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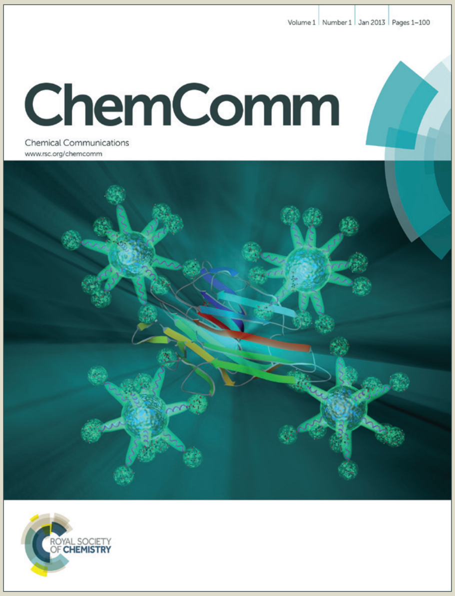

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Panchromatic Luminescence from Julolidine Dyes Exhibiting Excited State Intramolecular Proton Transfer

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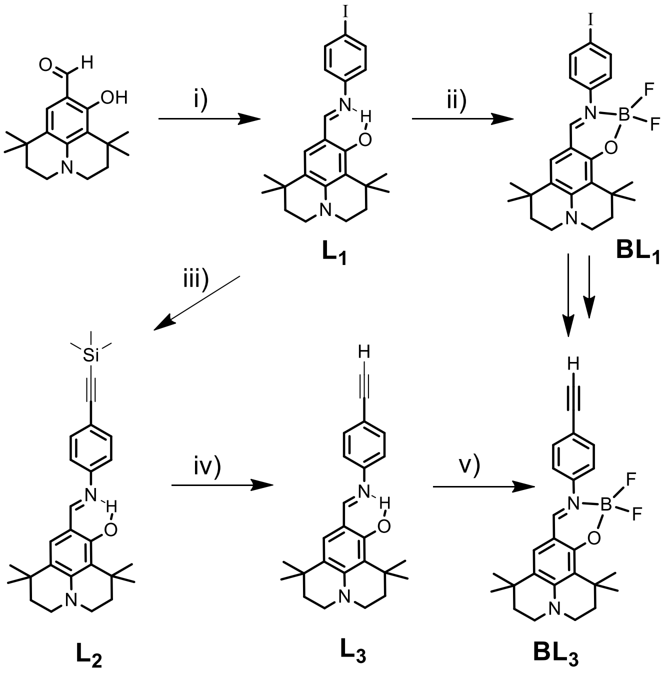
The preparation and the photophysical behavior of novel julolidine derivatives designed for displaying excited state intramolecular proton transfer (ESIPT) are reported. These dyes exhibit panchromatic photoluminescence covering the whole visible spectral range, both in organic solvents and in the solid state.

The search for white-light-emitting materials is strongly pursued in current chemistry because of the possibility to set disruptive progress in display and lighting technologies. Most of the materials reported so far rely on the mixing of different emitters (red/blue/green or blue/orange) to cover the whole visible spectral window (400-700 nm). However, this may cause problems such as diversified colour aging of individual components or demanding requirements in device fabrication. Compared to multicomponent emitters, white light output from an individual component can offer remarkable advantages, *e.g.* a more straightforward device fabrication and a better colour quality and reproducibility. Several approaches have been explored to obtain white-light emission from individual chemical entities. A common strategy entails the use of multichromophoric arrays where partial energy transfer occurs from a donor component to one or more acceptors.[1-3] Another exemplary approach is the combination of two complementary blue- and orange-emitting dyes exhibiting excited state intramolecular proton transfer (ESIPT).[4, 5] In the latter case, energy transfer cannot occur due to the transient nature of the ground state of the acceptor unit, and concentration-independent white emission occurs. Panchromatic luminescence from mixed excited states has also been reported for a simple Ir(III) complex.[6] An alternative approach takes advantage of concomitant blue luminescence from a monomeric species and red luminescence from the related excimeric form.[7-9] This method allows colour tunability by controlling the extent of association between monomers and hence the balance between the two emission bands.

