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# Synthesis, Cyclic Voltammetric Studies, and Electrogenerated Chemiluminescence of a New Phenylquinoline-Biphenothiazine Donor−Acceptor Molecule

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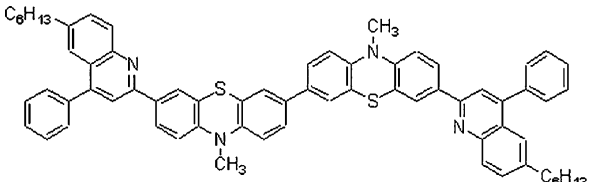
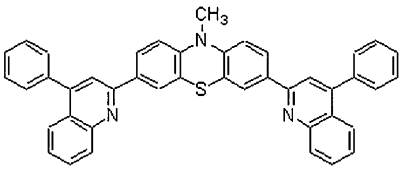
***Abstract:*** We report the synthesis, electrochemistry, and luminescence of a novel ECL emitting compound containing two electron-accepting hexyl-phenylquinoline groups covalently attached to the 3,3′-positions of the electron-donating 10,10′-dimethylbiphenothiazine group. The optimized geometry as determined from semiempirical MNDO calculations shows that the two quinoline groups are twisted 82.5° from the two phenothiazine rings, indicating a lack of electron delocalization among these groups. This unique geometry allows generation of localized radical cations and radical anions capable of generating ECL upon annihilation. However, the phenothiazine rings are twisted 46.5° relative to each other, suggesting possible interactions between the two moieties. This is evident in the electrochemical behavior in which two closely spaced one-electron oxidations, rather than a single two-electron oxidation wave, were observed. The photophysical properties of BHQ-BPZ show strong resemblances to the parent compound, BPQ-PTZ, which contains a single phenothiazine moiety. In addition, the ECL spectrum produced via radical ion annihilation shows good agreement with the fluorescence emission of the compound.

## Introduction

We report here the synthesis, the electrochemical and photophysical characterization of 7,7′-bis-(6-hexyl-4-phenylquinolin-2-yl)-10,10′-dimethyl-10*H*,10*H*′-[3,3′]biphenothiazinyl (BHQ-BPZ), as well as the electrogenerated chemiluminescence (ECL) that results from radical ion annihilation. Similar properties of the parent compound, BPQ-PTZ, have been previously reported.[1]



BHQ-BPZ



BPQ-PTZ

Radical ion annihilation ECL involves electron transfer between electrochemically generated radical ions resulting in an excited species that emits light. A typical reaction sequence can be represented as:

$$A + e^- \rightarrow A^{-\bullet} \quad \text{(reduction at electrode)} \tag{1}$$

$$D - e^- \rightarrow D^{+\bullet} \quad \text{(oxidation at electrode)} \tag{2}$$

$$A^{-\bullet} + D^{+\bullet} \rightarrow D^* + A \quad \text{(excited state formation)} \tag{3}$$

$$D^* \rightarrow D + h\nu \quad \text{(light emission)} \tag{4}$$

where D is frequently PAH.[2] In some situations, however, the radical cation or anion cannot be generated prior to the background oxidation or reduction of the solvent/supporting electrolyte used for electrochemistry. In this case, a second compound must be added to generate a stable radical counterion (a second reductant or oxidant to react with the radical cation or anion) required for annihilation.[2] In recent years, the field was advanced by the discovery of reaction schemes for generating ECL via the use of coreactants or other electrogenerated species capable of reacting with either the anion or the cation alone to produce the desired excited state. However, there are limitations in the choice of compounds or coreactants that can fulfill the energetic criteria as well as other solution criteria. Therefore, it is of great interest to investigate new compounds

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containing both donor and acceptor moieties that are capable of generating ECL. A few previous studies have investigated the generation of ECL through the direct attachment of a donor to an acceptor and have considered the possibility of the formation of charge-transfer states.[3,4] A previous study from our groups of the parent compound, BPQ-PTZ, showed that by attaching phenylquinoline to 10-methylphenothiazine (10-MP), we can electrochemically generate a stable radical anion upon the reduction of each individual quinoline group, which readily underwent electron transfer with electrochemically generated radical cations of phenothiazine to produce excited states that emit light.[1] In the present study, we investigated the photophysical, electrochemical, and ECL properties of the new donor−acceptor compound BHQ-BPZ, aimed at comparing the behavior of BHQ-BPZ and BPQ-PTZ, and especially noting the effect of the dimeric PTZ core in BHQ-BPZ. Both of these compounds are also important model systems for understanding the electronic processes and redox properties of related donor−acceptor conjugated polymers.[5,6]

## Experimental Section

**Materials.** 10-MP, acetyl chloride, anhydrous carbon disulfide ($CS_2$), 1,5-cyclooctadiene, 2,2′-bipyridine, bis(1,5-cyclooctadiene)nickel(0), *m*-cresol, triethylamine (TEA), anhydrous *N*,*N*-dimethylformamide, and diphenyl phosphate (DPP) were obtained from Aldrich and used as received. Bromine, sodium hydroxide, chloroform, and methanol were purchased from Fisher chemicals. The supporting electrolytes, $NBu_4B(C_6F_5)_4$ and $NBu_4B(C_6H_3(CF_3)_2)_4$, were prepared according to the published procedure.[7] The precursors, lithium tetrakis(pentafluorophenyl)borate etherate and sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, were obtained from Boulder Scientific Co. (Mead, CO). Other supporting electrolytes, tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) and tetra-*n*-butylammonium perchlorate (TBAP), were recrystallized twice and dried in a vacuum oven at 100 °C prior to transferring them directly into an inert atmosphere drybox (Vacuum Atmospheres Corp., Hawthorne, CA). Anhydrous benzene (Aldrich, ACS spectrophotometric grade), anhydrous acetonitrile (Aldrich, biotech grade), and anhydrous dimethylformamide (Aldrich, ACS spectrophotometric grade) were used without further purification. All solutions were prepared in a drybox with fresh anhydrous solvents and sealed in airtight vessels for measurements completed outside of the drybox.

**3-Bromo-10-methylphenothiazine (a).** This was prepared by following a reported method with a modified separation procedure.[8] Sodium hydroxide (4.12 g, 103 mmol) was dissolved in 250 mL of glacial acetic acid under argon. 10-MP (7.5 g, 35.15 mmol) was added, followed by chloroform (50 mL). The solution was cooled to 0−5 °C with an ice-water bath. Bromine (1.81 mL, 35.15 mmol) dissolved in glacial acid (30 mL) was added dropwise. The suspension was stirred at room temperature for 1 h. Acetic acid was removed by a rotavaporator, leaving behind a purple powder. The solid was dissolved in aqueous sodium bicarbonate (5% w/v, 100 mL) and dichloromethane (100 mL). The aqueous phase was separated from the organic phase and extracted with dichloromethane (100 mL). The combined organic phases were dried over $Na_2SO_4$ and filtered through a short silica gel column. The crude product was purified by flash chromatography on silica gel with ether−hexane (1:19) as eluent. Six grams of white crystals was obtained after recrystallization from toluene−ethanol (1:10). Yield: 63.3%. $^1$H NMR (200 MHz, $CDCl_3$), $\delta$ (ppm): 7.24 (m, 2H), 7.18 (m, 2H), 6.94 (m, 1H), 6.83 (d, 1H), 6.65 (m, 1H), 3.34 ($CH_3$, 3H). IR (KBr pellet), $\nu$ (cm$^{-1}$): 1587 (Ar), 1451. MS (ESI mode): Found M + 1, 292.2, 294.2; M − $CH_3$, 277.2, 279.2. $C_{13}H_{10}BrS$ requires M, 290.97, 292.97.

