

Synthesis and Electrogenenerated Chemiluminescence of Donor-Substituted Phenylethynylcoumarins

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Two series of donor-bearing phenylethynylcoumarins have been synthesized, and their photophysical properties have been evaluated. Chemiluminescence was observed through the annihilation of their electrogenerated radical ions and was found to be only slightly affected by the presence of various donor groups on the phenyl moiety linked through the C–C triple bond. The overall properties of the two series of compounds are discussed with respect to their structures. The observed electronic absorption properties are explained with the help of computational studies.

Introduction

Electrogenenerated chemiluminescence (ECL) is becoming increasingly important due to its potential application in immunoassay.¹ ECL is considered advantageous because it does not require a light source for excitation. Although a wide variety of organic molecules have been found to exhibit ECL,^{1b–f} most of them exhibit emission from the annihilation of their radical ions produced at the vicinity of electrodes in the presence of a co-reactant, especially tertiary amines. To study the ECL behavior of highly fluorescent laser dyes is of interest in view of their excellent fluorescence properties. The major requirements for compounds to be suitable for ECL include high fluorescence quantum yield, the electrochemical stability – that of radical anions and radical cations, and the efficiency of radical ion-annihilation and energy transfer. Park and Bard have studied² for the first time the electrochemical behavior and ECL of selected laser dyes, coumarin 2, coumarin 30, oxazine 1, Nile Blue, Rhodamin B, and Rhodamine 6G, which are well-known fluorescent molecules.

In our continued endeavor³ of finding new molecules for the ECL and for light-emitting devices, we became

interested in studying the effect of the extension of conjugation in coumarin compounds via introduction of a C–C triple bond with an electron push directed toward the coumarinyl moiety on ECL and other photophysical properties. Coumarin was chosen because of its excellent photochemical and photophysical nature⁴ especially in biological activity^{4e} as well as in organic light-emitting devices (OLED).^{4f,g} Despite remarkable properties and uses, there are no reports on the ECL properties of the ethynyl compounds of coumarins, although two reports are available on the syntheses and photophysical properties⁵ and one is available on the incorporation in the polymer backbone.⁶ For the present study, we chose two different positions of linkage, 3-coumarinyl and 7-coumarinyl derivatives. The donor groups were varied by substituting the *p*-hydrogen of the phenylethynylcoumarins with Me, OMe, OⁱPr, and NMe₂ groups. These groups have been chosen to study the effect of increasing donor strength in that order as well as of the introduction of steric hindrance at the donor site on the optical and ECL properties of the resultant molecules. We have observed that the OMe-substituted phenylquinolinylethynes showed excimer ECL due to the low twist angle, while the NMe₂-substituted counterpart exhibited monomeric intramolecular charge-transfer (ICT) ECL.^{3a} Our expectation in the present study is that the introduction of the OⁱPr group, a bulkier group than OMe, would

(1) References are only comprehensive and not extensive. (a) Richter, M. M. *Chem. Rev.* **2004**, *104*, 3003. (b) Kuwana, T. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1966; Vol. 1, Chapter 3. (c) Bard, A. J.; Faulkner, L. R. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1977; Vol. 10, p 1. (d) Hercules, D. M. *Acc. Chem. Res.* **1969**, *2*, 301. (e) Lai, R. Y.; Fabrizio, E. F.; Lu, L.; Jenekhe, S. A.; Bard, A. J. *J. Am. Chem. Soc.* **2001**, *123*, 9112. (f) Faulkner, L. R.; Bard, A. J. *Electrogenenerated Chemiluminescence*. In *Electrochemical Methods*; John Wiley & Sons: New York; 1980; pp 621–627. (g) Oyama M.; Okazaki, S. *Anal. Chem.* **1998**, *70*, 5079. (h) Kapturkiewicz, A. *J. Electroanal. Chem.* **1990**, *290*, 135. (i) Kapturkiewicz, A. *J. Electroanal. Chem.* **1991**, *302*, 13. (j) Knight, A. W.; Greenway, G. M. *Analyst* **1994**, *119*, 879 and references therein. (k) Miao, W.; Bard, A. J. *Anal. Chem.* **2003**, *75*, 5825.

