

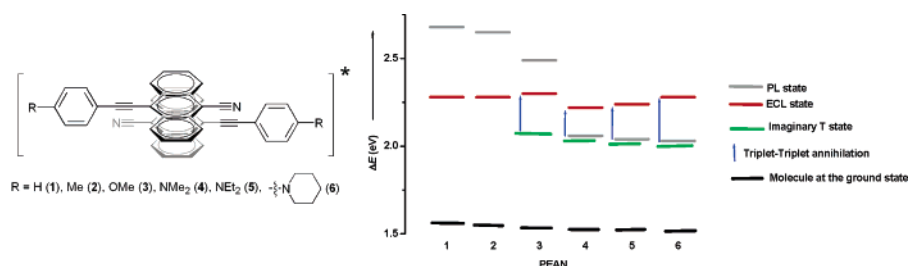
Synthesis, Electronic Properties, and Electrochemiluminescence of Donor-Substituted Phenylethynylanthronitriles

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A new series of π -conjugated donor–acceptor compounds (**1–6**) with inherent redox centers have been prepared and studied with respect to their electronic properties. The photophysical characteristics of these compounds have been studied in relation to their structures. Cyclic voltammetry and UV–vis spectroelectrochemistry were used to probe the ground-state electronic properties of the neutral and charged species. The observed electronic absorption properties of the neutral and charged molecules are explained with the help of frontier orbital structures and electrostatic potential maps obtained from density functional theory (DFT, B3LYP/6-31G^{*}) calculations. Electrochemiluminescence (ECL) of this series of donor-substituted phenylethynylanthronitriles with different donors was also studied. The structure–property relationship of all of the compounds is discussed.

Introduction

The use of π -conjugated organic materials has gained much attention because of their potential application in electronic devices such as light-emitting diodes¹ and field-effect transistors.² The structural flexibility and facile processing of these materials could potentially help to reduce the cost and enhance the applicability of these materials in various fields. Ethyne-based donor–acceptor molecules are emerging as new organic materials for luminescent applications.^{3,4} Apart from the most com-

monly anticipated luminescence applications, there is a special and unique application which involves production of light by chemiluminescence via an encounter reaction of radical ions formed by electrolysis of redox active molecules. Annihilation of radical ions, which are generated sequentially with a time interval at the surface of an electrode, can lead to the formation of electronically excited states of molecules by energetic electron-transfer reactions at the electrified interface. These excited species emit energy in the form of fluorescence at a certain wavelength. This technique is called as electrogenerated

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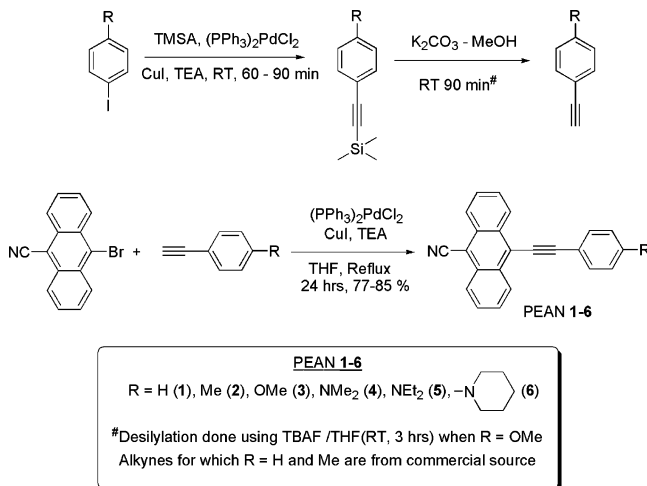
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chemiluminescence or, often, electrochemiluminescence (ECL).^{5–15} ECL emission can occur directly from the singlet excited state (S route), via triplet–triplet annihilation (T route), or via excimer formation (E route).^{5b}

Excimers are homodimers of molecules in solution which exist in the photoexcited state.¹⁶ Many excimers are formed between molecules whose π -systems interact effectively leading to the formation of appropriate states, and they possess structures prominently governed by their monomer chemical structures. The formation of excited states in the solid state by application of an electric field (as in OLED) has been shown to follow a mechanism similar to that followed in solution (ECL).^{4d–f} An understanding of the process occurring at the molecular level (even at the plasma level) is important for enhancing our ability to control and manipulate the emissive state. Design, synthesis, and study of new organic molecules for ECL are, therefore, a live research area. Recently, the radical ions of some water-soluble porphyrins and zinc porphyrins were produced, and we recorded the ECL emissions.¹⁰ A series of intramolecular charge-transfer (ICT) donor–acceptor stilbenoid systems with the *N,N*-dialkylamino group as the donor and with a pyridyl, thiophenyl, or aryl group as the acceptor were prepared, and their ECL emissions were studied.¹¹ It was found that most of the stilbenoids showed ICT–ECL through direct annihilation of radical ions. Only poor ICT compounds with weak electron-demanding thiophene as the acceptor showed excimer ECL. The coplanarity of the donor and the quinolinyl and isoquinolinyl acceptor moieties with respect to the conjugated triple bond plays a role in determining the type and emission wavelength of ECL.^{12a,b} Formation of the *H*-type excimer has been proposed to be responsible for the observed blue-shifted ECL emission with respect to photoluminescence in *p*-*N,N*-diethylaminophenyl-4-quinolinylethyne^{12b} and *p*-*N,N*-dimethylaminophenylethyne^{12b} and *p*-*N,N*-dimethylaminophenylethyne^{12b} and *p*-*N,N*-dimethylaminophenylethyne^{12b} (see text and ref 27).

In the present work, a series of new diarylethyne molecules with donor-substituted phenyls and anthroni-

SCHEME 1. General Synthetic Route for the Preparation of PEANs 1–6



trile acceptor moieties was synthesized, and the ECL and other photophysical properties were studied.

The anthronitrile moiety was chosen because of the following: (i) It is a fluorophore and a good electron acceptor, and when connected appropriately with an electron donor through conjugation, it will portray photophysical characteristics, such as absorption and emission in the visible region; in other words, the HOMO–LUMO gap can be reduced advantageously. (ii) 9-Cyano-10-haloanthracenes have been found to produce, upon electroreduction, radical anion intermediates stable enough for the electrochemical studies, and all the related activation parameters could be determined with sufficient accuracy even at room temperatures;¹³ substitution of the halogen with donor groups via conjugation would help realize the tunable properties. (iii) Anthracene and diphenylanthracene have been among the very early aromatic compounds to be studied¹⁴ for ECL, and now our attention has been drawn to the extension of π -conjugation through the molecule seeking for new aspects. (iv) The anthronitrile moiety can impart intermolecular π – π interactions, and hence, the chromophore activity can be controlled and the emission tuned by the appropriate conditions.

