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Synthesis and electrogenerated chemiluminescence of donor-substituted phenylquinolinylethynes and phenylisoquinolinylethynes: effect of positional isomerism †

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In furtherance of our research on the design, synthesis and study of electrogenerated chemiluminescence (ECL) of new donor substituted phenylquinolinylethynes, we report here more new series with the aim of studying the effect of positional isomerism on their overall photophysical properties with a special focus on ECL. For this study we have chosen 2-, 3-, and 4-(*p*-substituted phenyl)ethynylquinolines, and 1- and 4-(*p*-substituted phenyl)ethynyl*iso*quinolines. These ethynes were synthesized in good yields by modified Sonogashira coupling of the corresponding terminal alkyne with the respective haloquinolines. The photophysical properties and ECL were studied in acetonitrile solvent and the various results are discussed.

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 the ECL active molecules in biological assays has prompted many analytical chemists to venture into the synthesis and study of several new molecular systems.[3] Integral unit molecules bearing donor and acceptor groups are very limited with respect to the study of ECL.

ECL can be regarded as a field that is still growing. Emission from certain annihilation reactions has thus far been achieved by the involvement of a co-reactant, especially amines which are well known fluorescence quenchers. Further advancements are still required in terms of finding new emitters that do not require a co-reactant, new applications and new detection techniques as well as mechanistic understanding of the phenomenon.

Recently, new interest in the design, synthesis and photophysical properties of donor-acceptor luminescent molecules with ethynyl linkage has evolved.[4] Access to facile and efficient methods of synthesis encouraged by ready availability of relatively inexpensive starting compounds make it possible to realize simple yet unknown fluorophores. After the publication of articles on organic light emitting diodes (OLED) based on aluminium(tris-8-hydroxyquinoline) (Alq_3) by Tang and VanSlyke,[5] the design and preparation of numerous fluorescent organic compounds have spurred on active research in the creation of organic and organometallic compounds for electroluminescent (EL) applications.[6]

Reports of donor and acceptor moieties linked by a conjugated triple bond are only emerging now as suitable molecular systems for electrogenerated chemiluminescence studies. The introduction and extension of conjugation affords opportunities for investigating variations and new phenomena alike. For example, introduction of a double bond through *N,N*-dimethylaminophenyl-4-quinoline (*i.e.*, *p*-*N,N*-dimethylaminostyryl-4-quinoline) has imparted unexpected ECL properties to the resultant molecule.[7] Similarly, the introduction of a triple bond between the donor and acceptor moieties has also imparted ECL character to the resultant molecule. These studies prompted more intrigue and promoted more interest. A thorough investigation into the phenomenon is undertaken here by choosing positional isomers of the acceptor moieties, namely quinolines and isoquinolines, with respect to ethyne (Chart 1).

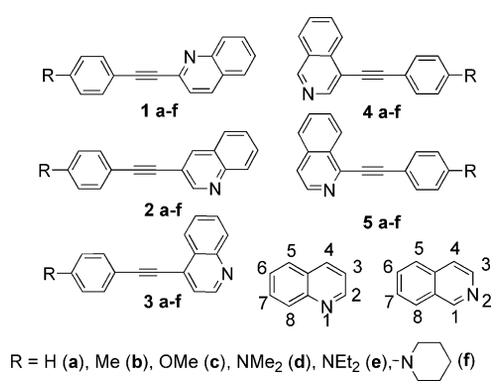

Chart 1 Structures of new series of donor-substituted phenylquinolinylethynes '**na–nf**' (where '**n**' stands for series **1**–**5**) and the common numbering convention of quinoline and isoquinoline.

Quinoline and isoquinoline have been chosen in view of the fact that they are good electron acceptors and are known fluorophores. They can be easily and reversibly reduced and their reduction potentials fall within the measurable electrochemical window of major solvents used for electrochemical cycling. Their absorption and emission properties can be tailored by suitable substitution in the heterocyclic and homocyclic rings.