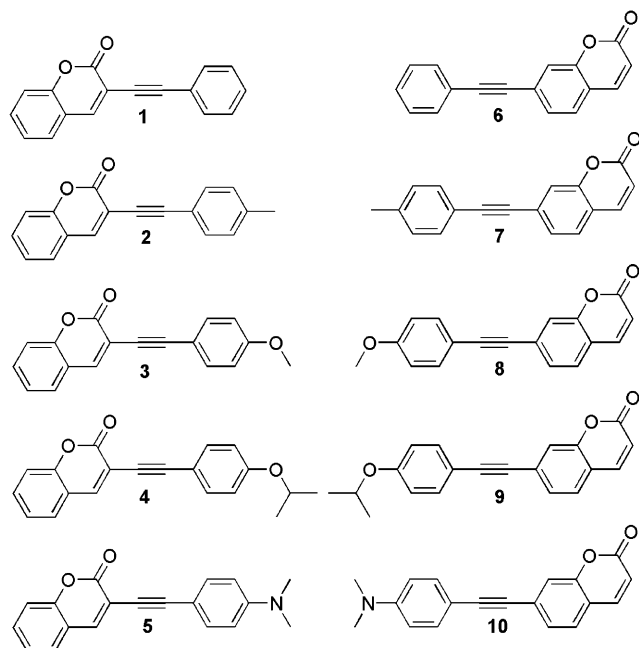
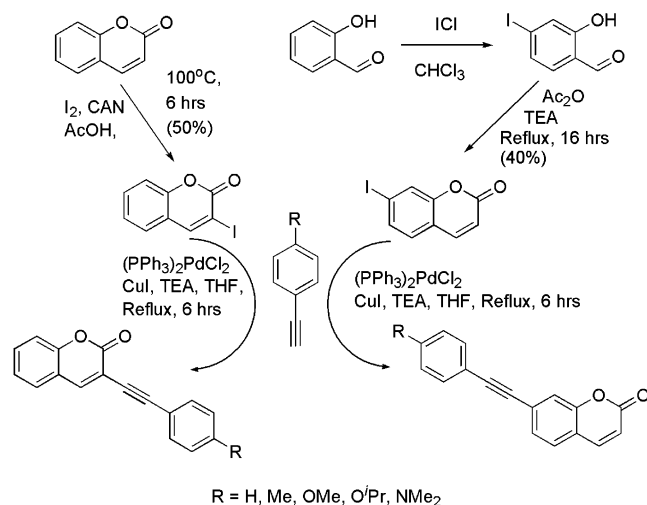
(2) Park, S. M.; Bard, A. J. *J. Electroanal. Chem.* **1977**, *77*, 137.

(3) (a) Elangovan, A.; Chen, T.-Y.; Chen, C.-Y.; Ho, T.-I. *Chem. Commun.* **2003**, 2146. (b) Chen, C.-Y.; Ho, J.-H.; Wang, S.-L.; Ho, T.-I. *Photochem. Photobiol. Sci.* **2003**, *2*, 1232. (c) Elangovan, A.; Yang, S.-W.; Lin, J.-H.; Kao, K.-M.; Ho, T.-I. *Org. Biomol. Chem.* **2004**, *2*, 1597.

(4) (a) Reynolds, G. A.; Drexhage, K. H. *Opt. Commun.* **1975**, *13*, 222. (b) Maeda, M. *Lasers and Dyes*; OHM: Tokyo, 1984. (c) Elderfield, R. C., Ed. *Heterocyclic Compounds*; John Wiley: New York; 1951; Vol. 2, p 173. (d) Katritzky, A. R.; Rees, C. W., Eds. *Comprehensive Heterocyclic Chemistry*; Pergamon Press: Oxford, 1984; Vol. 3, Part 2B, p 641. (e) See, for example: *Coumarins-Biology, Applications and Mode of Action*; O'Kennedy, R., Thornes, R. D., Eds.; Wiley: Chichester, 1997. (f) Kido, J.; Lizumi, Y. *Appl. Phys. Lett.* **1998**, *73*, 2721. (g) Tasch, S.; Brandstätter, C.; Meghdadi, F.; Leising, G.; Froyer, G.; Athouel, L. *Adv. Mater.* **1997**, *9*, 33. (h) Muthuramu, K.; Ramamurthy, V. *J. Org. Chem.* **1982**, *47*, 3976.

(5) (a) Schiedel, M.-S.; Briehn, C. A.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 4677. (b) Mori, A.; Ahmed, M. S. M.; Sekiguchi, A.; Masui, K.; Koike, T. *Chem. Lett.* **2002**, 756.

(6) Fomine, S.; Fomina, L.; Sánchez, C.; Ortiz, A.; Ogawa, T. *Polym. J.* **1997**, *29*, 49.

SCHEME 1. Structures of Donor-Substituted Phenylethynylcoumarins 1–10

SCHEME 2


impart a higher twist between the donor and coumarin acceptor moieties and thus alter the ECL maxima. The structures of the compounds studied in the present work are listed in Scheme 1.

Result and Discussion

Compounds **1–5** were readily prepared by the modified Sonogashira coupling of 3-iodocoumarin and donor-substituted phenylacetylenes,⁵ while **6–10** were prepared from 7-iodocoumarin and the same donor-phenylacetylenes under a mild reducing atmosphere of hydrogen and argon⁷ according to Scheme 2. The synthetic yields and melting point are summarized along with the photo-physical data in Table 1.

(7) (a) Elangovan, A.; Wang Y.-H.; Ho, T.-I. *Org. Lett.* **2003**, *5*, 1841.
 (b) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467.

Solution-Phase Photophysical Properties. The UV–visible absorption spectra of all of the compounds were recorded in acetonitrile solvent (except **5** which was recorded in CH₂Cl₂) at a concentration of 10 μM, and the long wavelength absorption maxima are given in Table 1. From the spectra of **1–5** (Figure 1), it can be seen that there is a minimal and gradual increase in the λ_{max} values upon increasing the donor strength in both of the series. The maximum red shift can be observed for **5**. Figure 2 shows the UV spectra of **6–10**, for which the longest wavelength absorption appears as a very weak tail around 330–340 nm. This may be due to the fact that the donors in compounds **6–10** are not in effective communication with the coumarinyl acceptor unit as compared to the 3-coumarinyl systems (**1–5**), and hence poor charge-transfer transition was observed for **6–10**.