**3-Acetyl-7-bromo-10-methylphenothiazine (b).** First, 5.84 g of **a** (20 mmol) and 5.34 g of $AlCl_3$ (40 mmol) were dissolved in 20 mL of anhydrous $CS_2$ and cooled to 0−5 °C with an ice-water bath. Next, acetyl chloride (2.5 mL, 35.4 mmol) was added. The mixture was stirred for 3 h and poured into a mixture of ice (100 g) and concentrated HCl (20 mL). The organic phase was extracted with dichloromethane (50 mL), washed with water, and dried over anhydrous sodium sulfate. After the solvent was removed, 5.28 g of yellow solid was purified by flash chromatography on silica gel with chloroform as the eluent. Yield: 79.0%. $^1$H NMR (200 MHz, $CDCl_3$), $\delta$ (ppm): 7.78 (s, 1H, Ar−H), 7.69 (s, 1H, Ar−H), 7.26 (s, 2H, Ar−H), 6.80 (s, 1H, Ar−H), 6.66 (s, 1H, Ar−H), 3.37 (s, 3H, $CH_3N$), 2.52 (s, 3H, $CH_3CO$). IR (KBr pellet), $\nu$ (cm$^{-1}$): 3078, 2965, 2888, 1676 (C═O), 1593. MS (ESI mode): Found M + 1, 334.3, 336.3; M + Na, 356.2, 358.2; $C_{15}H_{12}BrNOS$ requires M, 332.98, 334.98.

**7,7′-Diacetyl-10,10′-dimethyl-10*H*,10′*H*-[3,3′]-biphenothiazinyl (c).** First, 1.65 g of $Ni(COD)_2$ (6 mmol) and 0.937 g of 2,2′-bipyridine (6 mmol) were added to a flask in a glovebox under argon. Next, degassed 0.74 mL of 1,8-cyclooctadiene (6 mmol) and 20 mL of anhydrous DMF were injected in with a syringe. The mixture was stirred for 30 min at 60 °C to form a dark blue catalytic solution. In another flask, 3.342 g of **b** (10 mmol) was dissolved in dry DMF under argon. The catalytic solution was slowly transferred into solution **b** by a double-ended needle. The mixture was stirred overnight and finally was poured into 100 mL of methanol containing 1 mL of concentrated HCl. A yellow powder was precipitated and filtered out. The crude product was purified by silica gel chromatography with ether/chloroform (v/v: 1/9) as the eluent, and 3.81 g of product was obtained. Yield: 75%. $^1$H NMR (499 MHz, $CDCl_3$), $\delta$ (ppm): 7.79 (b, 4H, Ar−H), 7.26 (b, 12H, Ar−H), 6.86 (b, 4H, Ar−H), 3.45 (s, 6H, 2 × $CH_3N$), 2.54 (s, 6H, 2 × $CH_3CO$). IR (KBr pellet), $\nu$ (cm$^{-1}$): 1665 (C═O), 1602, 1575 (C═C stretching in Ar). MS (ESI mode): Found M + 1, 509.2. $C_{30}H_{24}N_2O_2S_2$ requires M, 508.13.

**Synthesis of BHQ-BPZ.** This compound was prepared by following the reported procedure for the synthesis of oligoquinolines and polyquinolines.[9] First, 0.675 g of 2-amino-5-hexylbenzophenone (2.4 mmol) and 0.509 g of **c** (1 mmol) were added along with 5 g of diphenyl phosphate (DPP) and 5 g of *m*-cresol in a glass reactor fitted with a mechanical stirrer, two glass inlets, and a sidearm. Next, the reaction mixture was purged with argon for 20 min, and then the temperature was gradually raised to 90 °C under argon atmosphere for 1 h and then to 140 °C for 12 h. After being cooled, the product was precipitated in a solution of 100 mL of methanol/40 mL of triethylamine (TEA). The yellow powder was extracted with 10% TEA/methanol solution overnight and recrystallized in a mixture of toluene/ethanol (2/8 v/v), and 720 mg of BHQ-BPZ was obtained. Yield: 72%. No melting transition was observed by a differential scanning calorimetry (DSC) scan under nitrogen; however, an apparent onset of decomposition was observed at 220 °C. $^1$H NMR (200 MHz, $CDCl_3$), $\delta$ (ppm): 8.14 (s, 1H), 8.10 (s, 1H), 8.04 (s, 3H), 8.01 (s, 1H), 7.71 (s, 2H), 7.56 (m, 14H), 7.36 (m, 4H), 6.90 (m, 4H), 3.46 (s, 6H), 2.71 (t, $J$ = 18.7 Hz, 4H, 2 × $CH_2$−Ar), 1.64 (m, 4H), 1.30 (m, 12H, 6$CH_2$), 0.87 (t, 6H, 2$CH_3$). IR (KBr pellet), $\nu$ (cm$^{-1}$): 2955 ($CH_3$ asy stretch), 2923 ($CH_2$ stretching), 2852 ($CH_2$ stretching), 1584 (C═C stretching). MS (ESI mode): Found M + 1, 999.8; (M + 2)/2, 500.6. $C_{68}H_{62}N_4S_2$ requires M: 998.44. UV−vis, $\lambda_{max}$ (nm) (benzene): 396 (log $\epsilon$ = 4.67).

**Characterization.** The FT-IR spectra were obtained with KBr pellets by using a Bruker Vector 33 Fourier transform infrared spectrometer under nitrogen. $^1$H NMR spectra were measured at 200 MHz on a

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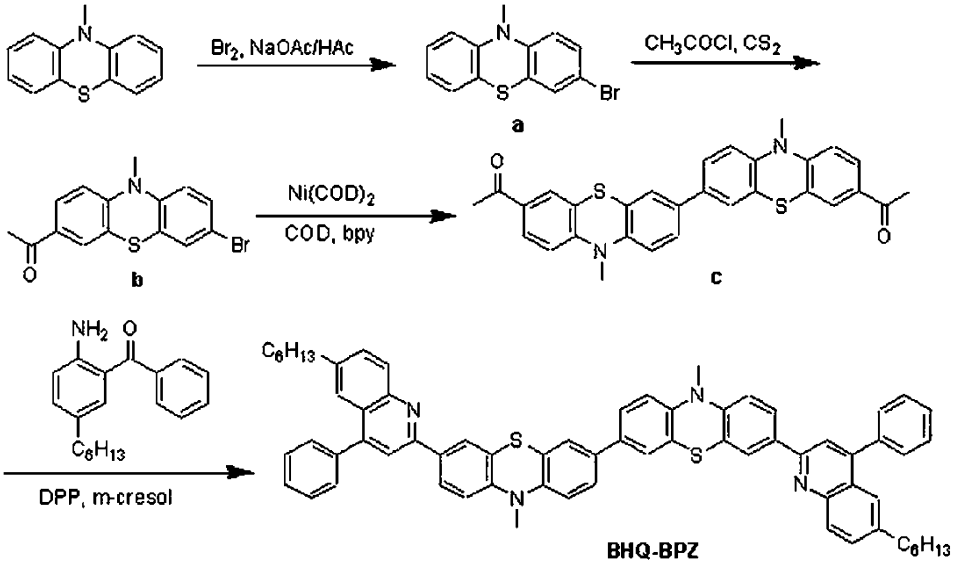
***Scheme 1***




Bruker DPX200 or at 499 Hz on a Bruker DRX499 instrument. Mass spectra were recorded on a Bruker Esquire LC/ion trap mass spectrometer using ESI mode.