Results and Discussion

Compounds 1–6 were synthesized by coupling the corresponding terminal aryl acetylenes with 9-bromo-10-anthronitrile under modified Sonogashira conditions¹⁷ as shown in Scheme 1. A summary of photophysical data is presented in Table 1, and the electrochemical characteristics of these compounds are furnished in Table 2.

Photophysical Properties. UV–vis absorption spectra of all of the compounds (1–6) exhibited β -band absorption at about 275 nm. As can be seen from Figure 1, for those phenylethyneanthronitriles (PEANs) with

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
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TABLE 1. Photophysical Data of 1–6

PEAN	R	$\lambda_{\max}^{\text{Abs}}$ (nm) ^a	$\Delta E_{\text{H-L}}$ (eV) ^b	ϵ_{\max}^c	$\lambda_{\max}^{\text{Flu}}$ (nm, eV) ^d	Φ^e
1	H	442	2.63	1.32	460, 2.68	0.58
2	CH ₃	444	2.63	1.55	466, 2.65	0.73
3	OCH ₃	448	2.62	1.62	496, 2.49	0.64
4	NMe ₂	480	2.15	9.91	603, 2.06	0.10
5	NEt ₂	488	2.15	11.12	604, 2.04	0.08
6		470	2.15	8.93	608, 2.03	0.05

^a Maxima at the longest-absorption wavelength. ^b $\Delta E_{\text{H-L}}$ is the HOMO–LUMO gap calculated from the onset of the visible absorption maxima. ^c In units of $\times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. ^d Emission spectra for 4–6 were recorded in CH₂Cl₂ because no emission was noticed in CH₃CN; emission spectra for 1–3 in CH₂Cl₂ showed little shift in the maxima. ^e Using coumarin 334 as the standard ($\Phi = 0.69$ in MeOH).¹⁸

TABLE 2. ECL and Electrochemical Data for PEANs 1–6 Recorded in Acetonitrile with 50 mM TBAP

PEAN	$\lambda_{\max}^{\text{ECL}}$ (nm, eV)	$E_{\text{p,ox}}$ (V)	$E_{\text{p,red}}$ (V)	$-\Delta H^\circ$ (eV) ^a
1	542, 2.28	1.62	−0.92	2.38
2	541, 2.28	1.62	−0.91	2.37
3	536, 2.30	1.49	−0.89	2.22
4	556, 2.22	0.90	−0.90	1.64
5	550, 2.24	0.87	−0.90	1.61
6	540, 2.28	0.91	−0.90	1.65

^a Calculated using the equation $\Delta H^\circ = E_{\text{p,ox}} - E_{\text{p,red}} - 0.16$.¹⁵

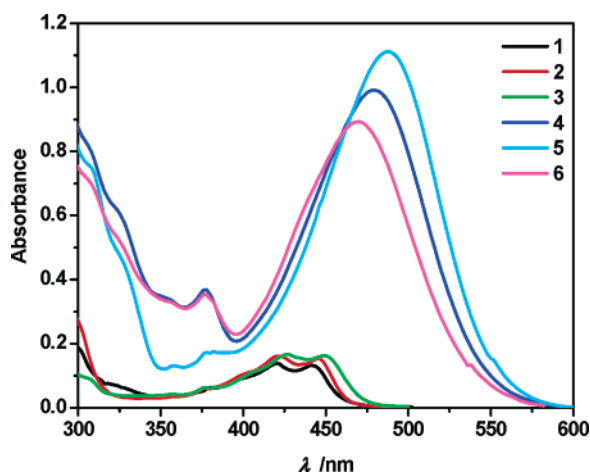


FIGURE 1. UV–vis absorption spectra of PEANs 1–6 in ACN (10^{-5} M).

poor donors (R = H, Me, OMe), the longest wavelength of the absorption maximum is about 440 nm as a structured band (3 broadens slightly because of the enhancement of donor strength). This implies that the vertically excited lowest singlet state (the Franck–Condon state) has little or no charge transfer. From the approximate spacing of about 1250 cm^{-1} , the transition is likely the result of the stretching contribution $\nu(\text{CC})$ from the polyaromatic anthranitrile unit. For those PEANs which have stronger donors (R = NMe₂, NEt₂, piperidyl), the maximum shifts to >480 nm with a structureless feature. This vast red-shift can be attributed to the absorption from the charge-transfer transition at the lowest Franck–Condon excited state.

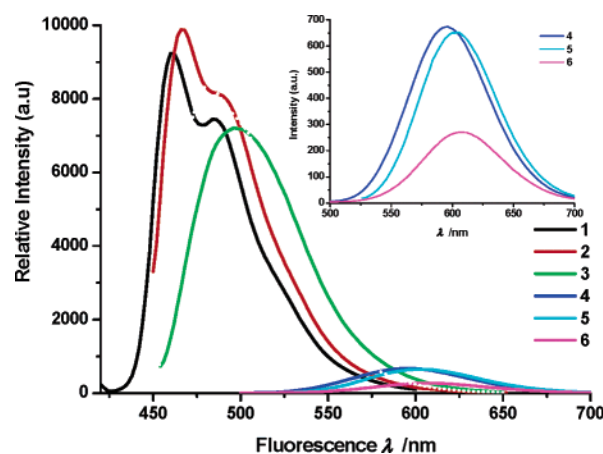


FIGURE 2. Fluorescence emission spectra of PEANs 1–6. Spectra of 1–3 were recorded in ACN and those of 4–6 in CH₂Cl₂ (10^{-5} M); inset is a magnified view of the spectra of 4–6.

The preceding argument is supplemented by the emission characteristics as well. Compounds 1 and 2 emit closely at the same maximum with vibrational fine structure while 3 attains a moderate charge transfer given its structureless emission band in ACN again caused by the increase in donor strength (Figure 2). Although the amine substituted compounds 4–6 beneficially exhibited longer red-shifts and higher intensities in the absorption spectra, their emission intensities were diminished in polar ACN when compared to those of 1–3 with no or weaker donors. In polar solvents such as ACN, for the stronger ICT compounds, the energy level of the ICT state becomes so low that back-electron transfer occurs to populate the ground state, and therefore 4–6 did not show fluorescence in ACN. In less polar methylene chloride, 4–6 show emission with a Stokes shift of >100 nm. In general, the increased Stokes shift is indicative of better stabilization of the emitting state of the acceptor moiety that is in communication with the donor moiety at remote.

