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Donor-substituted phenyl-π-chromones: electrochemiluminescence and intriguing electronic properties†

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Phenylethynylchromones bearing different donor groups at the phenyl moiety have been prepared and their photophysical and electrogenerated chemiluminescence (ECL) properties have been studied with respect to their structural features. Intriguingly, the presence and variation of donor groups do not much influence the absorption spectra, which can be compared with the spectrum of unsubstituted chromone, whereas the photoluminescence (PL) spectra show pronounced changes. Density functional theory (DFT) calculations indicate enhancement of HOMO energy levels upon increasing the donor strength. The photophysical properties have also been studied in various solvents, and the PL spectra in particular show the anticipated trend. The introduction of π-extension imparts ECL to the new molecules and the electronic coupling between the donor and the acceptor moieties through C–C triple bond influences ECL emission maxima. Weaker donors impart excimer ECL while stronger donors impart monomeric intramolecular charge transfer (ICT) ECL.

Introduction

Chromones form a class of compounds whose importance arises from their wide natural occurrence as subunits in flavonoids[1,2] and the latter's biological activities.[3] However, reports on the photophysical properties of chromones are limited,[4–6] and the study of potentially useful optical and optoelectronic properties, and application of chromone derivatives in functional devices are nascent.[7,8] Emission of light by recombination of charged radicals generated by electrolysis of organic molecules having redox centers is termed as electrogenerated chemiluminescence (or electrochemiluminescence, ECL).[9–29] This emission may arise either from a singlet (S) state or *via* a triplet (T) state of the electroactive molecule. The formation of these energy states depends on the annihilation enthalpy change ($-\Delta H^0$) during the intramolecular charge transfer (ICT)/electron transfer reaction.[11] The singlet state is generated if the $-\Delta H^0$ is equal to or in excess of the energy needed for the excited singlet state (S-route). On the other hand, if the $-\Delta H^0$ is lower than energy required for the S state, but is sufficient only to populate the triplet state, then the annihilation of radical ions will lead to the formation of the T state. The singlet excited state can also be achieved through triplet–triplet annihilation, and this route is called the T-route. There is yet another pathway called the E-route, wherein the emission is observed from the excimer of the electronically excited molecules through the annihilation of radical ions. The emission maxima of the ECL can ordinarily be overlain on the photoluminescence maxima and likewise the excimer ECL on the excimer photoluminescence. Unlike fluorescence, ECL does not require a light source in order to excite molecules, and hence it is considered superior.[12,13] While many molecules have been known to exhibit ECL activity, most requiring amines as co-reactants, simple molecules emitting ECL, especially without the use of any co-reactant, are of interest to study.

We have been involved in the design, synthesis and study of the ECL properties of novel π-bridged donor–acceptor systems.[20–22,30] A variety of donor-bearing phenyl-2-quinolinylethynes have been studied by us and were found to exhibit ECL behavior, varying with the twist angle between the donor and acceptor groups along the ethyne back-bone. Weak donor bearing compounds exhibited excimer ECL while strong donor systems show monomeric ICT emission as compared to photoluminescence.[21] Donor-bearing phenyl-4-quinolinylethynes were found to show ECL emissions whose maxima are considerably blue shifted with respect to the corresponding photoluminescence maxima.[22] Similar behavior was also observed in the case of donor-substituted phenylethynylanthracene, whose ECL maximum also appears at a wavelength that is also blue shifted with respect to the photoluminescence maximum.[30] The reason for this observation was derived from the π–π interaction between the two proximally parallel acceptors moieties in adjacent molecules lying in head-on-head-tails-away fashion. This proposal was supported by the single crystal X-ray analysis of compounds that exhibit aggregate ECL. In order to determine the real cause for the occurrence of twist, we studied the ECL of a series of donor-bearing phenylethynylacridines with varying degrees of steric hindrance as well as of donor strength. We found that steric bulk is not essential to cause the twist and it is the strength of the donor and that of the acceptor that causes it. From these observations we arrive at a rationally plausible conclusion that weaker donors at the *para*-position of the phenyl group do not impart torsion but stronger donors do. In consequence, the position of ECL maxima of donor–acceptor ethynes are largely determined by the nature of the donor groups in normal cases, and by π–π stacking interaction in abnormal cases. The ethyne-bridged donor–acceptor systems based on chromones are rare and there are no reports on the photophysical characteristics so far; however, directly linked 2-arylchromones have been reported.[6]

In the present work we studied the ECL and general photophysical studies of a new variety of donor–acceptor systems with the previously studied donors and chromone (as the new) acceptor linked by C–C triple bond and their structures are shown in Chart 1.