Free coumarin has been known to show an absorption maximum at 310 nm.⁸ This intriguing absorption behavior of 7-coumarin systems can be interpreted with the help of semiempirical calculations. Two molecules from each family of 3- and 7-isomers, **1**, **5**, **6**, and **10**, were chosen for the study. Structures were built and minimized at the PM3 level, and the various properties and orbital surfaces were obtained for singlet molecules at the ground state. Molecule **1** has a planar structure in C_s symmetry (dihedral angle 0°) with a heat of formation of 38.10 kcal/mol and a dipole moment of 4.06 D. The HOMO and LUMO levels were found spread all over the molecule, indicating uniform distribution of π-electrons throughout the molecule (see Supporting Information for figures).

On the contrary, molecule **6**, which also has a C_s point group with a heat of formation of 37.35 kcal/mol and a dipole moment of 4.56 D, is twisted at a dihedral angle of 90°. The HOMO and LUMO levels are not spread throughout the molecule but localized on the coumarin subunit, indicating that there is no contribution from the phenyl moiety. Upon imposing a dihedral angle constraint of 0°, the molecule attains planarity, although with an infinitesimal change in energy and dipole moment, and shows orbital distributions similar to those of **1**.

The molecule **5** also has a planar structure in C₁ symmetry with an energy of formation of 34.32 kcal/mol and a dipole moment of 4.07 D. The HOMO level indicates partial π-electron distribution at the acceptor coumarin end with major distribution at the donor-bearing phenyl group. Molecule **10** too has a twisted structure at the ground state in C₁ symmetry with a heat of formation of 33.54 kcal/mol and a dipole moment of 4.36 D. The dihedral angle between the planes of the donor-substituted phenyl and coumarinyl acceptor units was measured to be 90.01° with HOMO localized on the donor part and LUMO localized on the acceptor coumarin part. As a result, the donor and acceptor moieties do not couple effectively and remain electronically detached from each other. Imposing a dihedral angle constraint of 0° enhanced the energy of the molecule to 37.77 kcal/mol and the dipole moment to 6.05 D. The planarized molecule has a C_s symmetry and shows the HOMO and LUMO levels similar to the 3-coumarin derivative, with moderate π-electron distribution over acceptor and donor moieties, respectively.

TABLE 1. Synthetic Yield, Melting Point, and Photophysical Data of Compounds 1–10

compound	yield (%)	mp (°C)	$\lambda_{\max}^{\text{abs}}$ (nm), ^a [ϵ] ^b	$\lambda_{\max}^{\text{flu}}$ (nm), ^a eV	Φ ^c	Stokes shift (nm)
1	89	176–177	342 [2.36]	406	0.88	64
2	88	127–128	345 [2.81]	416	0.73	71
3	85	162–165	353 [2.41]	456	0.55	103
4	83	147–148	356 [2.87]	464	0.43	108
5	88	205–206	406 [2.44] ^d	550 ^d	0.009	144
6	86	74–76	300 [3.26]	364	0.011	64
7	90	183–186	304 [3.03]	440	0.016	136
8	85	102–107	308 [3.16]	465	0.029	157
9	85	112–116	310 [2.59]	470	0.034	160
10	92	125–129	333 [3.63]	438	0.009	105

^a $c = 10 \mu\text{M}$ in CH_3CN . ^b ($\times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). ^c Measured in CH_2Cl_2 with reference to coumarin 1 ($\Phi = 0.99$ in CH_3COOEt). ^d Spectra of compound **5** recorded in CH_2Cl_2 .

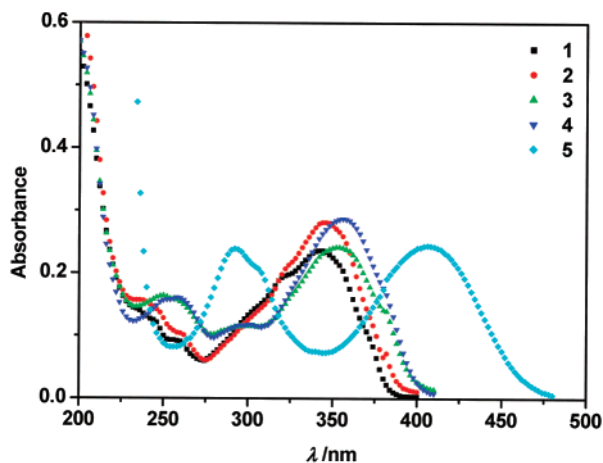


FIGURE 1. UV-visible spectra of 3-coumarin derivatives 1–4 in CH_3CN and **5** in CH_2Cl_2 ($10 \mu\text{M}$).

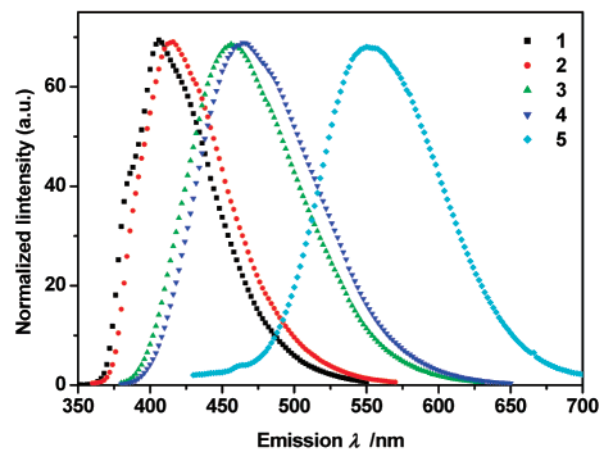


FIGURE 3. Fluorescence spectra of 3-coumarin derivatives 1–4 in CH_3CN and **5** in CH_2Cl_2 ($10 \mu\text{M}$).

