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RESEARCH ARTICLE

Synthesis, Photophysical, Electrochemical and Thermal Studies of 2,3-Bithienylpyrazino[2,3-*b*]phenazine

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Abstract: In this work, 2,3−bithienylpyrazino[2,3−*b*]phenazine [BTPP] was synthesized and its photophysical, electrochemical and thermal properties was studied and compared with 2,3−bithienylquinoxaline [BTQ] and 2,3−bithienylbenzo[*g*]quinoxaline [BTBQ]. The photophysical studies revealed that BTPP emit in the green region at λ_{max} 551 nm. Electrochemical studies show that the ionization potential (HOMO) and electron affinity (LUMO) of BTPP are −5.49 eV and −3.15 eV respectively and are comparable to commonly used electron acceptor/transporter. The optical energy band gap of BTPP is 2.34 eV. Thermogravimetric analysis showed that BTPP possess good thermal stability.

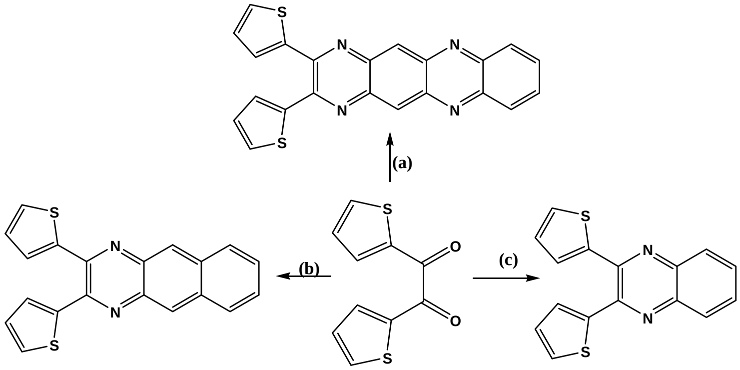
Keywords: Phenazine, BTTP, OLEDs

Introduction

In last few decades there has been significant progress in the field of organic semiconductors particularly larger acenes[1,2] because of their potential application in organic light-emitting diodes (OLEDs)[3], organic field effect transistors (OFETs)[4] and photovoltaic cells[5]. However most of the larger acenes[6] always display *p*-type semiconducting properties (electron donor, hole transporter). *N*-type (electron acceptor, electron transporter) organic and polymer semiconductors are also needed for developing more efficient and high performance organic electronics. Heteroaromatic molecules containing imine nitrogen atoms (C=N) are promising candidates for electron transporting materials because of their valence state, high electron affinity[7] and less sensitivity to oxidation and dimerization[8]. However very few heteroaromatics have been explored as electron transport (n–type) materials in organic electronics. Hence there is need to prepare new class of *N*-heteroacenes as an electron acceptor/transporter. BTQ and BTBQ have been used as electron transport materials to varied degree of success in organic electroluminescent devices[9,10]. Here we report the synthesis of BTPP and compared its photophysical, electrochemical and thermal properties with BTBQ and BTQ.

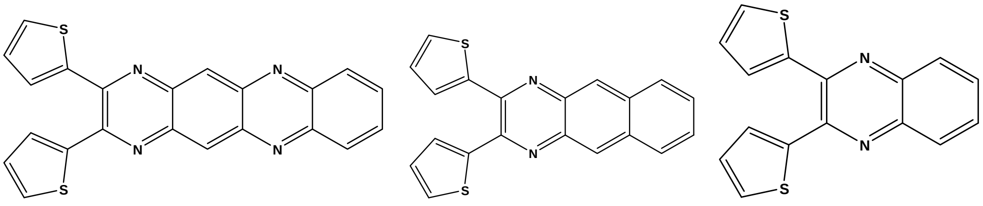
Experimental

The BTQ, BTPP and BTBQ is synthesized by condensing 2,2'-thenoin and corresponding aromatic diamines in acetic acid. Formation of BTQ is confirmed by its melting point 143 ^{0}C (Lit = 143-144 ^{0}C)[9]. The detailed synthetic route adopted for the synthesis of BTPP and BTBQ is depicted in Scheme 1 and were characterized by spectrometry methods. Molecular structures of BTQ, BTBQ and BTPP are illustrated in Figure 1.