Experimental

All the chemicals and reagents were purchased from Acros Organics, unless specified otherwise, and were used as received. Dichlorobis(triphenylphosphine)palladium(II) was

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† Electronic supplementary information (ESI) available: Characterization data, UV-visible absorption and fluorescence emission spectra of **1**–**5** in various solvents, CV curves for **1**–**5** and X-ray data for **4**. See http://www.rsc.org/suppdata/pp/b4/b416319b/

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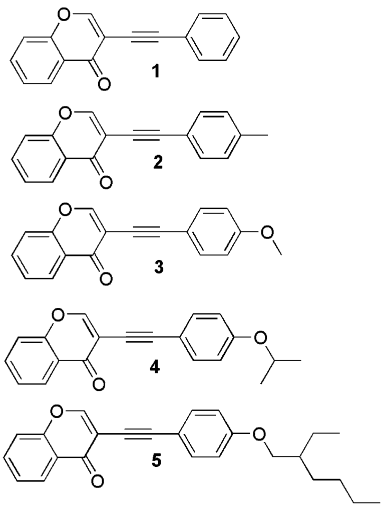

Chart 1 Structures of donor-substituted phenylethynylchromones.

either prepared in-house or from commercial source (Acros). 3-Iodochromone was prepared from iodination of the propenone intermediate obtained from reaction between 2-hydroxyacetophenone (Acros) and dimethylformamide dimethylacetal (Acros) as per the reported procedure.[31] 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 and hydrogen before use. ^{1}H NMR spectra of the samples were recorded with 400 MHz Varian instrument and ^{13}C NMR spectra were recorded with the same instrument at 100.1 MHz operator 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 Jeol SX 102A instrument on nitrobenzyl alcohol matrix. TLC was run on Merck pre-coated aluminium plates (Si 60 F_{254}). Column chromatography was run on Merck silica gel (60–120 mesh) or neutral alumina (Merck) 70–230 mesh.

All UV-visible spectra and fluorescence spectra were recorded on Cintra® 10c UV Spectrophotometer and Aminco-Bauman® Luminescence spectrometer respectively with 10 μM solution of the compounds in hexane, benzene, CH_2Cl_2, ethanol, CH_3CN and DMSO. Fluorescence quantum yields (Φ) were determined using coumarin 1 standard (Φ = 0.5 in MeOH). Cyclic voltammetry (CV) measurements were done for compound solutions in acetonitrile [1 μM containing 50 mM tetrabutylammonium perchlorate (TBAP) as supporting electrolyte] on CH Instruments Electrochemical Analyzer. The cell used is three-electrode cell consisting of carbon disc (2.0 mm) working electrode, a platinum wire counter electrode and an Ag/AgCl reference electrode. The scan rate was 50 mV s^{-1}. ECL spectra were recorded at room temperatures using a setup consisting of F-3010 fluorescence spectrophotometer, CV-27 Voltammograph with a computer interface. Typically 1 mM concentration of the compound solution in acetonitrile containing 50 mM TBAP was used. To generate annihilation reaction, the platinum electrodes [a Pt wire (0.25 mm diameter, Aldrich) and a Pt gauss (100 mesh, 0.5 × 0.5 cm, Aldrich)] were pulsed between first reduction and first oxidation potentials and the potential pulse interval was controlled using a computer.[19–21]

