Spectroscopic and DFT Studies of Donor–Acceptor Molecules Containing Phenylquinoline and Phenothiazine Moieties in Various Redox States

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ABSTRACT: We report the ultraviolet (UV)-Vis, Fourier transform-infrared (FT-IR), and FT-Raman spectroscopic study of an electrogenerated chemiluminescence (ECL) emitting compound containing two electron-accepting phenylquinoline end groups covalently attached to an electron-donating 10-methylphenothiazine central moiety. The optimized molecular geometry of the neutral compound as determined from quantum chemical density functional theory (DFT)//B3LYP/3-21G* calculations shows that the phenyl groups appended onto the quinolines are twisted by ~62° from these moieties. The sulfur atom is also tilted with respect to the plane defined by the phenyl rings of the phenothiazine, in both the neutral and singly oxidized species. The highest occupied
molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of the neutral systems partially overlap, so that the lowest-energy visible absorption band implies a certain degree of charge transfer from the phenothiazine toward the phenylquinolines. In contrast, the removal of the first electron mainly affects the structure and equilibrium charge distribution of the phenothiazine, and much less in those of the quinolines. In addition, the DFT//UB3LYP/3-21G* topologies of the molecular orbitals around the bandgap region of the radical cation reveal no molecular orbital overlap between the two types of constituent building blocks, thus inhibiting the delocalization of the injected positive charge over the whole molecule. This feature could be in line with the ability of this system to generate localized radical ions capable of displaying chemiluminescence upon annihilation, as previously observed experimentally. The UV-Vis and FT-Raman spectra of the singly oxidized species generated upon treatment with FeCl₃ in CH₂Cl₂ solution have also been recorded. The experimental data were interpreted with the help of DFT calculations. © 2005 Wiley Periodicals, Inc. Int J Quantum Chem 104: 635–644, 2005

**Key words:** Raman spectroscopy, in situ UV-Vis spectroelectrochemistry; density functional theory calculations

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**Introduction**

Emission of light by the generation of excited-state molecules through the annihilation of electrogenerated radical ions in solution is called electrogenerated chemiluminescence (ECL) [1]. The advent of ECL is a remarkable event, as this technique is considered superior to conventional optical techniques in analytical chemistry [2]. The usefulness of ECL active molecules in biological assays has prompted many chemists to venture into the synthesis and study of several new molecular systems [3]. However, so far integral unit molecules bearing both donor and acceptor moieties are very limited with respect to the study of ECL.

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:

1. \( A + e^- \rightarrow A^- \) (reduction at electrode) \( (1) \)
2. \( D - e^- \rightarrow D^+ \) (oxidation at electrode) \( (2) \)
3. \( A^- + D^+ \rightarrow D^* + A \) (excited state formation) \( (3) \)
4. \( D^* \rightarrow D + h\nu \) (light emission), \( (4) \)

where D is frequently an aromatic hydrocarbon (PAH) [4]. 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 [4]. In recent years, the field was advanced by the discovery of reaction schemes for generating ECL through the use of co-reactants (i.e., especially amines, which are well-known fluorescence quenchers) or other electrogenerated species capable of reacting with either the anion or the cation alone to produce the desire excited state. However, there are limitations in the choice of compounds or co-reactants that can fulfill the energetic criteria as well as other solution criteria. Therefore, it is of great interest to investigate new systems containing both donor and acceptor groups that are capable of generating ECL.

After the publication of some articles on organic light-emitting diodes (OLEDs) based on aluminum-(tris-8-hydroxyquinoline) (Alq₃) by Tang and VanSlyke [5], the design and preparation of numerous fluorescent organic compounds spurred active research in the creation of organic and organometallic compounds for electroluminescent (EL) applications [6].

Some studies have already 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 [7,8]. Furthermore, the introduction of various types of \( \pi \)-conjugated bridges in donor–acceptor luminescent molecules affords opportunities for investigating variations and new phenomena alike [9].

One compound that requires the addition of a second species is 10-methylphenothiazine (10-MP)
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[10, 11]. Some of us have previously demonstrated that by attaching phenylquinoline to 10-methylphenothiazine, it was possible to generate electrochemically 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 underwent electron transfer with electrochemically generated radical cations of phenothiazine to produce excited states that can emit light [12]. In the present work, we further study this ECL-emitting 3,7{-bis[4-phenyl-2-quinolyl]}-10-methylphenothiazine system (i.e., hereafter referred to as BPQ-PTZ) by means of FT-Raman, Fourier transform infrared (FT-IR), FT-IR, and Vis-NIR spectroscopies both in the neutral state and upon oxidative treatment with FeCl3 in dichloromethane solution. DFT//B3LYP/3-21G* quantum chemical calculations have also been performed as a guide for the analysis of the electronic absorption and vibrational spectroscopic data, for both the neutral and doped forms, and to derive useful information about the minimum-energy structure, molecular orbital (MO) topologies, and equilibrium atomic charge distributions.