Reaction conditions: (a) 2,3-diaminophenazine, CH_3COOH, Reflux, 5 h. (b) 1,2-diaminonaphthalene,CH_3COOH, Reflux, 3 h. (c) 1,2-phenylenediamine, CH_3COOH, Reflux, 3 h

Scheme 1. Synthesis of BTPP, BTBQ and BTQ



BTPP BTBQ BTQ

Figure 1. Molecular structures of BTPP, BTBQ and BTQ

UV-Visible spectra were recorded on SHIMADZU UV-2401PC at room temperature. The excitation and emission spectra were carried out on a Perkin Elmer LS 55 Fluorescence spectrophotometer. Cyclic voltammetry studies was carried out on a computer controlled AUTOLAB PGSTATE 30 electrochemical analyzer equipped with USB electro chemical interface using GPES software version 4.9.005. Typically, a three electrode cell equipped with a glassy carbon working electrode, Ag/AgCl (non-aqueous) reference electrode and platinum (Pt) wire as counter electrode was employed. The measurements have been carried at room temperature in anhydrous acetonitrile with tetrabutyl ammonium hexafluoro phosphate solution (0.1 M) as supporting electrolyte with a scan rate of 100 mVs^{-1}. The potential of Ag/AgCl reference electrode was calibrated by using ferrocene/ferrocenium redox couple which has the known oxidation potential of +4.8 eV. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Frontier 91579. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded using $CDCl_3$ on a Bruker 300 Ultrashield spectrometer with Tetramethylsilane (TMS) as internal reference at a working frequency of 300 MHz and 75 MHz respectively. Elemental analysis was recorded on Euro EA elemental analyzer and Mass spectra were recorded on Thermo scientific GC-MS.

General procedure for the synthesis of BTPP, BTBQ and BTQ

A mixture of 2,2’-thenoin (1 mmol) and aromatic diamines (1 mmol) was dissolved in glacial acetic acid (10 mL). The reaction mixture was continuously stirred at 100 ^{0}C for 3-5 hours. After completion of reaction, reaction mixture is poured in cold distilled water and filtered, and washed with water. The solid thus obtained was then purified by column chromatography (eluent: *n*-hexane: chloroform ratio as 70:30) to obtain a yellow to brown solid.

2,3-bithienylpyrazino[2,3-b]phenazine (BTPP)

Yield 40% MP: >300 ^{0}C. MS: $C_{22}H_{12}N_4S_2$, *m/z*: 396.41 $[M]^+$. Anal.Calcd for $C_{22}H_{12}N_4S_2$: C (66.64), H (3.05), N (14.13), S (16.18). Found: C (66.63), H (3.06), N (14.13), S (16.18). IR (neat, ν_{max} cm^{-1}):1495, 1604, 3026; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.30 (q, 2H, ArH, *J* = 1.2 Hz, 3.6 Hz), 7.41 (d, 2H, ArH, *J* = 1.2 Hz, 2.7 Hz), 7.66 (d, 2H, ArH, *J* = 1.2 Hz, 2.7 Hz), 7.89 (dd, 2H, ArH, *J* = 3.3 Hz, 3.6 Hz), 8.26 (dd, 2H, ArH, *J* = 3.3 Hz, 3.6 Hz), 9.06 (s, 2H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 130.01, 131.64, 131.97, 132.08, 134.57, 139.90, 142.16, 145.19, 154.49, 162.10, 165.43.

2,3-bithienylbenzo[g]quinoxaline (BTBQ)

Yield 70% MP: 157 ^{0}C Anal.Calcd for $C_{20}H_{12}N_2S_2$: C (69.74), H (3.51), N (8.13), S (18.62). Found: C (69.72), H (3.53), N (8.13), S (18.62). IR (neat, ν_{max} cm^{-1}): 1420, 1520, 3064; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.04 (q, 2H, ArH, *J* = 1.2 Hz, 3.9 Hz), 7.28 (d, 2H, ArH, *J* = 0.9 Hz, 2.7 Hz), 7.50–7.55 (m, 4H, ArH,), 8.05 (dd, 2H, ArH, *J* = 3.3 Hz), 8.60 (s, 2H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 126.80, 127.14, 127.54, 128.51, 129.17, 129.83, 134.17, 137.24, 141.79, 147.28.

