J. *J Appl Phys*, 2009, 106: 044509
- 118 Ellinger S, Graham KR, Shi P, Farley RT, Steckler TT, Brookins RN, Taranekar P, Mei J, Padilha LA, Ensley TR, Hu H, Webster S, Hagan DJ, Van Stryland EW, Schanze KS, Reynolds JR. *Chem Mater*, 2011, 23: 3805–3817
- 119 Tang X, Li XL, Liu H, Gao Y, Shen Y, Zhang S, Lu P, Yang B, Su SJ, Ma Y. *Dyes Pigm*, 2018, 149: 430–436
- 120 Li Y, Yao J, Wang C, Zhou X, Xu Y, Hanif M, Qiu X, Hu D, Ma D, Ma Y. *Dyes Pigm*, 2020, 173: 107960
- 121 Liu T, Zhu L, Zhong C, Xie G, Gong S, Fang J, Ma D, Yang C. *Adv Funct Mater*, 2017, 27: 1606384

- 122 Liu T, Xie G, Zhong C, Gong S, Yang C. *Adv Funct Mater*, 2018, 28: 1706088
- 123 Murto P, Minotto A, Zampetti A, Xu X, Andersson MR, Cacialli F, Wang E. *Adv Optical Mater*, 2016, 4: 2068–2076