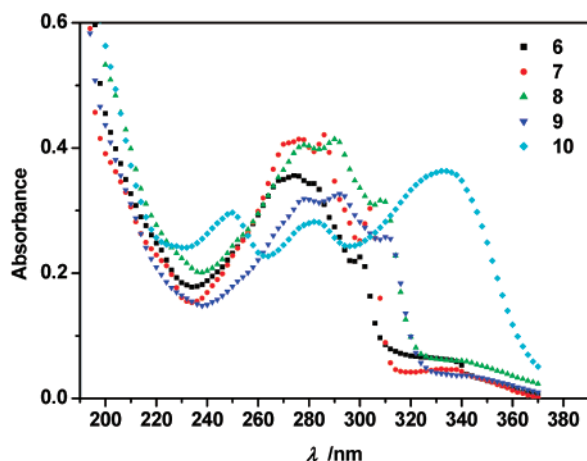


FIGURE 2. UV-visible spectra of 3-coumarin derivatives 6–10 in CH_3CN ($10 \mu\text{M}$).

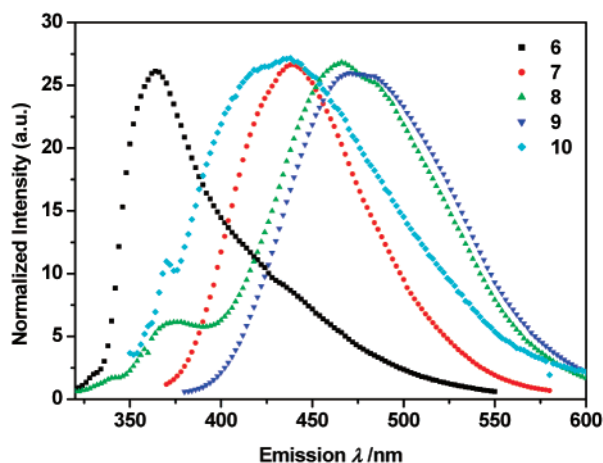


FIGURE 4. Fluorescence spectra of 7-coumarin derivatives 6–10 in CH_3CN ($10 \mu\text{M}$).

From these observations, it can be inferred that the electronic coupling between the donor and the acceptor is more pronounced in the 3-coumarin derivatives than in the 7-coumarin derivatives, although the latter apparently has a longer resonance conjugation than the former. This could also be a reason for observing better overall properties in the former system of compounds than in the latter (vide infra). The reason for the appearance of the strong structureless long-wavelength absorption band at 333 nm for **10** is due to the intramo-

lecular charge transfer from the HOMO of the donor-bearing phenyl moiety to the LUMO of the coumarin subunit during electronic absorption.

The fluorescence spectra of **1–4** and **6–10** were recorded in acetonitrile, while that of **5** was recorded in CH_2Cl_2 as it is not fluorescent in highly polar CH_3CN . As in the case of absorption spectra, fluorescence spectra (Figures 3 and 4) also take the similar course of shifting the maxima of emission to the red upon increasing the donor strength with **5** showing the longest wavelength of emission in the series. Comparing the Stokes shift, **1**

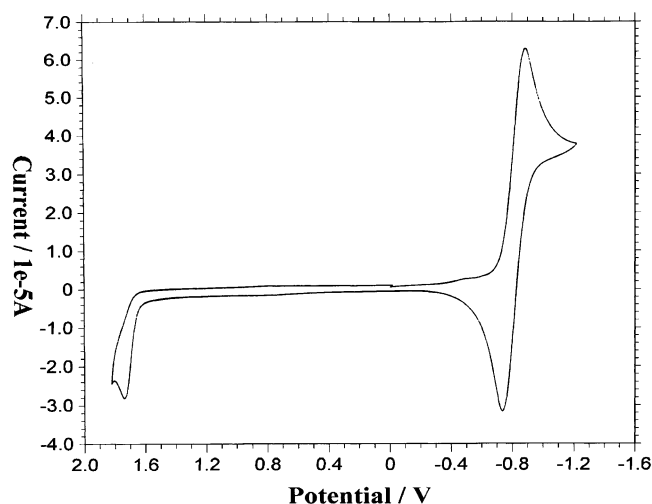


FIGURE 5. Cyclic voltammogram of **7** in CH_3CN (1.0 mM with 50 mM TBAP) at 50 mV/s scan rate.

and **2** (3-coumarinyl family) bearing H and Me groups do not show a great shift, whereas their counterparts in the 7-coumarinyl family, **6** and **7**, show a large Stokes shift. In general, the Stokes shift of the 7-coumarinyl family is larger than that of the 3-coumarinyl family (except **10**). In the case of 3-coumarin derivatives, a stronger donor is required to induce larger Stokes shift. This indicates that the charge-transfer interaction is more facilitated with the introduction of stronger donors than weaker donors in these systems (cf., **2** and **4**). In the case of 7-coumarin derivatives (**6–10**), there seems to be a periodical increment in the Stokes shift values upon increasing the donor strength. Here, the shift is sensitive to even milder push–pull enhancement (cf., **7** and **9**).