Typical and general procedure[32–34] for the synthesis of 3-*p*-tolylethynylchromen-4-one (**2**): 3-iodochromone 272 mg (1 mmol), $(PPh_3)_2PdCl_2$ 14 mg (2 mol%), CuI 4 mg (2%), PPh_3 26 mg (10%) and a stirring bar 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 (8–10 mL) was introduced *via* a syringe into the reaction flask followed by six equivalents of TEA and finally by a solution of the terminal acetylene (1.1 mmol) [4-tolylacetylene (Aldrich) 127 mg] in 5 mL THF *via* a syringe under the mild reducing atmosphere at about 60 °C. After the addition of the alkyne, the reaction mixture was refluxed for 10–12 h. When the TLC indicated disappearance of starting compounds, the volatiles were evaporated and the residue was purified by column chromatography followed by recrystallization from benzene to get pure **2** as off-white crystals (yield: 175 mg, 67%); mp: 136–138 °C; ^{1}H NMR (400 MHz δ, ppm): 8.26,(d, *J* 8 Hz, 1H), 8.20 (s, 1H), 7.67 (t, *J* 8 Hz, 1H), 7.43 (m, 4H), 7.13 (d, *J* 8.4 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR: (100.1 MHz, $CDCl_3$, δ, ppm): 21.66, 78.75, 95.18, 111.45, 118.07, 119.43, 123.42, 125.56, 126.13, 128.91, 131.56, 133.78, 138.67, 155.72, 157.52, 175.17; HR MS (*m*/*z*): 260.0839 (M^+) (calculated for $C_{18}H_{12}O_2$: 260.0837). The rest of the compounds were synthesized in similar manners and were ascertained by satisfactory spectral characteristics (see the supplementary information†).

Crystal data for **4**: formula $C_{20}H_{16}O_3$; formula weight: 304.33; unit cell parameters with standard deviations: a 14.2400(7); b 6.3210(4); c 36.476(2) Å; α 90(0); β 98.92(0); γ 90(0)°; V 3243.58(30) Å^3; symmetry space group $P2_1/c$; cell formula units Z 8; temperature of study 295(2) K; absorption coefficient 0.083 mm^{-1}; reflections collected 10293; independent reflections 5291 (R_{int} 0.1081); final R indices [$I > 2\sigma(I)$]: R_1 0.1601, wR_2 0.3582; R indices (all data): R_1 0.2998, wR_2 0.3932.

CCDC reference number 253696.

See http://www.rsc.org/suppdata/pp/b4/b416319b/ for crystallographic data in CIF or other electronic format.

Theoretical calculations were performed using Spartan'04™ for Windows, Wavefunction Inc., Irvine, CA 92612, USA. Molecules were built and optimized at B3LYP level with density functional theory (DFT) using 6-31G* basis set for ground state, and orbital energies and HOMO–LUMO energy gaps were calculated subsequently. Excited state orbital maps for **1** were calculated under CIS at 6–31G* level of basis set. All molecules were optimised at gaseous state geometry for ground and excited states as provided in the Spartan program (optimization was done under the self consistent field (SCF) model with restricted hybrid HF-DFT calculations using Pulay DIIS extrapolation). No solvent environment was considered for geometry optimization. It may be noted that the rotation with respect to the C–C triple bond axis in the excited state was not considered because we assumed that the theory provided by Spartan for both ground and excited states would yield the appropriate output in both of the cases.

Results and discussion

All compounds were prepared by palladium catalyzed cross-coupling of 3-iodochromone with the corresponding terminal alkyne under modified Sonogashira conditions.[32–34] The photophysical studies initially done in acetonitrile (ACN) solutions afforded some interesting observations: the absorption maxima of all the compounds showed little variation with respect to either π-extension or to the nature of donors, as all structured maxima were found to be centered at 300 nm (Table 1). The HOMO–LUMO energy gap values ($\Delta E_{H\text{-}L}$) calculated with density functional theory (DFT) at B3LYP/6–31G* level of theory show that there is variation in the calculated energy gaps as compared to those obtained from the UV-Vis spectra (3.5 eV, from the onset of the absorption ≈350 nm for all molecules). This variation may be due to the fact that the calculations were done for the molecules in the gas phase; *i.e.*, in the absence of any solvent matrix. The calculated HOMO energy increases from **1** through **5** while the LUMO energy remains little affected by the substituents (Table 1 and Fig. 1).