Experimental and Theoretical Details

The synthesis and characterization of a donor-acceptor ECL emitter, BPQ-PTZ, used in the present study as well as related molecules and polymers have been previously reported [12]. FT-IR absorption spectra were recorded on a Bruker Equinox 55 spectrometer, and using a Golden Gate ATR accessory from Specac (i.e., as the average of 50 scans with a spectral resolution of 2 cm−1). Interference from atmospheric water vapor was minimized by purging the instrument with dry argon before beginning the data collection. FT-Raman scattering spectra were collected on a Bruker FRA106/S apparatus and a Nd:YAG laser source (λexc = 1064 nm), in a backscattering configuration. The power of the exciting laser radiation was kept at 100 mW, and solid samples were analyzed in sealed capillaries. Typically, 500 scans with a spectral resolution of 2 cm−1 were averaged to optimize the signal-to-noise (S/N) ratio. UV-Vis-NIR absorption spectra were recorded on an Agilent 8453 instrument equipped with a diode array for a fast record of all the electronic absorption bands appearing in the 190–1100-nm spectral region. The oxidation of the ECL emitting compound was accomplished by using a FeCl3/CH2Cl2 solution.

Density functional theory (DFT) calculations were carried out by means of the Gaussian 98 program [13] running on an SGI Origin 2000 supercomputer. We used Becke’s three-parameter exchange functional combined with the LYP correlation functional (B3LYP) [14]. It has already been shown that the B3LYP functional yields similar geometries for medium-size molecules as MP2 calculations do with the same basis sets [15, 16]. Moreover, the DFT force fields calculated using the B3LYP functional yield IR spectra in very good agreement with experiments [17, 18]. We also made use of the standard 3-21G* basis set [19]. Optimal geometries were determined on isolated entities. All geometrical parameters were allowed to vary independently, apart from planarity of the aromatic rings. On the resulting ground-state optimized geometries, harmonic vibrational frequencies and infrared intensities were calculated analytically whereas Raman intensities were calculated numerically with the B3LYP functional.

We used the often-practiced adjustment of the theoretical force fields in which calculated harmonic vibrational frequencies are uniformly scaled down by a factor of 0.98 for the 3-21G* calculations, as recommended by Scott and Radom [17]. This scaling procedure is often accurate enough to disentangle serious experimental misassignments. All quoted vibrational frequencies reported in the manuscript are thus scaled values. The theoretical spectra were obtaining by convoluting the scaled frequencies with Gaussian functions (10 cm−1 width at the half-height). The relative heights of the Gaussians were determined from the theoretical Raman scattering activities.

Vertical electronic excitation energies were computed by using time-dependent DFT (TDDFT) formalism [20, 21]. The 12 lowest-energy electronic excited states were at least taken into consideration. The computational cost of TDDFT is roughly comparable to that of single-excitation theories based on a HF ground state, such as single-excitation configuration interactions (CIS). Numerical applications reported so far indicate that TDDFT approach employing current exchange-correlation functionals performs significantly better than HF-based single excitation theories for the low-lying valence excited states of both closed-shell and open-shell molecules [22, 23]. In the present work, TDDFT calculations for the neutral system were performed by using the B3LYP functional and the 3-21G* basis set on the optimized molecular geom-
etries previously obtained at the same level of theory. On the other hand, radical cations were treated as open-shell systems and computed by using spin-unrestricted UB3LYP wavefunctions. The maximum value obtained for $S^2$ was 0.76, quite close to the 0.75 theoretically expected for a doublet, showing that spin contamination was almost absent.

Results and Discussion

UV-Vis ABSORPTION DATA

The chemical structure of the ECL-emitting BPQ-PTZ compound studied in this article is depicted in Figure 1. Its UV-Vis absorption spectrum, in CH$_2$Cl$_2$ solution, is displayed in Figure 2 (i.e., the resulting spectral features are concentration independent in the range examined, indicating that the molecules are not in an aggregated phase).

