

Efficient Deep Blue Electroluminescence Based on Phenanthroimidazole-Dibenzothiophene Derivatives with Different Oxidation States of Sulfur Atom

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Abstract: Developing efficient deep blue materials is a long term research focus in the field of organic light emitting diodes (OLEDs). In this paper, we report two deep blue molecules, PITO and PISF, which share similar chemical structures but exhibit different photophysical and device properties. These two molecules consist of phenanthroimidazole and dibenzothiophene analogues. The distinction of their chemical structures lies in the different oxidation states of the S atom. For PITO, the S atom is oxidized and the resulting structure dibenzothiophene S,S-dioxide becomes electron deficient. Therefore, the PITO displays remarkable solvatochromism, implying a charge transfer (CT) excited state formed between the donor (D) phenanthroimidazole and acceptor (A) dibenzothiophene S,S-dioxide. For PISF, it is constituted by phenanthroimidazole and dibenzothiophene of which the S atom is not oxidized. The PISF displays locally excited (LE) emission with little solvatochromism. Compared to PISF, the D-A molecule PITO with electron deficient group shows much lowered LUMO energy level which is in favor of electron injection in device. In addition, the PITO exhibits more balanced carrier transport. However, the PISF is capable of emitting in the shorter wavelength region which is beneficial to obtain better color purity. The doped electroluminescence (EL) device of the D-A molecule PITO manifests deep blue emission with a CIE coordinates of (0.15, 0.08) and maximum external quantum efficiency (EQE) of 4.67%. The doped EL device of the LE molecule PISF, however, reveals an even bluer emission with CIE coordinates of (0.15, 0.06) and a maximum EQE of 4.08%.

Introduction

Organic light emitting diodes (OLEDs) is expected to be the next-generation of lighting and display technique because of its unique advantages such as light weight, flexibility, energy conservation and so on.^[1] Though great progress has been made since the pioneering work of C. W. Tang and co-workers,^[2] some issues are still not well resolved, and one of which is the realization of efficient deep blue electroluminescence (EL).^[3] Deep blue emission can not only provide one of the RGB primary colors and enhance the color gamut for full color display, but also lower power consumption for white lightings.^[4]

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According to the National Television System Committee (NTSC), deep blue emission should have a Commission International de L'Eclairage (CIE) coordinates (x, y) of (0.14, 0.08). The European Broadcasting Union (EBU) puts forward even more rigorous requirement on deep blue emission with CIE coordinates of (0.15, 0.06). To achieve efficient deep blue emission. fluorescent materials may be superior to phosphorescent materials. Though heavy metal (commonly Ir or Pt) based phosphorescent materials can harvest 100% electrical injected excitons,^[5] it still remains a bottleneck to develop efficient phosphorescent materials with high triplet energy levels to meet the NTSC deep blue CIE coordinates,^[6] probably due to the increasing nonradiative process via metal dorbitals when elevating the metal-ligand charge transfer (MLCT) state into the deep blue region,^[7] and the most classic blue phosphorescent material FIrpic is in fact a sky blue emitter.^[8] In contrast, there are a wide variety of fluorescent materials that can emit in the deep blue region with high photoluminescence quantum efficiency (PLQY).^[3] Several short conjugated aromatic rigid rings such as anthracene,^[9] phenanthrene,^[10] pyrene^[11] and fluorene^[12] are good building blocks for efficient deep blue materials and some of them exhibit fairly good device performance. For example, Kim and co-workers recently reported an anthracene derivative 2-(2,5-dimethyl-4-(10-

(naphthalen-1-yl)anthracen-9-yl)phenyl)-4,6-diphenyl-1,3,5triazine (NAXPT) with horizontal emitting dipoles.^[13] The nondoped device based on NAXPT exhibits deep blue emission with CIE coordinates of (0.145, 0.068) and a high external quantum efficiency (EQE) of 6.6%. Ma et al designed and synthesized a triphenylamine-phenanthrene molecule. It shows efficient deep blue EL with a CIE coordinates of (0.157, 0.073) and a high EQE of 7.23% in the nondoped device.^[10a] In addition donor-acceptor (D-A) molecules with limited charge transfer (CT) strength are also attracting emitters for high performance deep blue OLEDs.^[14] The proper energy alignments of D-A molecules can effectively reduce charge injection barrier in device. Moreover, their bipolar attribute is beneficial for a balanced carrier transport.^[15] Especially, some D-A molecules possess sufficient small singlet-triplet energy splitting which is in favor of triplet harvesting via reverse intersystem crossing (RISC).^[16] For example, Adachi et al developed a blue emitting molecule consists of 3,6-di-tertbutylcarbazole and sulfone with thermally activated delayed fluorescence (TADF) character.^[17] The doped device displays deep blue EL with CIE coordinates of (0.15, 0.07). Though the efficiency is as high as 9.9%, it decreases rapidly at high luminescence. Zhang and co-workers also reported a carbazole-sulfone analogue. The nondoped device achieves a CIE coordinates of (0.157, 0.055) and a maximum EQE of 4.21%.^[18] Among so many deep blue materials,

