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COMMUNICATION

Solvent-tuned Dual Emission: a Structural and Electronic Interplay highlighting a novel planar ICT (OPICT)

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Displaying a dual emission, Phen-PENMe$_2$ compound can be foreseen as a new model for fundamental studies. It is based on an excited state cumulene-type structure, involving perpendicular π orbital (OPICT). By contrast to the "Twisted Intramolecular Charge Transfer" (TICT) emission, the OPICT emissive state is planar. This new compound is also a potential candidate for local *ratiometric* probes of the medium polarity (mixture of solvents, and biological systems), and white emission

Intramolecular charge transfer (ICT) is a phenomenon widely reported in the literature and it is present in a large number of donor-acceptor systems. The first report of dual emission linked to ICT[1] was described by Lippert et al in 1959[2] involving the 4-N,N-(dimethyl)aminobenzonitrile molecule (DMABN). Starting from this seminal work, recently largely commented and revisited in the literature[3], several other systems were designed and proved to exhibit this feature. Most of these actually consist of a molecular scaffold, such as phenanthridine[4], benzoic acid[5], pyrrole[6], aminoacridine[7], pyrene[8], butadiene[9], or stilbene[10] functionalized with electron- donating and/or withdrawing groups[11]. In addition to a localized excited-state (LE), the existence of a Twisted Intramolecular Charge Transfer (TICT) is usually proposed to explain this dual emission,[12] concerning DMABN and related molecules. Among other proposals, one of the most relevant is the planar ICT model with no twisting of the dimethylamino group[13]. The compound 9-amino-10-cyanoanthracene (ACAN)[14] was also recently reported to result in two emissions due to the largely different conformational geometries in the two states. Nonetheless, in most cases, the reported dual-emission is due to the existence of two species in solution, such as species in different protonation states (i.e. pH sensors), in the ground or at the excited state.[15]

In this manuscript, the existence of a dual emission stemming from the presence of two main emissive excited-states (LE and ICT) is proven by a combined experimental and theoretical approach in the case of the 5-(4-dimethylaminophenylethynyl)-1,10-

phenanthroline compound (Phen-PENMe$_2$, Figure 1), a prototype molecule belonging to the Phen-PEZ family.[16]

The UV-visible absorption spectrum of Phen-PENMe$_2$ shows an intense band in the visible range and no sizable change of the absorption maximum as a function of the solvent (See Figure S1 in supplementary material, ESI), probably due to the similar polarity of the ground and vertical excited-states as demonstrated by the similar dipole moment computed at DFT level for the ground and localized excited state (10.7 and 13 Debye, respectively; for computational details refer to the ESI). DFT calculations showed that, independently of the solvent considered, the most stable conformation of the molecule in the ground state is planar.
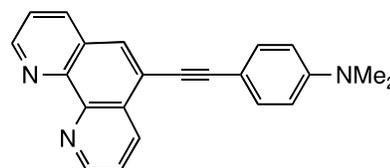
Figure 1: Molecular structure of Phen-PENMe$_2$

Interestingly, following 380 nm excitation, Phen-PENMe$_2$ indeed exhibits significant solvatochromism in its emission spectra when considering aprotic solvents. For instance, a shift of 8220 cm^{-1} is measured going from cyclohexane to DMSO (Figure S2 in ESI). This behaviour already points out the possible existence of an ICT state involved in fluorescence.[17] This finding is also in agreement with the calculated TD-DFT vertical absorption spectrum, which shows two intense vertical transitions around 420, and 310 nm, with a marked HOMO $\rightarrow$ LUMO, and HOMO $\rightarrow$ LUMO+2 character, respectively, both of ICT character (Table S1 in ESI). Furthermore, a lower intensity transition is additionally computed at 388 nm (F =0.05 a.u.) whose presence could be at the origin of the non-Gaussian profile observed for the longest wavelength band observed in the absorption spectrum.

At higher excitation energy (340 nm), a dual emission is observed in the most polar aprotic solvents (i.e. acetone, acetonitrile, DMSO

refer to Figure S3 in ESI) and the relative intensity of the two bands can be modulated in different mixtures of solvents. Emission spectra were recorded (after excitation at 340 nm) in mixtures of CH_3CN/DMSO (Figure S4). Since Phen-PENMe$_2$ displays a different quantum yield according to the solvent used, (Table S2) these spectra were normalized by area to eliminate quantum yield differences. On the normalized spectra, an *iso*-emissive point appears (Figure 2).
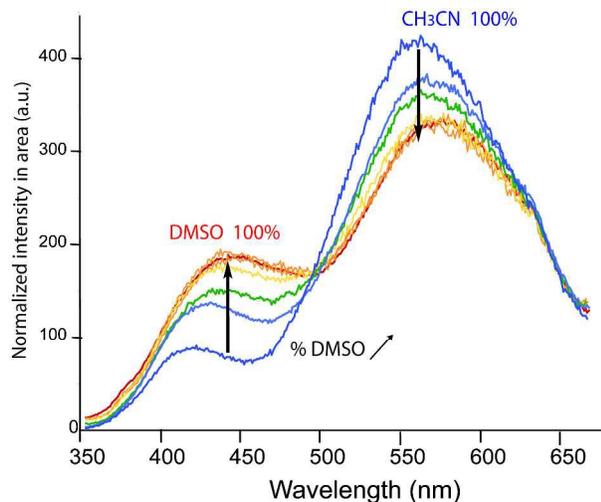
Figure 2: Normalized emission spectra of Phen-PENMe$_2$ recorded in different mixtures of DMSO/CH_3CN (% DMSO: 100, 82, 64, 46, 28, 10, and 0) upon an excitation at 340 nm.

