# Synthesis, Cyclic Voltammetric Studies, and Electrogenerated Chemiluminescence of a New Donor—Acceptor Molecule: 3,7-[Bis[4-phenyl-2-quinolyl]]-10-methylphenothiazine

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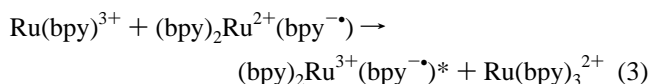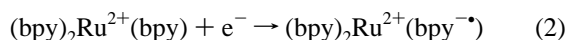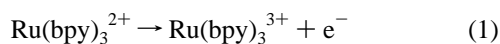
**Abstract:** We report here the synthesis of a novel compound that contains two electron-accepting phenylquinoline groups covalently attached to the 3,7-positions of a light-emitting electron donor, 10-methylphenothiazine. The optimized geometry as determined from semiempirical MNDO calculations shows that the phenylquinoline moieties are twisted ~77.5° from the phenothiazine central ring. As a result, no molecular orbital overlap between these two groups exists, inhibiting any delocalization of the charge upon electrochemical oxidation or reduction. Comparison between cyclic voltammograms obtained of this compound as well as of the individual compounds, 10-methylphenothiazine and 2-phenylquinonine, did indeed show no change in the electrochemical behavior of these two groups upon the covalent attachment, confirming the results obtained from the semiempirical calculations. A shift to lower energy wavelengths of phenothiazine was observed upon the addition of the electron-deficient phenylquinoline moieties. Overall, this unique geometry allows us to electrochemically produce the stable radical ions needed to generate the light-emitting excited state of phenothiazine within a potential window not obtainable with just 10-methylphenothiazine. ECL spectrum produced by annihilation between the radical cation of phenothiazine and the radical anion of phenylquinoline shows good agreement with the fluorescence emission of 10-methylphenothiazine.

## Introduction

We report here the synthesis and the electrochemical and photophysical characterization of 3,7-[bis[4-phenyl-2-quinolyl]]-10-methylphenolthiazine (BPQ-PTZ) as well as the electrogenerated chemiluminescence (ECL) that results from the annihilation reaction between its oxidized and reduced forms.



BPQ-PTZ
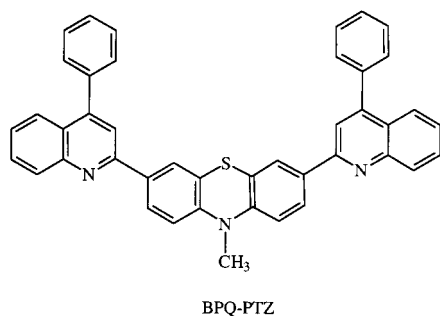
In ECL, electron transfer between electrochemically generated radical ions results in an excited species that emits light. A widely studied case involves the reaction between the oxidized and reduced forms of Ru(bpy)$_3{}^{2+}$ (where bpy represents 2,2′-bipyridine).[1]

$$Ru(bpy)_3{}^{2+} \rightarrow Ru(bpy)_3{}^{3+} + e^- \quad (1)$$

$$(bpy)_2Ru^{2+}(bpy) + e^- \rightarrow (bpy)_2Ru^{2+}(bpy^{-\bullet}) \quad (2)$$

$$Ru(bpy)^{3+} + (bpy)_2Ru^{2+}(bpy^{-\bullet}) \rightarrow$$
$$(bpy)_2Ru^{3+}(bpy^{-\bullet})^* + Ru(bpy)_3{}^{2+} \quad (3)$$

$$(bpy)_2Ru^{3+}(bpy^{-\bullet})^* \rightarrow Ru(bpy)_3{}^{2+} + h\nu \quad (4)$$

In this case the oxidized form is a Ru(III) center and the reduced form is a bipyridine radical anion. The excited state can be written as the well-known charge transfer state shown in eqs 3 and 4.

In some situations, however, the radical anion cannot be generated prior to the reduction of most nonaqueous solvents used for electrochemistry so that a second compound must be added to generate a stable radical counterion (a second reductant to react with the radical cation) required for annihilation.[1] One compound that requires the addition of such a species is 10-methylphenothiazine (10-MP).[2,3] Therefore, it is of particular interest to examine the case where this second compound is attached directly to a light-emitting compound. Two 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.[4,5]

(1) For reviews on ECL see: (a) Knight, A. W.; Greenway, G. M. *Analyst* **1994**, *119*, 879. (b) Faulkner, L. R.; Bard, A. J. In *Electroanalytical Chemistry*; Marcel Dekker; New York, 1977; Vol. 10, p 1; (c) Bard, A. J.; Debad, J. D; Leland, J. K.; Sigal, G. B.; Wilbur, J. L.; Wohlstadter, J. N. In *Encyclopedia of Analytical Chemistry: Applications, Theory and Instrumentation*; Meyers, R. A., Ed., John Wiley & Sons: New York, 2000; Vol. 11, p 9842 and references therein.
(2) Freed, D. J.; Faulkner, L. R. *J. Am. Chem. Soc.* **1971**, *93*, 2097.
(3) Freed, D. J.; Faulkner, L. R. *J. Am. Chem. Soc.* **1971**, *93*, 3565.
(4) Kapturkiewicz, A.; Grabowski, Z.; Jasny, J. *J. Electroanal. Chem.* **1990,** *279*, 55.
(5) Kapturkiewicz, A.; Herbich, J.; Nowacki, J. *Chem. Phys. Lett.* **1997**, *275*, 355.