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phenanthroimidazole (PI) derivatives have attracted great attention recently.^[19] The PI mainly consists of phenanthrene and imidazole rings. The relatively short conjugation of PI gives rise to a near ultraviolet emission.^[20] Besides, the rigid PI plane can reduce nonradiative vibrational and rotational processes, leading to a high PLQY. What's more, the different bonding mode of the two nitrogen atoms in the imidazole ring endows PI with bipolar character.^[21] Various strategies have been applied to design efficient blue-emitting PI derivatives.^[22] By linking two PI in different modes, efficient blue emission can be expected.^[23] For instance, Cheng et al connected two PI via a stilbene linker.^[23a] The resultant molecule is doped into DMPPP host and a blue emission with CIE coordinates of (0.14, 0.14) is obtained with a maximum EQE of 8.1%. PI can also serve as acceptor to construct blue emitting D-A molecules.^[24] Ma and co-workers employed triphenylamine as donor and PI as acceptor to construct a blue-emitting molecule TPA-PPI.^[24a] The nondoped device exhibits a maximum EQE of 5.02% and CIE coordinates of (0.15, 011). Besides. PI is also used as electron donor due to its bipolar character.^[25] Tong et al adopted polycyclic aromatic hydrocarbon units as electron acceptor and PI as donor and achieved a maximum EQE of 5.25% with a CIE coordinates of (0.16, 0.07).^[25a] We recently employed PI as a weak donor and sulfone as acceptor to construct a D-A molecule PMSO with deep blue emission.^[25b] The doped device gives a maximum EQE of 6.8% and a CIE coordinates of (0.152, 0.077). This positive result inspires us to further develop other analogues in order to obtain efficient deep blue OLEDs. We note that dibenzothiophene S,S-dioxide (DBTSO) as an acceptor constitutes many efficient blue-emitting D-A polymers and small molecules.^[26] For example, Perepichka et al introduced DBTSO into oligofluorene and attained stable and efficient blue emission with improved electron affinity.^[26a] However, the color purity of many DBTSO based D-A materials cannot satisfy the NTSC deep blue standard.^[27] This is due to a pronounced CT character between donor and acceptor DBTSO according to previous researches.^[28] Considering the weak donating ability and high PLQY of PI, efficient deep blue emission would be expected from a D-A molecule in which PI acts as the donor and DBTSO as acceptor. In general, there are two kinds of linking modes for DBTSO, i.e., at the 3,7-positions (para sites) or 2,8-positions (meta sites).^[28d] Previous study has shown that if the para sites of DBTSO are substituted by donors, the whole molecule will present a linear configuration and the donor/acceptor share good conjugation which will lead to a bathochromic emission.^[28d] By contrast, if the DBTSO is substituted by donors at the metasites, the donors are twisted against DBTSO, therefore the conjugation between them is partially interrupted, making it possible to obtain blue emission. Herein, the PI is connected to the meta-positions of DBTSO as a weak donor to construct a D-A-D molecule termed as PITO. The PITO behaves relatively strong CT strength as evidenced by the remarkable solvatochromism. The nondoped device exhibits sky blue emission with a CIE coordinates of (0.17, 0.31) and a maximum EQE of 3.88%. To tune the emission into deep blue region, PITO is doped into host and the doped device shows a CIE coordinates of (0.15, 0.08) which is very close to the NTSC

requirement for deep blue emission. The maximum EQE is 4.67%. To realize emission at even shorter wavelength and smaller CIE_v value, another molecule analogue to PITO is also synthesized. As shown in Scheme 1, the molecule is termed as PISF in which the S atom of dibenzothiophene (DBT) is not oxidized to weaken the CT strength of the whole molecule. As a result, the PISF exhibits much bluer emission compared to PITO. No obvious solvatochromism is observed for PISF indicating much reduced CT strength. The nondoped device of PISF gives a deep blue emission with a CIE coordinates of (0.16, 0.09) and a maximum EQE of 2.60%. The doped device of PISF emits at even shorter wavelength with a CIE coordinates of (0.15, 0.06) and a maximum EQE of 4.08%. The EL of PISF doped device has reached the EBU deep blue criterion and the efficiency is high among the reported deep blue OLEDs that meet the EBU deep blue requirement.^[29]



Scheme 1. Synthetic procedures of PITO and PISF. (a) CHCl₃, Br₂, 0 °C to room temperature, overnight; (b) H₂O₂, acetic acid, 120 °C, overnight; (c) bis(pinacolato)diboron, Pd(dppf)Cl₂, KOAc, 1,4-dioxane, 90 °C, N₂ protection, 72 h; (d) 4-bromobenzaldehyde, CH₃COONH₄, aniline, acetic acid, 120 °C, N₂ protection, overnight. (e) Pd(PPh₃)₄, K₂CO₃ (aq, 2 M), toluene, 90 °C, N₂ protection, 72 h.