Experimental

Materials and measurements

All the chemicals and reagents were purchased from Acros Organics unless otherwise indicated and were used as received. Dichlorobis(triphenylphosphine)palladium(II) was either prepared in-house or from a commercial source (Acros). 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 approx-

† Electronic supplementary information (ESI) available: synthetic procedures, measurement details and characterization data of all compounds. See http://www.rsc.org/suppdata/ob/b4/b403775h/

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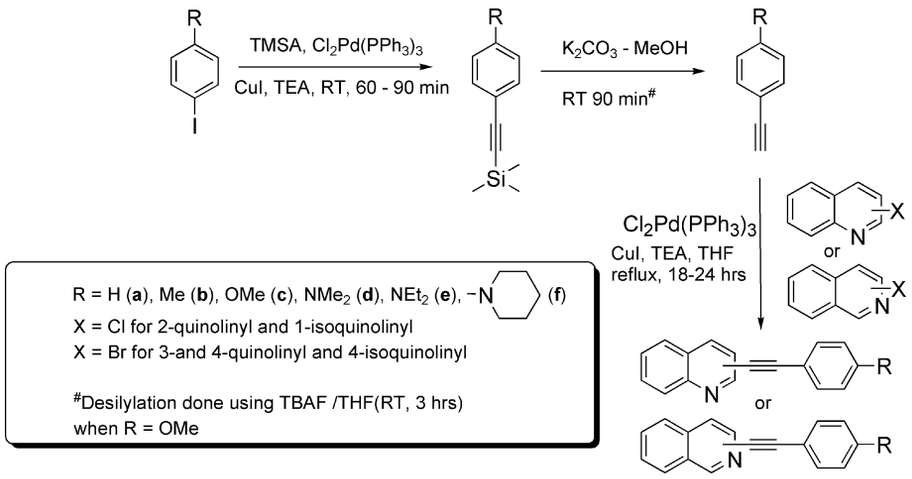


Scheme 1 General synthetic scheme for the preparation of **na–nf**.

imately 1 : 1 argon and hydrogen before use. ^{1}H-NMR spectra of the samples were recorded with a 400 MHz Varian instrument and ^{13}C-NMR spectra were recorded with the same instrument at 100.1 MHz operating frequency in $CDCl_3$ solvent (Merck) with $CHCl_3$ internal standard (δ 7.24 ppm for ^{1}H and 77 ppm, middle of the three peaks, for ^{13}C spectra). Mass spectra were recorded with a Jeol SX 102A instrument on a nitrobenzyl alcohol matrix. TLC was run on Merck precoated aluminium plates (Si 60 F_{254}). Column chromatography was run on silica gel (Merck, 60–120 mesh) and neutral alumina (Merck, 70–230 mesh). All UV-Visible spectra were recorded on a HITACHI U-2000 spectrophotometer with 10 μM solution of the compounds in CH_3CN and all fluorescence spectra on a HITACHI F-3010 fluorescence spectrophotometer with 0.5 nm slit width using the same solution concentrations. CV measurements for series **1** were done on a Voltammograph CV-27 with X-Y recorder with a scan rate of 100 mV s^{-1}. The cell used was a three-electrode cell consisting of a carbon disc (2.0 mm) working electrode, a platinum wire counter electrode and an Ag/AgCl reference electrode. CV measurements for **2**–**5** were done on a CH Instruments Electrochemical Analyzer with the aid of a PC using the CHI 405 Time Resolved Electrochemical Quartz Crystal Microbalance program using the same cell system with scan rates of 50 and 100 mV s^{-1}. ECL spectra were recorded using a setup consisting of a F-3010 Fluorescence spectrophotometer, CV-27 Voltammograph with a PC interface. Typically, 1 mM concentration of the compound solution in acetonitrile with 0.05 M tetrabutylammonium perchlorate (TBAP) was used.

Synthetic procedures

I. General procedure for the synthesis of terminal alkynes. A 50 mL round bottom flask was charged with the halide (1 m mol), dichlorobis(triphenylphosphine)palladium(II), the catalyst (1 mol%), and CuI (1 mol%) along with a magnetic stirring bar and degassed and back-filled three times with a mixture of approximately 10–50% hydrogen and nitrogen/argon from a balloon. TEA (8 mL) was introduced into the reaction flask using a syringe under the gaseous mixture atmosphere. Then trimethylsilylacetylene (TMSA, 1.1 mmol) was added to the reaction flask using a syringe with stirring. After the required stirring time, the solvent was evaporated and the residue was shaken with 10 mL saturated aqueous sodium bicarbonate solution and ether/hexane (10 mL). The organic layer was washed with water and then dried over anhydrous sodium sulfate. Evaporation of the solvent left a brown residue which was chromatographed on a short neutral alumina column using hexane eluant to get the trimethylsilyl derivative. The trimethylsilyl compound was dissolved in methanol (8–10 mL) and stirred with > 2 equivalents of K_2CO_3 for 2 hours (tetrabutylammonium fluoride, TBAF/THF 3 h, rt for R = OMe) with exclusion of air and then the solvent was evaporated to half its original volume, shaken with water (15–20 mL) and the product was extracted with ether (20 mL + 2 × 10 mL). The combined ether solutions were washed with brine, dried over anhydrous sodium sulfate and then passed through a short alumina column. Evaporation of the solvent afforded the analytically pure terminal alkyne.