While the absorption maxima of 1–6 were found to be >40 nm red-shifted in comparison with that of the parent, 9-cyanoanthracene ($\lambda_{\max}^{\text{Abs}} = 400 \text{ nm}$, $\lambda_{\max}^{\text{Flu}} = 440$), the emission maxima were found to be shifted from 40 to 140 nm. Compounds 1–3 showed intense green emission, while 4–6 showed beautiful orange-red fluorescence in solution (CH₂Cl₂/CHCl₃). Since molecules showing a preferably narrow emission typically close to 600–650 nm would be suitable for red-emitting LEDs^{4,19} and those emitting at about 500 nm would be suitable for green-emitting LEDs, the reported compounds may be of use as dopants in an EL device. The photoluminescence quantum yields (Φ measured in CH₂Cl₂) are moderate to quite high (from 0.05 to 0.73, those of 1–3 were the highest). The reduction in the Φ values of 4–6 may be the result of the lower energy of the emitting states which may facilitate nonradiative decay or produce low-energy states that decay to the ground state by back-electron donation.

The electronic absorption spectral properties can be better understood by analyzing the calculated highest-

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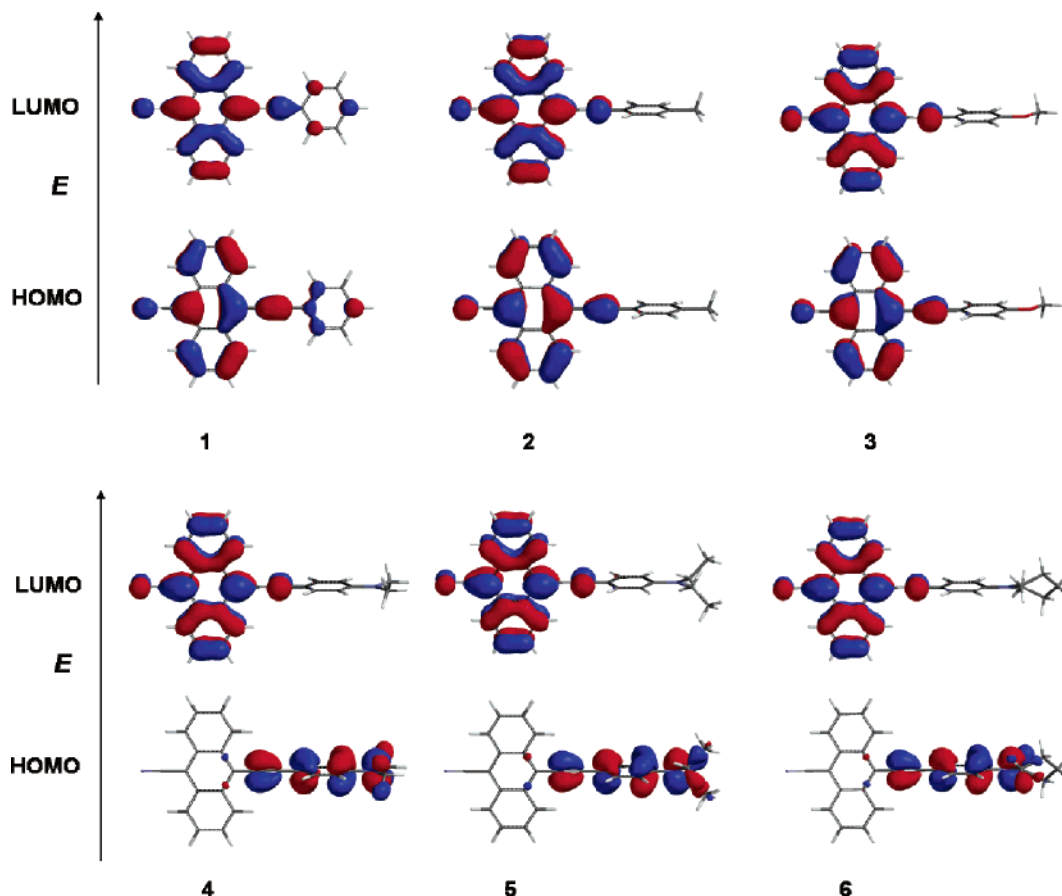


FIGURE 3. HOMO and LUMO levels of PEANs 1–6 calculated at the B3LYP/6-31G* level of density functional theory with a 6-31G* basis set using Spartan'04 for Windows.

occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) surfaces of the molecules (Figure 3). Molecule 1 (B3LYP/6-31G*) has a planar structure with frontier orbital distributed throughout the backbone. Thus, this compound has an absorption spectrum that shows a weak structured transition as the longest-wavelength absorption. Molecules 2 and 3, though they have moderate electron-donating groups, such as Me and OMe, their B3LYP/6-31G*-optimized structures at the ground state are not planar but twisted with a dihedral angle of 90°. Their HOMO and LUMO are mainly localized on the acceptor anthronitrile subunit, and there is no contribution from the donor-bearing phenyl moiety. Thus, their electronic absorption implies a vertical excitation of the electron from the HOMO of the anthronitrile to the LUMO of the same unit.

The entire scenario takes a turn in the case of molecules 4–6. It is interesting that these molecules, although they are twisted in a manner similar to 2 and 3, have their HOMO and LUMO at different locations; namely, the HOMO is localized on the donor-bearing phenyl moiety, and the LUMO is localized on the acceptor anthronitrile subunit. Thus, these molecules experience intramolecular charge transfer during electronic absorption, and hence, their absorption spectra show a strong structureless band at the longest wavelength. These molecules make good examples of systems with remotely communicating groups that can be applied in molecular electronics.

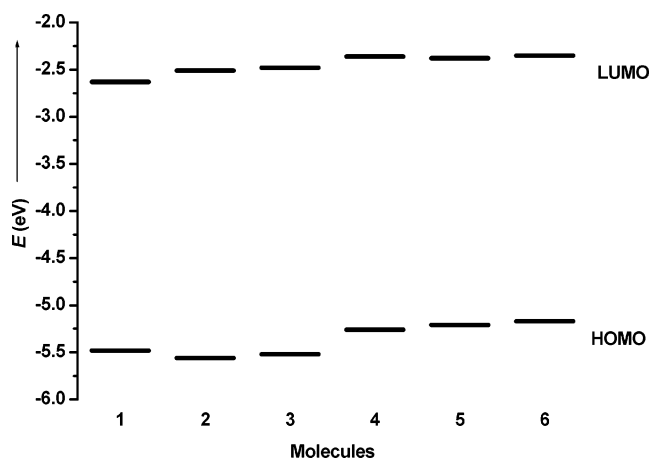


FIGURE 4. Energy level diagram showing the influence of the donor substituents on the HOMO and LUMO energies.

By comparing the B3LYP/6-31G* HOMO and LUMO energy levels of compounds 1–6 (Figure 4), one can see that both HOMO and LUMO energies are higher by 0.2–0.3 eV for the strong donor-substituted PEANs 4–6 than those for 1–3 which indicates the moderate influence of the strong donor moieties; they are also consistent with the experimental results observed in the absorption and emission spectra.