All fluorescence spectra were recorded on a Fluorolog-3 spectrofluorimeter (ISA-Jobin Yvon Hariba, Edison, NJ) using a slit width of 1 nm and a resolution of 1.5 nm. All UV−visible spectra were recorded on a Milton Roy Spectronic 3000 array spectrophotometer. The absorbance and fluorescence spectra of BHQ-BPZ were obtained with a 20 $\mu$M solution prepared with 1.5:1 PhH/MeCN. The relative fluorescence efficiency was measured using a 20 $\mu$M solution in PhH/MeCN (1.5:1) and calibrated with diphenylanthracene (DPA) as a standard ($\lambda_{exc}$ = 380 nm; $\Phi_{dpa}$ = 0.91 in benzene).[10]

Cyclic voltammograms were recorded on a CH Instruments Electrochemical Work Station (Austin, TX). The working electrode in all cases consisted of an inlaid platinum disk (2.0 mm diameter) that was polished on a felt pad with 0.05 $\mu$m alumina (Buehler, Ltd, Lake Bluff, IL) and sonicated in water and absolute EtOH for 2 min and then dried in a oven at 100 °C before being transferred into an inert atmosphere drybox. A platinum ultramicroelectrode (25 $\mu$m) was also utilized as a working electrode to obtain steady-state cyclic voltammograms. A platinum wire served as a counter electrode, and a silver wire served as a quasi reference electrode. The concentrations and solvents used to obtain each voltammogram are given in the corresponding figure caption. All potentials were calibrated versus an aqueous SCE by the addition of ferrocene as an internal standard taking $E_{(Fc/Fc^+)}{}^0$ = 0.424 V vs SCE.[11] Digital simulations were performed using Digisim V 3.03 (Bioanalytical Systems Inc., West Lafayette, IN). All electron-transfer reactions were considered fast ($k_o$ = 10 000 s$^{-1}$); all $\alpha$ values were taken to be 0.5. Other parameters used for the digital simulations are given in the figure caption.

All ECL measurements were performed as previously reported.[12] Measurements were obtained with 1 mM BHQ-BPZ solutions, 0.1 M in supporting electrolyte in several different solvent mixtures. To generate the annihilation reaction, the working electrode was pulsed between the first oxidation and reduction peak potentials of BHQ-BPZ with a pulse width of 0.1 s. The resulting emission spectra were obtained with a charged coupled device (CCD) camera (Photometrics CH260, Photometrics-Roper Scientific, Tucson, AZ) that was cooled to −100 °C. Integration times were 2 min. The CCD camera and grating system were calibrated with a mercury lamp prior to each measurement.

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## Results and Discussion

**Synthesis and Characterization.** Scheme 1 describes the synthetic route to BHQ-BPZ. After monobromination of 10-methylphenothiazine, we prepared 3-acetyl-7-bromo-10-methylphenothiazine by the Friedel−Crafts acylation reaction. The 3,3′-biphenothiazine **c** was obtained by the Yamamoto coupling reaction of **b**. We first tried to synthesize a derivative of BHQ-BPZ without the hexyl groups; however, the resulting product was not soluble in normal solvents such as benzene, toluene, and chloroform. Introduction of hexyl groups into the BHQ-BPZ substantially improved the solubility in these solvents.

The molecular structures of all of the intermediates and BHQ-BPZ were confirmed by $^1$H NMR, FTIR, and mass spectra. The NMR and FTIR spectra, which were summarized in the Experimental Section, confirmed the attachment of phenylquinoline rings to the biphenothiazine moiety and the completion of the cyclization reaction forming the quinoline rings. In particular, the strong carbonyl peak in the FTIR spectrum of 3,7-diacetyl-10-methylphenothiazine (1666 cm$^{-1}$), due to the acetyl groups, was completely absent in the spectrum of BHQ-BPZ. Instead, new strong bands in the 1400−1600 cm$^{-1}$ range that are characteristic of the quinoline ring imine (C=N) group were observed in BHQ-BPZ.[9] Proton resonance due to the acetyl group was also completely absent in the spectrum of BHQ-BPZ, while new aromatic proton resonances characteristic of quinoline ring appeared. The ratio of the integration of the biphenothiazine methyl proton resonances to those of the hexyl ones in the $^1$H NMR spectrum was in accord with the proposed structure. Furthermore, the electrochemical and photophysical properties of BHQ-BPZ described below are all in agreement with the molecular structure.

**Absorption and Emission Spectroscopy.** Absorption and fluorescence spectra of BHQ-BPZ in 1.5:1 PhH:MeCN are shown in Figure 1. The absorption spectrum shows a broad band ranging from 350 to 460 nm with a $\lambda_{max}$ at around 396 nm. The same solution emitted in the green-yellow region when excited at 393 nm ($\lambda_{max}$ = 550 nm) with a fluorescence efficiency, $\Phi$ = 0.29, smaller than that of BPQ-PTZ which shows a fluorescence efficiency of 0.70 under the same experimental conditions.[1] This compound shows evidence of

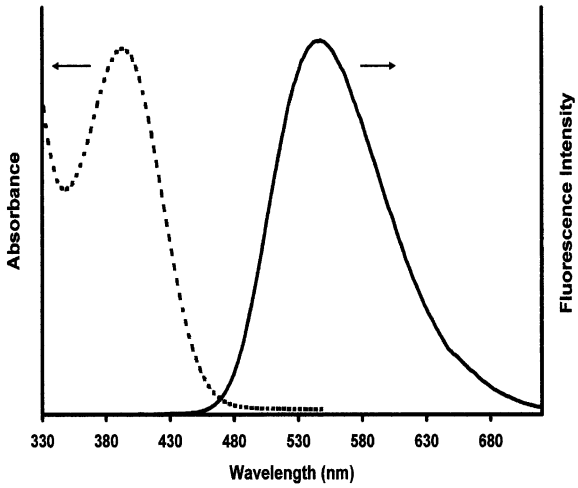


***Figure 1.*** Optical absorption (dotted line) and fluorescence spectrum (solid line) of a 20 $\mu$M solution of BHQ-BPZ in 1.5:1 PhH/MeCN (excitation wavelength, 393 nm).