The Φ values for **1–4** are much higher than those of **6–10**. The emission quantum yield decreases upon increasing the donor strength and is the highest for **1** and lowest for **5** (and for **10**). Possible quenching by intermolecular electron transfer from the *N,N*-dimethylanilino group to the coumarin of the neighboring molecule or even the strong excited state ICT itself could be the reason for this reduction in quantum yield. Surprisingly, while the fluorescence quantum yields decrease upon increasing the donor strength in **1–5**, it increases in **6–9**. Again, as revealed by the π -electron distribution from PM3 level calculations, the twisted geometry of the 7-coumarin family of compounds disturbs the electronic communication between the donor and acceptor groups, and this could be one of the reasons for the observed photophysical properties. This is also supported by the observation that compound **10**, which contains an NMe_2 group as donor, did in fact show photoluminescence from MeCN, whereas **5**, which also contains the same donor group, did not.

Electrochemistry. Cyclic voltammetry was employed to study the electrochemical behavior and to determine the reduction and oxidation peak potentials of compounds **1–10**, and a typical CV trace of **7** is shown in Figure 5. All compounds exhibited reversible first reduction peak and an irreversible oxidation peak. The peak oxidation ($E_{p,OX}$) and peak reduction ($E_{p,RED}$) potentials are given in Table 2. The reduction peak potentials in the range of

–0.85 to –0.93 V are attributable to the reduction of the coumarin moiety. The reduction potential values are closely the same as the acceptor is the same in each family, with very minor variations caused by the presence of substituents, but these substituents seem to have no regular impact on them. The first oxidation peak potentials can be regarded as due to the oxidation at the donor-bearing phenyl group. The oxidation peak potentials show a gradual downward trend upon increasing the donor strength. The unsubstituted phenylethynylcoumarins have the highest oxidation potentials [1.93 V (for **6**) to 1.95 V (for **1**)], while the strongest donor-bearing compounds show the lowest oxidation peak potentials [0.89 V (for **10**) to 0.90 V (for **5**)]. The minor reduction in the reduction potential of –0.07 to –0.17 V is indicative of mild influence from the donor groups.

Electrochemiluminescence. ECL spectra were recorded with a sample concentration of 1.0 mM in the presence of TBAP (50 mM) in CH_3CN with varying pulse rates and intervals to obtain an optimum ECL spectra. The enthalpy change of the radical ion annihilation reaction ($-\Delta H^\circ$) calculated from the equation⁹

$$-\Delta H^\circ = E_{p,OX} - E_{p,RED} - 0.16 \text{ eV}$$

for radical ion-annihilation reactions, along with the ECL maxima, are given in Table 2. The unsubstituted coumarin shows a photoluminescence maximum at 363 nm,¹⁰ whereas ECL shows a maximum at 428 nm under similar conditions of measurements. Extending conjugation along the molecular axis with the triple bond coupled with various donors is found to shift the maxima to the red. The ECL maxima of **6** seem little affected by the extension of conjugation. It can be seen from Table 2 that the position of ECL maxima for **1–4** and **6–9** appear at 440–456 nm. Their relative positions of ECL are not much altered by the presence of substituents unlike the solution photoluminescence maxima wherein there is a gradual increase in the shift that ranges from 364 to 470 nm. In this situation, there seems to be no pronounced role for the donors in these systems. Only for strong donor group-substituted molecules **5** and **10** are the ECL maxima shifted considerably. It appears from these observations that the ECL emitting species emits light from a state that is different from that of the photoluminescent state. It may be a special type of excimer state/aggregation state. An *H*-type excimer or a trans excimer formation (Figure 6) in high concentration can be considered responsible for this behavior under ECL experimental conditions. It may be noted for comparison that the excimer emission maximum of the α,ω -biscoumarin long-chain compound has been observed at 450 nm.¹¹ Considering the energy of the ECL emission maxima in eV and the enthalpy change for the annihilation reaction ($-\Delta H^\circ$ in eV), it is clear that the emission is generated via triplet–triplet annihilation because the electrogenerated radical ions do not have sufficient energy to populate the singlet state. Hence, triplet–triplet an-

(8) (a) Lewis, F. D.; Barancyk, S. V. *J. Am. Chem. Soc.* **1989**, *111*, 8653. (b) Kim, H.-C.; Kreiling, S.; Greiner, A.; Hampp, N. *Chem. Phys. Lett.* **2003**, *372*, 899.

(9) Faulkner, L. R.; Tachikawa, H.; Bard, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 691.

(10) Wood, P. D.; Johnston, L. J. *J. Phys. Chem. A* **1998**, *102*, 5585.

TABLE 2. ECL Maxima and Electrochemical Data of 1–10

compound	$\lambda_{\text{max}}^{\text{ECL}}$ (nm), eV	relative intensity ^a	$E_{\text{p,OX}}$ (V)	$E_{\text{p,RED}}$ (V)	$-\Delta H^{\circ}$ (eV)
1	439, 2.82	0.60	1.95	-0.93	2.72
2	456, 2.72	0.03	1.88	-0.83	2.55
3	438, 2.83	0.20	1.59	-0.89	2.32
4	451, 2.75	0.50	1.55	-0.92	2.31
5	505, 2.45	0.06	0.90	-0.88	1.62
6	456, 2.72	0.008	1.93	-0.91	2.68
7	448, 2.77	0.005	1.74	-0.89	2.47
8	454, 2.73	0.003	1.55	-0.92	2.31
9	455, 2.73	0.004	1.49	-0.85	2.18
10	478, 2.59	0.0001	0.89	-0.91	1.64
coumarin ^b	428, 2.89	0.096	2.29	-1.00	3.13

^a Relative to $\text{Ru}(\text{bpy})_3^{2+} = 1.0$. ^b Unsubstituted free coumarin.