Herein, we report the preparation and photophysical behaviour of novel julolidine derivatives, properly designed for displaying ESIPT. Suitable reference dyes in which ESIPT is blocked through boranylation have been also prepared. The julolidine unit has been chosen because of its strong electronic donating properties[10, 11] which will make the N^O chelating centre favourable either for boron(III) or metal coordination. The presence of four methyl groups on the julolidine increases the solubility and prevents the concentration quenching in the solid state or in concentrated solutions. Julolidine based materials have been previously used as red emitters in OLED's when linked to dicyanomethylpyran modules[12] and in push-pull systems for exciplex emission at low energy.[13] Our ESIPT dyes exhibit broad luminescence covering the whole visible range after photoexcitation, both in solution and in the solid state.

The protocols for the synthesis of the targeted dyes are sketched in Scheme 1. The pivotal ligand L_1 was synthesized by the condensation of julolidinyl-aldehyde[14-16] and 4-iodoaniline in ethanol in the presence of catalytic amount of *p*-TsOH under reflux, as previously described for anils derivatives.[17-19] The terminal alkyne was introduced by a Sonogashira cross-coupling reaction promoted by Pd/CuI catalysts between L_1 and trimethylsilyl(TMS)-acetylene. A large excess of KF was necessary for the deprotection of the TMS group of **L_2** in polar conditions to yield the key arylacetylide **L_3**. Complexation of **L_3** with $BF_3{\cdot}Et_2O$ in 1,4-dichloroethane gave the boranil derivative **BL_3** in 94 % yield. **BL_3** can also be obtained from **BL_1** in two steps using similar synthetic methods but it was more difficult to functionalize the iodo group after the BF_2 complexation has occurred. The proton NMR spectra of **L$_1$**, **L$_2$** and **L$_3$** in $CDCl_3$ show a characteristic signal at ~14.0 ppm which is safely assigned to OH proton. This is shifted downfield, due to the strong hydrogen bond formed with the free doublet of nitrogen atom. The IR spectrum of **L$_3$** and **BL$_3$** exhibit a strong absorption around 3300 and 2100 cm^{-1} for the ν(C-H) and ν(C≡C) stretching vibration, respectively. Routine elemental analysis, ESI-MS and NMR unambiguously confirm the molecular structure of these novel compounds.



Scheme 1. Synthetic pathways for compounds L_1 to BL_3. *i)* *p*-TsOH cat., dry EtOH, 95 °C, 12 hrs, 75%. *ii)* $BF_3{\cdot}Et_2O$ (6 eq.), 1,4-dichloroethane, rt, 30 min.; $^{i}Pr_2NH$ (6 eq.), 3 hrs, 89%. *iii)* $[Pd(PPh_3)_2Cl_2]$ 10 mol%, CuI 10 mol%, TMS acetylene, $^{i}Pr_2NH$, THF, rt 12 hrs, 99%. *iv)* KF (100 eq.), $MeOH/H_2O$, THF, rt, 12 hrs, 76%. *v)* $BF_3{\cdot}Et_2O$ (6 eq.), 1,4-dichloroethane, rt, 30 min.; $^{i}Pr_2NH$ (6 eq.), 3 hrs, 94%.

All compounds **L$_n$** and **BL$_n$** (n = 1, 3) absorb up to 450 nm with relatively high extinction coefficients (Figure SI11 and Table SI1). The strongest and broad absorption band, peaking at about 400 nm, is assigned to $^1\pi,\pi^*$ transitions[20] and is not influenced by solvent polarity (Figures SI12-13). On going from **L$_n$** to **BL$_n$**, this band is red shifted by approximately 20 nm and its intensity increases (ε_{max} = 49400, 40300, 64000 and 64500 M^{-1}cm^{-1}, for **L$_1$**, **L$_3$**, **BL$_1$** and **BL$_3$** respectively).