II. General procedure for the synthesis of internal ethynes. The respective haloquinoline (1 m mol), the palladium catalyst (2 mol%), CuI (1 mol%) and a stirring bar were placed in a two neck round bottom flask fitted with a condenser. The whole set up was degassed and back-filled with the gaseous mixture as before. To the reaction flask was added previously degassed TEA (6 eq.) using a syringe. The terminal acetylene was dissolved in 8 mL THF and added to the reaction mixture at about 80 °C. The reaction was stirred at reflux for 24 h under the atmosphere of the gas mixture. The solvents were evaporated; saturated aqueous sodium bicarbonate solution (10 mL) was added to the mixture at room temperature and it was extracted with ether (20 mL + 2 × 10 mL). The combined organic layers were washed with water followed by brine before drying and evaporating. The residue after evaporation was chromatographed on silica gel using ethyl acetate/hexane mixture (1 : 9–1 : 7–1 : 4) to separate the by-product, the butadiyne and the crosscoupled product. Synthesis and characterization data of individual compounds are given in the electronic supplementary information.† Compound **1d** is representative: yield: 99% (conversion: 76% based on recovered starting compounds) mp: 126–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$)/δ, ppm: 3.00 (s, 6H), 6.65 (d, *J* 9.2 Hz, 2H), 7.48 (m, 1H), 7.54 (m, 4H), 7.69 (t, *J* 6.8 Hz, 1H), 7.75 (d, *J* 8.0 Hz, 1H), 8.08 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$)/δ, ppm: 40.5, 88.4, 92.6, 108.7, 111.9, 124.5, 126.8, 127.0, 127.6, 129.3, 130.0, 133.8, 136.0, 144.6, 148.4, 150.7. MS (M^+): 272.09 (calculated for $C_{19}H_{16}N_2$ 272.13).

Results and discussion

All the ethynes were synthesized according to modified Sonogashira coupling reaction[8] of the corresponding alkyne with appropriate chloro/bromo quinolines as outlined in Scheme 1. Initial attempts under original conditions resulted in very low yields of the products. Employing a mild reducing atmosphere enhanced cross-coupling and yield. However, while the conditions are not optimized, the yields are also determined by the steric hindrance caused by *peri*-hydrogens of quinoline rings adjacent to the halogen atom[9] and thus chlorides generally afforded better yields than bromides under the chosen conditions.

Table 1 Photophysical and electrochemical data of aryl-quinolinyl- and aryl-isoquinolinyl-ethynes **na–nf**

Compound	λ_{max}^{Abs}/nm, eV	λ_{max}^{Flu}/nm, eV	Stokes shift/nm	Relative fluorescence intensity (%)[a]	λ_{max}^{ECL}/nm, eV	ECL Intensity (%)[b]	$E_{p,\,RED}$/V	$E_{p,\,OX}$/V	$-\Delta H°$/eV[c]
1a	326, 3.80	361, 3.44	35	5.33	463, 2.66	1.3	−1.88	2.16	3.88
1b	316, 3.92	364, 3.41	48	0.89	472, 2.62	0.5	−2.16	2.11	4.11
1c	346, 3.58	405, 3.06	59	2.41	479, 2.59	37.8	−1.94	1.71	3.49
1d	373, 3.32	527, 2.35	154	98.50	540, 2.30	2.0	−1.97	0.92	2.73
1e	379, 3.27	528, 2.35	149	10.78	539, 2.30	7.6	−1.89	0.96	2.69
1f	366, 3.39	531, 2.34	165	16.16	527, 2.35	7.5	−1.84	0.98	2.66
2a	340, 3.65	354, 3.50	15	32.76	448, 2.76	0.1	−1.95	1.90	3.69
2b	342, 3.63	370, 3.35	32	98.39	460, 2.69	0.1	−0.90	1.80	2.54
2c	342, 3.63	406, 3.05	64	100.00	[d]	—	−1.00	1.59	2.43
2d	366, 3.39	534, 2.32	168	12.09	[e]	—	−0.97	0.88	1.69
2e	374, 3.32	532, 2.33	158	14.94	[e]	—	−0.87	0.85	1.56
2f	359, 3.45	534, 2.32	175	10.86	[e]	—	−0.88	0.91	1.63
3a	320, 3.87	378, 3.28	58	0.21	451, 2.75	5.0	−0.85	2.0	2.69
3b	324, 3.83	374, 3.32	50	1.32	449, 2.76	4.8	−0.90	1.90	2.64
3c	334, 3.71	422, 2.94	88	17.99	450, 2.76	15.0	−0.93	1.65	2.42
3d	381, 3.25	538, 2.30	157	1.06	448, 2.77	2.8	−0.87	0.96	1.67
3e	388, 3.19	536, 2.31	148	1.57	500, 2.48	3.6	−0.87	0.94	1.65
3f	382, 3.24	540, 2.29	158	0.51	481, 2.58	1.0	−0.88	0.96	1.68
4a	340, 3.64	372, 3.33	32	6.66	463, 2.67	1.0	−0.91	0.81	1.56
4b	344, 3.60	382, 3.25	38	40.93	553, 2.24	1.0	−0.88	1.65	2.37
4c	334, 3.71	414, 2.99	80	95.62	[d]	—	−0.91	0.58	1.33
4d	368, 3.37	534, 2.32	166	9.83	[e]	—	−0.89	0.89	1.62
4e	376, 3.29	534, 2.32	158	12.00	[e]	—	−0.92	0.89	1.65
4f	362, 3.42	536, 2.31	174	6.98	[e]	—	−0.89	0.55	1.28
5a	334, 3.71	372, 3.33	38	0.47	440, 2.81	6.5	−0.96	0.86	1.66
5b	347, 3.57	376, 3.29	29	0.73	524, 2.36	7.2	−0.91	1.76	2.51
5c	350, 3.54	404, 3.07	54	11.44	457, 2.71	22.0	−0.93	1.64	2.41
5d	382, 3.24	530, 2.34	148	5.36	525, 2.36	12.0	−0.91	0.94	1.69
5e	383, 3.24	528, 2.35	145	7.27	527, 2.35	0.9	−0.89	0.92	1.65
5f	370, 3.35	530, 2.34	160	5.33	[e]	—	−1.04	0.94	1.82