solvatochromism in which both the absorption and the emission wavelengths red shifted slightly with increasing polarity of the solvent. In PhH/DMF (1:2), the absorption maximum was at 399 nm, while the emission maximum was at 558 nm. In both solvent mixtures, the absorption and emission bands are very broad and without any vibrational structure. The breadth of the absorption and emission bands can be attributed to the decreased planarity of the molecules caused by the large steric interactions within the molecule. A relatively large Stokes shift of 150 nm was observed between the absorption and emission spectra maxima. This large shift was also observed with the parent molecule, BPQ-PTZ, as well as with 10-MP. This shift can be attributed to changes in the molecular structure of the phenothiazine moieties upon excitation, in which the difference in energy between the geometrically relaxed ground state and the nonrelaxed excited singlet state is larger than the energy difference between the geometrically relaxed excited state and the nonrelaxed ground state.[13] Additionally, the fluorescence spectrum of BHQ-BPZ is slightly red shifted (~10 nm) when compared to those of BPQ-PTZ obtained under the same experimental conditions. This shift could be due to a different rearrangement of solvent molecules in the transient ground state and singlet-excited state, because of the presence of two flexible aliphatic chains in addition to an extra phenothiazine moiety. Based on the absorption and emission wavelength of the compound, the energy needed to generate the first singlet-excited state is about 2.68 eV; therefore, it is this energy that must be generated in the electrochemical annihilation reaction of the radical ions to generate the singlet-excited state and ECL emission. The singlet energy of BHQ-BPZ is comparable to that of the parent compound, BPQ-PTZ, which suggests that the two phenothiazine groups are not in the same plane and that their molecular orbitals do not interact strongly with each other. More extensive delocalization between the two PTZ groups would have caused a significant shift in the absorption and emission bands.

**Electrochemical Properties of BHQ-BPZ.** Cyclic voltammograms of BHQ-BPZ in various solvent−electrolyte systems obtained at a platinum electrode are shown in Figures 2 and 3. As observed, the cyclic voltammograms obtained in PhH/MeCN (1.5:1) and PhH/DMF (1:2) showed similarities. The oxidation of BHQ-BPZ in PhH/DMF (1:2) with $TBAPF_6$ was characterized by two broad oxidation waves observed at peak potentials of +0.81 and +1.30 V vs SCE. Upon close examination, the first broad wave is composed of two closely spaced oxidation waves, with an irreversible wave superimposed onto a quasi-reversible one. The wave separation is more pronounced in Figure 2b where only the first broad oxidation wave and the first reduction wave are present. These two closely spaced oxidation waves probably correspond to the formation of the radical cation at $E_p$ of +0.69 V vs SCE (representing oxidation of one PTZ) and the less stable dication at $E_p$ of +0.81 V vs SCE (representing oxidation of the second coupled PTZ). Due to the instability of the dication in this solvent system, the reverse wave observed at −0.63 V vs SCE most likely represents the reduction of the cation radical and some of the dication. At higher scan rates, the wave separation between the first and second oxidation was more pronounced; however, no defined reversal wave was observed for the second oxidation in this solvent−electrolyte system. The fact that these two closely spaced oxidation waves are one-electron waves ($n \approx 1$) suggests that the two PTZ groups are not completely electronically decoupled, so that these two waves represent individual one-electron oxidation of each PTZ at a slightly different potential. The overlapping oxidation waves indicate that the two PTZ moieties have some molecular orbital interactions; however, these are not strong enough to significantly alter the photophysical properties of the compound.

The broad irreversible oxidation wave observed at a peak potential of +1.39 V vs SCE corresponds to the formation of the highly reactive trication and tetracation. Similar to the first two oxidations, this broad wave is also composed of two closely spaced oxidations, although this is not as apparent as the separation of the first two waves. The irreversibility in the oxidation of the dication, trication, and tetracation is probably due to a following chemical reaction with trace water or the solvent, MeCN.[14] Prolonged cycling at potentials where the dication is generated leads to film formation on the surface of the electrode. Moreover, the solution color changes from yellow to red upon bulk electrolysis at a potential sufficiently positive to generate both trications and tetracations.

Upon scanning in the negative direction to −3.0 V vs SCE, three reduction waves were observed: one reversible wave with a half wave potential of −2.00 V vs SCE and two irreversible waves with peak potentials of −2.58 and −2.84 V vs SCE. In a separate experiment where a non-ion pairing electrolyte was used, the steady-state voltammograms obtained with a 25 $\mu$m platinum electrode showed that the first two oxidations are consecutive one-electron oxidations, while the first reduction wave displayed characteristics of a single two-electron wave (Supporting Information). This reversible reduction wave, therefore, corresponds to the formation of the radical anion on each of the PQ groups that are reduced at essentially the same potential. This wave was near nernstian with $i_{pa}$ and $i_{pc}$ proportional to $v^{1/2}$ indicating diffusion control. Additionally, the ratio of the peak currents ($i_{pc}/i_{pa}$) was unity, indicating no following chemical reactions. However, $E_{pa}$ and $E_{pc}$ shifted

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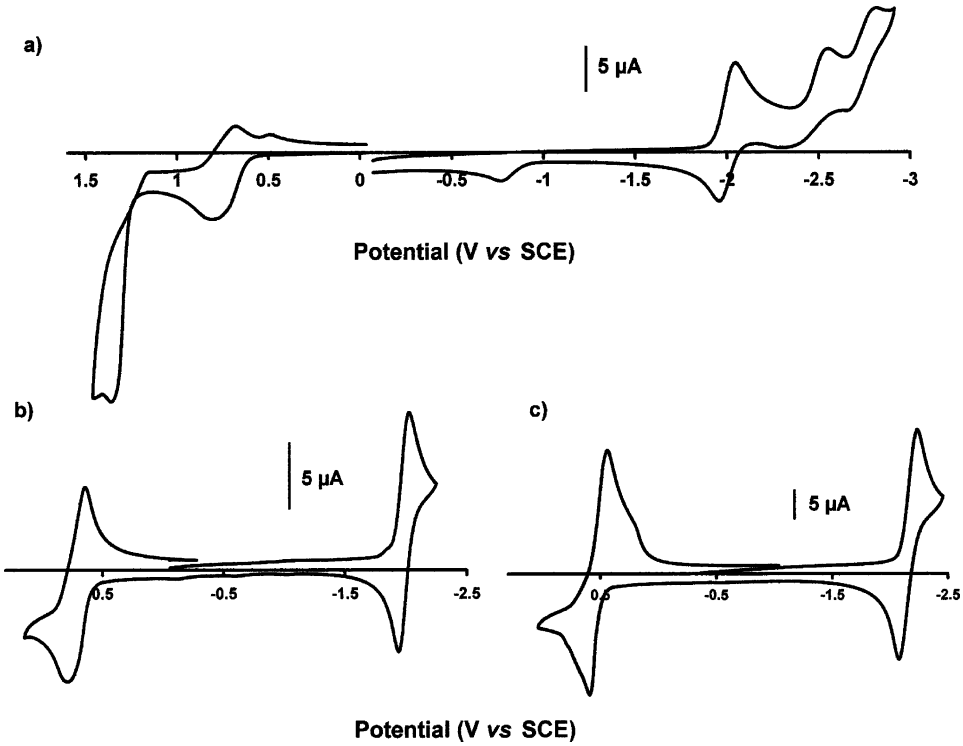


***Figure 2.*** Cyclic voltammograms of a 1 mM solution of BHQ-BPZ in (a,b) 0.1 M $TBAPF_6$ in 1:2 PhH/DMF, with different scan limits, and (c) 0.1 M $TBAPF_6$ in 1.5:1 PhH/MeCN at a platinum electrode (area = 0.015 $cm^2$) (scan rate, 200 mV/s).