Results and Discussion

Synthetic procedures

The molecular structures and synthetic routes of PITO and PISF are shown in Scheme 1. To begin with, PPIBr was prepared via one-pot reaction mode using our previous procedure.^[20] Then PPIBr was reacted with bis(pinacolato)diboron through palladium catalyzed Suzuki coupling to get PPIB. DBTBr was obtained by the bromination of DBT.^[30] Afterwards, DBTBr was

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oxidized by H_2O_2 to get DBTSOBr. The DBTB was produced by the borylation reaction of DBTBr. In the end, the target compound PITO was accessible by using PPIB and DBTSOBr as starting materials via palladium catalyzed Suzuki coupling. Likewise, PISF was acquired by Suzuki coupling using PPIBr and DBTB as reaction substrates. The molecular structure and purity of PITO and PISF were fully characterized by NMR, MS, and elemental analysis.

> a) - PITO 100 PISF **1** 90 Weight | % 04 PITO: T_=554 °C PISF: T_=526 °C 60 200 400 800 600 °C Temperature | b) - PITO PISF Endothermic = 225 °C 100 150 200 250 300 350 400 50 Temperature |

Figure 1. (a) TGA and (b) DSC curves of PITO and PISF.

Thermal properties

Thermal stability is very important to organic light-emitting materials because once the device is working, the electric current can generate large amount of joule heat which may decompose the emitter or destroy the morphology of the thin film. As displayed in Figure 1a, the decomposition temperature (T_{d} , corresponding to 5% weight loss) of PITO and PISF are 554 °C and 526 °C, respectively. Such high T_d means that PITO and PISF would not decompose during evaporation and have proper endurance for joule heat. Another issue is the morphology stability under high temperature. As can be seen in Figure 1b, PITO does not show any glass transition or melting points during the temperature rising process, revealing that PITO tends to form amorphous morphology and would not undergo

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morphology changes easily at high temperature. The PISF

exhibits a glass transition temperature (T_q) of 225 °C which is

comparable to that of other organic light-emitting materials with good thermal stability.^[31] No melting point is observed for PISF.

From the thermal stability point of view, PITO and PISF are

suitable for evaporation fabricated OLEDs and have proper

endurance for joule heat.

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Figure 2. (a) PITO: the absorption spectrum in dilute THF (10^{-5} M), the PL in dilute THF (10^{-5} M), neat film and doped film; (b) PISF: the absorption spectrum in dilute THF (10^{-5} M), the PL in dilute THF (10^{-5} M), neat film and doped film; (c) Emission spectra of PITO in different solvents; (d) Emission spectra of PISF in different solvents.

Photophysical properties

As shown in Figure 2a and Figure 2b, the absorption spectra of PITO and PISF are similar in dilute THF. Both PITO and PISF show an absorption peak around 262 nm which can be attributed to the π - π transition of the phenyl ring anchored at N atom of the imidazole group.^[32] The 348 and 366 nm absorption bands of PITO can be assigned to the π - π transition of the conjugation backbone of the molecule. Likewise, the 335 and 365 nm absorption bands of PISF also arise from the π - π transition of the conjugation backbone of PISF. The excited state properties of PITO and PISF can be evaluated by the emission behavior in different solvents with various polarities (Figure 2c and 2d). For PITO, it shows remarkable solvatochromism, suggesting relatively strong CT between PI and DBTSO. The photoluminescence (PL) of PITO shows vibronic structure in non-polar solvent *n*-hexane which implies a locally excited (LE) state. However, as the solvent alters from ether to THF and acetone, the emission peaks greatly red shift from ~406 nm in nhexane to ~496 nm in acetone. Besides, the PL spectra become structureless and broadened, indicating the formation of a CT excited state. The solvatochromism of PITO disclose an evolution from a LE state to a CT excited state as the solvent polarity increases. On the contrary, PISF constantly displays LElike emission in the four solvents, as evidenced by the PL with fine vibronic structure. In addition, the PL spectra do not red shift with increasing solvent polarity, further conspicuously demonstrating the LE character of the S₁ state of PISF. Specifically, the fine vibronic structure becomes vague in high polar solvent acetone. We can conclude that the CT emission between the donor DBT and acceptor PI is initiated for PISF in high polar solvent. Similar spectroscopic behavior is also observed in literatures of DBT and DBTSO derivatives which have demonstrated that an oxidation state of the sulfur atom is crucial for the CT process and the evolution from a LE to a CT excited state as the solvent polarity increases.^[28] The PLQY of PISF in dilute THF is close to unity, proving the highly emissive

nature of the S₁ state. As shown in Figure 2a, the PITO emits at the sky blue region in neat film with an emission peak of ~482 nm and the PLQY is measured to be 31%. To suppress intermolecular interactions and gain deep blue emission, PITO is dispersed into a wide band gap host matrix 1,3-di(9H-carbazol-9-yl)benzene (mCP) with a doping concentration of 10%. The emission peak of PITO doped film blue shifts to ~450 nm and the corresponding PLQY is improved to 82%. The neat film of PISF shows an emission peak of 447 nm (Figure 2b). The corresponding PLQY is 26%. To tune the emission of PISF into even shorter wavelength region, PISF is also doped into mCP at a doping level of 25%. The emission peak is dragged to ~430 nm and the PLQY is 60%. Considering the deep blue emission and high PLQY of PITO and PISF in doped films, they may be good candidates as deep blue emitters for OLEDs application.