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However, these did not involve the type of donor and acceptors described here. By attaching phenylquinoline to 10-MP, we can now electrochemically generate a stable radical anion upon the reduction of each individual quinoline group at potentials more positive than the nonaqueous solvent background. Under the appropriate pulsing conditions, the charge localized phenylquinoline radical anions, generated upon reduction, readily undergo electron transfer with electrochemically generated radical cations of phenothiazine to produce excited states that can emit light. In the existence of such a donor−acceptor structure, the excited state could be visualized, under appropriate structural and electronic conditions, to contain charge-transfer characteristics analogous to those of $Ru(bpy)_3^{2+}$.

## Experimental Section

**Materials.** Acetyl chloride, anhydrous carbon disulfide ($CS_2$), *m*-cresol, 2-aminobenzophenone, triethylamine (TEA), methanol, chloroform ($CHCl_3$), deuterated chloroform, deuterated dimethyl sulfoxide (DMSO), and diphenyl phosphate (DPP) were obtained from Aldrich (St. Louis, MO) and used as received. Tetra-*n*-butylammonium perchlorate (TBAP) was used as received and dried in a vacuum oven at room temperature prior to transferring directly into an inert atmosphere drybox (Vacuum Atmospheres Corp., Hawthorne, CA). 2-phenylquinoline (2-PQ, Aldrich), 10-methylphenothiazine (10-MP, Aldrich), anhydrous benzene (Aldrich, ACS spectrophotometric grade), and anhydrous acetonitrile (Aldrich, ACS spectrophotometric grade) were also used as received. All solutions were prepared in the drybox with fresh anhydrous solvents and sealed in airtight vessels for measurements completed outside the drybox.

**3,7-Diacetyl-10-methylphenothiazine.** The synthesis of this compound by Friedel−Crafts reaction of 10-MP with acetyl chloride has been reported by Gipstein et al.[6] Their procedure was followed starting with 10-MP (12 g, 56.1 mmol), 100 mL of anhydrous $CS_2$, and $AlCl_3$ (20 g, 0.15 mmol) with addition of acetyl chloride (2.5 mL, 35.4 mmol). We obtained 5 g of greenish crude solid. After recrystallizing the crude product in 120 mL of 1:1 ethanol/acetic acid three times, 2.5 g of greenish powder was obtained. Mp: 206−208 °C (lit.[6] mp 205−206 °C). $^1H$ NMR (400 MHz/CDCl$_3$) $\delta$: 7.82 (d, $J = 10.6$ Hz, 2H), 7.72 (s, 2H), 6.85 (d, $J = 10.6$ Hz, 2H), 3.48 (s, 3H), 2.56 (s, 6H).

**Synthesis of BPQ-PTZ.** 2-Aminobenzophenone(1.11 g, 6.68 mmol) and 3,7-diacetyl-10-methylphenothiazine (0.815 g, 2.74 mmol) were added along with 9.5 g of diphenyl phosphate (DPP) and 5 g of *m*-cresol in a glass reactor fitted with mechanical stirrer, two glass inlets, and a sidearm. 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 15 h. After cooling, the product was precipitated in a solution of 360 mL of methanol/40 mL of triethylamine. The yellow powder was purified by recrystallizing in 100 mL of 1:1 mix of THF/methanol, extracting it with 10% TEA/ methanol solution overnight, and drying in a vacuum at 40 °C. The yield was greater than 89%. A melting transition was not observed in differential scanning calorimetry (DSC) scan in flowing $N_2$; however, an apparent onset of decomposition was observed at ≥180 °C. UV− vis, $\lambda_{max}$ (nm) (CHCl$_3$): 396 (log $\epsilon$ = 4.38). $^1H$ NMR (400 MHz/ DMSO-$d_6$) $\delta$: 8.24 (d, $J = 10.7$ Hz, 2H), 8.22 (s, 2H), 8.15 (d, $J = 10.3$ Hz, 2H), 8.06 (s, 2H), 7.80 (m, 4H), 7.56 (m, 12 H), 7.15 (d, $J = 10.7$ Hz, 2H), 3.45 (s, 3H). See Supporting Information for the numbering of carbons used to assign $^{13}C$ NMR (200 MHz, CD$_2$Cl$_2$) $\delta$: 35.9 (CH$_3$) 114.7 (C3); 118.8 (C11); 123.7(C6); 127.13 (C5); 128.8-(C2); 129.9 (C13, C13′); 134.2(C10); 146.7(C1); 149.2, 149.4, 155.5 (C7, C8, C9); 126,0 (C4); 126.5 (C12, C12′); 126.3, 130.0, 130.3, 138.8 (C14, C15, C16, C17). FT-IR (KBr pellet, cm$^{-1}$) 3061, 2966, 1589, 1545, 1482, 1460, 1357, 1265, 1165, 823, 775, MS (FAB) *m/z* 620.0 (M$^+$). Elemental analysis, calculated values for C$_{43}$H$_{29}$N$_3$S: C, 83.33; H, 4.72; N, 6.78; S, 5.17; found: C, 82.69; H, 4.62; N, 6.87; S, 5.06.