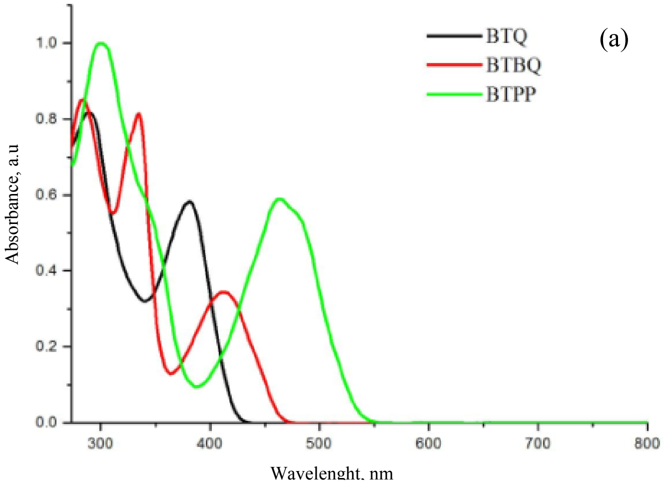
2,3-Bithienylquinoxaline (BTQ)

Yield: 90% MP: 143 ^{0}C (Lit = 143-144 ^{0}C)[9].

Results and Discussion

Photophysical properties

The absorption and fluorescence properties of BTPP were studied in dichloromethane and toluene and compared with BTQ and BTBQ. The synthesized molecules show similar UV-Vis absorption spectra in both the solvents (Figure 2).



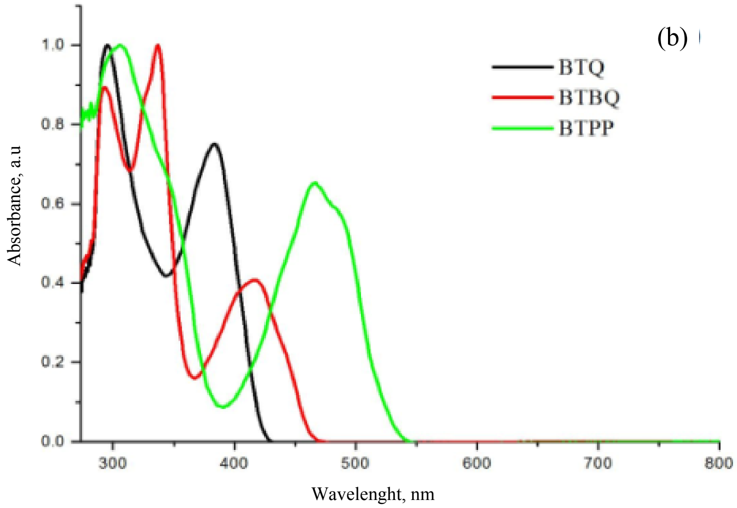
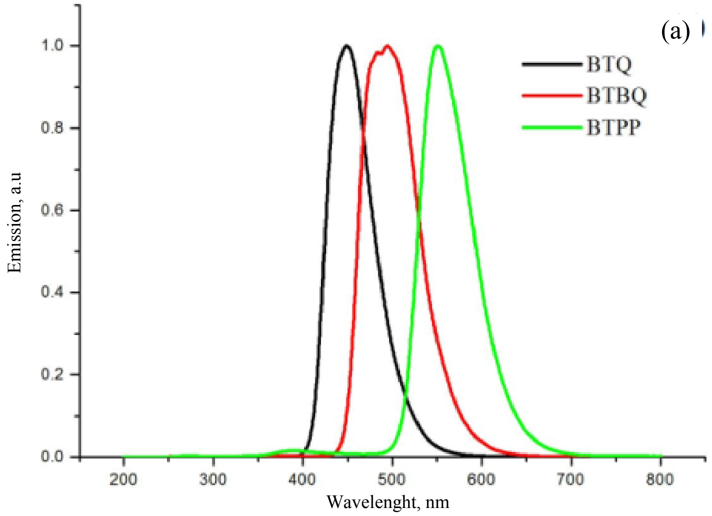


Figure 2. Absorption spectra of BTQ, BTBQ and BTPP in CH_2Cl_2 (**a**) and toluene (**b**)

The absorption spectra of BTPP reveal two major bands arising from the π-π^* transition (300-304 nm) and lower energy charge transfer transition (461-466 nm). In addition, an n-π^* transition originating from the terminal thiophene moiety is expected to appear below 300 nm, but it is probably overlapping with the intense π-π^* transitions.