[a] Relative to **2c** for which the fluorescence quantum yield was determined to be 0.25 using coumarin 1 as standard ($\Phi = 0.50$ in MeOH[10]). [b] Relative to tris(2,2′-bipyridyl)ruthenium(II)oxalate complex = 100%. [c] Calculated from $-\Delta H° = E_{p,OX} - E_{p,RED} - 0.16$ eV.[11] [d] Too weak to be considered as signal. [e] Very weak and not reproducible as decomposition was observed.

The photophysical and ECL data, and electrochemical peak reduction and oxidation potential values are summarized in Table 1. We have chosen the following numbering scheme for convenience of discussion: the five series of compounds are given the numbering '**nx**' where '**n**' ranges from **1** to **5**, and '**x**' from '**1a**–**1f**' in Chart 1. The UV-Visible spectra were recorded in acetonitrile solvent and a typical graph of those of **3a**–**3f** is depicted in Fig. 1, and their maxima are recorded in Table 1. All the compounds show two groups of maxima in their UV-Vis absorption spectra corresponding to the β-band and long-wavelength absorptions. The absorption maxima gradually shifted to red when the electron donor became stronger. The β-band absorptions (λ = 230–270 nm) were stronger for **na–nc** whereas the long-wavelength bands were stronger in the case of **nd–nf**. This indicates that the charge transfer is more facilitated in the latter systems (*i.e.*, strong donor systems) than in the former (weak donor) systems.

All the compounds are blue-green fluorescent in acetonitrile and more strongly in dichloromethane, with the '**nd–nf**' systems being the most prominent emitters. The fluorescence spectra of all the compounds were recorded in acetonitrile and a typical graph showing the fluorescence spectra of **3a**–**3f** is depicted in Fig. 2, and all the maxima are recorded in Table 1 along with relative intensity. Among the fluorescence spectra of the five series of compounds, those bearing no or weak donors (H, Me, OMe) *i.e.*, '**na–nc**' (where **n** = **1**–**5**) show low Stokes shifts in the range of 25–88 nm. Those bearing strong donors *i.e.*, '**nd–nf**' (where **n** = **1**–**5**) show larger Stokes shifts in the range of 150–188 nm consistent with intramolecular charge transfer (ICT) and they exhibit solvatochromism which is also indicative of the ICT behavior of these molecules. This character arises due to the presence of strong electron donor moieties linked to the quinolinyl acceptor through the ethynyl bridge. It is interesting to note that the introduction of an electron donating substituent raises the highest occupied molecular orbital (HOMO)