The fluorescence spectra on the other hand exhibited red-shift upon increasing the donor strength; from H and Me to OMe, an increment of about 50 nm, and to O^{i}Pr about 60 nm was noticed. It is indeed surprising, in the present system of compounds, that the vertical excitation to the singlet state encounters little

Table 1 Photophysical data of **1**–**5** in acetonitrile and calculated energies

Compound	λ_{max}^{abs}/nm	$\varepsilon_{max}/10^4$ M^{-1} cm^{-1}	λ_{max}^{flu}/nm	Stokes shift/cm^{-1}	Φ^{flu}	$E_{HOMO}{}^a$/eV	$E_{LUMO}{}^a$/eV	$\Delta E_{H\text{–}L}{}^a$/eV
1	298	1.09	406	8927	6.6×10^{-3}	−5.73	−1.61	4.12
2	298	1.99	404	8805	4.5×10^{-4}	−5.61	−1.57	4.04
3	300	2.52	454	11307	5.5×10^{-3}	−5.38	−1.52	3.86
4	298	2.01	462	11912	9.3×10^{-3}	−5.32	−1.50	3.82
5	296	1.21	456	11854	8.4×10^{-3}	−5.32	−1.51	3.81
Chromone	302	0.48	335	3262	5.4×10^{-5}	−6.57	−1.50	5.07

[a] E_{HOMO}: HOMO energy; E_{LUMO}: LUMO energy; $\Delta E_{H\text{–}L}$: HOMO–LUMO gap calculated using DFT at B3LYP/6-31G* level. All calculations were performed using Spartan'04 (W).

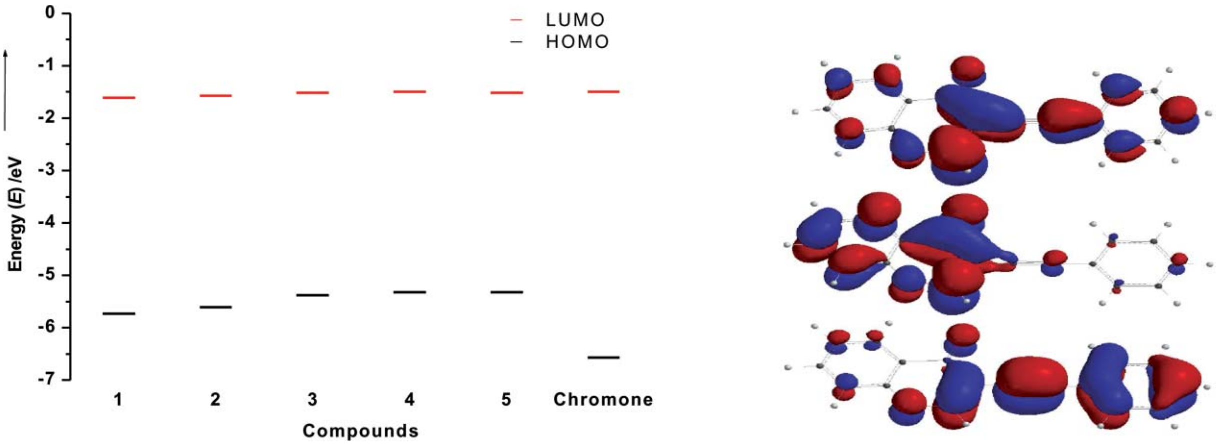

Fig. 1 Graphical representation of HOMO–LUMO energy levels for **1**–**5** and free chromone (left), and the excited state SOMO (right-top, CIS 6-31G*), ground state LUMO (right-middle B3LYP 6–31G*) and HOMO (right-bottom B3LYP 6-31G*) of 3-phenylethynylchromone (**1**). Note that the excited state SOMO experiences enhanced π-delocalization throughout the molecule as compared to the ground state LUMO. All surfaces represent ≈90% electron density probability.

interference from the auxochrome that is generally expected to be in effective communication with the chromophore through π-conjugation, and little charge transfer is noticed even in high polar ACN. The Frank–Condon state in the present systems appears to be less polar and is almost identical with that of free chromone while the excited state alone experiences charge transfer as seen from structure-less fluorescence maxima and is influenced by the presence of donor groups. This is also evident from the theoretical singly occupied MO (SOMO) in the excited state (CIS) which has better π-orbital distribution throughout the molecule than in the ground state (see Fig. 1 top-right).