**Characterization.** Elemental analysis was performed by Oneida Research Services (Whitesboro, NY). The FT-IR spectra were obtained

with KBr pellets using a Nicolet Model 20SWC Fourier transform infrared spectrometer under nitrogen. $^1H$ NMR spectra were measured at 400 MHz on a Bruker Avance-400 instrument and at 200 MHz on a Bruker DPX200 instrument. $^{13}C$ NMR spectra were measured at 200 MHz on a Bruker DPX200 instrument. All fluorescence spectra were recorded on a Fluorolog-3 spectrofluorimeter (ISA-Jobin Yvon Hariba, Edison, New Jersey) using a slit width of 0.5 nm and a resolution of 1 nm. All UV−visible spectra were recorded on a Milton Roy Spectronic 3000 array spectrophotometer. The absorbance spectrum of BPQ-PTZ was obtained with a 10 $\mu$M solution prepared with 1.5:1 benzene/acetonitrile (PhH/MeCN), and the fluorescence spectrum of the same compound was obtained with a 20 $\mu$M solution in 1.5:1 PhH/ MeCN. The relative fluorescence efficiency was measured using a 20 $\mu$M solution in PhH/MeCN (1.5/1) and determined with diphenylanthracene (DPA) as a standard ($\lambda_{exc} = 380$ nm; $\Phi_{dpa} = 0.91$ in benzene).[7]

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 ethanol for 3 min and then dried in a oven at 100 °C before transferring into the inert atmosphere drybox. A platinum wire served as a counter electrode and a silver wire contained in a glass tube closed off with a porous Vycor rod was utilized as a quasi reference electrode. The concentrations 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$^+$) = 0.424V vs SCE.[8]

All ECL measurements were performed as previously reported.[9] Measurements were obtained with BPQ-PTZ solution concentrations of 1 mM in 0.1 M TBAP in 1.5:1 PhH/MeCN. To generate the annihilation reaction, the working electrode was pulsed between the first oxidation and reduction peak potentials of BPQ-PTZ with a pulse width of 0.5 s. The resulting emission spectra were obtained with a charged coupled device (CCD) camera (Photometrics CH260, Photometrics-Roper Scientific, Tuscon, AZ) that was cooled to −100 °C. Integration times were 5 min. The CCD camera and grating system were calibrated with a mercury lamp prior to each measurement.

## Results and Discussion

**Synthesis and Characterization.** Scheme 1 describes the synthesis of BPQ-PTZ. A reaction of 2 equiv of 2-aminobenzophenone with 1 equiv of 3,7-diacetyl-10-methylphenothiazine gave the desired BPQ-PTZ in good yield (>89%). The final compound was soluble in a number of organic solvents including CHCl$_3$, toluene, THF, and DMSO. The molecular structure was confirmed by elemental analysis, $^1H$ NMR, $^{13}C$ NMR, FTIR, and mass spectroscopy and compared with previously reported phenylquinoline-containing oligomers and polymers.[10] The NMR and FTIR spectra, which were summarized in the Experimental Section, confirmed the attachment of phenylquinoline rings to the 10-MP moiety and the completion of the cyclization reaction forming the quinoline rings.[10] In particular, the strong carbonyl peak in the FTIR spectrum of 3,7-diacetyl-10-methylphenothiazine (1687 cm$^{-1}$), due to the acetyl groups, was completely absent in the spectrum of BPQ-PTZ. 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 BPQ-PTZ. Proton resonance due to the acetyl group was also completely absent in the spectrum of BPQ-PTZ while new aromatic proton resonances characteristic of quinoline ring

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(6) Gipstein, E.; Hewett, W. A.; Need, O. U, *J. Polym. Sci. A-1* **1970**, *8*, 3285.

**Scheme 1**
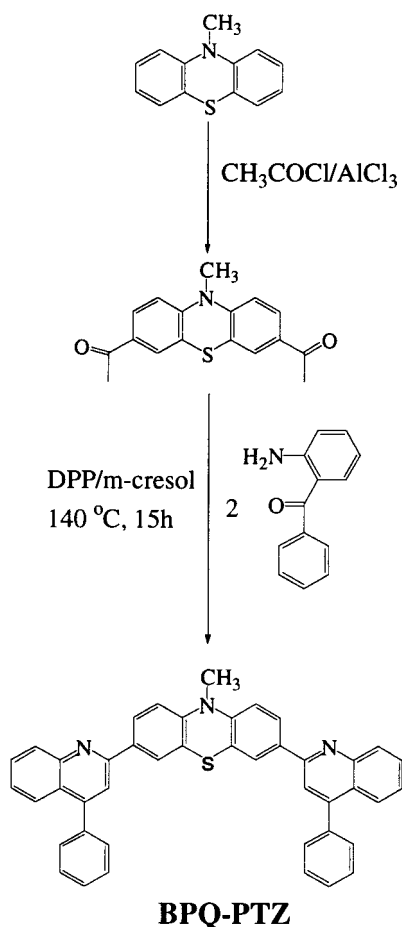


**BPQ-PTZ**

appeared.[10a,b] The ratio of the integration of the methyl proton resonances to that of the aromatic ones in the ^{1}H NMR spectrum was in accord with the proposed structure. Assignment of the ^{13}C NMR spectrum of BPQ-PTZ was also facilitated by comparisons with the ^{13}C NMR spectra of quinoline and 2-PQ in $CD_2Cl_2$ and the ^{13}C NMR and DEPT 135- NMR spectra of 10-MP in $CD_2Cl_2$ (see Supporting Information). The later spectra of 10-MP allowed assignment of the quarternary carbons in BPQ-PTZ. Furthermore, the electrochemical and photophysical properties of BPQ-PTZ described below are all in agreement with the molecular structure.