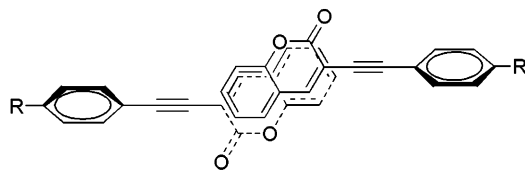


FIGURE 6. Proposed structure of the *H*-type excimer or the trans excimer.

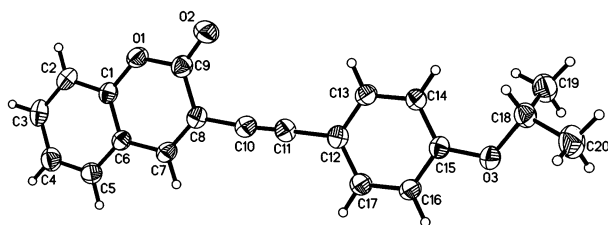


FIGURE 7. X-ray crystal structure of 4 with thermal ellipsoids drawn at the 50% probability level.

nihilation must have occurred to provide sufficient energy to generate the ECL emitting state.^{1a,e,9} It is of interest to note that the intensities of ECL emission for 1–5 are very much higher than those for 6–10. Compound 5 does emit electrochemiluminescence, while it does not emit photoluminescence in the same solvent. This observation also supports our argument that the ECL is from a completely different state as compared to the photoluminescent state for this and other systems as well. Comparing the photoluminescence quantum yield and relative intensities of ECL, there appears to be close consistency between the two series in that the 3-coumarin derivatives are better luminescent materials than 7-coumarin derivatives. However, the lesser relative ECL intensity for some compounds as compared to their photoluminescence quantum yield could be due to the formation of (trans) excimer and self-quenching.

From the X-ray crystal structure of compound 4 (Figure 7), it can be seen that the molecule has a planar structure, indicating effective conjugation through the molecular axis. Further, an intermolecular distance of 3.6 Å was measured between two molecules in the crystal unit cell, suggesting pronounced interaction between π -faces of adjacent molecules¹⁶ in a head-on-head tails-away fashion (Figure 8).

This kind of π -stacking in the solid state may be extended to high-concentration solutions under ECL measurements (10^{-3} M, 100-folds higher than for fluo-

rescence measurements). In view of the fact that the configurational twist can occur in solution, which is not possible in the solid crystalline state, it may be assumed that the donor tail groups can lie twisted away from the two π -stacked coumarin acceptor headgroups. Scheme 3 provides a probable pathway by which an *H*-excimer can be formed during the annihilation reaction of the radical ions under ECL conditions. The tendency of the molecules to undergo π -stacking should naturally favor alignment of the chromophore to fit in the most comfortable motif. The motif shown in Figure 6 would be plausible. Similar observations were made with donor-substituted phenyl-4-quinolinylethyne.^{3c} In addition, it may be noted that there are a few reports of reduction in the emission intensity with a blue shift in the maxima of excimer fluorescence of 9-anthronitrile.¹⁴ While there are some reports of excimer emission of certain alkyl-tethered bisarenes,¹⁵ there are no reports of excimer emission for free coumarin so as to have substantial correlation between the observed ECL and photoexcimer emissions of coumarin. Hence, we prefer to arrive at a modest inference that the only way by which the chromophores studied here can exhibit excimer (in ECL) would be by formation of an *H*-type or a trans excimer, as shown in Figure 6, which would also amount to the reduction in dipole moment and hence the ECL blue shift in comparison with photoluminescence. Theoretical treatment of the

(11) Liu, T.; Wu, S. *Wuli Huaxue Xuebao* **1996**, *12*, 677; *Chem. Abstr.* **125**: 300343.

(12) Sharma, J.; Singh, P. K.; Singh, K. P.; Khanna, R. N. *Org. Prep. Proced. Int.* **1995**, *27*, 84.

(13) Iodosalicylaldehyde was prepared according to: Klein, S. I.; Guertin, K. R.; Spada, A. P.; Pauls, H. W.; Gong, Y.; McGarry, D. G. U.S. patent, 2001, 6323227. 4-Iodosalicylaldehyde was cyclized with acetic anhydride to obtain 7-iodocoumarin in 40% yield according to: Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*; Wiley: New York, 1989; p 1040.

(14) (a) Morsi, S. E.; Carr, D.; El-Bayoumi, M. A. *Chem. Phys. Lett.* **1978**, *58*, 571. (b) Ebeid, E. M.; El-Bayoumi, M. A.; Williams, J. O. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1457. (c) Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371.

(15) (a) Lewis, F. D.; Zhang, Y.; Liu, X.; Xu, N.; Letsinger, R. L. *J. Phys. Chem. B* **1999**, *103*, 2570. (b) Chandross, E. A.; Dempster, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 3586. (c) Lim, E. C. *Acc. Chem. Res.* **1987**, *20*, 8. (d) DeSchryver, F. C.; Collart, P.; Vandendriessche, J.; Goedeweck, R.; Swinnen, A. -M.; Van der Auveraer, M. *Acc. Chem. Res.* **1987**, *20*, 159 and references therein.