Electrochemistry. Cyclic voltammograms (CV) were recorded to determine the electrochemical activity and the reduction and oxidation potential values of these

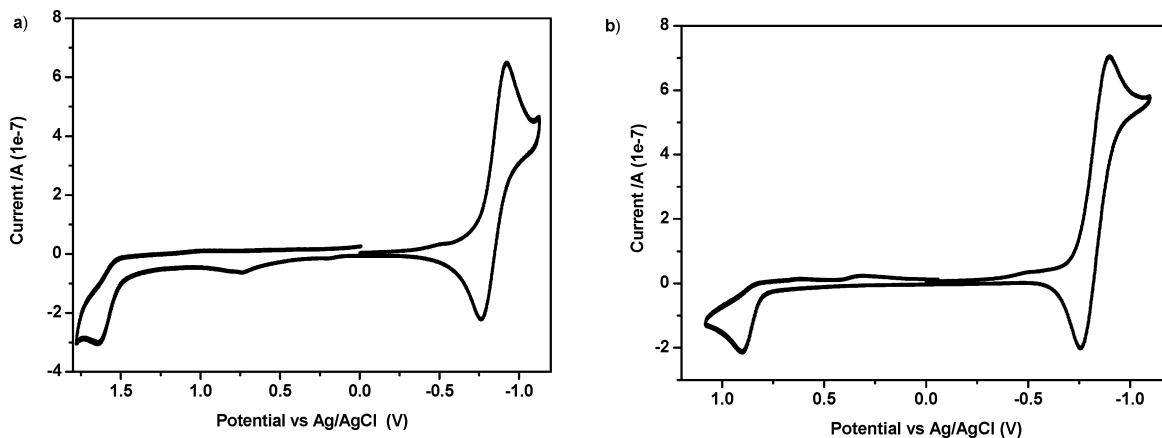


FIGURE 5. CV traces for PEANs **1** (a) and **4** (b) recorded in ACN containing 50 mM TBAP at a scan rate of 50 mV/s.

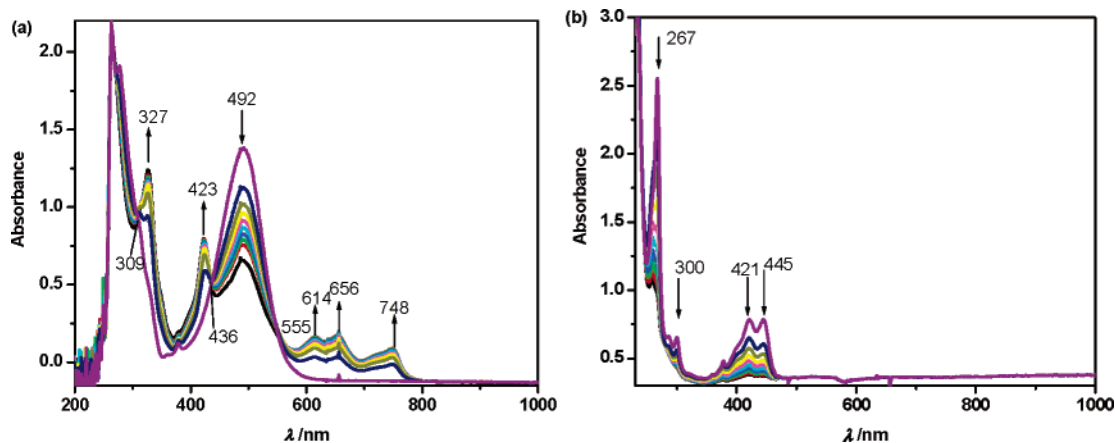


FIGURE 6. UV-vis spectra of the radical anion (a) and radical cation (b) of PEAN **1**.

compounds. CV of **1–6** (1.0×10^{-3} M) were recorded in acetonitrile with 50 mM tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte at a scan rate of 0.05 V/s, and the reduction and oxidation peak potentials are recorded in Table 2.

The reversible reduction peak potentials occur in the vicinity of -0.9 V which corresponds to the reduction at the 9-cyanoanthracene moiety. The extension of conjugation through a triple bond has altered the reduction potential significantly in comparison to the reported reduction potential of -1.27 V for the unsubstituted parent, 9-cyanoanthracene.²⁰ As seen in Figure 3, PEANs **2–3** have the HOMO and LUMO localized mainly on the acceptor anthronitrile unit with delocalization extending up to the $C\equiv C$ triple bond. Hence, the redox process occurring in these compounds can be assumed to take place mainly on the part of the π -extended acceptor anthronitrile. The oxidation curve is irreversible for **1–3**; however, a well-defined peak corresponding to the peak potential could be observed, and the reduction curves are fully reversible (Figure 5).

PEANs **4–6** showed quasi-reversible oxidation peaks and fully reversible reduction peaks. The HOMOs for PEANs **4–6** are localized on the donor-neighboring phenyl moiety, and the LUMOs are localized on the acceptor anthronitrile subunit with the $C\equiv C$ triple bond contri-

buting to both HOMO and LUMO which indicates the involvement of the bridging unit in the redox processes. All compounds are found to show stability for about 8–10 electrochemical cycles.

UV-Vis Spectroelectrochemistry. UV-vis spectroelectrochemical experiments were carried out on all of the compounds to obtain more information about the redox process and the eventual products of the reaction. The UV-vis spectra were recorded for the radical ions generated by electrolysis. All compounds, when reduced, showed the formation of a new band at about 320 nm and another set of long-wavelength bands centered at about 650 nm with the tail extending up to 750–800 nm. The intensity of the longest-wavelength band also increases with an increase in the voltage (-0.3 V every 30 s for 4–5 min). This increase in intensity is accompanied by a decrease in the intensity of bands at 260 and 450 nm. Figures 6 and 7 are typical UV-vis absorption spectra of PEANs **1** and **4** (reduced and oxidized), respectively, as representative cases of weak and strong donor-substituted PEANs (the spectra for the rest are provided in the Supporting Information). The appearance of two isosbestic points in the reduction spectra indicates the existence of two species, namely, the neutral and radical anions of the respective compounds, in equilibrium.