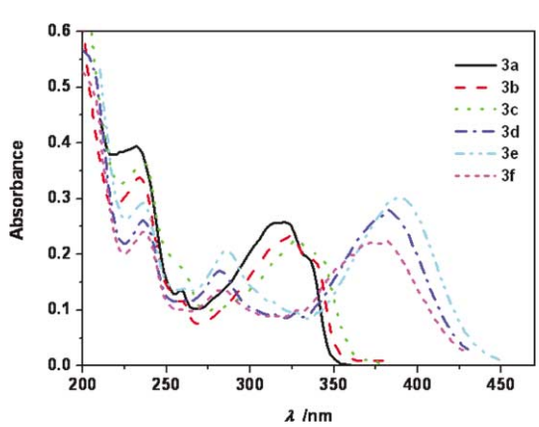


Fig. 1 UV-Vis spectra of **3a**–**3f** recorded in acetonitrile (1.0×10^{-5}M).

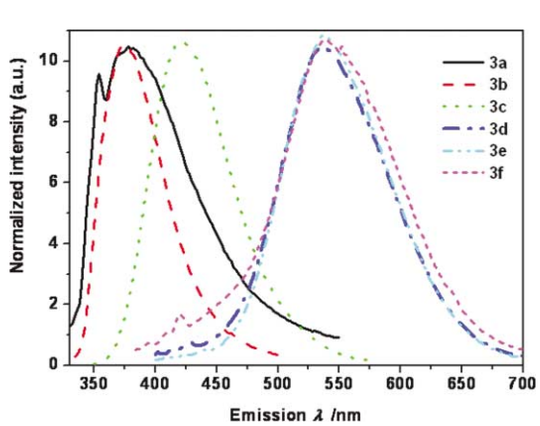


Fig. 2 Fluorescence emission spectra of **3a**–**3f** recorded in acetonitrile.

energy and hence reduces the HOMO–LUMO energy gap in these systems.

To determine the reduction and oxidation potentials of these compounds, cyclic voltammograms were recorded for **na–nf** in acetonitrile at a concentration of typically 1 mM of compound with 50 mM tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The scan rates varied from 50 mV s^{-1} to 100 mV s^{-1}. All the CV curves show reversible reduction potentials whereas the oxidation potentials are irreversible. A typical CV trace of **2d** is shown in Fig. 3 and peak potential values of all compounds are furnished in Table 1. The first reduction peak potential values obtained from the CV of all the compounds lie in the range of −0.8 V to −2.16 V and the first oxidation peak potentials range from 0.55 V to 2.16 V. The first reduction and oxidation potentials can be ascribed to reduction at the quinolinyl acceptor moiety and oxidation at the donor substituted phenyl moiety respectively. Compounds **1a**–**1f** have the highest reduction potential (from −1.84 V to −2.16 V) as compared to the rest of the compounds, indicating that they have lower LUMO energy. Compounds with weak electron donors (**1a**–**1c**) have larger oxidation potentials than those with strong electron donors (**1d**–**1f**). The variation in the oxidation potentials may be due to the intramolecular charge transfer interactions through the triple bond. The smaller oxidation potentials observed for the strong electron donating substituents may provide further evidence for the increase of HOMO energies caused by the introduction of electron donating substituents. On the other hand, since the electron acceptors are similar (*i.e.*, quinolines/isoquinolines) the LUMO energies remain almost the same. As a result we observe little variation in the reduction potentials except for one compound, **2a**, whose reduction potential is unusually large due to unknown reasons.

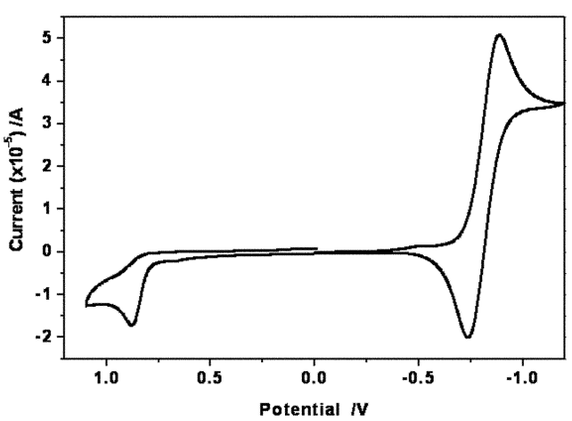


Fig. 3 Cyclic voltammogram of **2d** (1 mM with 50 mM TBAP in CH_3CN) *vs.* Ag/AgCl.