The dyes under investigation display a manifold emission behaviour: the proton bridged systems **L$_1$** and **L$_3$** have completely different luminescence features with respect to the related boranils **BL$_1$** and **BL$_3$**. The highest photoluminescence quantum yields (PLQYs) were found for the closed ring derivatives **BL$_1$** and **BL$_3$** (Table SI2), likely due to boron chelation.[20-24] Indeed, recently, tetrahedral boron-complexes, incorporating N^N or N^O chelation, were found to be highly luminescent.[20] The short-lived emission in solution of **BL$_1$** and **BL$_3$**, peaking at about 480 nm, does not display large shift or shape modification by changing the solvent. On the contrary, lifetimes and PLQYs are remarkably affected by the medium. An increase in solvent polarity brings about an enhancement of PLQYs (Table SI2), as observed for similar systems.[25, 26] The proton bridged ligands **L$_1$** and **L$_3$** display dual luminescence, due to ESIPT (*vide infra*). In general, this phenomenon occurs upon photoexcitation of systems containing a proton donor and a nearby proton acceptor group. Light irradiation triggers a redistribution of the electronic charges, inducing a fast proton transfer reaction from the donor to the acceptor group, mediated by the intramolecular H-bond. This migration is ultimately a keto-enol tautomerization, transforming the excited enol form (E*) in the excited keto form (K*). After the radiative deactivation of the latter, the system goes back to the initial E form, through reverse proton transfer.[27, 28] The ESIPT process generally induces a reduction of PLQY of the K form, because it makes non-radiative deactivation pathways more competitive, favouring internal conversion and vibrational relaxation. The extent of ESIPT is dramatically affected by the medium, as intermolecular H-bond formation in protic solvents competes with the intramolecular proton transfer process.[29]

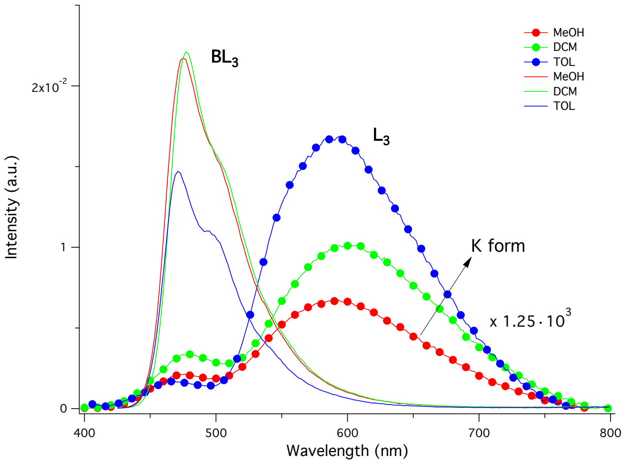


Figure 1. Emission spectra in different solvents at rt of **BL$_3$** (full line) and **L$_3$** (full line and markers). Spectra are normalized for the quantum yield.

Figure 1 compares the room temperature luminescence spectrum of ESIPT compound **L$_3$** with that of the corresponding non-ESIPT boranil analogous **BL$_3$** in 3 solvents of different polarity and proticity. The same comparison for **L$_1$** and **BL$_1$** is reported in Figure SI14 top. Emission bands from both tautomers can be observed in different ratio depending on the solvent: luminescence from E form appears at 470–480 nm whereas K form emission is strongly red-shifted at 600 nm. The global luminescence quantum yields for **L$_1$** and **L$_3$** decrease from ~10^{-3} in aprotic solvents to around 10^{-4} in methanol (MeOH) because of the reduced formation of the stronger emitting K form (Table SI2).[29] On the other end, the K form is longer lived in less polar solvents and displays a mono-exponential decay (Table SI2). Its formation (rise) is not discernible because the ESIPT process takes place at an ultrafast rate. Accordingly, the lifetime of the E tautomer is too short and under the limits of detection of our apparatus.