The UV-vis spectra of the radical cations of PEANs **1–3**, with no or weak donors, produce long-wavelength

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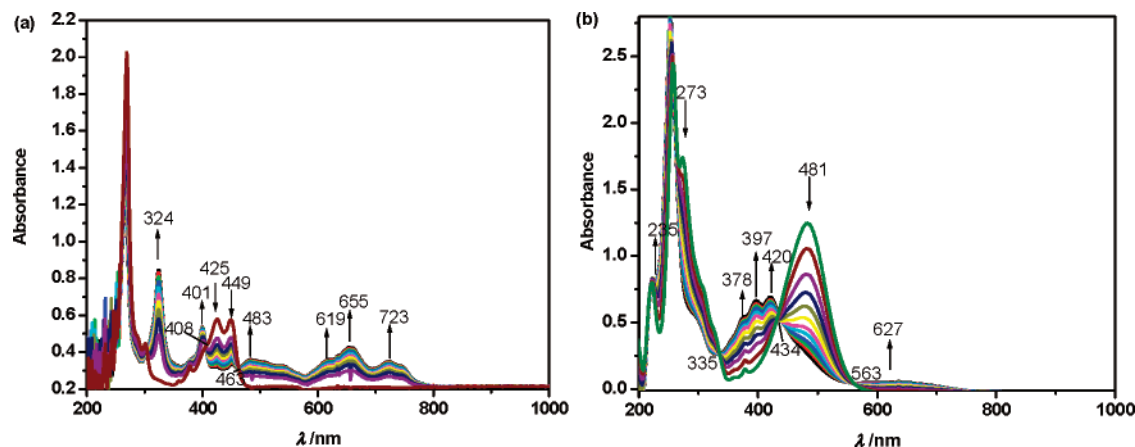


FIGURE 7. UV-vis spectra of the radical anion (a) and radical cation (b) of PEAN 4.

maxima that are too weak or do not show (e.g., Figure 7b), whereas PEANs 4–6, which have oxidizable amine groups, exhibit the formation of new long-wavelength bands centered at about 630 nm. They have features which signify the existence of mixtures of free and radical cations of the reactant molecules in equilibrium as revealed by the noticeable formation of two isosbestic points at about 335 and 430 nm. The trend observed in the UV-vis spectroelectrochemistry is rationalized with the help of the HOMO and LUMO frontier orbital diagrams in Figure 3. As discussed earlier, since the HOMO and LUMO are localized at the acceptor part for PEANs 2 and 3, the radical ions in these systems are generated only within this subunit of the molecule. However, the formation of long-wavelength maxima beyond the photoabsorption maxima can be attributed to the formation of the charge resonance state wherein resonance occurs between the reducible center (the anthronitrile moiety) and the other end (the phenyl moiety) facilitated by conjugation through the triple bond. The formation of new long-wavelength bands in PEANs 4–6 is plausible given the occurrence of the HOMO on the donor part of these molecules; this is not the case with PEANs 2 and 3 in which there are no such oxidizable groups and the HOMOs are found on the acceptor part. Thus, the appearance of long-wavelength bands in PEANs 4–6 indicates that radical ions are indeed formed and involved in resonance with the acceptor moiety, and hence, these groups are electrochemically active. More prominent absorption bands appear for the reduced states as well, and the charge resonance in such cases leads to stronger absorption which results in the appearance of bands more intense than those in the oxidized states. The electrochemical reversibility, as confirmed by the reproducibility of the absorption spectra of the neutral compound solution from the electrochemical cycling for all of the compounds, was satisfactory.

The preceding discussion is supported by computational DFT calculations for the charged molecules. Figure 8 depicts the electrostatic potential density maps for the representative molecules **1** (no donor) and **6** (strong donor). Charged molecule **1** has a planar geometry similar to that of the neutral state; the radical anion carries more negative charge at the center of the acceptor anthronitrile moiety (red, more negative), and the radical cation carries less electron density (blue, more positive)

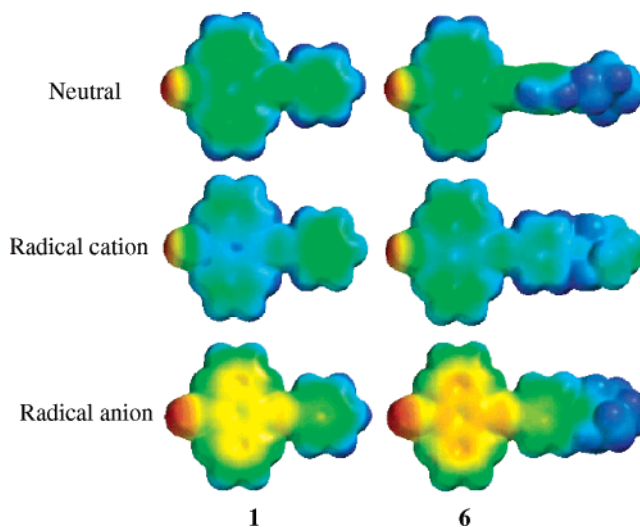


FIGURE 8. Electrostatic potential maps for the PEAN (from top to bottom): **1**, **1⁺**, and **1⁻** (left) and **6**, **6⁺**, and **6⁻** (right). The maps for the radical ions were obtained using density functional theory (DFT-B3LYP/6-31G*). Red is more negative. Blue is less electronegative and more electropositive.

at the center of the molecule. Both radical ions have very different charge densities in comparison to that of the neutral molecule. PEAN **6** attains planarity in the charged state; the radical anion carries more negative charge at the acceptor anthronitrile unit (red), and the radical cation carries more positive charge at the donor site (less green and more blue, more positive). The planarization caused by charging, together with the electrostatic difference, can induce charge resonance between the communicating groups, namely, the donor and the acceptor, and thus produce new absorption bands.²¹

Figure 9 shows the HOMO and LUMO surfaces for the charged species of **1** and **6**. As seen from this figure, the radical anion of **1** carries the HOMO coefficient at the acceptor unit and the LUMO at the phenyl moiety. Thus, the electronic absorption involving charge resonance can be expected and has been observed (Figure 7a). The radical cation has an orbital coefficient almost uniformly distributed in both the HOMO and LUMO, and therefore, no charge resonance can be expected for electronic absorption; hence, the spectrum is flat at the region

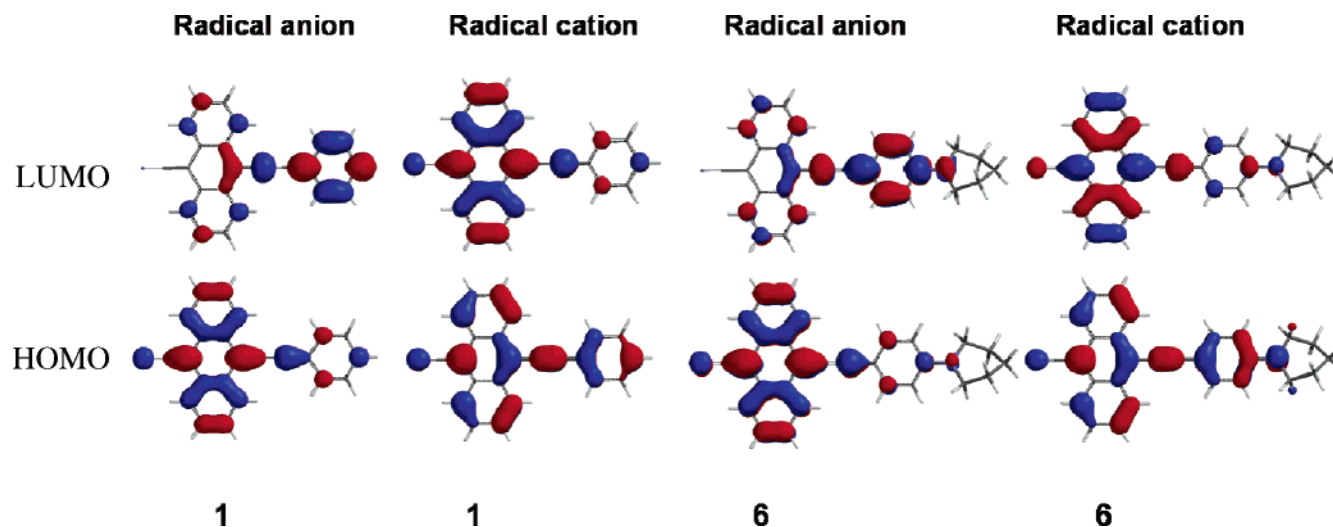


FIGURE 9. HOMO (bottom) and LUMO (top) surfaces for radical ions of **1** and **6** (DFT-B3LYP/6-31G^{*}).