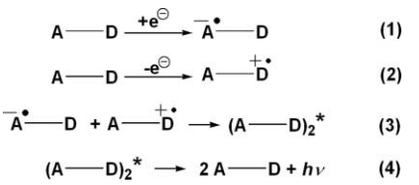
Comparing the oxidation potentials of all the compounds, we observe that those compounds with weaker electron donating groups (**na–nc**) have larger oxidation potentials, the exceptions being **4a**, **4c** and **5a**. Compounds with strong electron donating substituents **nd–nf** have similar oxidation potentials (ranging from 0.84 to 0.98 excepting **4f**) irrespective of the acceptor moiety. In general, the redox potential values are more regular in the case of quinolines (**1**–**3**) than in the case of isoquinolines (**4** and **5**). Compounds **1a**–**f** have the largest reduction potentials and compounds **1a**–**c** have the largest oxidation potentials. This is a unique property of 2-quinolinyl systems.

ECL spectra were recorded with typically 1 mM concentration of the compound dissolved in acetonitrile with 0.05 M TBAP as supporting electrolyte. To generate the reaction, the platinum electrode was pulsed between the first reduction and oxidation potentials and the pulse interval was controlled on a PC using home-made time controller software. All measurements were carried out at room temperature. ECL emission could be well observed for those compounds with ethynyl bridged donor groups attached at the carbon which has an *ortho*- and *para*- like relationship with respect to the ring nitrogen heteroatom in the quinolinyl/isoquinolinyl moiety, while very weak to no ECL was observable for those compounds in which the donors are linked through the triple bond with a *meta*-like relationship.

The annihilation enthalpy change ($-\Delta H^\circ$) for the radical ion reaction can be calculated from the following equation:

$$-\Delta H^\circ = E_{p,OX} - E_{p,RED} - 0.16\ eV^{10}$$

The calculated annihilation enthalpy change for the compounds **na–nf** are listed in Table 1. Compounds **1a**–**1f** show the largest enthalpy change values. Within this series, compounds **1a**–**1c**, bearing weaker donors, have larger enthalpy change values than **1d**–**1f** which bear strong electron donors. The ECL emission from **1a**–**1c** can be ascribed the to the excimer emission due to the planar nature of these molecules (Scheme 2).[12] For compounds **1d**–**1f** the ECL emission has been ascribed to intramolecular charge transfer (ICT) through direct annihilation of radical ions. For **1a**–**1f**, their annihilation enthalpy of reaction is sufficiently larger than their singlet energies and the ECL are derived from their singlet state. For the rest of the quinolinyl systems (**2** and **3**) their annihilation enthalpy changes for the radical ion reactions are not sufficient to populate their singlet excited states. Thus triplet–triplet annihilation must have occurred to provide the energy (T-route). This also results in a weaker to even no ECL emission for these systems especially when the donor arylethynyl groups are in *meta*-relation to the ring nitrogen. The compounds bearing weak donors (**2a**,**2b**,**3a**–**3c**,**4a**–**4b**,**5a**–**5c**) exhibit excimer ECL (E-route) due to very low twist angle between the donor and acceptor moieties, while those bearing strong donors like NMe_2 show ICT ECL (higher twist angle *cf* Chart 2 and Scheme 3) from direct annihilation, albeit with exceptions (**3d**–**3f**) wherein the ECL emission maxima were 40–90 nm blue-shifted as compared with the solution photoluminescence maxima with reduced intensity. This may be due to the formation of an *H*-type excimer[12] in which two quinolinyl moieties are stacked face to face with donor-bearing phenyl groups projecting perpendicularly away from



Scheme 2 Mechanism for the excimer ECL emission of **na–nc** (where **n** = **1**–**5**).

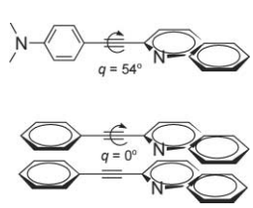
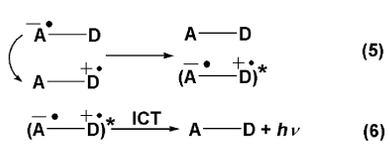


Chart 2 Probable spatial occurrence of the luminophores in solution especially during ECL: monomeric (top, **1d**) and excimeric (bottom pair, **1a**). Strong donors exert twist while weaker ones do not. Twist angle of energy minimized structure was calculated using the Spartan 4.0 molecular modeling program.



Scheme 3 Mechanism for the ECL emission of **1d**–**1f**.

each other (Scheme 4). Figs. 4 and 5 are typical of normal excimer ECL (of **3b**) and ICT ECL (of **1e**) respectively depicted compared with the corresponding fluorescence curves. A survey of the literature on the excimers of common fluorophores revealed that only alkyl spacer linked bisarenes of a specific type (*e.g.*, naphthalene, phenanthrene *etc.*) exhibit excimer photoluminescence while the free arene counterparts do not.[13,14] Free quinoline is not known to exhibit excimer emission. Further, the reduction in intensity of ECL accompanied by the blue-shift (as compared to photoluminescence) is indicative of aggregation.[13] In the case of **3d**–**3f** the only possibility by which they can form a blue-shifted excimer is by *trans* excimer formation.