**Absorption and Emission Spectroscopy.** Absorption and fluorescence spectra of BPQ-PTZ are shown in Figure 1a. The absorption spectrum that was obtained in the same solvent mixture used for all electrochemical measurements shows a very broad band ranging from 350 nm to 460 nm with a $\lambda_{max}$ at ~400 nm while the same solution emitted in the green-yellow region when excited at 380 nm ($\lambda_{max}$ = 540 nm) with a moderately high fluorescence efficiency, $\Phi$ = 0.70. In addition to the broad absorption, a relatively large Stokes shift of 100 nm was observed between the absorption and emission spectral maxima. Both of these effects can be attributed to changes in the molecular structure of the phenothiazine center upon the excitation. In particular, 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.[11] This large Stokes shift is also observed in the fluorescence spectrum of 10-MP, as shown in Figure 1b.[12] Additionally,

(11) Mehlhorn, A.; Schwenzer, B.; Schwetlick, K. *Tetrahedron* **1977**, *33*, 1489.

the absorption and fluorescence spectra of BPQ-PTZ are red shifted by about 0.8 eV when compared to those of 10-MP. While a portion of this shift (~0.4 eV) can be attributed to the through $\sigma$-bond inductive effects caused by nitrogen lone pairs located on the quinoline substituents, the balance of this shift suggests structural changes in coplanarity of BPQ-PTZ that influence the electronic properties of the phenothiazine group. On the basis of the emission wavelengths in the fluorescence spectrum, the energy needed to generate the first singlet-excited state is about 2.3 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.

**Electrochemical Properties of BPQ-PTZ.** A cyclic voltammogram of BPQ-PTZ in 0.1 M TBAP in PhH/MeCN obtained at a platinum electrode is shown in Figure 2a. Upon scanning the potential positive, two one-electron oxidation waves were observed; one reversible wave at half-wave potential of +0.69 V vs SCE and another irreversible wave at peak potential of +1.32 V vs SCE. These waves correspond to the formation of the radical cation ($i_{pa1}$ = −14.5 $\mu$A) and the highly reactive dication ($i_{pa2}$ = −14.0 $\mu$A). The observed peak separation for the reversible waves was ~100 mV, larger than that expected for nernstian behavior where a one-electron wave is expected to have a peak separation of 59 mV. However, the internal standard, ferrocene, which is known to show nernstian behavior showed a similar peak separation under these same electrolyte conditions; thus, the observed peak separation can be attributed to ohmic drop (~1 kohm) that is often observed within aprotic solvents. Scan rate studies showed that the anodic and cathodic peak currents ($i_{pa}$, $i_{pc}$) of the first oxidation wave were proportional to the square root of scan rate ($v^{1/2}$) while the corresponding peak potentials ($E_{pa}$, $E_{pc}$) were proportional to scan rate ($v$). Additionally, the peak current ratio ($i_{pa}/i_{pc}$) was approximately unity down to a scan rate of 50 mV/s, indicating the absence of a following chemical reaction. This suggests that the first oxidation to the stable radical cation is near nernstian. This was not the case for the second oxidation. No reverse oxidation wave was found for scan rates up to 10 V/s. The irreversibility in the oxidation of the radical cation is due to a following chemical reaction with trace water or the solvent, acetonitrile.[13]

Upon scanning in the negative direction, two reduction waves were observed; one reversible wave with a half wave potential of −1.96 V vs SCE and another irreversible wave with a peak potential of −2.61V vs SCE. Direct comparison to the one-electron oxidation waves indicates that each reduction wave appears to be a single two-electron wave ($i_{pc1}$ = 28.9 $\mu$A, $i_{pc2}$ = 20.0 $\mu$A). These waves, therefore, correspond to the formation of the dianion and the tetraanion. The first reduction was near nernstian with $i_{pa}$ and $i_{pc}$ proportional to $v^{1/2}$ indicating diffusion control; however, $E_{pa}$ and $E_{pc}$ shifted with scan rate because of uncompensated resistance. Additionally, the ratio of the peak currents ($i_{pc}/i_{pa}$) was unity, indicating no following chemical reactions. The fact that the reduction wave is a two-electron wave ($n \approx 2$) suggests that the two phenylquinoline groups are not electronically coupled through the PTZ moiety, so that this wave represents individual one electron reduction of each PQ at essentially the same potential.[14] As discussed below, this

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(13) Perichon, J. In *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Lund, H., Eds., Marcel Dekker: New York, 1978; Vol. 11, Chapter 1, pp 132−135.

(14) (a) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248.; (b) Ammar, F; Savéant, J.-M., *J. Electroanal. Chem.* **1973**, *47*, 215.

a)