shown in Figure 7b. The situation changes when a strong donor is substituted for the weak donor. With a piperidinyl unit at the phenyl moiety (PEAN **6**), the radical anion carries the HOMO and LUMO at two different locations; the radical cation seems to have an almost uniform distribution throughout the charged molecule. Thus, this molecule (as well as the other strong donor-substituted molecules **4** and **5**) experiences a charge difference in their charged state, and therefore, they undergo charge resonance during absorption.

Electrochemiluminescence. ECL spectra were recorded in acetonitrile at 1.0 and 0.10 mM concentrations with 50 mM tetrabutylammonium perchlorate as the supporting electrolyte in a cell setup similar to one that was previously published.¹⁰ The electrodes were pulsed between the first oxidation and first reduction peak potentials at various pulse intervals to generate radical ions and the subsequent annihilation reaction. Satisfactory ECL spectra were obtained at a 10⁻⁴ M concentration of the sample, while no ECL was observed at the lower concentrations used for photoluminescence measurements. Moreover, the ECL emission intensity diminished greatly at higher concentrations (10⁻³ M) when compared with those of photoluminescence (10⁻⁵ M). A typical ECL spectrum of compound **3** is depicted in Figure 10, and the maxima of all compounds are recorded in Table 2.

As can be seen from Tables 1 and 2, the ECL maxima for **1–3** are red-shifted by 40–80 nm, and for compounds

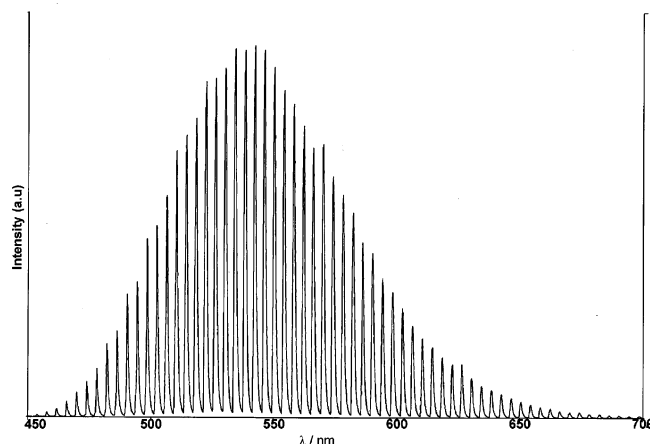
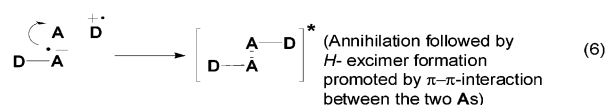
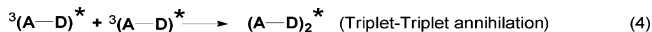
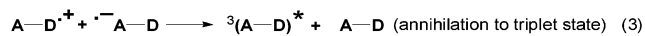


FIGURE 10. ECL spectrum of **3** in ACN (10⁻⁴ M).

SCHEME 2



A stands for acceptor and D for donor

4–6, the ECL maxima are blue-shifted by 40–68 nm when compared with their fluorescence maxima. The enthalpy change ($-\Delta H^\circ$) values for the radical ion annihilation, calculated from the peak potentials, are greater than the ECL maximal energies for **1** and **2**, and hence, they can follow the S route. The annihilation enthalpy changes for **3–6** are not sufficient to populate the excited emission state. The direct annihilation of radical ions can generate a triplet state instead, and

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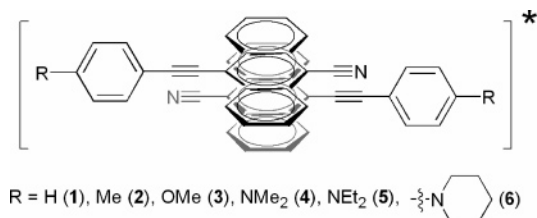


FIGURE 11. *H* excimer or trans excimer formation proposed for the ECL-emitting state of PEAN.

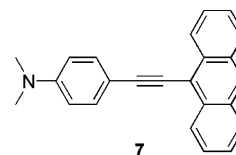
hence the emission state can be generated by the triplet–triplet annihilation process (T route, Scheme 2).

The possibility of the excimer formation in step 5 of the above mechanism can be thought to be promoted by the π – π interaction between the two acceptor subunits as shown in eq 6 of Scheme 2. The excited state may have a structure in which the two acceptor headgroups align head to head with the donor tailgroups projecting away from one another in an anti H–H fashion as shown in Figure 11.

The parent 9-cyanoanthracene is known to form an excimer in solution, glass, and crystalline matrixes, and the energy of excimer-type ECL emission, in general, is in agreement with the published photoexcimer energy of parent 9-cyanoanthracene.²² Further, it is interesting to note that the ECL maxima of **1–6** occur very closely at about 540–550 nm regardless of the nature of the donor groups. In view of the preceding discussions, we infer that the ECL emissions in **1–6** are all from a similar type of species, and we presume it to be from a special type of excimer as shown in Figure 11. A remarkable recent publication by Ketter and Wightman²³ has indicated the possibility of an annihilation reaction producing as yet unknown excited states other than the photoluminescence state. These authors have studied the tuning of the emission states of the benzophenone/phenoxathiin or benzophenone/4-methoxythioanisole system among others. They have discovered the formation of an excimer of benzophenone in the ECL; it was a species that was not found in its photoluminescence upon increasing the concentration of benzophenone 100 fold.