(16) (a) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885. (b) Coates, G. W.; Dunn, A. R.; Henling, L. M.; Ziller, J. W.; Lobkovsky, E. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 3641. (c) Hunter, C. A.; Lawson, K. R.; Perkins, J.; Urch, C. J. *J. Chem. Soc., Perkin Trans. 2* **2001**, 651.

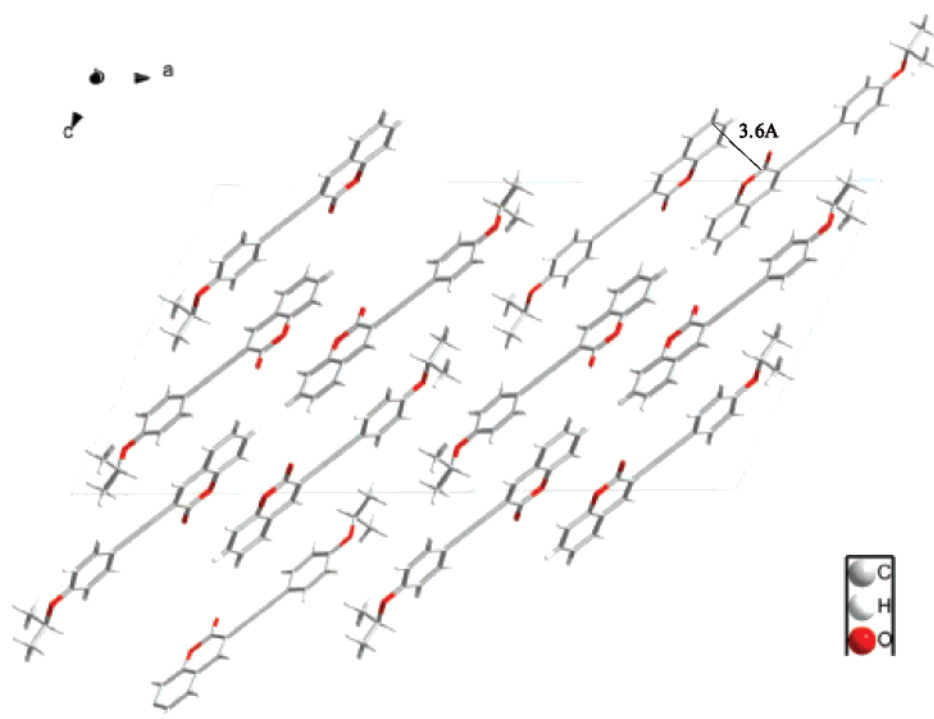
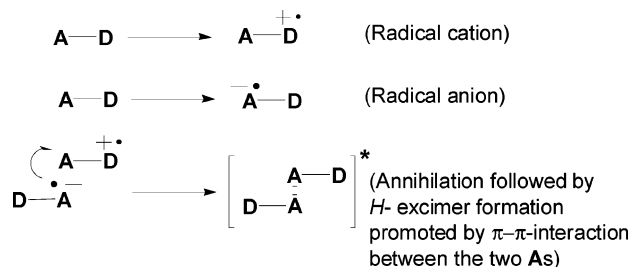


FIGURE 8. Head-on-head tails-away mode of crystal packing with the π -stacking interaction viewed along the “b” axis.

SCHEME 3. Probable Mechanism for the Formation of the *H*-Excimer



A is the acceptor and D is the donor

ECL state would require expensive calculations as the species may be a singlet or triplet and an open shell.

Conclusion

Donor-substituted phenylethynylcoumarins have been synthesized in good yields by the modified Sonogashira coupling reaction, and the ECL and other photophysical properties of the ethynes were studied. Compounds **1–5** showed expected UV–vis absorption spectra, whereas those of **6–10** are quite intriguing as they exhibit the highest absorbance maxima reminiscent of free coumarin with very weak long-wavelength absorption regardless of their apparent longer conjugation. This character has been analyzed with the aid of the PM3 level of theory, which predicted planar geometry for 3-isomers (**1–5**) but twisted geometry for 7-isomers (**6–10**). As a result of this twist, orbital contributions to the electronic absorption of these molecules were very weak, and the absorption spectra appeared close to that of free coumarin. While the photophysical properties showed some trend consistent with the structure–property relationship, the ECL

behavior seems to be affected only by the presence of strong donors such as the NMe_2 group. All compounds are believed to show ECL emission via the triplet–triplet annihilation pathway as deduced from their lower annihilation reaction enthalpy. No co-reactant was used throughout to generate ECL. The effect of the twist angle between the donor and acceptor could not be ascertained due to the formation of the probable trans excimer whose ECL emission maxima are vastly independent of the donor groups in these systems under ECL experimental conditions. The present study, however, supports our view that the photoluminescent state and electrochemiluminescent state may be not the same, but different.¹⁷ Studies on the possible application of these compounds in light-emitting devices are underway.