Figure 3. Cyclic voltammetry of PITO and PISF.

Electrochemical properties

Cyclic voltammetry (CV) is employed to determine the HOMO/LUMO energy levels which are derived from the onset oxidation/reduction potentials during positive/negative scans. As shown in Figure 3, the reduction potential of PITO against Fc⁺/Fc is -1.95 V whereas that of PISF is lowered to be -2.54 V. Comparing the difference of molecular structure between PITO and PISF, the electron deficient group DBTSO has the strongest electron affinity compared to PI and DBT which leads to the higher reduction potential of PITO in comparison with that of PISF. The LUMO energy levels of PITO and PISF are calculated to be -2.85 eV and -2.26 eV, respectively. This reveals that by oxidation of S atom, the resultant electron deficient group DBTSO can lower LUMO energy and reduce electron injection barrier in device. The oxidation potential of PISF against Fc⁺/Fc is 0.61 V and is a little bit lower than that of PITO (0.72 V). The oxidation onset takes place on PI for PITO. By contrast, for PISF, the oxidation preferentially occurs on DBT instead of PI. This can be rationalized that the DBT is "electron richer" than PI and therefore is easier to be oxidized. In fact, DBT is commonly used as hole transporting and hosting functional group in many OLEDs materials.^[33] The HOMO energy levels of PITO and PISF are estimated to be -5.52 eV and -5.41 eV, respectively. The

introduction of electron rich group DBT can improve the HOMO energy level and therefore facilitate hole injection. By oxidation of DBT, the resultant group DBTSO turns to be electron deficient and can lower electron injection barrier in device.

Table 1. Photophysical data of PITO and PISF.									
Compound	$T_d / T_g (^{\circ}\mathrm{C})^{[a]}$	$\lambda_{\max, abs} (nm)^{[c]}$	$E_{g} \left(\mathrm{eV} \right)^{\mathrm{[d]}}$	$\lambda_{\max, PL} (nm)^{[e]}$	PLQY (%) ^[f] HOMO / LUMO $(eV)^{[i]}$				
PITO	554 / n.o. ^[b]	262 / 348 / 366	3.02	482 ^[g] / 450 ^[h]	31 ^[g] / 82 ^[h] -5.52 / -2.85				
PISF	526 / 225	262 / 335 / 365	3.16	447 ^[g] / 430 ^[h]	26 ^[g] / 60 ^[h] -5.41 / -2.26				

[a] $T_{d'}$ decomposition temperature; $T_{g'}$ glass transition temperature. [b] n.o. = not observed. [c] Absorption peaks in dilute THF (10⁵ M). [d] Optical gap calculated from the absorption onset in dilute THF (10⁵ M). [e] Emission peaks. [f] PLQY measured by integrating sphere. [g] Values of neat film. [h] Values of doped film. [i] HOMO / LUMO energy levels estimated from cyclic voltammetry measurement.

Single Carrier Devices

Single carrier devices were fabricated to investigate whether the PITO and PISF possess balanced carrier transporting ability. The hole-only device consists of ITO / HATCN (6 nm) / NPB (10 nm) / PITO or PISF (80 nm) / NPB (20 nm) / AI (100 nm) in which HATCN is hexaazatriphenylenehexacabonitrile and NPB is N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine. A thin layer of HATCN and NPB near anode ITO is used to facilitate hole injection and NPB near cathode AI is applied to block electron. The electron-only device constitutes of ITO / TPBi (20 nm) / PITO or PISF (80 nm) / TPBi (10 nm) / LiF (1 nm) / AI (100 nm) in which TPBi is 1,3,5-tris(1-phenyl-1H-benzimidazol-2vI)benzene. A thin layer of LiF and TPBi near cathode AI is designed to enhance electron injection while TPBi near anode ITO is aimed at preventing hole injection. For both the hole- and electron-only devices, the PITO or PISF layer is much thicker than that of NPB / TPBi so that the hole / electron transporting of the whole device is predominated by PITO or PISF. As shown in Figure 4, PITO exhibits balanced carrier transporting character in a wide range of voltages. With increasing voltages, the electron density increases more rapidly than the hole density, demonstrating that the electron mobility is better than hole mobility for PITO. However, even at the voltage as high as 20 V, the current density of electron-only device is only about as threefold as that of hole-only device which gives a further proof that PITO possesses balanced carrier transporting ability with electron mobility being a little more higher. As for PISF, the distinction of the opposite carrier mobility is greater than that of PITO which reveals less balanced carrier transporting property of PISF. The current density of hole-only device is close to an order of magnitude higher than that of electron-only device for PISF at the voltage of 20 V. Considering the fact that the hole mobility of many organic molecules is often several orders of magnitude higher than electron mobility,^[34] we may conclude that the carrier transport of PISF is balanced to some extent. Note that the hole mobility of PISF is higher than that of PITO while vice versa for the electron mobility. Such distinction between PITO and PISF is closely in correlation with their respective chemical structures. For PITO, the DBTSO is a strong electron withdrawing group which is responsible for the electron