The effect of substitution on chromone is only observed from the increment in molar extinction coefficient which is found to be more than twice as much as for free chromone, and is still higher for donor-substituted phenylethynylchromone systems (**2**–**4**) than for unsubstituted phenyethynylchromone (**1**). This indicates that these compounds have higher oscillator strength than for free chromone.[35] The smaller value for **4** as compared to **3** indicates slight deviation for planarity caused by the increased donor strength. In fact compound **4** was found, from single crystal X-ray analysis, to be twisted with a dihedral angle of 45.2° between the plane of the donor-bearing phenyl moiety and that of the chromone acceptor moiety (Fig. 2).

The lower ε_{max} for **5** may be a consequence of the modest deviation from planarity, reflected in the diminished oscillator strength; it is probably the lower limit among **2**–**5**. Interestingly enough, a longer Stokes shift of more than 100–150 nm is observed for all the π-extended chromones indicating better stabilization of the excited state, and the excited states of **1**–**5** are extremely more stabilized by 6000–9000 cm^{-1} than that of free chromone itself (*cf.* Stokes shift). The π-extended chromones exhibit higher photoluminescence quantum yield than the free chromone itself.

Intrigued by these preliminary solution photophysical observations in ACN, we carried out solvatochromic studies of compounds **1**–**5** in solvents of varying polarity. Fig. 3a depicts the typical UV spectra of **1** recorded in six different solvents in the order of increasing polarity. As has been mentioned earlier, all the absorption spectra show maxima centered at about 300 nm though the absorbance values (and the molar extinction coefficients in turn) are irregular and not concomitant. However the emission spectra (Fig. 3b) clearly show the influence of solvent polarity on the emission behavior. Going from hexane through to DMSO, there is a periodical red shift with loss of band structure and increase in intensity. Similarly, compounds **2**–**5** also portray the same behavior and typical spectra of **5** are shown in Fig. 3c (UV) and Fig. 3d (fluorescence), and the spectra for the rest of the molecules are provided in the supplementary information.† The equilibrium state (*i.e.*, after the Frank–Condon state) experiences more planarity and hence better delocalization of π-orbitals, which is not possible in the twisted ground (S_0) state. Thus the compounds studied here (especially **2**–**5**) make new examples of twisted ICT (TICT) systems *ie.*, TICT in the ground state and planar ICT in the excited state.

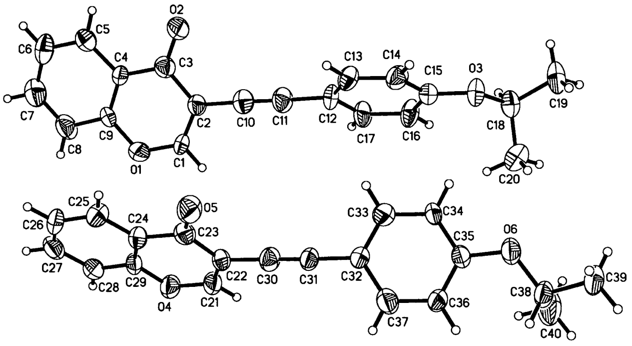

Fig. 2 X-Ray crystal structure of **4** showing twist between donor phenyl and acceptor moieties (two molecules lie in two different fashion in a unit cell as depicted; thermal ellipsoids were drawn at 50% probability level).