This latter phenomenon can be attributed to the existence of two species at the excited state identical in all mixtures but possessing different quantum yield values. Following 340 nm excitation, the shorter wavelength emission band (ca. 430 nm) corresponds to emission from a locally excited (LE) state, (see Figure 3 for a qualitative description of the related phenomena, based on calculations and spectroscopic data). According to TD-DFT calculations, this transition is of $\pi \rightarrow \pi^*$ character, centred on the 1,10-phen moiety, and associated with a twisted conformation of the molecule ($\phi \sim 90°$) in the excited-state. It should be stressed that the torsional motion associated to a change in ϕ is easily accessible, with an estimated barrier of c.a. 1 kcal.mol^{-1}.

An ICT state, on the other hand, is responsible for the longer wavelength emission band (at ca. 550 nm). Actually, and according to the TD-DFT calculations, two emissive ICT states exist which show a similar, planar ($\phi \sim 0°$) structure, with close emission energies (0.27 eV of difference) but different intensity (oscillator strengths of 1.36 a.u. and 0.11 a.u., see Table S3 in the ESI), thus justifying the broad profile observed for this emission band. At the lower excitation energy (380 nm), the only emissive excited states are the ICT ones (with associated important solvatochromism). When the molecule is excited at a higher energy (340 nm), the LE state can be reached, giving rise to LE emission and ICT emissions after non-radiative de-excitation. The ICT state displays a high charge separation (calculated dipolar moment is 28 Debye) and is consequently stabilized in more polar solvents. From the slope of the experimental Lippert-Mataga plot (Stokes shift according to the solvent orientation polarizability), and using a calculated Onsager radius of 5.6 Å, a value of 20 D was found for the difference between ICT and the fundamental dipolar moment, which is in good agreement with the calculated value (28.0 - 10.7 = 17.3 D, see calculation, and Figure S5 in ESI). This value can be explained by

the non-conjugated "cumulene-like" mesomeric character of the ICT excited-states (see calculations and Bond Length Alternation value – BLA-, Table S4).
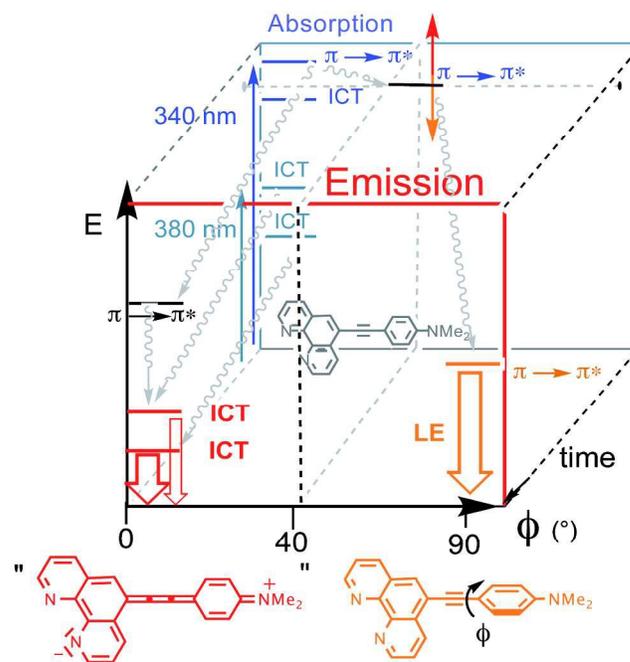
Figure 3: 3D schematic representation of the electronic energy levels in Phen-PENMe$_2$ and the related observed transitions; non radiative relaxations are also indicated as grey arrows (a larger version of this figure is provided in the ESI).

The lowest lying emissive states actually stem from the relaxation of two ICT excited states existing in the Franck-Condon region corresponding to excitations from the dimethylaminophenyl to the 1,10-Phen moiety. Both of these states are also accessible after 380 nm excitation whereas two additional states, vertically computed at 310 (ICT character), and 298 nm ($\pi \rightarrow \pi^*$), become accessible only after an experimental 340 nm excitation.