The visible absorption spectrum shows a very broad and unstructured feature ranging from 350 nm to 460 nm, with a $\lambda_{\text{max}}$ at 396 nm (3.13 eV). In addition, a relatively large Stokes shift of 100 nm was observed between the absorption and emission spectral maxima of neutral BPQ-PTZ (i.e., the same solution used for the electronic absorption measurements emitted in the green-yellow region under excitation at 380 nm, again giving rise to a broad and unstructured feature with its $\lambda_{\text{max}}$ at 540 nm and a moderately high fluorescence efficiency of $\Phi = 0.70$). These experimental observations can be attributed to the decreased planarity of the ECL emitter caused by the large steric interactions between its various constituent building blocks and also to changes in the molecular structure of the phenothiazine central moiety upon excitation. In particular, the difference in energy between the geometrically relaxed ground electronic state and the nonrelaxed excited singlet state is larger than the energy difference between the geometrically relaxed excited state and the nonrelaxed ground state [24]. A large Stokes shift was also observed in the case of 10-MP [25]. Additionally, the absorption and fluorescence features of BPQ-PTZ are red-shifted by about 0.8 eV with respect to those of 10-MP, which can be attributed in part to the $\sigma$-bond inductive effects caused by nitrogen lone pairs located on the quinoline substituents.

OPTIMIZED GEOMETRY AND THEORETICAL ELECTRONIC ABSORPTIONS OF THE NEUTRAL COMPOUND

To gain deeper insight into the structure and equilibrium charge distribution of the neutral form of BPQ-PTZ, we have performed molecular geometry optimizations, within the framework of DFT, by using DFT//B3LYP/3-21G* model chemistry (namely, the main skeletal bond lengths obtained for the neutral form of BPQ-PTZ are reported in Table I together with the corresponding theoretical values for the radical cation). The C–S bonds are predicted to be sizeably longer (by 0.37 Å) than its nearest CC bonds, which causes a tilting of the former two bonds by 42° out of the least-squares plane defined by the phenyl rings of the phenothiazine. In contrast, the phenyl groups appended onto the quinolines are also found to be largely...
twisted by \( \approx 62^\circ \) relative to these moieties in the minimum-energy structure of the neutral system.

Figure 3 shows the overall summations of the natural population analysis (NPA) atomic charges on various molecular domains, which can be hypothesized within BPQ-PTZ. The sulfur and nitrogen atoms of the phenothiazine unit are predicted to bear NPA charges of 0.36 and -0.42 e, respectively, in the neutral state, whereas the overall charges on the phenyl and quinoline groups are in any case lower than -0.1 e. Thus, the ground-state 1.71 D dipole moment is mainly due to the asymmetric polarization of the heteroatoms of the phenothiazine.

As a help in the analysis of the UV-Vis absorption spectrum of the ECL emitter in neutral state, TDDFT calculations were performed on the previously optimized B3LYP/3-21G* structure. Two main absorptions are theoretically expected to be recorded in the visible spectral region at 4.03 and 2.81 eV, with oscillator strengths of 0.94 and 0.44, respectively. Their description in terms of the main one-electron vertical excitations involved shows that the former is mostly built up from a combination of the highest occupied molecular orbital (HOMO)-1 \( \rightarrow \) lowest unoccupied molecular orbital (LUMO) and HOMO \( \rightarrow \) LUMO+6 transitions, whereas the latter arises from the HOMO \( \rightarrow \) LUMO transition.

Figure 4 presents a diagrammatic sketch of the absolute energies of the molecular orbitals around the bandgap, whereas Figure 5 shows the topologies of the frontier MO of BPQ-PTZ. We observe that (i) the HOMO is concentrated almost exclusively on the phenothiazine (with a small contribution by part of the other two nitrogens of the molecule), while the quinolines largely contribute to LUMO; and (ii) an effective overlap occurs between both frontier orbitals; so that the lowest-energy optical absorption recorded in the visible spectral re-
gion implies a partial degree of charge transfer from the central phenothiazine moiety toward the quinoline electron–acceptor end groups.

It is noteworthy that the computed TDDFT//B3LYP/3-21G* energy required for the vertical one-electron transition from the highest-energy doubly occupied MO to the lowest-energy vacant MO, 2.81 eV, is predicted to be smaller by 0.45 eV than the DFT//B3LYP/3-21G* HOMO–LUMO energy gap, 3.27 eV, which must be ascribed to the reduced interelectronic interaction upon the single one-electron excitation. That is, the interaction can be conceptually interpreted in a simple way as the balance between Coulomb and exchange terms, and it is expected to decrease as the distance between the two interacting electrons grows longer.