BTPP emits in green region with λ_{emi} at 540-551 nm (Figure 3) upon excitation at their corresponding absorption maxima in dichloromethane and toluene. On comparing emission peak of BTPP with BTQ and BTBQ it has been found that increase in conjugation along with imine (C=N) group in quinoxaline skeleton of BTPP lead to bathochromic shift of around 103 and 58 nm respectively.

Other basic photophysical characteristics such as the molar extinction coefficient (log ε), optical band gaps (E_g^{opt}), Stokes shift ($\nu_{Abs} - \nu_{Em}$) and fluorescent quantum yield (Φ_F) of the molecules were determined and pertinent data is summarized in Table 1.



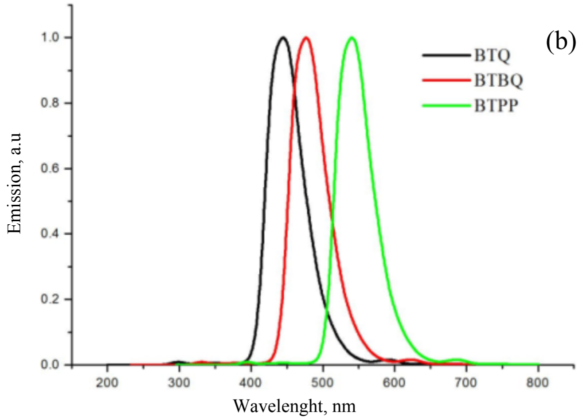


Figure 3. Emission spectra of BTQ, BTBQ and BTPP in CH_2Cl_2 (**a**) and toluene (**b**)

Table 1. Photophysical data of BTQ, BTBQ and BTPP

Compd	λ_{abs}, nm[a]		λ_{emi}, nm[a]		log ε[b]	E_g^{opt} (eV)[c]	Stoke shift[d]	Φ_F^e
	CH_2Cl_2	toluene	CH_2Cl_2	toluene				
BTQ	290,379	293,383	448	445	4.438	3.01	16741	0.21
BTBQ	282,335,411	294,333, 415	493	472	4.536	2.72	20868	0.21
BTPP	300,461	304,466	551	540	4.297	2.34	20461	0.20

[a] *Recorded in* 10^{-5} *mol* L^{-1} *in* CH_2Cl_2 *and toluene.* [b] *Extinction coefficient (* $L^{-1} mol^{-1} cm^{-1}$ *) measured in* CH_2Cl_2*.* [c] *Optical bandgap estimated from the optical edge of solution form* ($E_g^{opt} = 1240/\lambda_{opt\ edge}$) eV. [d] *Stokes shift calculated from absorption and emission wavelength observed in solution form.* [e] *Quantum yield with reference to* Alq_3 *(*$\Phi_F = 0.16$ *in benzene)*

Electrochemical properties

Electrochemical properties of the synthesized molecules were studied by cyclic voltammetry. On anodic sweep BTBQ and BTQ shows one irreversible wave corresponding to one electron oxidation of thiophene segment. No wave was observed for the BTPP on anodic sweep. However on cathodic sweep BTBQ and BTQ show one reversible wave corresponding to one electron reduction of quinoxaline segment and BTPP shows one irreversible wave suggesting stable one radical anion formation[11]. The reduction potential of BTPP is –1.26 V which is lower than BTQ and BTBQ. The HOMO and LUMO levels of BTPP are –5.76 eV and –3.15 eV respectively. Thus BTPP may acts as electron acceptor/transporter material since it has low reduction potential and its LUMO value is above 3.0 eV[12]. The observed parameters are reported in Table 2 and cyclic voltammogram is displayed in Figure 4a.