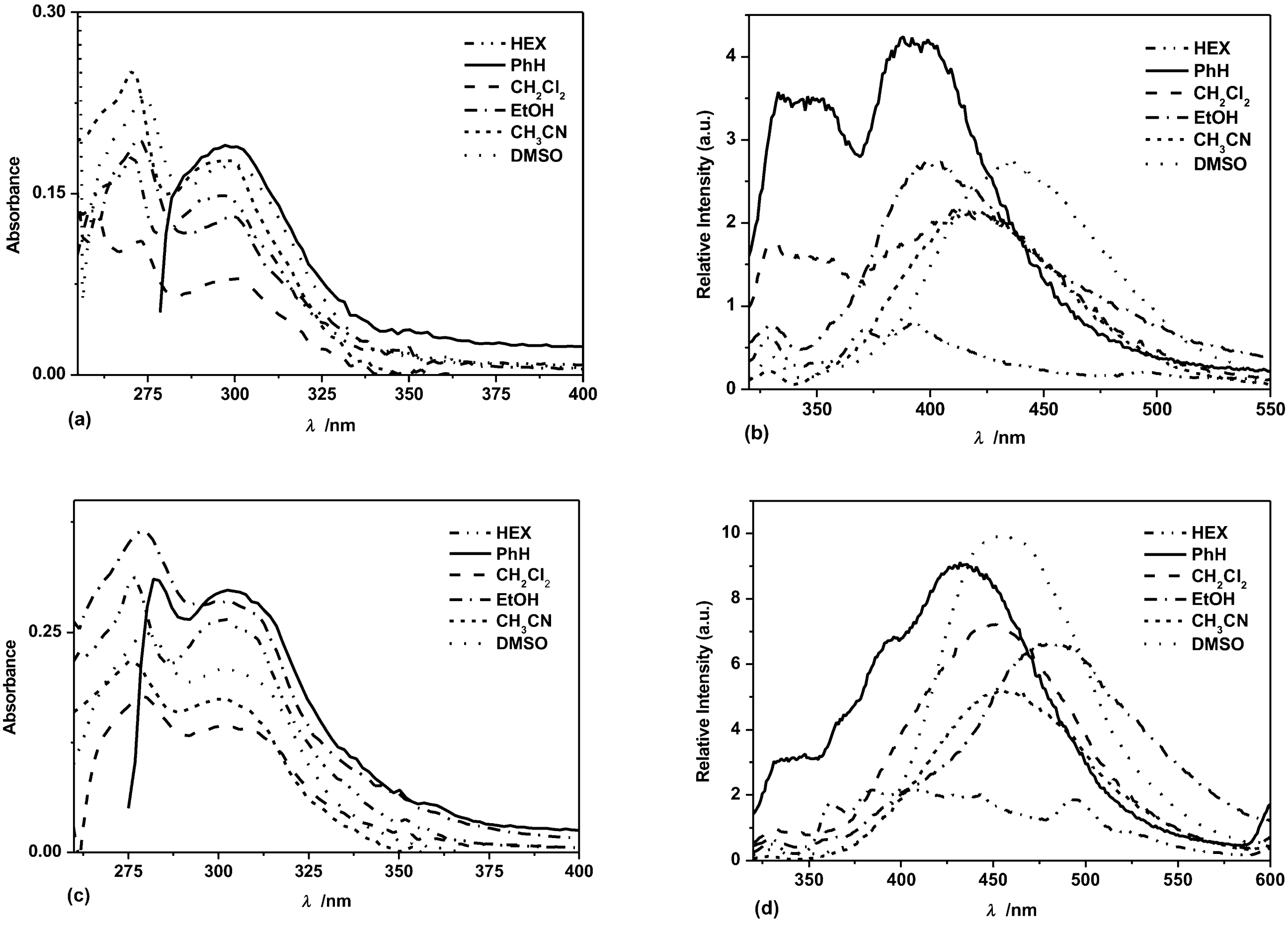

Fig. 3 (a) UV absorption spectra of **1** in various solvents of increasing polarity (the trace before 275 nm for benzene have been neglected to clear absorption due to the solvent). (b) Fluorescence emission spectra of **1** in various solvents with increasing polarity. (c) UV spectra of **5** in various solvents. (d) Fluorescence spectra of **5** in various solvents.