The excitation spectrum recorded at the emission at 560 nm (see Figure 4), essentially corresponds to the UV-vis absorption spectra. By contrast, the excitation spectrum of the emission centred at 416 nm is quite different, particularly for the highest wavelengths.
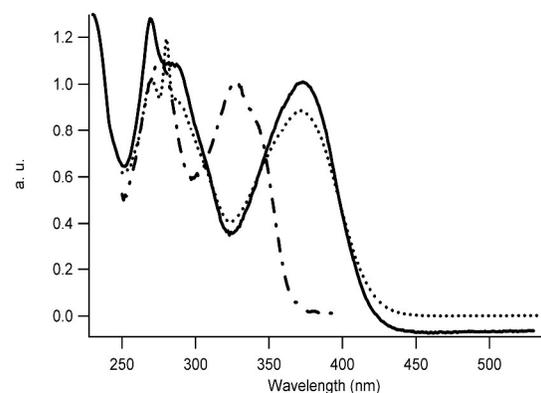
Figure 4: Excitation spectra of Phen-PENMe$_2$ in CH_3CN for emission at 416 (-·-) and 560 (…) nm, and compared to the absorption spectra (-).

In good agreement with the TD-DFT calculations, it can be deduced that an excited state around 330 nm close to the conformation of the LE emissive state (non planar) is related to a nearly forbidden electronic transition from the ground (planar) state.

In less polar solvents, this "twisted" state is expected to be higher in energy as a consequence of its rather high dipole moment (for a twist angle of 40°, the dipole moment is computed to be 19 D); therefore it can not be reached via de-excitation processes (see Figure 3), and this may explain the single ICT-character emission observed in those solvents.

Time-resolved fluorescence spectra of Phen-PENMe$_2$ were also recorded in different mixture of acetonitrile/DMSO (Table S2). The estimated ICT emission lifetime is ca. four times longer than the LE (4.5 ns and 1.9 ns, respectively), and a decrease of the k$_r$ (radiative de-excitation) constant for the ICT is observed going from ACN to DMSO. On the other hand the k$_{nr}$ constant (associated to non-radiative relaxation processes) seems to be rather insensitive to the solvent mixture.

Quenching of the ICT band is observed after addition of water to a solution of Phen-PENMe$_2$ in DMSO (Figure 5). As previously reported in the literature,[7] this behaviour may be attributed to the existence of new fluorescence deactivation pathways involving the lone pair of the nitrogen (amino group) in hydrogen bonding and inhibiting the donor character of the nitrogen. These data thus further supports the presence of the CT from the lone electron pair of the dimethylamino group to the 1.10-Phen moiety.
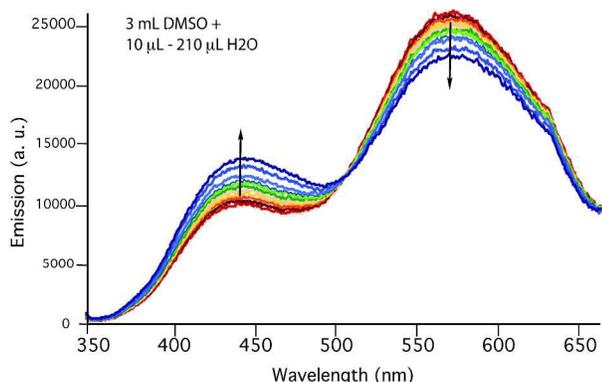
Figure 5: Normalized emission spectra of Phen-PENMe$_2$ in DMSO and after successive add of water.

More interestingly, the simultaneous presence of two emission bands allows a measure of the ratio of the two solvents more accurately than the direct monitoring of absolute quantum yields. Figure 5 shows how it is possible to use Phen-PENMe$_2$ as a sensitive ratiometric probe able to quantify amounts of water (between 200 and 7000 ppm) in a solvent (here DMSO). The same holds for other mixtures of solvents as depicted in Figure 2.

Conclusions

The presence of a dual emission in Phen-PENMe$_2$ related to the population of LE and ICT states has been demonstrated by a joint experimental and theoretical analysis. The ICT to LE excited state ratio is mostly triggered by solvent polarity, which modulates the relaxation of Franck-Condon excited states to a twisted localized emissive state (TLE). For the ICT emission, both ground and excited-states are planar. The large solvatochromism observed may be explained by the conjugation disruption induced by an excited state cumulene-type structure involving perpendicular π orbital

(OPICT). On the contrary to the TICT, the geometries of the emissive ICT excited and fundamental states are planar. The dual emission observed for this compound opens the route of a fundamental in depth study, but also for potential application as *ratiometric* optical probe of local polarity (or of microscopic electric fields), viscosity[8b] or water in solvents. The potential of such molecules was also pointed out for electro-optical molecular switches,[18] white light emitting diodes[19] by the use of pertinent media conditions, and field effect diodes.[20] Finally, interesting nonlinear optical properties can be anticipated for Phen-PENMe$_2$ and its use as a ligand for metal ions is currently under analysis although they are permitted in communications submitted to other journals.

Notes and references

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