The situation outlined above must be stressed. First, despite being commonly applied as a direct measure of the HOMO-LUMO gap and the extent of conjugation of a system, UV-Vis absorption spectra are not unambiguous in this use. This should also hold when analyzing a homologous series of linear \( \pi \)-conjugated oligomers. It is not infrequent that the optical properties reach saturation for quite short chain lengths, while the orbital energies still continue to change for longer oligomers (see Ref. [28d]). As mentioned above, the Coulomb and exchange integrals must decrease with increasing chain length (this trend of variation is in line with the expectation that in longer systems the interelectronic repulsion is smaller). However, the narrowing of the HOMO-LUMO gap with increasing number of units in a \( \pi \)-conjugated chain is usually more pronounced, so that the Coulomb and exchange terms play a minor role in determining the energy of the singlet excited state associated to the HOMO–LUMO transition for the ever growing members of the set of oligomers. As a result, it is desirable that analysis of the experimental UV-Vis data not be based on the spectroscopic intuition only, but guided by some type of quantum-chemical calculation about the energies and topologies of the molecular orbitals involved and of the multiconfigurational character of the different optical absorptions.

**EXPERIMENTAL AND THEORETICAL VIBRATIONAL SPECTRA OF THE NEUTRAL COMPOUND**

Figure 6 compares the FT-IR and FT-Raman spectral profiles of neutral **BPQ-PTZ**. We observe that the IR spectrum displays several features with similar intensities between 1600 and 700 cm\(^{-1}\), while the appearance of the Raman scattering profile is much simpler, since only four lines, at 1605, 1585, 1366, and 1245 cm\(^{-1}\), appear to be strongly enhanced among the very many Raman-active vibrational normal modes predicted by the optical selection rules. Nonetheless, the exciting laser radiation used for the Raman experiments (i.e., 1064 nm) is still rather far from the lowest-energy optical absorption bands of the neutral molecule.
absorption of the neutral ECL emitter at 442 nm. Thus, it can be excluded the eventuality that the selective gain in intensity of the four Raman scatters mentioned above arises from a fortuitous matching between the monochromatic NIR excitation employed and an optical absorption of the compound.

Figure 7 plots the B3LYP/3-21G* Raman spectrum of neutral BPQ-PTZ in the 1700–700-cm\(^{-1}\) Raman shift spectral region. The agreement between theory and experiments is quite satisfactory both in the peak positions and relative intensities. From the B3LYP/3-21G* vibrational eigenvectors (Fig. 8), we learn that: (i) the 1605-cm\(^{-1}\) Raman line is to be associated with a totally symmetric, TS, \(\nu(C\equiv C)\) stretching mode mostly located on the phenyl rings of the phenothiazine; (ii) those at 1385 and 1366 cm\(^{-1}\) arise, respectively, from a TS \(\nu(C\equiv C)\) stretching and a TS in-plane \(\delta(C\equiv H)\) bending modes, but this time being both located mainly on the phenyl groups appended onto the quinoline end groups; whereas (iii) the Raman scattering at 1245 cm\(^{-1}\) is due to a TS in-plane \(\delta(C\equiv H)\) bending mode located only on the quinolines. It follows that these totally symmetric skeletal vibrations of the “\(\pi\)-conjugated backbone” give rise to the largest changes in the molecular polarizability, whereas many other types of non-TS molecular vibrations such as out-of-plane \(\gamma(C\equiv H)\) bending modes and in-plane and out-of-plane oscillations of the partially charged (i.e., either positively or negatively) heteroatoms with respect to their equilibrium positions sizeably contribute to the infrared absorption spectral pattern of the neutral ECL emitter. Finally, we would like to stress that the Raman vibrational characteristics of this BPQ-PTZ compound are reminiscent of those commonly observed for many classes of \(\pi\)-linked \(\pi\)-conjugated oligomers and polymers even with rather complex chemical structures (namely, for quasi one-dimensional systems in which a few totally symmetric collective skeletal vibrations of the \(\pi\)-conjugated path are known to give rise to overwhelmingly strong Raman lines experimentally observed) [26–29].

**DFT calculations on the singly oxidized species and in situ spectrochemistry**

The main skeletal bond lengths for BPQ-PTZ\(^{\bullet}\), as deduced from the UB3LYP/3-21G* calculations performed for the open-shell species, are summarized in Table I, as well as the relative differences with respect to the neutral form of the ECL emitter.

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The largest structural changes take place for the central phenothiazine moiety, but the phenylquinoline groups are little affected by the removal of the first electron. The C–S bonds are predicted to shorten by 0.032 Å in passing from BPQ-PTZ to BPQ-PTZ\(^{\bullet}\); while the nearest CC bonds (i.e., those numbered as 2 and 4 in Table I) lengthen by 0.011 and 0.021 Å, respectively. In addition, this second set of DFT calculations shows us that the structural relaxation taking place in the neighborhood of the sulfur upon oxidation leads to a lowering of the tilting of this heavy atom with respect to the least-squares plane defined by the two phenyl rings of

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the phenothiazine moiety from 42° in the neutral form to 23° in the radical cation.