transporting whereas the hole transporting is mainly undertaken by PI considering its bipolar property.^[21] Since the hole mobility are much higher than electron mobility for many organic molecules, the existence of electron withdrawing group DBTSO can therefore enhance electron mobility and narrow down the mobility gap between hole and electron, making these opposite carriers being transported evenly at the price of sacrificing a certain extent of hole mobility. For PISF, the DBT is an electron donating group which can further improve the hole mobility of the molecule while the electron transporting may mainly occur on PI group. Thanks to the bipolar property of PI, the PISF still displays balanced carrier transport. But the difference of the opposite carrier mobility of PISF is much obvious than that of PITO.



Figure 4. Single carrier devices of PITO and PISF.

Electroluminescence properties

To investigate the application potential of these two molecules as solid state emitter, we fabricated OLEDs using PITO and PISF as emitting layer. We firstly fabricated the nondoped devices of PITO with the configuration of ITO / HATCN (6 nm) / NPB (40 nm) / TCTA (5 nm) / emitting layer (PITO, 20 nm) /

TPBi (50 nm) / LiF (0.5 nm) / Al (120 nm) (Device A) where ITO (indium tin oxide) is the anode, HATCN is hole injecting layer, NPB is hole transporting layer, TCTA (tris(4-carbazoyl-9ylphenyl)amine) is the buffer layer, TPBi is the electron transporting layer, LiF is the electron injecting layer and Al is the cathode. The nondoped device shows sky blue emission with a CIE coordinates of (0.17, 0.31) at 7 V (Table 2). The EL spectrum corresponds well with the PL counterpart with an emission peak at ~480 nm (Figure S3b), indicating the emission comes from the emitting layer. The EL spectra are stable at various voltages which proves that the carriers are recombined exactly within the emitting layer (Figure S3a). The turn-on voltage is 3.2 V and is only a little higher than PITO optical gap (see in Table 1 and Table 2), disclosing effective charge injection. The maximum luminescence is ~39000 cd m⁻². The maximum EQE is 3.88% which is achieved at very high luminescence of ~24000 cd m⁻² (Figure 5a). The EQE at 100 and 1000 cd m⁻² are 3.22% and 3.57%, respectively. To adjust the emission of PITO into deep blue region, we also fabricated doped device. mCP is selected as host considering the good overlap between the absorption spectrum of PITO and the emission band of mCP (Figure S1a). The doped device consists of ITO / HATCN (6 nm) / NPB (40 nm) / TCTA (5 nm) / emitting layer (PITO: mCP, wt. 10%, 20 nm) / TPBi (50 nm) / LiF (0.5 nm) / AI (120 nm) (Device B). The EL is successfully dragged into the deep blue region with a CIE coordinates of (0.15, 0.08) at 7 V which is very close to the NTSC requirement of blue emission (Table 2). The doped EL spectra is in agreement with the PL counterpart and is very stable at a wide range of voltages (Figure S3c and S3d), indicating that the carrier is recombined in the emitting layer and the EL originates from the dopant PITO. The turn-on voltage of doped device is also 3.2 V. The doped device can reach a maximum luminescence of ~10000 cd m⁻². The maximum EQE is 4.67% which is obtained at a luminescence of ~60 cd m⁻² (Figure 5a). The improvement of

maximum EQE of doped device can be rationalized by the increase in PLQY of the doped film as shown in Table 1. The EQE at 100 and 1000 cd m⁻² are 4.44% and 3.25%, respectively. The performance of the doped device is good among the reported deep blue fluorescent OLEDs which can meet the NTSC deep blue requirement.^[35] The PISF exhibits bluer emission than PITO. Therefore we also fabricated PISF based nondoped EL device with the structure of ITO / HATCN (6 nm) / NPB (40 nm) / TCTA (5 nm) / emitting layer (PISF, 20 nm) / TPBi (20 nm) / LiF (0.5 nm) / Al (120 nm) (Device C). The CIE coordinates is (0.16, 0.09) under a driving voltage of 7 V. The EL is stable at various voltages and matches with the PL spectrum with an emission peak of ~444 nm (Figure S4a and S4b). The turn-on voltage is 3.2 V, reflecting a low charge injection barrier. The maximum luminescence is ~15000 cd m⁻². The maximum EQE is 2.60% which is attained at a luminescence of ~100 cd m⁻ ² (Figure 5c). The EQE at 1000 cd m^{-2} is 2.27%. To enhance the device efficiency, PISF is doped into mCP host. The doped device consists of ITO / HATCN (6 nm) / NPB (40 nm) / TCTA (5 nm) / emitting layer (PISF: mCP, wt. 30%, 20 nm) / TPBi (20 nm) / LiF (0.5 nm) / AI (120 nm) (Device D). The device shows extremely deep blue emission with a CIE coordinates of (0.15. 0.06) which is in accordance with the EBU requirement on deep blue emission. The EL locates at the deep blue region with an emission peak of ~427 nm and corresponds with the PL spectrum of doped film (Figure S4c and S4d). The turn-on voltage is 3.3 V indicating relatively low charge injection barrier. The maximum luminescence is ~6000 cd m⁻². The maximum EQE is 4.08% which is achieved at a luminescence of ~20 cd m⁻ (Figure 5c). The EQE at 100 and 1000 cd m⁻² are 3.92% and 3.22%, respectively. Though there is a certain degree of efficiency roll-off, the overall device performance is positive and is comparable to many other deep blue fluorescent materials that can reach EBU standard.^[29]