In order to study ECL for the synthesized compounds, the electrochemical activity was studied and the redox behavior analyzed. Cyclic voltammetry was employed to measure the reduction and oxidation potentials and the values are furnished in Table 2 together with ECL data. All the reduction peaks caused by one electron reduction at the acceptor chromone moiety are found to be electrochemically reversible whereas the oxidation peaks caused by the one electron oxidation are not. All the new compounds show reduction potentials ranging from −0.84 to −0.90 V and oxidation potentials ranging from 0.91 to 1.84 V. There is only a marginal change in the reduction potentials but there is a drastic reduction in oxidation potential values upon increasing donor strength. This suggests a gradual increase in the electronic coupling between the donor and acceptor groups through π-conjugation with increase in donor strength. The observed trend in the oxidation potential is also reflected in the calculated HOMO energy levels which increase (lesser negative value) upon going down from **1** through **5** (Table 1, Fig. 1). The little change in the calculated LUMO energy levels is reflected in the equally unchanged reduction potential measured with CV (ground state). Thus the HOMO–LUMO gap reduction can be ascribed to the rise in the HOMO energy level upon increasing donor strength.

As can be seen from Tables 1 and 2, the π-extension, coupled with electron push through C–C triple bond, indeed reduced the energy gap between the HOMO and the LUMO. It is evident, from the comparison of the reduction and oxidation potential values of the donor–acceptor compounds **1**–**5** with those of the parent chromone, that there is a moderate to strong electronic coupling between the communicating moieties, suggesting possible charge transfer in the ground state. The calculated HOMO and LUMO as well indicate mild interaction as seen from a small coefficient of HOMO distribution at the acceptor and LUMO distribution at the donor. This observation is quite contradictory to that made in the UV absorption studies wherein no coupling is observed in the ground state; and the

Table 2 Electrochemical and ECL data for **1**–**5** in acetonitrile

Compound	$E_{\mathrm{p,ox}}$/V	$E_{\mathrm{p,red}}$/V	$-\Delta H^0$/eV[a]	$\lambda_{\mathrm{max}}{}^{\mathrm{ECL}}$/nm (eV)	Intensity[b](%)
1	1.84	−0.84	2.52	450 (2.75)	1.4
2	1.80	−0.88	2.52	447 (2.77)	3.0
3	1.60	−0.87	2.31	440 (2.82)	4.6
4	1.53	−0.87	2.24	445 (2.78)	7.0
5	1.56	−0.90	2.30	445 (2.78)	4.0
Chromone	2.54	−0.82		—	—

[a] Calculated from $-\Delta H^0 = E_{\mathrm{p,ox}} - E_{\mathrm{p,red}} - 0.16$.[29] The peak potentials were used as if they were reversible assuming a slow follow-up kinetics since the annihilation leading to light emission is faster. [b] Relative to $\mathrm{Ru(bby)_3}^{2+}$.

reason for this intriguing behavior is derived from the DFT orbital surface maps which show, for example in **1**, that the LUMO is vastly localized on the acceptor chromone unit and the HOMO on the phenyl moiety with weak coefficient at the opposite sides. Both HOMO and LUMO have extended distribution only up to acetylenic triple bond with very weak coefficient on the other side of the molecule. However, it is plausible that the nature of the electrolyzed species (and in turn the ECL emissive species, see below) and the photoactive species is not one and the same. Interestingly, the calculated HOMO–LUMO energy difference ($\Delta E_{\text{H–L}}$ in Table 1) agrees well with the concomitant reduction in the oxidation potentials from **1** down to **5** ($E_{\text{p,ox}}$ in Table 2) upon increasing the donor strength. The LUMO levels remain almost unaltered whereas the HOMO levels are raised for **1**–**5** (less negative values in Table 1 and Fig. 1) which indicate facility of oxidation.

It is probable that the radical ions generated by electrolysis experience higher charge difference than the photoirradiated molecule in the cases under study. This charge difference may induce planarity between the two communicating groups and attain a state of better charge delocalization.

