

First synthesis and electrogenerated chemiluminescence of novel *p*-substituted phenyl-2-quinolinylethyne^{†‡}

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Received (in Cambridge, UK) 28th May 2003, Accepted 30th June 2003

First published as an Advance Article on the web 15th July 2003

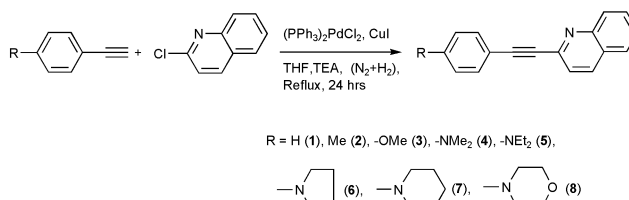
A series of *p*-substituted phenyl-2-quinolinylethyne as blue-green emitters were synthesized using a modified Sonogashira coupling reaction and their electrogenerated chemiluminescence properties are reported.

Electrogenerated chemiluminescence (ECL) is an important property of organic molecules and coordination compounds of Ru ions. ECL can be realized by the annihilation of radical cations and radical anions.¹ ECL has been found to be better than conventional chemiluminescence, in that it is characterized by high sensitivity, selectivity and it is convenient to generate the required reagents in solution in the vicinity of an electrode.² Development of new analytical systems has been a topic of current interest.^{3–5} Recently ECL from intramolecular charge transfer (ICT) systems has drawn much attention.^{3,6–7}

We have studied the photophysical properties of ICT systems consisting of an *N,N*-dialkylaminophenyl donor and a 2-quinolinyl acceptor connected by a double bond.^{8–11} We found that the quinoline moiety can act as a good electron acceptor, especially if it is connected through a double bond to a good electron donor. These systems show larger bathochromic shifts in the absorption and emission spectra.¹¹ However ECL properties of alkynes are rare and, to the best of our knowledge, no ECL properties have been reported for arylquinolinylethyne so far. We became interested in studying donor–acceptor systems with a triple bond as connector since the acetylenic bond has been shown to be a good connector for these donors and acceptors and in photoactive molecular conductors.^{12,13}

We have shown¹⁴ that diarylethyne can be conveniently prepared by Sonogashira crosscoupling of alkynes and aryl halides with diminished homocoupling by using a dilute hydrogen atmosphere. This, coupled with our quest for new simple compounds exhibiting ECL, prompted us to attempt the synthesis of arylquinolinylethyne with donor substituents and study their electrochemiluminescence properties. A series of novel ICT compounds from *N,N*-dialkylaniliny donors and 2-quinolinyl acceptor linked by a triple bond were synthesized using our modified Sonogashira reaction conditions (Scheme 1).[§]

The absorption and emission maxima for **1–8** are given in Table 1. **4–8** show ICT behavior¹¹ through solvatochromic studies. **4–8** show larger Stokes' shifts in their fluorescence and



Scheme 1 Synthesis of arylquinolinylethyne.

absorption maxima consistent with ICT emission behavior. Minimized ground state molecular modelling calculations carried out using SpartanTM 4.0 indicated increasing twisting between the donor and acceptor moieties as the electron donating ability is increased (Table 1, θ , the twist angle between the quinoline–triple bond plane and the donor bearing phenyl). **1–3** show small θ while **4–8** show larger θ .

The CV curve for **3** recorded[¶] between +2.7 V and –3 V is shown in Fig. 1. The reduction potentials (–1.94 V and –2.3 V) correspond to reduction at the quinoline moiety and acetylene function respectively.^{16,17} The positive potential at +1.71 V is ascribed to oxidation at the methoxyphenyl site (for **4–8** the donor is the *N,N*-dialkylaminophenyl moiety and they show similar oxidation potentials 0.85–1.05 V). The first reduction and oxidation potentials which correspond to the reduction of the quinoline and oxidation of the donor moiety respectively are recorded in Table 1.

ECL for **1–8** was measured according to our previously published method.¹⁸ The ECL spectrum for **5** between –1.8 V (0.2 s) and +0.9 V (0.2 s) with 2 s intermission is shown in Fig. 2, and the ECL maxima for **1–8** are summarized in Table 1.