Table 2. Electrochemical and thermal data of BTQ, BTBQ and BTPP

Compd	E_{ax}^{peak} (V)	E_{red}^{peak} (V)	HOMO[a](eV)	LUMO[b](eV)	T_m ^0C[c]	T_d (^0C)[d]
BTQ	1.76	−1.69	−5.734	−2.717	143	262(283)
BTBQ	1.62	−1.39	−5.753	−3.033	157	293(321)
BTPP		−1.26	−5.496	−3.156	>300	190(221)

[a] *HOMO energy calculated from* E_{HOMO}= *Optical bandgap+LUMO,* [b] *LUMO energy calculated* $E_{LUMO} = -[E_{red}^{peak} - E_{red}(Fc/Fc^+) + 4.8]eV$*.* [c] *Melting point (Open capillary Method).* [d] *Decomposition temperature [5% and 10% (in parentheses) weight loss] derived by TGA.*

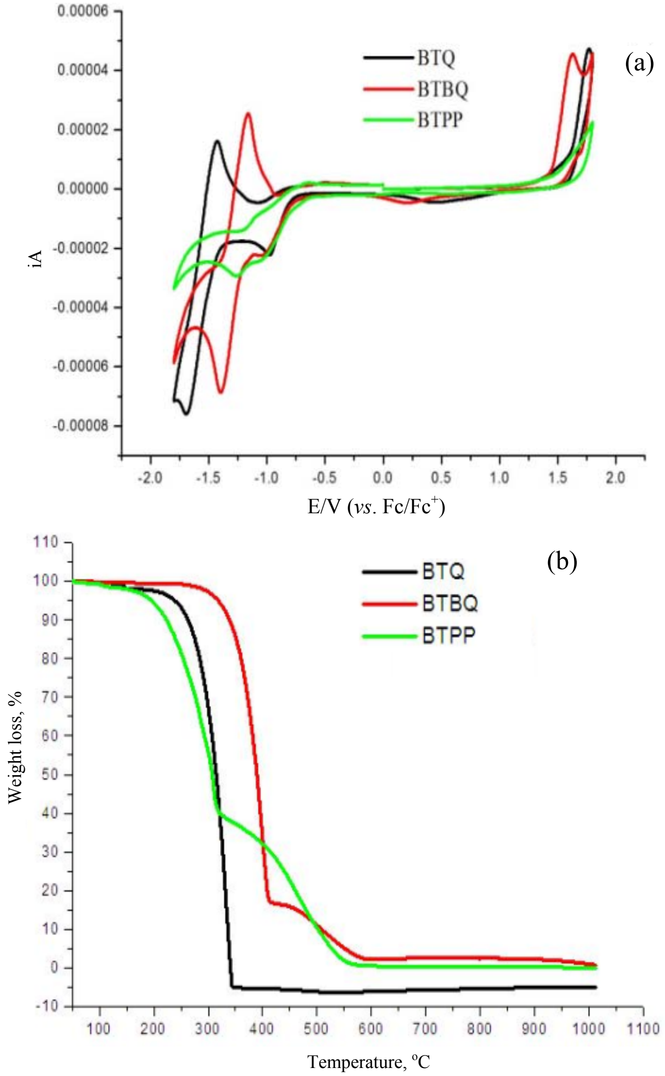


Figure 4. Cyclic voltammogram (**a**) and TGA thermogram (**b**) of BTQ, BTBQ and BTPP under nitrogen atmosphere

Thermal properties

Despite being relatively low molecular weight BTTP show amorphous nature and good thermal stability. The thermal stability of BTQ, BTBQ and BTPP (Figure 4b) was determined by Thermogravimetric analysis (TGA) at the temperature range of 30–1000 ^{0}C at a constant heating rate of 10 ^{0}C min^{-1} under nitrogen atmosphere. While the melting point of target molecules were less approximately determined by open capillary method. The decomposition temperature corresponding to 5% and 10% weight loss of BTPP are 190 ^{0}C and 221 ^{0}C (Table 2) respectively. However decomposition temperature of BTBQ and BTQ is slight higher than that of BTPP.

Conclusion

We have synthesized BTPP and compared its optoelectronic properties with BTQ and BTBQ. BTPP emits in green region in solution with good electron affinity. The above studies indicate that the increase in conjugation along with imine (C=N) group in quinoxaline skeleton of BTPP significantly lead to increase in electron affinity and decrease in band gap compared with BTQ and BTBQ. Hence based on above studies BTPP may act as electron acceptor/transporter material.

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