Table 2. Electroluminescence data of PITO and PISF based devices.											
Device	$V_{\rm on}~({ m V})^{[{ m a}]}$	L _{max} (cd m ⁻²) ^[b]	CE _{max} (cd A ⁻¹) ^[c]	EQE _{max} / 100 / 1000 (%) ^[d]	EL λ_{\max} (nm) ^[e]	$CIE (x, y)^{[f]}$					
А	3.2	39000	7.17	3.88 / 3.22 / 3.57	480	0.17, 0.31					
В	3.2	10000	3.35	4.67 / 4.44/ 3.25	444	0.15, 0.08					
С	3.2	15000	1.96	2.60 / 2.60 / 2.27	444	0.16, 0.09					
D	3.3	6000	1.98	4.08 / 3.92 / 3.22	427	0.15, 0.06					

[a] Turn on voltage at the luminescence of 1 cd m⁻². [b] Maximum luminescence. [c] Maximum current efficiency. [d] External quantum efficiency: maximum / at 100 cd m⁻² / at 1000 cd m⁻². [e] Emission peaks of EL spectra. [f] CIE coordinates of EL devices.

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Conclusions

To conclude, we have successfully designed and synthesized two blue-emitting molecules PITO and PISF. They share similar chemical structures with different oxidation states of the S atom. For PITO, the S atom is oxidized and the resultant structure DBTSO is electron deficient. Therefore, using PI as donor and DBTSO as acceptor, the D-A molecule PITO reveals strong solvatochromism, disclosing a CT excited state. In contrast, the PISF in which the S atom is not oxidized shows typical LE emission probably resulting from the π conjugation of the whole molecule. The D-A molecule PITO shows a much lowered LUMO energy level than PISF, demonstrating that the S,S-dioxide is in favor of reducing electron injection barrier. In addition, the PITO also shows more balanced carrier transport than PISF at the price of sacrificing a part of the hole mobility.

However, the emission color of PITO is red-shifted compared with that of PISF. The CIE coordinates of PITO nondoped device is (0.17, 0.31) and the maximum EQE is 3.88%. By doping PITO into appropriate host, the EL of doped device can be tuned into deep blue region with a CIE coordinates of (0.15, 0.08) which is close to the NTSC requirement on deep blue emission. The maximum EQE is improved to 4.67%. On the other hand, the PISF displays bluer EL but a little lower efficiency. The CIE coordinates of PISF nondoped device is (0.16, 0.09) and the maximum EQE is 2.60%. The doped device of PISF exhibits deep blue emission with CIE coordinates of (0.15, 0.06) and meets with the EBU standard of deep blue emission. The maximum EQE of PISF doped device is 4.08%. Overall, both PITO and PISF show deep blue EL in doped device and their efficiency is comparable to many other deep blue materials which can satisfy the NTSC and EBU standard.

Experimental Section

General information

All the reagents and solvents were used as received. ¹H NMR was recorded on Bruker AVANCE 500 spectrometer with tetramethylsilane (TMS) as the internal standard and DMSO-d₆ as solvent. Elemental analysis was carried out on a Flash EA 1112, CHNSO elemental analysis instrument. MALDI-TOF-MS mass spectra were obtained from an AXIMA-CFRTM plus instrument. Thermal gravimetric analysis (TGA) was performed on a Perkin-Elmer thermal analysis system from 30 °C to 900 °C. NETZSCH (DSC-204) unit was applied to measure differential scanning calorimetry (DSC) from 30 °C to 370 °C. Cyclic voltammetry (CV) were measured by using BAS 100B/W electrochemical analyzer with standard one-compartment, three-electrode electrochemical cell. The CV was performed in solutions. The working electrode was a glasscarbon disk electrode. The counter electrode was a Pt wire. The reference electrode was Ag/Ag⁺. The scan rate was 100 mV s⁻¹. The electrolyte for negative or positive scan was tetrabutylammoniumhexafluorophosphate (TBAPF6) dissolved in anhydrous dimethylformamide (DMF) or anhydrous dichloromethane (0.1 M). Following the IUPAC recommendation,[36] ferrocenium/ferrocene (Fc⁺/Fc) redox couple was used as the internal standard and the formal potential of Fc⁺/Fc is 4.8 eV below vacuum.^[37] All potentials relative to Ag/Ag⁺ electrode obtained from CV measurement were eventually referenced against Fc⁺/Fc to calculate HOMO/LUMO levels. As a result, the Ag/Ag⁺ electrode is just a pseudo reference. The HOMO/LUMO levels are calculated according to the following formalism:

HOMO = - (E_{ox} vs. Fc⁺/Fc + 4.8) eV

LUMO = - (E_{red} vs. Fc⁺/Fc + 4.8) eV.

where the $E_{\rm ox}$ vs. Fc⁺/Fc and $E_{\rm red}$ vs. Fc⁺/Fc are oxidation and reduction onset potentials relative to Fc/Fc⁺ reference, respectively. UV-vis and PL spectra were recorded on a Shimadzu UV-3100 spectrophotometer. The PLQY ($\Phi_{\rm F})$ in solutions and solid films were measured by integrating sphere.

Device fabrications and measurements

ITO coated glasses were used as the substrates and the sheet resistance was 20 Ω square⁻¹. The ITO glasess were cleaned by deionized water, isopropyl alcohol, acetone, toluene, treated with UV-zone for 30 min, and then transferred to a vacuum deposition system with a base pressure lower than 5×10⁻⁶ mbar for organic and metal deposition. The hole injecting layer (HATCN, 6 nm) was deposited at 0.1 Å s⁻¹. The deposition rate of all other organic layers was 1.0 Å s⁻¹. The electron injecting layer LiF (0.5 nm) was deposited at a rate of 0.1 Å s⁻¹ and then the capping Al metal layer (120 nm) was deposited at a rate of 4.0 Å s⁻¹. The EL characteristics were measured using a Keithley 2400 programmable electrometer and a PR-650 Spectroscan spectrometer under ambient condition.

Synthesis and characterization

2,8-dibromodibenzo[b,d]thiophene (DBTBr)

Dibenzo[b,d]thiophene (DBT) (1.85 g, 10 mmol) was dissolved in 80 mL CHCl₃ and then 1.1 mL Br₂ (22 mmol) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature overnight. Upon completion, the reaction mixture was washed by aqueous K_2CO_3 and then extracted by dichloromethane. After evaporating the solvent, the

crude product was purified by column chromatography using petroleum ether as eluent to give white solid. Yield: 3.10 g (90%). ¹H NMR (500 MHz, DMSO-d₆, δ ppm): 8.77 (s, 2H), 8.04 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 8.7 Hz, 2H). MALDI-TOF (m/z): [M⁺] Calcd: 339.86; Found: 341.01.

2,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)dibenzo[b,d]thiophene (DBTB)

A mixture of DBTBr (3.4 g, 10 mmol), bis(pinacolato)diboron (10.16 g, 40 mmol), Pd(dppf)Cl₂ (467 mg, 0.6 mmol), KOAc (5.9 g, 60 mmol), 60 mL 1,4-dioxane was stirred at 90 °C under N₂ protection for 72 h. The reaction was quenched by water and the mixture was extracted by dichloromethane. After evaporating the solvent, the crude product was purified by column chromatography (petroleum ether : dichloromethane = 5 : 1, v/v) to give white solid. Yield: 2.62 g (60%). ¹H NMR (500 MHz, DMSO-d₆, δ ppm): 8.64 (s, 2H), 8.02 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 1.32 (s, 24H). MALDI-TOF (m/z): [M⁺] Calcd: 436.21; Found: 437.82.

2,8-dibromodibenzo[b,d]thiophene 5,5-dioxide (DBTSOBr)

A mixture of DBTBr (2.05 g, 6 mmol), 40 mL acetic acid, 5 mL 30% H_2O_2 was stirred at 120 °C. After about half an hour, large amount of white sediment occurred. The reaction mixture was continued stirring overnight Upon completion, the mixture was cooled and filtered. The product was purified by recrystallization to get white solid. Yield: 2.12 g (95%). ¹H NMR (500 MHz, DMSO-d₆, δ ppm): 8.65 (s, 2H), 8.00 (d, J = 8.2 Hz, 2H), 7.91 (d, J = 8.5 Hz, 2H). MALDI-TOF (m/z): [M⁺] Calcd: 371.85; Found: 373.14.