Scheme 4 Proposed structure of the *H*-type dimer of **3e**.

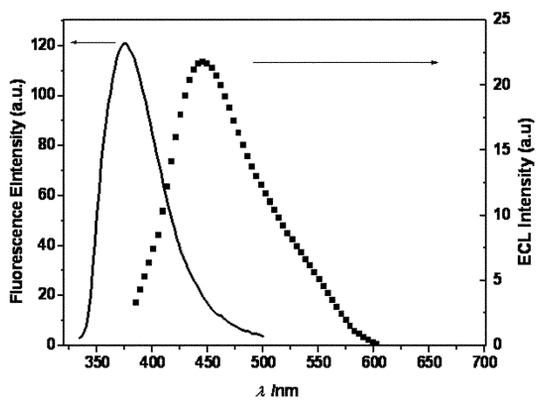


Fig. 4 Typical comparative fluorescence (solid line) and ECL (squares) spectra of **3b** showing red shifted (excimer) ECL.

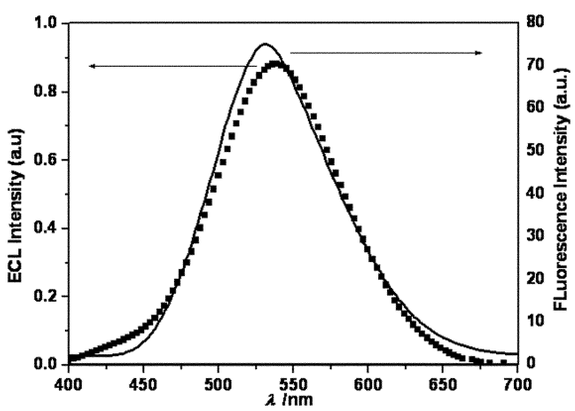


Fig. 5 Typical comparative fluorescence (solid line) and ICT ECL (squares) spectra of **1e** showing close overlap of both solution fluorescence and ECL spectra.

Direct formation of excimers by radical ion comproportionation reactions is more probable under the ECL experimental conditions since the radical ions, when annihilated, should be in close proximity with the appropriate geometry. The ECL for **1d**–**1f** is derived from the annihilation arising from collisions between the radical cations and radical anions of these compounds to generate ICT states. The requirement for the generation of the ICT state is provided by the large twist angle between the plane of the quinoline moiety and the donor bearing phenyl moiety as seen from the larger calculated twist angle.

From the foregoing discussions, the mechanism of ECL emission can be divided into three categories. For '**na–nc**' with no or weak electron donating substituents and no/small twist angle (Chart 2), it is less favorable to populate the ICT state. Due to the planar geometry, they tend to show excimer type ECL emission albeit with less efficiency. The mechanism is similar to that already reported for poly(9,9-dioctylfluorene)[3] and is shown in Scheme 2 where A represents the acceptor (quinoline) moiety and D the donor (substituted phenyl) moiety of the same molecule. During electrochemical redox reaction the radical anion and radical cation are formed (eqns 1 and 2). Then they collide to form an excimer (eqns 3 and 4). For '**1d**–**1f**' the ECL mechanism (Scheme 3) is quite different from that for '**na–nc**'. The radical ions collide neck-to-neck to generate the ICT state directly (eqn. 5). The third blue-shifted ECL for **3d**–**3f** is a sequel to *H*-type excimer or *trans* excimer as shown in Scheme 4. This is a unique property of the 4-quinolinyl system due to the symmetrical nature of the excimer.