No excimer peaks were observed in the ECL spectra, as seen from Fig. 2. The ECL spectra of **1** and **2** showed very low intensity. Therefore a strong donor group on the phenyl moiety is found to be essential for the detection of ECL.

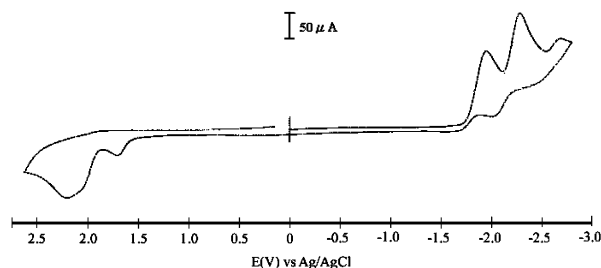


Fig. 1 Cyclic voltammogram of **3**.

[†] Electronic supplementary information (ESI) available: experimental. See <http://www.rsc.org/suppdata/cc/b3/b305943j/>

[‡] Dedicated to Professor F. D. Lewis on the eve of his 60th birthday.

Table 1 Photophysical and electrochemical data of arylquinolinylethyne^a

Product	$\lambda_{\max}^{\text{Abs}}/\text{nm}$	$\lambda_{\max}^{\text{Flu}}/\text{nm}$, eV	Shift/nm	$\lambda_{\max}^{\text{ECL}}/\text{nm}$, eV	$E_{\text{p,RED}}/\text{V}$	$E_{\text{p,OX}}/\text{V}$	$-\Delta H^0/\text{eV}^b$	$\theta/^\circ$
1	326	361, 3.44	35	463, 2.66	–1.88	2.16	3.88	0.0
2	316	364, 3.41	48	472, 2.62	–2.16	2.11	4.11	0.0
3	346	405, 3.06	59	479, 2.59	–1.94	1.71	3.49	0.5
4	373	527, 2.35	154	540, 2.30	–1.97	0.92	2.73	53.8
5	379	528, 2.35	149	539, 2.30	–1.89	0.96	2.69	7.6
6	380	533, 2.33	153	547, 2.27	–1.91	1.11	2.86	8.5
7	366	531, 2.34	165	527, 2.35	–1.84	0.98	2.66	18.9
8	359	523, 2.37	164	531, 2.33	–1.94	1.01	2.79	33.3

^a Conditions of optical and CV measurements: CH₃CN, 25 °C. ^b Calculated from $-\Delta H^0 = E_{\text{p,OX}} - E_{\text{p,RED}} - 0.16 \text{ eV}$.¹⁵

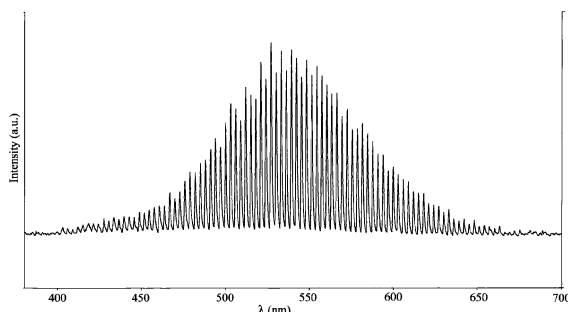
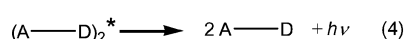
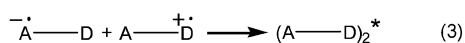
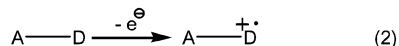
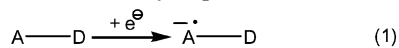


Fig. 2 ECL spectrum of 5.

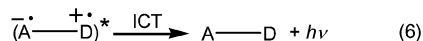
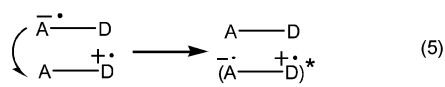
The annihilation enthalpy change ($-\Delta H^\circ$) calculated from the oxidation and reduction potentials¹⁵ (Table 1) is sufficient to populate the singlet state of 1–8 (S-route). The singlet excited state of 1–8 can be reached in the electron transfer reaction of the radical ions.