b)
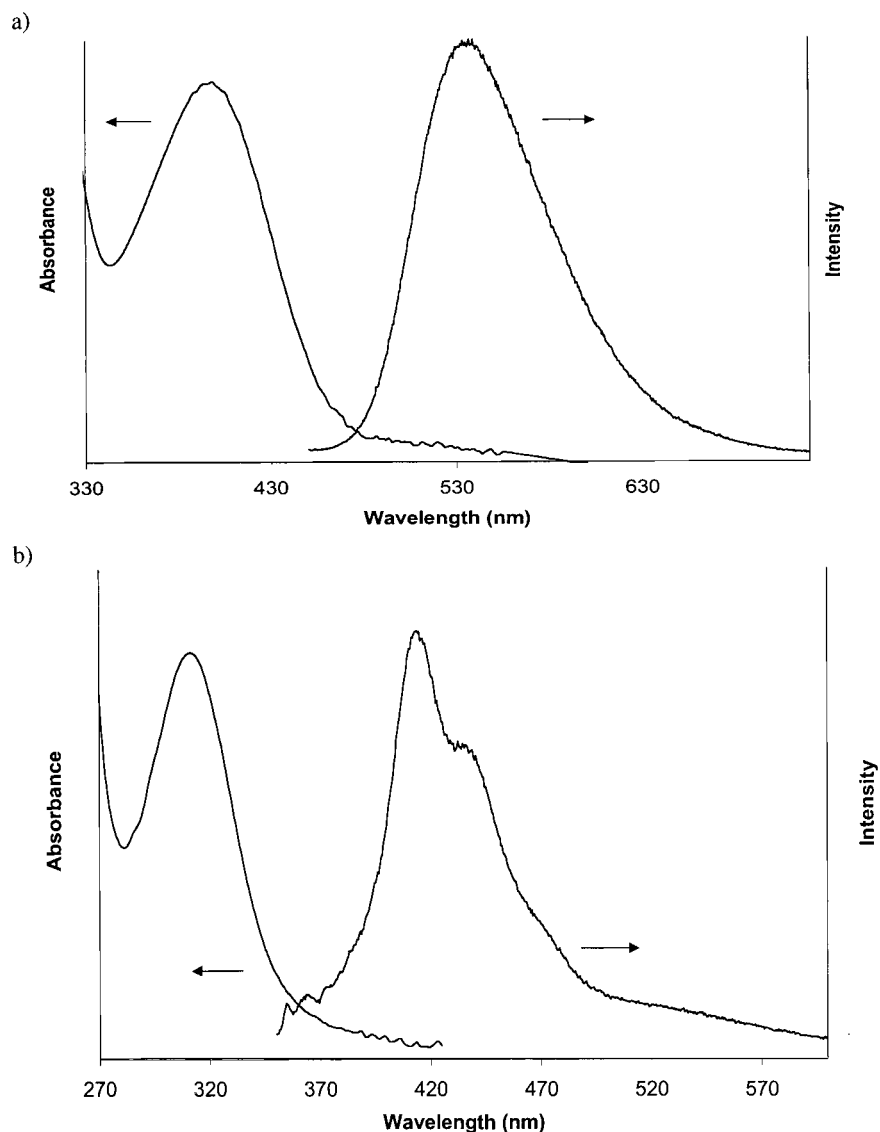


**Figure 1.** Optical absorption (10 $\mu$M) and fluorescence spectra (20 $\mu$M) of (a) BPQ-PTZ (excitation wavelength, 380 nm), and (b) 10-MP (excitation wavelength, 310 nm) in benzene/acetonitrile.

observation is consistent with the theoretically determined structure of the molecule.

The second reduction step, like the second oxidation, was an irreversible process, presumably because the tetraanion formed upon reduction of the dianion is basic enough 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 second reduction wave irreversible ($i_{pc} \gg i_{pa}$) at all measurable time scales.[15] Additionally, upon reversing potential, a new oxidation wave appears at $-0.7$ V vs SCE (Figure 2a). This wave most likely corresponds to the oxidation of a protonated compound that is easier to oxidize than the parent compound. To confirm that oxidation was indeed occurring on the phenothiazine and reduction on the quinoline groups, cyclic voltammograms of 10-MP and 2-PQ were obtained under the same electrochemical conditions.[3,15,16] These voltammograms are shown in Figures 2b and c. The observed reduction potentials of 2-PQ ($E_{1/2.1} = -1.99$ V, $E_{p.2} = -2.83$

V vs SCE) and the oxidation potentials of 10-MP ($E_{1/2.1} = +0.67$ V, $E_{p.2} = +1.37$ V vs SCE) are very close to the redox potentials of BPQ-PTZ suggesting no delocalization of charge between the phenylquinoline groups and the phenothiazine ring upon oxidation and reduction. This also indicates that the highest filled MO in the PTZ moiety is not greatly perturbed by the attached PQ groups and that the lowest unoccupied MO of the PQs are not perturbed by the PTZ. Additionally, the lack of a shift in the half wave potentials in the oxidation and reduction of the individual compounds when compared to BPQ-PTZ suggests the absence of any intramolecular and intermolecular charge-transfers occurring at this concentration.[17]

To determine a possible reason for the localization of charge upon the oxidation and reduction of BPQ-PTZ, the optimized molecular geometry of this compound was obtained using MNDO semiempirical calculations and is shown in Figure 3.[18] As one can see from this structure, the central phenothiazine ring is twisted $\sim$77.5° from the plane of the quinoline substit-uents while the phenyl groups appended onto the quinolines

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(16) Andruzzi, R.; Trazza. A.; Greci, L.; Marchetti, L. *J. Electroanal. Chem.* **1980**, *113*, 127.