Conclusion

In summary, we have disclosed a new family of compounds showing ECL based on quinoline and isoquinoline acceptors and aryl donors linked by a triple bond. Various donor substituted phenylquinolinylethynes and phenylisoquinolinylethynes were prepared in good yields and their ECL properties were studied. In all of the ECL active systems no co-reactant was used. The ECL for weak donor substituted compounds (**1a**–**1c**,**2a**,**2b**,**3a**–**3c**,**4a**,**4b**,**5a**–**5c**) is believed to be from the normal excimer formed by annihilation of radical ions generated electrochemically. Compounds with strong donor groups (**1d**–**1f**,**5d**,**5e**), show ECL from their ICT states. A strange aggregation of *H*-type excimer formation in **3d**–**3f** is believed to be responsible for the observed blue-shift of ECL in comparison with their solution fluorescence maxima. It can be seen that only the 4-quinolinyl systems show *H*-type excimers and this may be due to the favorable geometrical arrangement (with a center of symmetry) of the excimers of 4-quinolinyl derivatives. From the annihilation enthalpy changes of reaction, we understand that ECL for compounds **1a**–**1f** are derived from singlet states and the rest (**2**–**5**) from a triplet–triplet annihilation mechanism. Thus the present study has thrown light on the fundamental aspects governing the ECL phenomenon. The compounds reported here may have possible application as sensors in molecular recognition oriented towards immunoassay due to the presence of a hydrogen bonding site in the fluorophore moiety. Introduction of many binding sites at the fluorophore moiety would be more helpful for the studies. Efforts in this direction will be pursued by us in the future.

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References

1 (*a*) L. R. Faulkner and A. J. Bard, Electrogenerated Chemiluminescence, in *Electrochemical methods*, John Wiley & Sons, New York, 1980, pp. 621–627; (*b*) M. Oyama and S. Okazaki, *Anal. Chem.*, 1998, **70**, 5079; (*c*) A. Kapturkievicz, *J. Electroanal. Chem.*, 1990, **290**, 135; (*d*) A. Kapturkievicz, *J. Electroanal. Chem.*, 1991, **302**, 13.
2 (*a*) A. W. Knight and G. M. Greenway, *Analyst*, 1994, **119**, 879; (*b*) A. W. Knight, *Trends Anal. Chem.*, 1999, **18**(1), 47; (*c*) R. Y. Lai, E. F. Fabrizio, L. Lu, S. A. Jenekhe and A. J. Bard, *J. Am. Chem. Soc.*, 2001, **123**, 9112.
3 I. Prieto, J. Teetsov, M. A. Fox, D. A. Vanden Bout and A. J. Bard, *J. Phys. Chem. A*, 2001, **105**, 520.
4 (*a*) S. A. Odom, S. R. Parkin and J. E. Anthony, *Org. Lett.*, 2003, **5**, 4245; (*b*) A. Elangovan, T.-Y. Chen, C.-Y. Chen and T.-I. Ho, *Chem. Commun.*, 2003, 2146; (*c*) O. Lavastre, I. Illitchev, G. Jegou and P. H. Dixneuf, *J. Am. Chem. Soc.*, 2002, **124**, 5278; (*d*) A. Harriman and R. Zeissel, *Coord. Chem. Rev.*, 1998, **171**, 331; (*e*) J. G. Kushmerick, D. B. Holt, S. K. Pollack, M. A. Ratner, J. C. Yang,

T. L. Schull, J. Naciri, M. H. Moore and R. Shashidhar, *J. Am. Chem. Soc.*, 2002, **124**, 10654; (*f*) E. Galopini, W. Guo, W. Zhang, P. G. Hoertz, P. Qu and G. J. Meyer, *J. Am. Chem. Soc.*, 2002, **124**, 7801; (*g*) C. Hortholary and C. Coudret, *J. Org. Chem.*, 2003, **68**, 2167; (*h*) S. Huang and J. M. Tour, *J. Am. Chem. Soc.*, 1999, **121**, 4098.

5 (*a*) C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913; (*b*) C. W. Tang, S. A. VanSlyke and C. H. Chen, *J. Appl. Phys.*, 1989, **65**, 3610.

6 (*a*) H. D. Burrows, M. Fernandes, J. Seixas de Melo, A. P. Monkman and S. Navaratnam, *J. Am. Chem. Soc.*, 2003, **125**, 15310; (*b*) R. Pohl, V. A. Montes, J. Shinar and P. Anzenbacher Jr., *J. Org. Chem.*, 2004, **69**, 1723; (*c*) R. Métivier, R. Amengual, I. Leray, V. Michelet and J.-P. Genêt, *Org. Lett.*, 2004, **6**, 739.

7 C.-Y. Chen, J.-H. Ho, S.-L. Wang and T.-I. Ho, *Photochem. Photobiol. Sci.*, 2003, **2**, 1232.

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

9 K. Palat and M. F. G. Stevens, *J. Chem. Res. (S)*, 2000, 136.

10 G. A. Reynolds and K. H. Drexhage, *Opt. Commun.*, 1975, **13**, 222.

11 L. R. Faulkner, H. Tachikawa and A. J. Bard, *J. Am. Chem. Soc.*, 1972, **94**, 691.

12 E. A. Chandross, J. W. Longworth and R. E. Visco, *J. Am. Chem. Soc.*, 1965, **87**, 3259.

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

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