1–3 show larger shifts in the ECL maxima as compared with their fluorescence maxima, while ECL maxima for compounds 4–8 are pretty much the same as their fluorescence maxima. The ECL for 1–3 can be explained on the basis of excimer emission generated from the annihilation of the radical anions and radical cations of 1–3¹⁹ (E-route). No excimer emission is observed when higher concentrations of 1–3 were employed for photoexcitation. Even though there are reports^{4,19} that ECL excimer emissions can be observed, no excimer emission was recorded by direct photoexcitation. 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 4–8 derived from the annihilation arising from collisions between the radical cations and radical anions of these compounds to generate ICT states.⁷ 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.

The mechanism of ECL emission can be divided into two categories. For 1–3 with no or weak electron donating substituents and small twist angle, 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)⁴ and is shown in Scheme 2. A represents the acceptor (2-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 (eqn. 1 and 2). Then they collide to form an excimer (eqn. 3 and 4). For 4–8 the ECL mechanism (Scheme 3) is quite different from that for 1–3. The radical ions collide neck-to-neck to generate the ICT state directly (eqn. 5).



Scheme 2 Plausible mechanism of ECL emission for 1–3.



Scheme 3 Plausible mechanism of ECL emission for 4–8.

In summary we have uncovered a new family of compounds showing ECL based on quinoline acceptors and aryl donors linked by a triple bond. Donor substituted phenyl-2-quinolinylethyne (3–8) were prepared for the first time in good yields

with diminished homocoupling and their ECL properties were studied. The ECL for 1–3 is believed to be from the excimer formed by annihilation of radical ions generated electrochemically. For 4–8, due to their larger twisting donor–acceptor angle, the ECL can be generated by the annihilation of their radical ions to populate their ICT states. Preliminary studies on the usefulness of these compounds indicate possible application as anion sensors. For example, 4 was found to detect F^- ion by quenching of emission. Research in this direction will form a future study.

Financial support by the National Science Council, Taiwan, Republic of China is gratefully acknowledged.

Notes and references

§ Coupling without the use of hydrogen-degassing resulted in very low yields of products together with major diphenylbutadiynes. Typical experimental procedure:¹⁴ 4-iodo-*N,N*-diethylaniline (1 mmol), $(PPh_3)_2PdCl_2$ (1 mol%), CuI (1 mol%) were taken in a flask and degassed and back-filled with a mixture of $N_2 + H_2$ 3 times and triethylamine (8 mL, degassed with $N_2 + H_2$) followed by trimethylsilylethyne (1.1 mmol) were added. The resulting mixture was stirred for 2 h at rt. The solvent was evaporated and worked up with ether and saturated $NaHCO_3$ solution. The ether solution after drying was passed through a short alumina column and then evaporated to get the pure TMS derivative in 99.6% yield. This was hydrolyzed by stirring in MeOH with 0.4 g K_2CO_3 for 2 h followed by aqueous work-up to get fine low melting needles of pure 4-*N,N*-diethylaminophenylethyne in 94% yield. This acetylene was coupled with 2-chloroquinoline by refluxing in THF (degassed with $N_2 + H_2$) with 2 mol% Pd catalyst, 2 mol% CuI and 4 equiv. TEA. After 24 h, the volatiles were evaporated and the crude product was extracted with ether and evaporated. Column chromatography of the residue on silica gel afforded pure 5 in 95% yields for 70% conversion (details in ESI†).

¶ See ESI for details. † Typically a 1 mmol solution of the compound in dry degassed CH_3CN with 0.05 M tetrabutylammonium hexafluorophosphate (TBAP) was electrolysed under argon using a carbon disc (2.0 mm) working electrode, a Pt wire counter electrode and a Ag/AgCl reference electrode with a scan rate of 100 $mV s^{-1}$. The ECL spectra were recorded using a setup consisting of a F-3010 Fluorescence spectrophotometer, a CV-27 voltammeter with a PC interface under CV conditions. The ECL intensities were measured with 40 nm slit width relative to tris(2,2'-bipyridyl)ruthenium(II) chloride.

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