In the present study, we have noticed the formation of an ECL emission maximum that is either red-shifted (PEANs **1–3**) or blue-shifted (PEANs **4–6**) with respect to the photoluminescence maxima. The structure, proposed as a *H*-type or trans excimer with donor-bearing phenyl tails projecting perpendicularly away from the two inversely face-to-face aligned acceptor anthronitrile headgroups (resembling the letter H), also amounts to a decrease in the dipole moment of the species. Given the steric nature of the bimolecular complex, only the proposed supramolecular assembly is more plausible because they cannot form the normal cis excimer in which case the ECL maxima would be shifted more to the red (especially for **4–6**) than to the blue, compared to the photoluminescence maxima (see ref 12a). Attempts to draw evidence from the X-ray crystal structure analysis were unsuccessful because of the inability of these

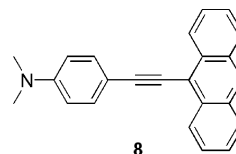
compounds to crystallize large enough for the X-ray diffraction analysis. Hence, a model compound, namely, *N,N*-dimethylaminophenylethynylanthracene (**7**),



was prepared so that a single-crystal X-ray analysis could be obtained.²⁴ Figure 12 shows the packing diagram of compound **7** which depicts the existence of two adjacent molecules in the proximity of the moieties of the molecule which are aligned in an anti H–H fashion with an interplanar distance of 3.48 Å.

The donor-bearing phenyl group is projecting in a near-perpendicular fashion relative to the anthracene moiety. The dihedral angle between the plane of the donor-bearing phenyl group and that of the anthracene group was determined to be 73.7°, and the interplanar distance between the two offset-parallel anthracene planes of adjacent molecules was measured to be 3.48 Å which is within the range of a typical π – π interaction.²⁵ The ECL of compound **7** has also been found to be blue-shifted by about 30 nm with respect to its own photoluminescence maxima (to be reported elsewhere along with many other related compounds).²⁶

A similar situation has also recently been encountered by us in the family of phenylethynylacridines.²⁷ The *N,N*-dimethylaminophenylethynylacridine (**8**),



which showed a blue-shift of about 35 nm compared to its photoluminescence maximum, crystallized in a triclinic prism with two acridinyl heads facing each other invertedly with *N,N*-dimethylaminophenyl groups projecting nearly perpendicularly in opposite directions (Figure 13), similar to the structure depicted in Figure 11. The dihedral angle between the plane of acridine and that of donor-bearing phenyl is measured to be 73.3°, and the interplanar distance between the two offset-parallel planes of the acridines at 91.83° was measured to be 3.59

(24) Crystal data for **7**: Formula C₂₄H₁₉N; formula weight 321.40. Unit cell parameters with standard deviations (unit cell lengths in angstroms): cell length *a* 9.2040(2) Å, cell length *b* 9.3250(2) Å, cell length *c* 11.0960(3) Å; cell angle α 72.871(2)°, cell angle β 80.4240(10)°, cell angle γ 71.4130(10)°; cell volume 859.86(4) Å³; symmetry space group *H*–*M*, *P*1; cell formula units *Z* 2; temperature of study 295(2) K; absorption coefficient 0.072 mm^{–1}; reflections collected 5163; independent reflections 2982 (*R*_{int} = 0.0226); final *R* indices [*I* > 2 σ (*I*)] *R* = 0.0451, *R*_w = 0.1232; *R* indices (all data) *R* = 0.0582, *R*_w = 0.1361.

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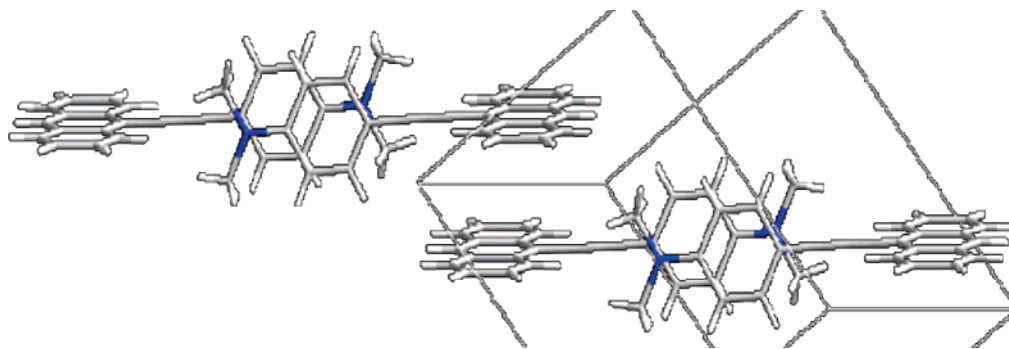


FIGURE 12. Crystal packing diagram of **7** showing the π - π interactions between the two adjacent anthracene moieties of the molecule. It is aligned in an anti H-H fashion with an interplanar distance of 3.48 Å.

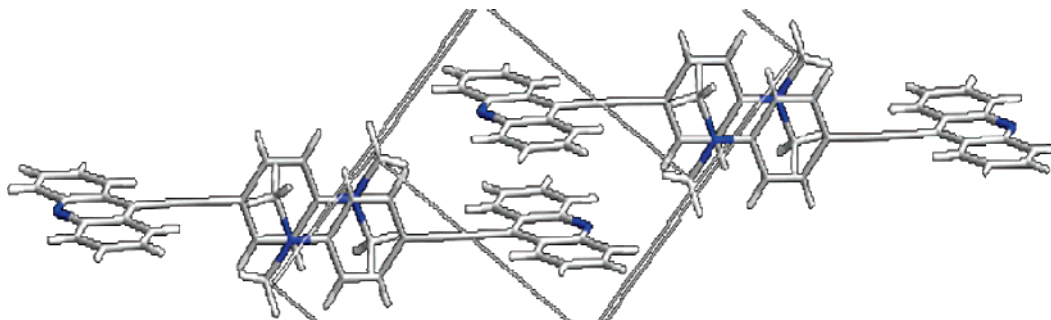
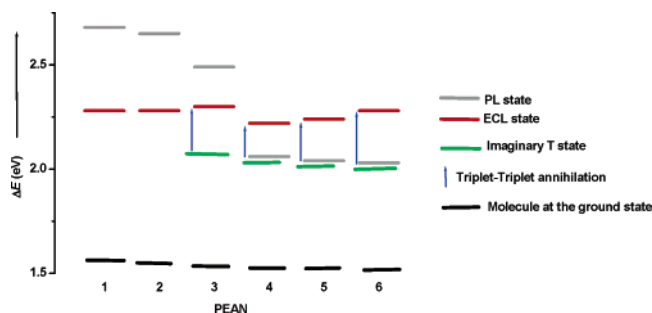


FIGURE 13. X-ray crystal packing diagram showing π -stacking interactions between the two adjacent acridinyl units. The interplanar distance between the two planes of acridine was measured to be 3.59 Å (from ref 27).

SCHEME 3. Schematic of Routes of Formation of the Various Energy States for the PL and ECL of the PEANs 1–6



Å.²⁸ A similar trend was also noticed in the case of donor-substituted phanyethynylcoumarins.²⁹ The extent of the ECL blue-shift from the PL maximum in the present family of compounds is the largest (up to 68 nm) in our studies so far.