Regarding the electrostatic picture of BPQ-PTZ•/H, we learn from the UB3LYP/3-21G* data that the phenothiazine moiety bears an overall NPA charge of +0.76 e (see Fig. 9), whereas the corresponding value for the neutral species amounted only to +0.04 e. Thus, the phenothiazine central building block is theoretically predicted to support ~76% of the positive charged injected into the system. (That is, the two innermost heteroatoms of the ECL emitter are able to store ~40% the excess of positive charge, with respect to the neutral compound since their NPA atomic charges increase by 0.22 and 0.12 e, as for the sulfur and the nitrogen atoms, respectively. Nonetheless, the remainder ~25% of the net charge of the singly oxidized species is predicted to be delocalized over the two quinolines and even the phenyl groups appended onto them. In any case, the polarization of the system leads to an increase of the molecular dipole moment from 1.71 D (BPQ-PTZ) to 4.49 D (BPQ-PTZ•).

Figure 2 shows the UV-Vis absorption spectrum of BPQ-PTZ•/H recorded after in situ treatment of a freshly prepared solution of neutral BPQ-PTZ in dichloromethane with one equivalent of FeCl3 already dissolved in CH2Cl2. The lowest-energy visible absorption of the doped compound is now recorded at 520 nm (2.38 eV), whereas that recorded at 396 nm for the neutral compound is completely absent. TDDFT calculations performed for BPQ-PTZ• at the UB3LYP/3-21G* level of theory predict the appearance of two subgap electronic transitions with their respective maxima located at 1.48 and 0.95 eV, the former being predominantly built up from the one-electron vertical excitation from the filled HOMO-3 to the now semi-occupied HOMO (i.e., SOMO), and the latter due to the HOMO-1 → HOMO transition. With respect to the atomic composition of the HOMO-3 orbital of BPQ-PTZ•/H, whereas the semi-occupied HOMO of this doped species greatly resembles that of the filled HOMO of the neutral form, we again observe that the SOMO is located mainly on the phenothiazine and the HOMO-3 on the quinolines, but this time, as opposed to the case of the HOMO → LUMO transition of the neutral system, no overlap takes place between HOMO-3 and SOMO of BPQ-PTZ•. Thus, the corresponding subgap absorption does not imply any charge transfer.

Finally, Figure 10 shows the FT-Raman spectrum of BPQ-PTZ•/H recorded after exhaustive oxidation with FeCl3. It is clear that the Raman scattering profile of the doped species still greatly resembles that of the neutral system, despite the fact that the strong optical absorptions of the latter completely disappeared upon oxidation.

DFT model chemistry has previously evidenced that the selectively enhanced Raman lines observed for neutral BPQ-PTZ were due to particular TS skeletal (CC) stretchings and in-plane δ(C–H) bendings located almost exclusively on the phenyl-quinoline groups, and that, on the other hand, the largest structural changes upon oxidation mainly take place in the phenothiazine central moiety. Thus, the great similarity between the experimental Raman spectra of BPQ-PTZ and BPQ-PTZ• is in full agreement with the theoretical expectations.
Conclusions

Organic molecules showing intramolecular charge transfer features are of great interest because of their versatility in photonic applications. In this study, the electronic and molecular structures of a ECL emitting compound containing two electron-accepting phenylquinoline end groups covalently attached to an electron-donating 10-methylphenothiazine central moiety have been explored by means of electronic absorption and vibrational Raman spectroscopies in combination with quantum chemical calculations within the framework of DFT. In this way, Raman spectroscopy has been demonstrated to be an incisive technique with which to analyze the electronic features of this complex π-conjugated system. The very few Raman lines and their intensities are distributed according to the involvement of each moiety in the electronic structure, otherwise consisting of an intramolecular charge transfer. This work establishes a valuable assignment of the Raman signals and provides significant evidence to their wavenumbers on the basis of detailed structural (bond lengths and dihedral angles), charge distribution, and orbital topologies. In this sense, future functionalization and improvement of these molecules can be related to the understanding of the electronic properties through analysis of the Raman spectra. As a prototypical example, the case of a radical cation has been selected as a reliable model of the charged species involved in the annihilation mechanism of forming excitons.

Since BPQ-PTZ is also a model compound for donor-acceptor conjugated copolymers of current interest as bipolar emitters for efficient OLEDs [6d, 12b, 12c], the present spectroscopic and DFT results have implications for the design of such donor-acceptor materials for OLED applications.

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References