In order to investigate the prototropic equilibrium and the photophysical properties of the protonated species, the proton bridged ligands **L$_1$** and **L$_3$** have been studied in acetonitrile solution upon acidification. Indeed, ESIPT molecules contain both proton donor and acceptor groups and they can be protonated or deprotonated depending on the pH of the solution. While for **BL$_1$** and **BL$_3$**, absorption and emission profiles are not affected by the acid addition, the absorption spectra of **L$_1$** and **L$_3$** are red-shifted compared to those of pure acetonitrile (ACN) solution (Figure SI15-16). The emission data reveals the disappearance of the K form and the corresponding appearance of a new species, between E and K emissions (Figure SI15-16). This new band can be ascribed to the cationic form, given by the protonation of imine nitrogen, and is very similar in shape and position (only slightly red shifted) to that of the related boranil compound. Indeed, the N-protonation is expected to interrupt the intramolecular H-bond (O-H···N).

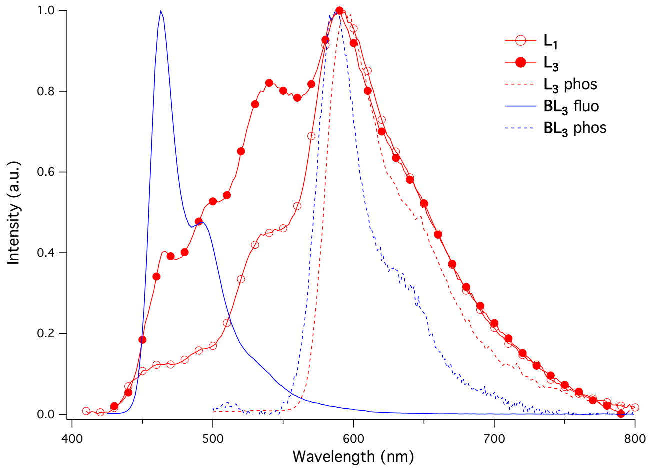


Figure 2. Normalized luminescence spectra of **L$_n$** and **BL$_n$** derivatives in $CH_3OH:CH_2Cl_2$ 1:1 glass at 77 K; the luminescence of **BL$_1$** is omitted for clarity.

In a condensed medium ($CH_3OH:CH_2Cl_2$ 1:1 glass at 77 K) the boranil compounds show a strongly blue-shifted fluorescence (peaking at around 460 nm) with respect to rt and a weak phosphorescence emission (λ_{max} = 584 and 572 nm, τ = 17.1 and 38.1 ms for **BL$_1$** and **BL$_3$**, respectively; Figure 2, Figure SI17 and Table SI3). The phosphorescence of **BL$_1$** is shorter-lived than that of **BL$_3$**, because of the heavy atom effect of the iodine substituent (ζ_I = 5069 cm^{-1}),[30] which promotes the $T \rightarrow S_0$ spin forbidden deactivation. On the contrary, the proton bridged julolidine derivatives **L$_1$** and **L$_3$** show a more complex emission behaviour, both displaying a panchromatic emission from a variety of excited states. By comparison with the emission behaviour of the boranil derivatives, the emission from the singlet and triplet states of the E form can be identified with the bands peaking at around 465 and 590 nm, respectively (Figure 2).[29, 31] The contribution of the intermediate band, peaking around 530 nm, can be attributed to the fluorescence of the K form. This assignment is also confirmed by the luminescence decay analysis at different emission wavelengths. At λ > 600 nm the decay is monoexponential with lifetimes in the order of ms (τ = 11.6 and 54.6 ms for **L$_1$** and **L$_3$**, respectively, Table SI3), which are typical for the phosphorescence of organic compounds and comparable to those observed for the related boranil derivatives. At shorter wavelengths (450 < λ < 550 nm) double exponential decays are observed both for **L$_1$** and **L$_3$**, with lifetimes in the ns region (Table SI3).