In light of the preceding discussion and in view of the energy states of both photoluminescence (PL) and electrochemiluminescence (ECL), we can draw a schematic of the whole picture (Scheme 3) which summarizes the processes taking place during the electronic transitions

(28) Crystal data for **8**: Formula $C_{23}H_{18}N_2$; formula weight 322.39. Unit cell parameters with standard deviations (unit cell lengths in Angstroms): cell length a 9.2827(2) Å, cell length b 9.3930(2) Å, cell length c 10.7357(3) Å; cell angle α 81.7260(10)°, cell angle β 72.9830(10)°, cell angle γ 71.801(2)°; cell volume 849.25(3) Å³; symmetry space group $P\bar{1}$; cell formula units Z 2; temperature of study 295(2) K; absorption coefficient 0.02(2) mm⁻¹; reflections collected 5997; independent reflections 3827 (R_{int} = 0.0192); final R indices [$I > 2\sigma(I)$] R = 0.0483, R_w = 0.1278; R indices (all data) R = 0.0671, R_w = 0.1449.

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and respective states. As discussed earlier, the ECL states for all of the compounds (represented by red bars in the scheme) appear at states with close to the same energy, whereas the PL states (represented by gray bars) occur at different energy levels consistent with the structure of free compounds (cf. Tables 1 and 2). The radical ion-annihilation reaction can thus produce new excited states other than the PL states.

Conclusion

We have synthesized a new series of donor-substituted phenylethynylanthonitriles (PEANs **1–6**) and studied their photophysical and ECL properties. Compounds **1–3**, bearing weak donor groups, exhibit no charge transfer, and their electronic absorption spectra are of Franck-Condon-type. Compounds **4–6** show strong ICT interactions in the ground and excited states. The energies of excited ICT states for **4–6** become so low that they are not fluorescent in high-polarity acetonitrile solvent. Density functional theory provided evidence for the observed electronic properties, in that the properties of **2** and **3**, bearing weak donors, are controlled by the acceptor anthronitrile moiety and those of **4–6** are of the ICT-type involving both the donor and acceptor moieties. The electronic absorption, electro reduction and oxidation, and UV-vis spectroelectrochemistry can be explained by the orbital distribution and electrostatic charge densities of these neutral compounds and their radical ions.

All compounds reported here exhibit electrogenerated chemiluminescence (ECL) without the use of a co-reactant. Surprisingly, all of the compounds emit ECL at almost the same maxima centered at 545 nm regard-

less of the nature of the donor subunits. The observation of ECL in high-polarity acetonitrile while photoluminescence was not observed in the same solvent at even higher concentrations of the fluorophore supports the notion that the ECL-emitting state is different from the photoluminescent state. The possibility of the formation of a new kind of arrangement in high-concentration solutions is rationalized by the ability of such structurally related compounds to undergo π - π interaction. Thus, it is possible to generate a new excited state by the appropriate structural modification of fluorophores and the choice of conditions. These compounds appear to have qualities suitable for further application of ECL, and some of them could be good candidates for light-emitting diodes. Preliminary EL studies involving PEAN **4** have indicated that this compound can be applied as a dopant in a device to emit red light. Fabrication of sophisticated devices with better multicolor tuning and extensive device property studies will be pursued in the future.

Experimental Section

Materials and Methods. Phenyl acetylene and tolyl acetylene were obtained from commercial sources and were used as received. The rest of the terminal alkynes were reported earlier from our lab.^{12,17a} Dichlorobis(triphenylphosphine)palladium(II) was either prepared in-house or obtained from a commercial source. Solvents were distilled as per the standard methods and purged with argon before use. Triethylamine (TEA) and tetrahydrofuran (THF) were distilled and purged with a mixture of approximately 1:1 argon/hydrogen before use. ¹H NMR spectra of the samples were recorded with a 300/400 MHz instrument, and ¹³C NMR spectra were recorded at 100.1 MHz operator frequency in CDCl₃ solvent with CHCl₃ as the internal standard (δ 7.24 for ¹H and 77 middle of the three peaks for ¹³C spectra). Mass spectra were recorded on a nitrobenzyl alcohol matrix. TLC was run on precoated aluminum plates (Si 60 F₂₅₄). Column chromatography was run on silica gel (60–120 mesh) and neutral alumina (70–230 mesh). All UV–vis spectra were recorded on a spectrophotometer with a 10 μ M solution of the compounds in CH₃CN, and all fluorescence spectra were recorded on a fluorescence spectrophotometer using similar solution concentrations. Quantum yields were determined using coumarin 334 as the standard ($\Phi = 0.69$ in MeOH).¹⁸ CV measurements were done on a voltammograph using a cell consisting of a carbon disk (2.0 mm) working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. The scan rates were 50 and 100 mV/s. UV–vis

spectroelectrochemistry was performed with an optically transparent thin-layer electrode cell coupled with an UV–vis spectrophotometer.²⁰ ECL spectra were recorded at room temperature using a setup consisting of a fluorescence spectrophotometer and a voltammograph with a computer interface. The electrode surfaces were prepared freshly before the CV and ECL experiments. The carbon disk electrode was rubbed against alumina paste, and the Pt wire and Pt mesh electrodes were cleaned by rinsing with dilute nitric acid followed by water; then they were finally fired with a naked flame to ensure maximum cleanliness of the electrode. Typically 0.1 and 1.0 mM concentrations of the compound in acetonitrile with 0.05 M tetrabutylammonium perchlorate (TBAP) were loaded into the quartz cell, degassed with pure argon, and electrolyzed between platinum wire and platinum mesh electrodes. The platinum electrode was pulsed between first reduction and first oxidation potentials to generate reaction, and the pulse interval was controlled on a computer. The general synthetic method and the characterization data of compounds **1–6** are provided in the Supporting Information.

Theoretical Calculations. Density functional theoretical and semiempirical calculations were performed using Spartan'04 (for Windows).³⁰ The structures were drawn at the entry-level of input and minimized. Equilibrium geometry was obtained at the B3LYP level of DFT for each molecule at the ground state from its initial geometry subject to symmetry with a 6-31G* basis set.³¹ The total charge was kept neutral, anionic, or cationic as required, and the multiplicity was set at singlet or doublet as required. Orbitals and energies, atomic charges, vibrational modes, and thermodynamic properties were chosen as output parameters. HOMO and LUMO orbital surfaces and electrostatic potential density maps were then obtained from the output.

Acknowledgment. Financial support for this work was provided by the National Science Council of Taiwan.

Supporting Information Available: Characterization data, UV–vis and fluorescence spectra in CH₂Cl₂, raw ECL, ¹H NMR, and ¹³C NMR spectra of all compounds, Cartesian coordinates for all neutral molecules and radical ions of **1** and **6**, and the UV–vis spectra of the radical ions of all compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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