The structure–electronic property relationship of these bipolar systems can be established by correlation between the calculated HOMO energies and the electrochemical oxidation potentials for **1**–**5**. Fig. 4 is one such plot which correlates the oxidation potential and DFT calculated HOMO energies of **1**–**5** (r^2 = 0.9774 and SD = 0.0226) and thus a good correlation is established.

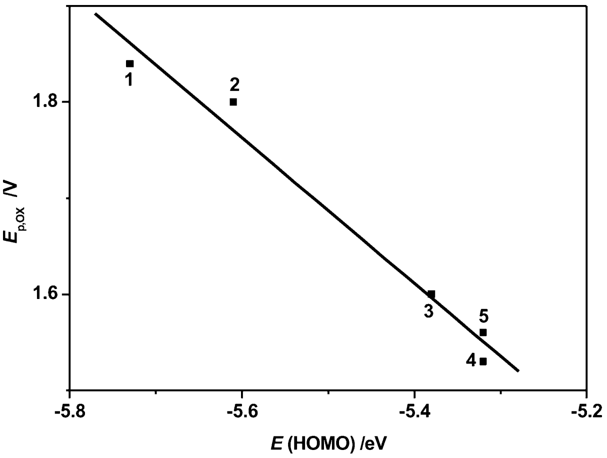

Fig. 4 Correlation of the oxidation potential ($E_{\text{p,ox}}$) and the calculated HOMO energies of **1**–**5** (r^2 = 0.9773).

Electrochemiluminescence was recorded for all the compounds **1**–**5** in ACN with a 1.0 mM concentration solution of each compound containing TBAP as supporting electrolyte (50 mM). The ECL maxima (Table 2) of compounds **1** and **2** occur at a wavelength of about 50 nm shifted to the red relative to their photoluminescence maxima (Table 1). The formation of excimers results from the generation of contact radical ion pairs (CRIP),[36] and hence these compounds can be regarded as emitting excimer ECL due to the formation of CRIP (E-route)[21] whereas the ECL of **3**–**5** can be closely overlain on the fluorescence spectra (see the supplementary information for a comparative ECL and PL spectra of representative compound **4**†). Hence they can be described as emitting from monomeric ICT state. The slight deviation may be a result of polar nature of the ECL active species.

From the values of enthalpy change of annihilation reaction of radical ions $-\Delta H^0$ and the energy of the ECL emission (in eV) it can be seen that the ECL emission for all the compounds is not from singlet state as the annihilation did not produce sufficient energy to populate the same. Hence triplet–triplet annihilation must have occurred to provide sufficient energy (T-route). It is interesting that these molecules emit ECL with appreciably higher intensities while the photoluminescence from them are too weak (*cf.* Φ^{flu}). Though the relative intensities of the ECL emission in each case is appreciably lower than the ECL intensity of the standard Ru(bpy)_3^{2+}, however, this is the first report that describes the chromone derivatives as showing ECL, and there are possibilities to tune the ECL emission wavelength and intensity *via* structural modification so that these compounds and derivatives can be made suitable for further application.

Conclusion

We have synthesized a new series of donor-substituted phenylethynylchromones and observed new photophysical properties and electrochemiluminescence that are quite different from that of the unsubstituted chromone. The steady-state photophysical nature of the new compounds is interesting and the non-interference of donor groups with the photo-absorption is a unique observation. While there is a full conformity between the theoretical results and electrochemical observation, there are variations between the theoretical results and the experimental elecronic absorption behaviour. While free chromone does not show ECL, π-extension imparts ECL character to the resultant molecules. Compounds **1** and **2**, having no or only a weak donor show excimer ECL, which is consistent with our previous observations. Compounds **3**–**5** exhibit monomeric ICT ECL. More interesting is the observation of intense ECL from molecules that are too weakly fluorescent. The electronic properties as studied by CV and DFT calculation correlate well. The present study provides a good deal of understanding of the mechanisms governing ECL in the still evolving field of electrogenerated chemiluminescence. The study also strengthens the principles and rationale of design and synthesis of fine-tunable electroactive, photoactive and electron communicating molecules for the advancement of molecular electronics.

Acknowledgements

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