It should be noted that the presence of the iodine atom promotes the intersystem crossing, altering the ratio between the singlet and triplet emission bands and hence the colour of the emitted light. This prompted us to determine the colour coordinates of **L$_1$** and **L$_3$** in the CIE 1931 colour space from the relevant irradiance spectra (Figure SI18). The results of the analysis are reported in Figure 3, together with the coordinates of the standard illuminants **A** (tungsten lamp) and **D65** (noon daylight) for comparison. There is a clear difference between the yellowish-orange emission of **L$_1$** (close to that of the standard illuminant A) and the yellowish-green emission of **L$_3$**, shifted towards the centre of the diagram. The emission output of **L$_3$** cannot be considered white but panchromatic, as all the colour components of the visible spectrum are present, but their balance is not optimized to generate white emission.

Notably, the panchromatic emission can also be observed from powder samples at rt (Figure SI18). In this case, **L$_3$** show colour coordinates similar to those already observed in glassy solution at 77 K (Figure 3). The situation is different for **L$_1$**: here the emission is mainly from the singlet state, while the red phosphorescence is depressed (Figure SI18). This leads to a more balanced white light emission having colour coordinates 0.341, 0.386 (Figure 3). This behaviour can be explained taking into account the phosphorescence quenching by the atmospheric oxygen, to which the powder samples are exposed during the measure. Unfortunately, it was not possible to determine the absolute photoluminescence quantum yield of the powder samples because it was below the detection limit of our apparatus (< 2%).

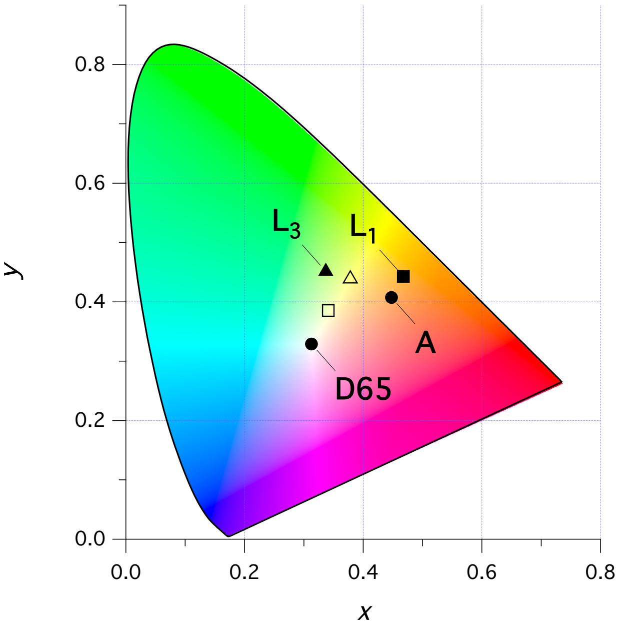


Figure 3. CIE 1931 spectral chromaticity coordinates of **L$_1$** (squares) and **L$_3$** (triangles) in $CH_3OH:CH_2Cl_2$ 1:1 glass at 77 K (full symbols) and as powder film at rt (hollow symbols) and of the standard illuminants **A** (tungsten lamp) and **D65** (noon daylight).

Conclusions

Here we have presented the panchromatic emission from modified julolidine dyes, achieved by taking direct advantage of the ESIPT effect. It must be emphasized that the present case is different from that of Park and coworkers, in which ESIPT was used to prevent the energy transfer between two chromophores.[4] Moreover, in our system the emission colour can be modulated by substituting the *para* position of the phenyl ring, whereas the now moderate PLQY of the K tautomer is expected to increase on passing to a 5-member ring system. Indeed, according to the literature, the PLQY of the K form in non-polar solvents is expected to be higher in 5-member systems than in 6-member rings for the less pronounced twisted intra-molecular charge transfer deactivation.[32] We believe that this approach can open the route to the synthesis of a new class of white light emitting single molecule systems, as promising luminescent materials in electro-optical devices for lighting (*e.g.* OLEDs and LECs).

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Notes and references

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