(17) Boulas, P. L.; Gomez-Kaifer, M.; Echegoyen, L. *Angew. Chem., Int. Ed.* **1998**, *37*, 216.
(18) MNDO Semiempirical calculations performed with HyperChem by Hypercube, Inc., Gainesville, FL.
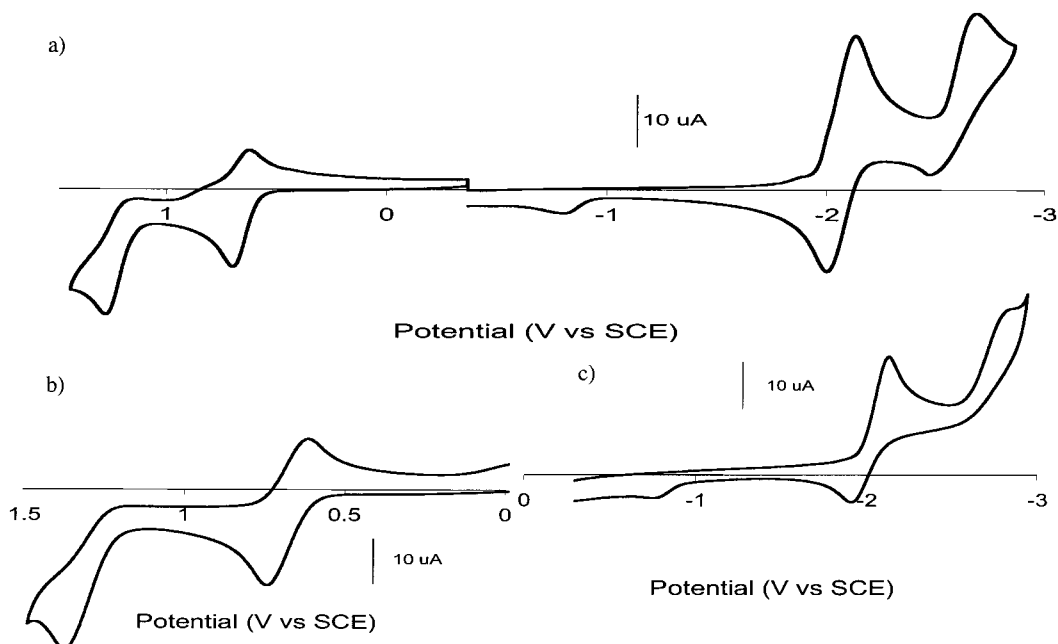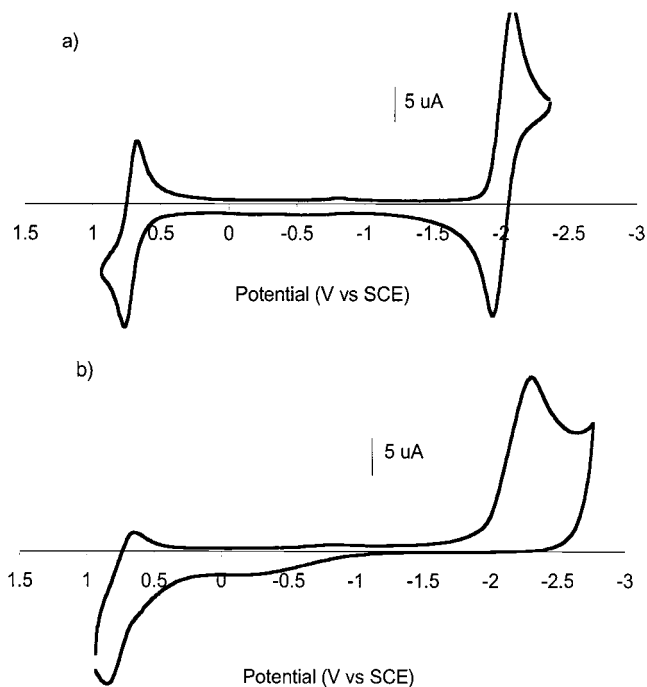
**Figure 2.** Cyclic voltammograms of (a) a 0.67 mM solution of BPQ-PTZ (scan rate 250 mV/s), (b) a 1 mM solution of 10-MP (scan rate 200 mV/s), and (c) a 1 mM solution of 2-PQ (scan rate 200 mV/s) in 0.1 M TBAP in benzene/acetonitrile at a platinum electrode.
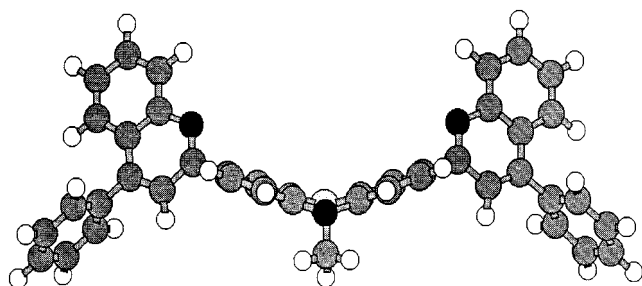


**Figure 3.** Optimized ground-state molecular geometry of BPQ-PTZ as calculated by MNDO semiempirical calculations.

are twisted ∼87.5° relative to these moieties. This geometry suggests minimal molecular orbital overlap between the π orbitals of the quinoline groups and the π orbitals of the phenothiazine inhibiting the delocalization of the electronic charge. On the basis of this calculated structure and the electrochemical results, we can conclude that the first two-electron reduction of BPQ-PTZ actually involves the formation of the radical anion on each of the quinoline groups while the second reduction is the formation of the dianion on each group.

We also noticed that upon continuous potential cycling of a solution of BPQ-PTZ over the range that encompassed the first oxidation and first reduction waves, the first two-electron reduction wave became irreversible, and the loss of reversibility became more pronounced as the number of scans increased. Figure 4 shows cyclic voltammograms that were obtained before and after numerous scans with the switching potential set at 300 mV past the peak potentials of the first oxidation and reduction waves of BPQ-PTZ (+1.0 and −2.3 V vs SCE). The loss of reversibility indicates a following chemical reaction involving the tetraanion or, more appropriately, the dianion of each quinoline moiety. Since this behavior is only observed upon scanning over both the oxidation and reduction waves (i.e., it is not found when cycling only over the first oxidation or only over the first reduction waves), the reaction also appears to involve the radical cation of phenothiazine. The products of this reaction form an insoluble film on the surface of the platinum-working electrode, which alters the electrochemical behavior



**Figure 4.** Cyclic voltammograms of a 1 mM solution of BPQ-PTZ in benzene/acetonitrile at a platinum electrode (0.1 M TBAP; scan rate 200 mV/s) (a) before potential cycling, (b) after 33 cycles between 0.90 V and −2.35 V (vs SCE).

of both BPQ-PTZ in solution as well as the internal potential standard, ferrocene (voltammogram not shown).