Experimental Section

All of the chemicals and reagents were purchased from a commercial supplier and were used as received. Dicholobis-(triphenylphosphine)palladium(II) was either prepared in-house or from a commercial source. 3-Iodocoumarin¹² and 7-iodocoumarin¹³ were prepared according to the reported methods. Solvents were distilled as per the standard methods and were purged with argon before use. Triethylamine (TEA) and tetrahydrofuran (THF) were distilled and purged with a mixture of approximately 1:1 argon and hydrogen before use. ¹H NMR spectra of the samples were recorded with a 400 MHz instrument, and ¹³C NMR spectra were recorded with the same instrument at 100.1 MHz operator frequency in CDCl_3 solvent with CHCl_3 internal standard (δ 7.24 ppm for ¹H and 77 ppm,

(17) Supporting evidence: When this paper was under review, a paper appeared that postulates the possibility of the annihilation reaction producing excited states other than the photoluminescence state. See: Ketter, J. B.; Wightman, R. M. *J. Am. Chem. Soc.* **2004**, *126*, 10183.

(18) *Spartan'04 Windows*; Wavefunction, Inc., 18401 Von Karman Ave., Suite 370, Irvine, CA 92612.

middle of the three peaks, for ^{13}C spectra). Mass spectra were recorded on nitrobenzyl alcohol matrix. TLC was run on precoated aluminum plates (Si 60 F₂₅₄). Column chromatography was run on silica gel (60–120 mesh) or neutral alumina 70–230 mesh. All UV–visible spectra were recorded for a 10 μM solution of the compounds in CH_3CN , and all fluorescence spectra were recorded using similar solution concentrations unless otherwise specified. CV measurements were done 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. ECL spectra were recorded at room temperature using a setup consisting of a fluorescence spectrophotometer and a cyclic voltammograph with a computer interface. Typically, 1 mM concentration of the compound solution in acetonitrile with 0.05 M tetrabutylammonium perchlorate (TBAP) were used. To generate the annihilation reaction, the platinum electrode was pulsed between first reduction and first oxidation potentials, and the pulse interval was controlled on a computer. All measurements were done at room temperatures (22–24 °C).

General Procedure for the Synthesis of 2. 3-Iodocoumarin (prepared according to ref 12), 272 mg (1 mmol), $(\text{PPh}_3)_2\text{-PdCl}_2$, 14 mg (2 mol %), CuI, 4 mg (2%), PPh_3 , 26 mg (10%), and a stirrer were charge in a two-neck round-bottomed flask equipped with a condenser, and the setup was degassed and back-filled three times with a gaseous mixture of Ar + H_2 . THF, 8 mL, was introduced from a still into the reaction flask followed by 6 equiv of triethylamine, and finally a solution of the terminal acetylene (1.1 mmol) (4-tolylacetylene 127 mg) in 5 mL of THF was added via a syringe under the mild reducing atmosphere at about 60 °C. After the addition of the alkyne, the reaction mixture was refluxed for 6 h. When the TLC indicated the disappearance of the starting iodo compound, the volatiles were evaporated and the residue was chromatographed to obtain 230 mg (88%) of analytically pure **2**. mp: 127–128 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.91 (s, 1H), 7.53–7.46 (m, 4H), 7.33–7.26 (m, 2H), 7.15 (d, J = 8 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 159.2, 153.0,

144.2, 139.3, 131.8, 131.7, 129.0, 127.5, 124.7, 118.9, 118.8, 116.6, 113.1, 96.1, 82.7, 21.7. MS (M^+) m/z , 260.0838; calculated for $\text{C}_{18}\text{H}_{12}\text{O}_2$, 260.0837. The characterization data for the rest of the compounds are provided in the Supporting Information.

Theoretical Calculations. Semiempirical calculations were performed using Spartan'04(W).¹⁸ Structures were drawn at the entry-level of input and minimized. Equilibrium geometry was obtained at the PM3 level of theory for each molecule at the ground state from its initial geometry subject to symmetry. The total charge was kept neutral, and the multiplicity was kept at singlet. Orbitals and energies, atomic charges, vibrational modes, and thermodynamic properties were chosen as output parameters. HOMO and LUMO orbital surfaces were then obtained from the output. Constraints were imposed for **6** and **10** by constraining the dihedral angle between the plane of the phenyl ring and that of the coumarinyl ring to "0°" and then were minimized. The calculation was resubmitted for the planarized structure, and the orbitals and properties were recalculated.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of compounds **1–10**; X-ray crystal data for **4**; CV trace for **1–10**; raw ECL spectra for the 3-coumarin family (**1–5**); selected ECL spectra for the 7-coumarin family (**6**, **8**, and **10**); details of theoretical calculations; HOMO–LUMO orbital surfaces for **1**, **5**, **6**, and **10**, (PM3) and their Cartesian coordinates for these molecules. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Arumugasamy Elangovan, Jui-Hsien Lin, Shu-Wen Yang, Hsien-Yi Hsu, and Tong-Ing Ho*. Synthesis and Electrogenerated Chemiluminescence of Donor-Substituted Phenylethynylcoumarins

Page 8086–8091. The structures of compounds **6–10** were incorrectly drawn as 7-substituted coumarins; they should instead be the 6-substituted isomers. All discussion of 7-coumarin derivative(s) and 7-isomer(s) should be to the corresponding 6-coumarin derivative(s) and 6-isomer(s). 4-Iodosalicylaldehyde should read and appear as 5-iodosalicylaldehyde. The PM3 calculations in the published paper are correct for the 7-substituted isomers. A corrected Supporting Information file is now available that includes the PM3 calculations for the 6-isomers (compounds **6** and **10**). The results of these new calculations are consistent with those reported in the published manuscript.

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