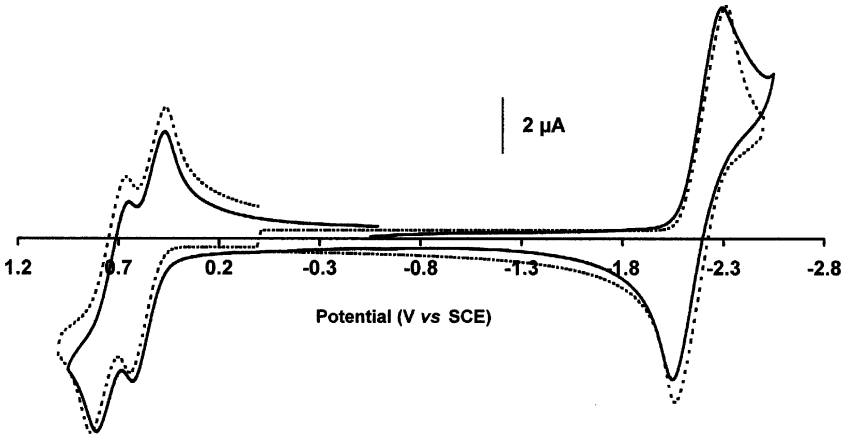


***Figure 3.*** Cyclic voltammogram of a 1 mM solution of BHQ-BPZ in 0.125 M $[NBu_4][B(C_6F_5)_4]$ in 20:1 PhH/DMF at a platinum electrode (area = 0.013 $cm^2$) (scan rate, 200 mV/s) (solid line). The dotted line shows a simulated voltammogram of BHQ-BPZ at a scan rate of 0.2 V/s. Parameters used in the simulation were $R$ = BHQ-BPZ, $E_{R/R^{2+}}{}^0 = 0.6$ V vs SCE, $E_{R/R^{2+}}{}^0 = 0.8$ V vs SCE, $E_{R/R^{\cdot-}}{}^0 = -2.13$ V vs SCE, $E_{R/R^{2-}}{}^0 = -2.18$ V vs SCE, $c_{(R)} = 1$ mM, $R_u = 10\,000\ \Omega$, $C_d = 1.5\ \mu$F, $T = 289.2$ F, planar electrode area = 0.013 $cm^2$. All species were assumed to have a diffusion coefficient of $1 \times 10^{-5}$ $cm^2/s$.

slightly with the scan rate because of uncompensated resistance. The fact that the first reduction occurs in a two-electron wave ($n \approx 2$) indicates that the two phenylquinoline groups are not electronically coupled through the PTZ moieties, so that this wave represents individual one-electron reduction of each PQ at essentially the same potential.[15] This also suggests that the highest filled MO in the PTZ moiety is not greatly perturbed by the attached PQ groups and that the lowest unoccupied MOs of the PQs are similarly not affected by the PTZ. This same observation was also found with the parent molecule, BPQ-PTZ, and is consistent with the theoretically determined structure of the molecule, which will be discussed in the next section.

The second and third reduction steps were irreversible processes, presumably because the more highly reduced species formed upon reduction of the dianion are sufficiently basic to abstract protons from any source present in the medium, including trace water and MeCN. Even in an aprotic medium, this protonation reaction is very fast in comparison to the time of the voltammetric experiments, thus making the reduction waves irreversible ($i_{pc} \gg i_{pa}$) at scan rates up to 50 V/s.[16] Additionally, upon reversing the sweep direction, after a scan beyond the second reduction wave, a new oxidation wave appeared at −0.7 V vs SCE (Figure 2a). This wave probably corresponds to the oxidation of a protonated species that is easier to oxidize than the parent compound. Similar redox behavior

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was observed with 1.5:1 PhH/MeCN as the solvent (Figure 2c), with one notable difference in the oxidation waves, where the cation radical and dication appear to form a precipitate, as indicated by the CV wave shape. This probably involves the anion of the supporting electrolyte, $TBAPF_6$, in this medium.

Certain weakly coordinating electrolytes have been shown by Geiger and co-workers to be very effective in solubilizing cations produced in anodic electrochemical reactions and minimizing ion pair formation.[7,17] On the basis of previous studies, $NBu_4B(C_6F_5)_4$ and $NBu_4B(C_6H_3(CF_3)_2)_4$ were chosen as the two non-interacting electrolytes in this study. The structures of these two electrolytes are shown in the Supporting Information. Figure 3 shows the cyclic voltammogram of BHQ-BPZ obtained in 0.125 M of $NBu_4B(C_6F_5)_4$ in PhH/DMF (20:1). A higher concentration of electrolyte was used to lower the resistance in this highly resistive medium. In this solution, two well-separated oxidation waves appeared with peak potentials of +0.63 and +0.83 V vs SCE, and the second oxidation showed a quasi-reversible behavior when compared to the cyclic voltammogram obtained in the presence of $TBAPF_6$ as the electrolyte. This indicates that both the cation radical and the dication are less ion-paired in the presence of this electrolyte, and this promotes separation of the two closed-spaced oxidation waves.[7] A third, irreversible, oxidation wave was observed at a peak potential of +1.53 V vs SCE. Similar to the behavior observed in the DMF/PhH system, this broad irreversible wave probably corresponds to the formation of the unstable trication and tetracation. The reduction of BHQ-BPZ in this solvent−electrolyte system was characterized by a reversible reduction wave at a half wave potential of −2.12 V vs SCE, a value slightly more negative than the reduction potential observed in the solvent−electrolyte systems discussed above. In this solvent−electrolyte system, the last two irreversible reduction waves were not observed prior to the reduction of the background. However, those redox reactions are not the focus of this study because the electrochemical stability of the first oxidation and reduction is most important in determining the compound's ECL efficiency.