To verify the formation of an insoluble film, the electrode surface containing the suspected film was characterized in the absence of BPQ-PTZ. Figure 5 shows two voltammograms obtained in PhH/MeCN (1.5:1) containing only electrolyte; one obtained from an electrode immediately after extensive cycling and rinsing with MeCN and one obtained immediately after the electrode was mechanically polished. The voltammogram after numerous scans shows a one-electron irreversible wave at −2.28 V vs SCE, and a one-electron oxidation wave at +0.66V vs SCE. From the observed redox potentials, the film appears to
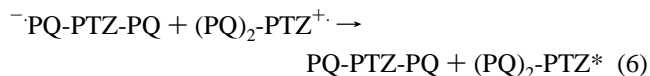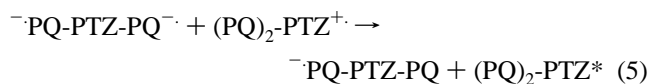
a)



b)

Potential (V vs SCE)
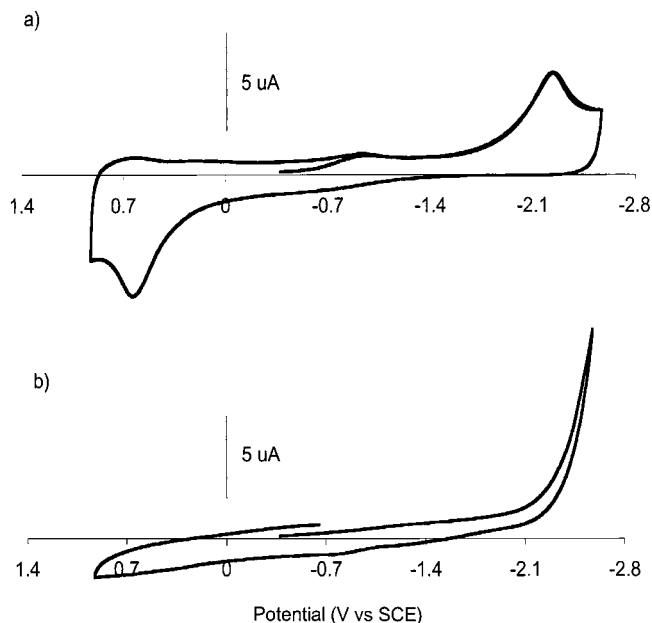
**Figure 5.** (a) Cyclic voltammogram of the insoluble film in 0.1 M TBAP in benzene/acetonitrile. (b) Cyclic voltammetric scan of the background at a platinum disk electrode.

have electrochemical properties that are similar to the original compound; however, both reduction and oxidation waves of the film exhibit irreversible electron transfer.
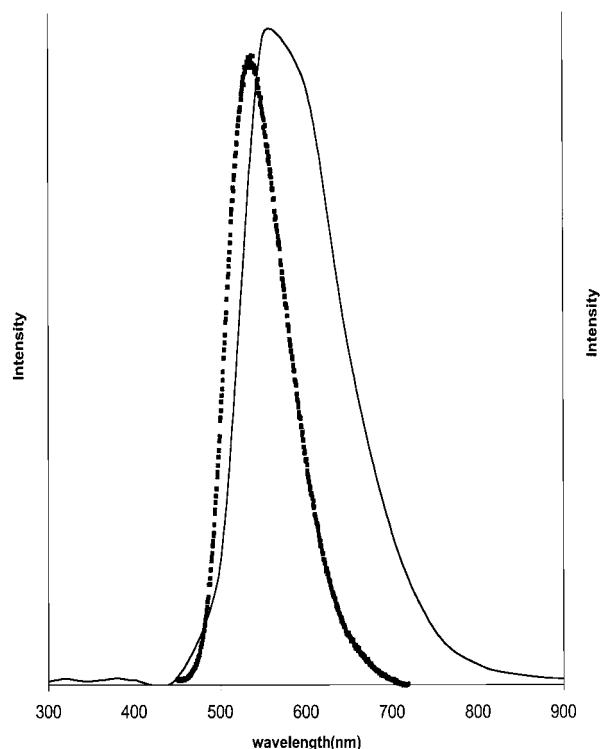
As a final note, the total free energy of the annihilation reaction ($\Delta G_{anni} = \Delta H_s - T\Delta S$), which is based on the difference between the peak potentials of the first oxidation and first reduction wave in the cyclic voltammogram ($\Delta E_{p(ox/red)} = 2.8$ eV) with entropy effects ($\sim 0.1$ eV) subtracted out, is about 2.7 eV.[1] This energy, which becomes available upon radical ion annihilation, is greater than that required to directly populate the singlet-excited state (2.3 eV) as previously determined from the fluorescence spectrum.