2-(4-bromophenyl)-1-phenyl-1H-phenanthro[9,10-d]imidazole (PPIBr)

A mixture of phenanthrene-9,10-dione (10.5 g, 50 mmol), 4-bromobenzaldehyde (9.25 g, 50 mmol), CH_3COONH_4 , (19.25 g, 250 mmol), aniline (18.3 mL, 200 mmol) was dissolved in 200 mL acetic acid and stirred at 120 °C overnight under N₂ protection. The mixture was poured into 100 mL water and then filtered to get grey solid. The product was purified by column chromatography (petroleum ether : dichloromethane = 2 : 1, v/v) to give white solid. Yield: 19.24 g (85%). ¹H NMR (500 MHz, DMSO-d₆, δ ppm): 8.94 (d, J = 8.2 Hz, 1H), 8.89 (d, J = 8.3 Hz, 1H), 8.69 (d, J = 7.9 Hz, 1H), 7.79 (t, J = 7.4 Hz, 1H), 7.72 (m, 6H), 7.58 (t, J = 8.3 Hz, 3H), 7.52 (d, J = 8.5 Hz, 2H), 7.35 (t, J = 7.2 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H). MALDI-TOF (m/z): [M⁺] Calcd: 448.06; Found: 449.84.

1-phenyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1H-phenanthro[9,10-d]imidazole (PPIB)

A mixture of PPIBr (2.24 g, 5 mmol), bis(pinacolato)diboron (2.54 g, 10 mmol), Pd(dppf)Cl₂ (117 mg, 0.15 mmol), KOAc (1.47 g, 15 mmol), 50 mL 1,4-dioxane was stirred at 90 °C under N₂ protection for 72 h. The reaction was quenched by water and the mixture was extracted by dichloromethane. After evaporating the solvent, the crude product was purified by column chromatography (petroleum ether : dichloromethane = 1 : 1, v/v) to give white solid. Yield: 1.62 g (65%). ¹H NMR (500 MHz, DMSO-d₆, δ ppm): 8.94 (d, J = 8.4 Hz, 1H), 8.89 (d, J = 8.3 Hz, 1H), 8.71 (d, J = 8.0 Hz, 1H), 7.79 (t, J = 7.4 Hz, 1H), 7.71 (m, 6H), 7.60 (dt, J = 19.6, 9.8 Hz, 5H), 7.35 (t, J = 7.5 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H), 1.30 (s, 12H). MALDI-TOF (m/z): [M⁺] Calcd: 496.23; Found: 497.73.

ΡΙΤΟ

A mixture of PPIB (2.24 g, 5 mmol), DBTSOBr (744 mg, 2 mmol), Pd(PPh₃)₄ (92 mg, 0.08 mmol), aqueous K₂CO₃ (15 mL, 2 M) and 30 mL toluene was stirred at 90 °C under N₂ protection for 72 h. Then the mixture was extracted by dichloromethane. After evaporating the solvent, the crude product was purified by column chromatography using dichloromethane as eluent to give light green solid. Yield: 1.06 g (55%). ¹H NMR (500 MHz, DMSO-d₆, δ ppm): 8.96 (d, J = 8.5 Hz, 2H), 8.91 (d, J = 8.4 Hz, 2H), 8.76 (m, 4H), 8.06 (dd, J = 24.3, 8.1 Hz, 4H), 7.95 (d, J = 8.1 Hz, 4H), 7.81 (d, J = 8.6 Hz, 16H), 7.73 (d, J = 7.9 Hz, 2H), 7.59 (t, J = 7.4 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.11 (d, J = 8.1 Hz, 2H). MALDI-TOF (m/z): [M⁺] Calcd: 952.29; Found: 953.58. Anal. Calcd. for C₆₆H₄₀N₄O₂S: C, 83.17; H, 4.23; N, 5.88. Found: C, 83.28; H, 4.29; N, 5.91.

PISF

A mixture of PPIBr (2.48 g, 5 mmol), DBTB (872 mg, 2 mmol), Pd(PPh₃)₄ (92 mg, 0.08 mmol), aqueous K₂CO₃ (15 mL, 2 M) and 30 mL toluene was stirred at 90 °C under N₂ protection for 72 h. Then the mixture was extracted by dichloromethane. After evaporating the solvent, the crude product was purified by column chromatography using dichloromethane as eluent to give white solid. Yield: 1.02 g (55%). ¹H NMR (500 MHz, DMSO-d₆, δ ppm): 8.97 (d, J = 8.4 Hz, 2H), 8.92 (d, J = 7.7 Hz, 2H), 8.76 (d, J = 7.4 Hz, 2H), 8.14 (d, J = 8.0 Hz, 2H), 7.96 (d, J = 7.8 Hz, 6H), 7.78 (m, 20H), 7.59 (s, 2H), 7.37 (s, 2H), 7.12 (d, J = 7.9 Hz, 2H). MALDI-TOF (m/z): [M⁺] Calcd: 920.30; Found: 921.69. Anal. Calcd. for C₆₆H₄₀N₄O₂S: C, 86.06; H, 4.38; N, 6.08. Found: C, 86.13; H, 4.36; N, 6.02.

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Two blue-emitting molecules, PITO and PISF, with different oxidation states of the S atom are reported. They share similar molecular structure but exhibit different photophysical and device properties. Both the PITO and PISF doped devices show deep blue emission with a maximum external quantum efficiency of 4.67% and 4.08%, respectively.



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Efficient Deep Blue Electroluminescence Based on Phenanthroimidazole-Dibenzothiophene Derivatives with Different Oxidation States of Sulfur Atom