Overall, the electrochemistry of BHQ-BPZ was similar to that of the parent compound, BPQ-PTZ, in all of the solvent−electrolyte systems studied. The observed reduction potentials ($E_{1/2.1}$ = −1.96 V, $E_{p.2}$ = −2.61 V vs SCE) and oxidation potentials of BPQ-PTZ ($E_{1/2.1}$ = +0.69 V, $E_{p.2}$ = +1.32 V vs SCE) are very close to the redox potentials of BHQ-BPZ. The redox potentials of BPQ-PTZ were previously shown to be very close to the redox potentials of the parent compounds, 10-MP and 2-phenylquinoline (2-PQ), indicating that oxidation was occurring in the PTZ moiety and reduction was occurring on the quinoline group.[1] Because of the electrochemical similarities between BPQ-PTZ and BHQ-BPZ, the oxidation of BHQ-BPZ probably also occurs at the two PTZ moieties and the reduction occurs at the two quinoline groups. The two major differences in their electrochemical properties are the presence of two closely spaced oxidations of the two PTZ rings and the presence of a third reduction wave. The overlapping, but split, oxidation waves suggest that the two PTZ moieties have some intramolecular interaction, so that oxidation of the first phenothiazine ring makes it somewhat more difficult to oxidize the adjacent phenothiazine ring. If the two PTZ groups were completely out of plane or orthogonal to one another, a single two-electron oxidation wave, similar to the two-electron reduction wave of the noninteracting quinoline groups, would be observed. As with BPQ-PTZ, the lack of a major shift in the half wave potentials in the oxidation and reduction of BHQ-BPZ when compared to 10-MP and 2-PQ suggests the absence of any intramolecular and intermolecular charge transfers occurring at this concentration.[18] To confirm the proposed electrochemical processes of BHQ-BPZ in this solvent−electrolyte system, digital simulations of the cyclic voltammetry were carried out. Figure 3 shows two simulated CVs (dotted line) in a 1 mM solution of BHQ-BPZ at a scan rate of 0.2 V/s, with the parameters shown in the figure caption. The good fit between the experimental and theoretical voltammograms supports the assumption that the first two oxidation waves obtained experimentally are two closely spaced consecutive one-electron oxidations, and the first reduction wave involves a two-electron reduction at essentially the same reduction potential or, more exactly, two one-electron reductions with a potential difference less than 50 mV.

MNDO semiempirical calculations were used to obtain the optimized molecular geometry of this compound to determine a possible reason for the localization of charge upon the oxidation and reduction of BHQ-BPZ.[19] As shown in Figure 4a and b, the phenothiazine rings are twisted by 82.5° from the plane of the quinoline substituents, while the phenyl groups appended onto the quinolines are twisted 87.5° relative to these moieties. This geometry suggests minimal molecular orbital overlap between the $\pi$ orbitals of the quinoline groups and the $\pi$ orbitals of the phenothiazine leading to little delocalization of the electronic charge. Moreover, one phenothiazine ring is twisted by 46.5° relative to the adjacent phenothiazine ring, suggesting some charge delocalization between the two rings. This is evident in the electrochemical behavior of BHQ-BPZ in which the two oxidation waves of the PTZ moieties were slightly separated instead of behaving like a single two-electron oxidation wave occurring at the same potential. Results obtained from the same calculation also confirmed the localization of the HOMO and HOMO−1 orbitals on the phenothiazine moieties and the LUMO and LUMO+1 orbitals on the phenylquinoline subunits, which further support the observed electrochemical behavior. However, the calculated energy difference between the HOMO and HOMO−1 orbitals was only 0.014 eV, slightly less than half of 0.035 eV, the energy difference between the LUMO and LUMO+1 orbitals. However, because of the importance of solvation effects and ion-pairing interactions, these small, calculated energy differences cannot be directly compared to the potential differences observed in the electrochemistry.

In addition, the MO energies were calculated as a function of the angles between the PTZ and PQ moieties in the molecule. When compared to the planar geometry where the PTZ and PQ groups are coplanar (angle = 0°) to each other, the calculated HOMO and LUMO energies of the molecule in its nonplanar ground-state geometry were slightly larger; that is, the HOMO and LUMO energies of the bent molecule were about 0.39 and 0.28 eV higher than the HOMO and LUMO energies of the

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(19) MNDO semiempirical calculations performed with HyperChem by Hypercube, Inc., Gainesville, FL.

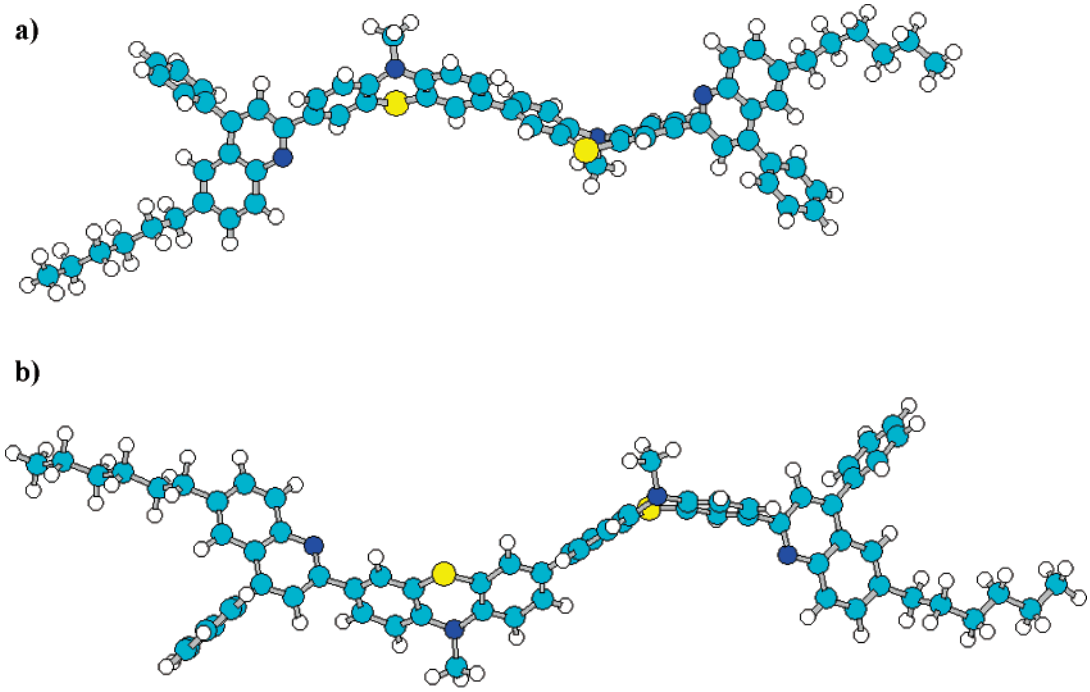


***Figure 4.*** Two views of BHQ-BPZ with optimized ground-state molecular geometry as calculated by MNDO semiempirical calculations.