**Electrogenerated Chemiluminescence.** Figure 6 shows the ECL spectrum of BPQ-PTZ in PhH/MeCN (1.5:1) containing 0.1 M TBAP as supporting electrolyte during repeated pulsing (pulse width = 0.5 s) between potentials where oxidized and reduced forms are produced alternately. The instability of the radical ions as well as the film may pose problems in obtaining ECL, however, by keeping the potential less than 100 mV past the first reduction peak potential, we should be able to observe relatively efficient ECL. In a typical ECL experiment, the radical anion reacts with the radical cation; however, in our case, we are generating the dianion or, more appropriately, the radical anion of each quinoline group upon reduction. The excited BPQ-PTZ can therefore be produced via two possible electron-transfer mechanisms:
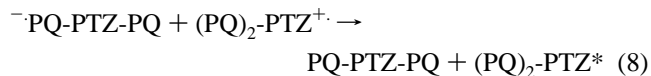
Mechanism I:

$$^-\text{PQ-PTZ-PQ}^{-\cdot} + (\text{PQ})_2\text{-PTZ}^{+\cdot} \rightarrow$$
$$^-\text{PQ-PTZ-PQ} + (\text{PQ})_2\text{-PTZ}^* \quad (5)$$

$$^-\text{PQ-PTZ-PQ} + (\text{PQ})_2\text{-PTZ}^{+\cdot} \rightarrow$$
$$\text{PQ-PTZ-PQ} + (\text{PQ})_2\text{-PTZ}^* \quad (6)$$

Mechanism II:

$$^-\text{PQ-PTZ-PQ}^{-\cdot} + (\text{PQ})_2\text{-PTZ} \rightarrow 2\ ^-\text{PQ-PTZ-PQ} \quad (7)$$



**Figure 6.** Fluorescence spectra (20 $\mu$M) of BPQ-PTZ in benzene/acetonitrile (squares) and ECL spectra of 1 mM BPQ-PTZ in 0.1 M TBAP in benzene/acetonitrile with pulsing (0.5 s) between 0.72 V and $-2.15$ V (vs SCE).

$$^-\text{PQ-PTZ-PQ} + (\text{PQ})_2\text{-PTZ}^{+\cdot} \rightarrow$$
$$\text{PQ-PTZ-PQ} + (\text{PQ})_2\text{-PTZ}^* \quad (8)$$

As shown in Figure 6, the ECL of BPQ-PTZ is characterized by a broad emission band between 450 nm and 800 nm, and the band appears to be composed of two overlapping peaks of similar intensity, one at 560 nm and another one at 600 nm. Upon comparison to the fluorescence spectra, the ECL spectrum is shifted approximately 20 nm to lower energy. This is probably due to self-absorption as a result of the high concentrations of BPQ-PTZ needed to obtain measurable ECL. In addition, the observed ECL emission band shows significant emission in the longer wavelength region 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. Another possible explanation is the presence of an intramolecular charge-transfer emission between radical anion of PQ and the radical cation of PTZ. The proposed mechanism is as follows:

$$(\text{PQ})_2\text{-PTZ}^{+\cdot} + \ ^{-\cdot} \rightarrow \text{PQ-PTZ-PQ}^-(\text{PQ-PTZ}^{+\cdot}\text{-PQ}^{-\cdot})^* \quad (9)$$

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

These reactions are analogous to the light emitting reactions of Ru(bpy)$_3^{2+}$ given in eqs 3 and 4 of the introduction. Preliminary measurement of fluorescence spectra of BPQ-PTZ in other solvents (toluene, chloroform, and DMSO) shows evidence of solvatochromism, suggesting intramolecular charge-transfer emission.

The relative ECL efficiency, defined as the ratio of the number of photons emitted to the number of annihilations

leading to emitting excited states, was estimated to be 8% in comparison to the ECL quantum efficiency of Ru(bpy)$_3{}^{2+}$ ($\Phi$ =0.05).[19] For BPQ-PTZ, the ECL efficiency is lower than similar polyaromatic compounds.[1] Additional ECL measurements taken as a function of time showed a significant drop in emission intensity that correlated with the cyclic voltammetry which became irreversible upon film formation. Even though ECL efficiency was determined for the very first pulse at a clean electrode, any film formation during this initial pulse may contribute to the lower than expected ECL efficiency.

## Conclusions

We report here the synthesis of a new quinoline-containing compound, 3,7-[bis[4-phenyl-2-quinolyl]]-10-methylphenothiazine (BPQ-PTZ), which allows us to generate ECL emission from phenothiazine without the addition of a coreactant or a second compound. Semiempirical MNDO calculations of this compound determined that the phenylquinoline is twisted ~77.5° relative to phenothiazine and indicated 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 radical cation onto phenothiazine. As a result, the oxidation and reduction potentials of BPQ-PTZ are very similar to the individual compounds, 2-PQ and 10-MP. The addition of the phenylquinoline groups to the 10-MP enables one to generate the radical

anion at potentials far more positive than the solvent as well as 10-MP. This, along with the charge separation, facilitates the electron transfer between the two electrochemically generated radical ions of BPQ-PTZ, thus eliminating the need to add a coreactant or a second compound. More importantly, the energy of this annihilation reaction is sufficient enough to generate the singlet-excited state and corresponding ECL emission of BPQ-PTZ. Donor−acceptor block architectures such as this may provide a general approach to design new materials exhibiting efficient ECL.

**Supporting Information Available:** Text giving additional characterization information on BPQ-PTZ, figure showing the numbering of the carbons of BPQ-PTZ, and figures showing ^{13}C NMR spectra of BPQ-PTZ and 10-MP, DEPT 135-NMR spectrum of 10-MP, and ^{1}H NMR spectrum of BPQ-PTZ. This material is available free of charge via the Internet at http://pubs.acs.org.

(19) Wallace, W. L.; Bard, A. J. *J. Phys. Chem.* **1979**, *83*, 1350.

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