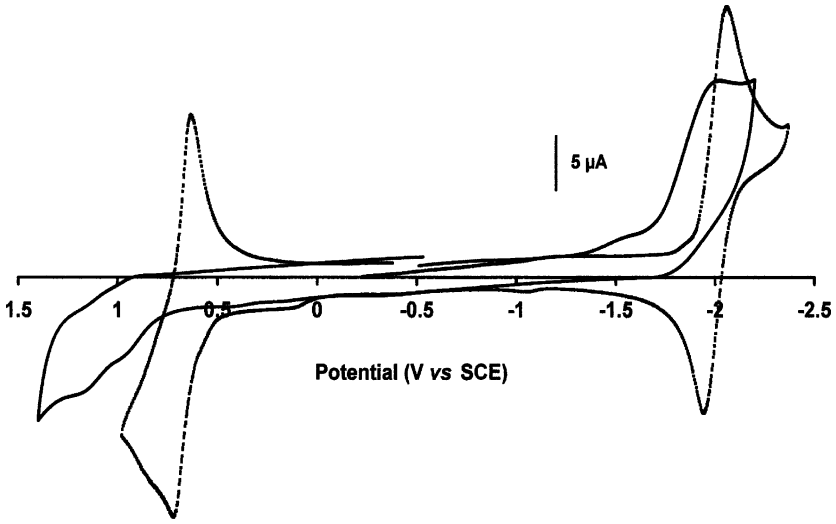


***Figure 5.*** Cyclic voltammograms of a 1 mM solution of BHQ-BPZ in 1:2 PhH/DMF at a platinum electrode before (dotted line) and after 200 cycles between 0.0 and 1.0 V (vs SCE) (solid line) (0.1 M $TBAPF_6$; scan rate, 200 mV/s).

planar molecule, respectively. This, again, suggests that the planar geometry promotes $\pi$ electron delocalization, making it easier to oxidize and reduce as well as decreasing the total annihilation energy of the molecule, while the optimized ground-state conformation limits MO interactions between the PTZ and PQ groups, leading to higher redox potentials. Thus, on the basis of the calculated structure, MO energies, and electrochemical results, we can conclude that the two closely spaced oxidations observed in the cyclic voltammogram involve the formation of the cation radical in each phenothiazine group, while the next two oxidations are the formation of the trication and tetracation. Furthermore, the structure shows that the two-electron reduction wave of BHQ-BPZ represents formation of the radical anion on each of the quinoline groups, while the second and third reductions represent formation of the dianion and trianion on each group.

As shown in Figure 5, upon continuous potential cycling over the range that encompassed the first two oxidations (0 to +1.0 V vs SCE), the two oxidation waves showed a pronounced loss of reversibility, as did the reduction wave. This loss of reversibility indicates a following chemical reaction involving the dication, that is, the radical cation of each phenothiazine moiety. Because the two oxidation waves are near one another, the radical cation cannot be generated without generating some unstable dication. Thus, even when the cycling was performed to a less positive potential than the oxidation potential of the radical cation (i.e., to +0.7 V vs SCE), a loss in reversibility was observed, but at a rate slower than when the cycling potential was positive enough to generate the dication. On the contrary, upon extensive cycling in the negative region where the dianion, tetraanion, and hexaanion were formed, no sign of loss of reversibility or film formation was present. The products

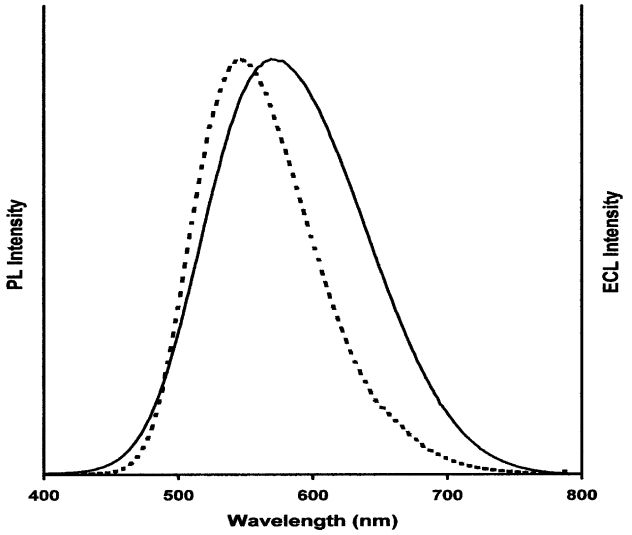


***Figure 6.*** Fluorescence spectra (20 $\mu$M) of BHQ-BPZ in 1.5:1 PhH/MeCN (dotted line) and ECL spectra (solid line) of 1 mM BPQ-PTZ in 0.1 M $TBAPF_6$ in 1:2 PhH/DMF with pulsing (0.1 s) between 0.70 and −2.05 V (vs SCE).

of the dication reaction form an insoluble film on the surface of the platinum-working electrode that alters the electrochemical behavior of both BHQ-BPZ and BPQ-PTZ in solution and that of the internal potential standard, ferrocene (voltammogram not shown). In the presence of the noninteracting electrolytes, the second oxidation wave was quasi-reversible instead of totally irreversible, as shown in Figure 3. In this case, the enhanced stability of the dication slowed the rate of electrode filming and the loss of reversibility of the redox waves.

As a final note, the total standard enthalpy of the annihilation reaction ($\Delta H_{ann}° = \Delta G_{ann}° + T\Delta S°$), which is based on the difference between the half peak potentials of the first oxidation and first reduction wave in the cyclic voltammogram ($\Delta E_{p(ox/red)} \approx 2.8$ eV) with entropy effects (~0.1 eV) subtracted out, is about 2.7 eV.[2] This energy, which is available upon radical ion annihilation, is greater than that required to directly populate the singlet-excited state (2.68 eV) as previously determined from the absorption and fluorescence spectra.

**Electrogenerated Chemiluminescence.** When an electrode immersed in a 1.0 mM solution of BHQ-BPZ is pulsed between the compound's first oxidation and reduction waves, a bright yellow light that is visible by eye in a darkened room is produced at the electrode surface. The ECL spectrum of BHQ-BPZ obtained in DMF:PhH (2:1) containing 0.1 M of $TBAPF_6$ as supporting electrolyte is shown in Figure 6. Although the light appeared to be fairly strong during the first few pulses, the instability of the dication as well as filming prevented obtaining stable ECL over a long period of time (i.e., 8 min) in this solvent−electrolyte system. However, by keeping the potential about 150 mV before the second oxidation peak potential, we could observe relatively efficient ECL. In systems containing $NBu_4B(C_6F_5)_4$ or $NBu_4B(C_6H_3(CF_3)_2)_4$, more stable ECL was observed due to the enhanced stability of the dication. In addition, the more pronounced separation between the two oxidation waves allowed generation of the radical cation without generating a large amount of dication. Thus, the observed ECL from these systems lasted about 20 min without a significant decrease in intensity or film formation. However, prolonged potential cycling or pulsing for about 1 h promoted generation of quenchers and film formation on the electrode surface, which eventually led to the loss of any observable light.

In a typical ECL experiment, the radical anion reacts with the radical cation; however, in our case, we are generating the radical cation, the dianion, and a small amount of dication upon oxidation and reduction. However, as shown in our group's previous studies on similar systems with rubrene and $Ru(bpy)_3^{2+}$ (where bpy represents 2,2′-bipyridine), the ECL efficiencies of such systems were lower when compared to systems where only the radical cation and anion were generated, because of the lack of unit probability of such reactions as well as the generation of a large amount of local quenchers (i.e., radical anions).[20,21] In this system, the dications are quite reactive and probably do not participate significantly in generating ECL via this route. Overall, the excited BHQ-BPZ can be produced via at least two possible electron-transfer mechanisms:

Mechanism I:

$$^{-\bullet}\text{PQ-PTZ-PTZ-PQ}^{-\bullet} + \text{PQ-PTZ}^{+\bullet}\text{-PTZ-PQ} \rightarrow {}^{-\bullet}\text{PQ-PTZ-PTZ-PQ} + (\text{PQ-PTZ-PTZ-PQ})^* \quad (5)$$

$$^{-\bullet}\text{PQ-PTZ-PTZ-PQ} + \text{PQ-PTZ}^{+\bullet}\text{-PTZ-PQ} \rightarrow \text{PQ-PTZ-PTZ-PQ} + (\text{PQ-PTZ-PTZ-PQ})^* \quad (6)$$

Mechanism II:

$$^{-\bullet}\text{PQ-PTZ-PTZ-PQ}^{-\bullet} + \text{PQ-PTZ-PTZ-PQ} \rightleftarrows 2\ {}^{-\bullet}\text{PQ-PTZ-PTZ-PQ} \quad (7)$$

$$^{-\bullet}\text{PQ-PTZ-PTZ-PQ} + \text{PQ-PTZ}^{+\bullet}\text{-PTZ-PQ} \rightarrow \text{PQ-PTZ-PTZ-PQ} + (\text{PQ-PTZ-PTZ-PQ})^* \quad (8)$$

The ECL of BHQ-BPZ is characterized by a broad emission band between 450 and 800 nm, with an emission maximum at 575 nm. When compared to the fluorescence spectrum, the ECL spectrum appears slightly broader in shape and slightly shifted to lower energy (25 nm). This is probably due to an inner filter effect as a result of the high concentrations of the compound needed to obtain measurable ECL, as well as the difference in resolution between the two instruments where the spectra were collected. In addition, the observed ECL emission band shows significant emission in the longer wavelength region as compared to the fluorescence spectrum. This emission might be due to the formation of side products generated during the annihilation. However, no change in the absorption and fluorescence spectra was observed before and after extensive potential cycling, eliminating this possibility. The longer wavelength component in the ECL could also be due to the formation of excited-state aggregates at the concentration used to obtain the spectrum. No shorter wavelength absorption band was present even at concentrations down to 1.25 $\mu$M in several solvent systems, suggesting the lack of ground-state aggregates. Moreover, due to steric hindrance, the ground-state molecular conformation appears to be nonplanar which discourages formation of ground-state aggregates; however, it is difficult to predict the conformation of the molecule in its excited state. Although we could not exclude the presence of excited-state

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(21) Tokel-Takvoryan, N. E.; Hemingway, R. E.; Bard, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 6582.

aggregates, no major shift in the fluorescence wavelength was observed even at concentrations up to 1 mM.

Another possible explanation is the presence of an intramolecular charge-transfer emission between the radical anion of PQ and the radical cation of PTZ. The proposed mechanism is as follows:

$$\text{PQ-PTZ-PTZ}^{+\bullet}\text{-PQ} + {}^{-\bullet}\text{PQ-PTZ-PTZ-PQ}^{-\bullet} \rightarrow {}^{-\bullet}\text{PQ-PTZ-PTZ-PQ} + (\text{PQ-PTZ-PTZ}^{+\bullet}\text{-PQ}^{-\bullet})^* \quad (9)$$

$$(\text{PQ-PTZ-PTZ}^{+\bullet}\text{-PQ}^{-\bullet})^* \rightarrow \text{PQ-PTZ-PTZ-PQ} + h\nu \quad (10)$$

Preliminary measurement of fluorescence spectra of BHQ-BPZ in solvents such as DMF, MeCN, and PhH shows evidence of solvatochromism, suggesting some intramolecular charge-transfer character.

Due to the enhanced stability of the dication in addition to a more pronounced wave separation in systems containing weakly coordinating electrolytes, the ECL efficiency of BHQ-BPZ was obtained in a PhH/DMF solvent mixture (20:1) containing $NBu_4B(C_6F_5)_4$. The ECL efficiency was determined by comparing the number of photons emitted per coulomb passed by comparison to a standard system with known ECL efficiency, $Ru(bpy)_3^{2+}$ (where bpy represents 2,2′-bipyridine), as a standard.[22] This yielded efficiency, $\Phi_{ECL} = 0.003$ for BHQ-BPZ, comparable to the ECL efficiency of BPQ-PTZ ($\Phi_{ECL} = 0.004$) obtained under slightly different experimental conditions. Because the fluorescence efficiency of BHQ-BPZ ($\Phi_{PL} = 0.28$) is significantly lower than that of BPQ-PTZ ($\Phi_{PL} = 0.70$), this suggests that BHQ-BPZ has a higher ECL efficiency (excited states produced per annihilation event) than BPQ-PTZ. This could be attributed to the enhanced solubility and stability of the dication in the presence of these weakly coordinating electrolytes. However, the ECL efficiency of BHQ-BPZ is about 6% of that of $Ru(bpy)_3^{2+}$ ($\Phi_{ECL} = 0.05$) and is much lower than similar polyaromatic hydrocarbons.[2,22]

As mentioned earlier, additional ECL measurements taken as a function of time showed a drop in emission intensity that correlated with the cyclic voltammetry becoming more irreversible upon film formation. Even when the anodic potential limit was kept at a less positive value to avoid generating the dication, it is possible that dication formation during this initial pulse and by disproportionation may contribute to the film formation, which would lower the observed ECL efficiency. In addition, the dianion itself could act as a quencher in this system, thus lowering the overall ECL efficiency.

## Conclusions

We report here the synthesis of BHQ-BPZ, a new donor−acceptor compound capable of ECL. The presence of phenothiazine dimer as the electron donor and phenylquinoline groups as the electron acceptors allows the generation of ECL without the addition of a coreactant or a second compound. On the basis of semiempirical MNDO calculations of this compound, the phenylquinoline group is twisted 82.5° relative to phenothiazine, indicating no molecular orbital overlap between these two groups. This molecular geometry, therefore, favors localization of the negative charge of the individual radical anions of the dianion onto each quinoline group and of the positive charge of the individual radical cation onto each phenothiazine group. In addition, the first phenothiazine is twisted 46.5° relative to the adjacent phenothiazine group, suggesting a possible delocalization of charge between these two moieties. However, this interaction is not strong enough to cause a pronounced effect in its photophysics. As a result of this slight interaction between the two phenothiazine groups, the oxidation of the first phenothiazine group creates a slight energetic barrier to the oxidation of the adjacent phenothiazine group, characterized by two closely spaced one-electron oxidation waves. Overall, BHQ-BPZ showed electrochemical, photophysical, and ECL properties similar to those of its parent compound, BPQ-PTZ. Most importantly, the energy of the annihilation reaction for BHQ-BPZ is sufficient enough to generate the singlet-excited state and corresponding ECL emission. Donor−acceptor block architectures such as this may provide a general approach to designing new materials exhibiting efficient ECL.

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**Supporting Information Available:** $^1$H NMR, FTIR, and mass spectra of BHQ-BPZ, and cyclic voltammogram of a 1 mM solution of BHQ-BPZ in 12:1 PhH/DMF at a 25 $\mu$m platinum microelectrode (0.125 M $[NBu_4][B(C_6F_5)_4]$; scan rate, 25 mV/s). This material is available free of charge via the Internet at http://pubs.acs.org.

JA036600Q

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