Triple fluorescence of 4-(1,4,8,11-tetraazacyclotetradecyl)benzonitrile

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Triple fluorescence is observed for DMABN-cyclam in EtOH, corresponding to a locally excited (LE) singlet state, a twisted intramolecular charge transfer (TICT) state, and an intramolecular exciplex (E).

More than 30 years ago, Lippert investigated the dual fluorescence of 4-(dimethylamino)benzonitrile (DMABN) in polar solvent.[1] Several models have been proposed to address the cause of the anomalous long-wavelength fluorescence, including bending of the cyano group,[2] solute–solvent exciplex formation,[3] and twisted intramolecular charge transfer (TICT).[4] The concept put forward by Grabowski of a TICT state, or charge transfer reaction which is accompanied by a twisting motion and orbital decoupling of the phenyl acceptor ring from the dimethylamino donor group, is generally favored.[4] In addition to TICT state formation, benzonitriles bearing flexible, alkylamino chains, *e.g.* 3-(4-cyanophenyl)-1-dimethylaminopropane (CNP3NM), can form intramolecular exciplexes which arise due to the conformational flexibility of the alkylamino chain, and its ability to form a sandwich configuration promoting excited state, charge transfer.[5] Van der Auweraer *et al.*[6] observed a correlation between intramolecular exciplex formation and Hirayama's rule,[7] which states that the most stable sandwich conformation will arise when $n = 3$ for a $Ph(CH_2)_nNMe_2$ system. We report here the triple fluorescence of 4-(1,4,8,11-tetraazacyclotetradecyl)benzonitrile (DMABN-cyclam), corresponding to the LE state, a TICT state, and an intramolecular exciplex (E) (Fig. 1).

The UV spectrum for DMABN-cyclam in EtOH shows a single absorption peak at 295 nm. Excitation at this wavelength leads to three emission peaks: 352 (LE state), 421 and 473 nm (Fig. 2). Intensity contributions from the three individual excited states were estimated using the Voigt Amplitude function of Jandel's PEAKFIT 4.0. Recently, Létard *et al.* reported the dual fluorescence of two compounds structurally similar to DMABN-cyclam, 4-(1-aza-4,7,10-trioxacyclododecyl)benzonitrile (DMABN-crown4) and 4-(1-aza-4,7,10,13-tetraoxacyclopentadecyl)benzonitrile (DMABN-crown5).[8] DMABN-crown5 exhibited a TICT emission that red-shifted and increased in intensity as the solvent polarity increased from hexane (where the emission band was too weak to be measured accurately) to toluene (λ_{max} = 406 nm), to acetonitrile (λ_{max} = 466 nm). Similarly, DMABN-cyclam, which differs from DMABN-crown4 primarily in the replacement of nitrogen binding sites for the oxygen atoms of the crown ether, reports a similar trend in the emission spectra (Fig. 2): hexane (λ_{max} = 390 nm), toluene (λ_{max} = 413 nm) and EtOH (λ_{max} = 473 nm). We, therefore, attribute the third emission band in EtOH at 473 nm to a TICT state. Unlike DMABN-crown4, however, DMABN-cyclam has two pendant amine groups linked by a short chain (n = 3 and 4) to the benzonitrile acceptor. Despite the cyclic nature of cyclam, this molecule exhibits sufficient flexibility to form a sandwich complex in the excited state that gives rise to an intramolecular exciplex peak (E) (Fig. 1). The peak position identified for the exciplex peak of DMABN-cyclam in hexane (λ_{max} = 392 nm) compares favorably with that found for CNP3NM in isopentane (λ_{max} = 390 nm).[9]

Several trends are evident from Fig. 2 with regards to the effect of solvent polarity on the triple fluorescence of DMABN-cyclam. The TICT emission band red-shifts by more than 80 nm and increases in intensity relative to the LE emission as solvent polarity is increased. The relative intensity of the TICT band increases with solvent polarity due to a stabilization of the charge separation. The exciplex emission does not red-shift quite as severely (34 nm), due to a smaller dipole moment compared with the TICT configuration, and reflects a maxima in the solvent, toluene. Apparently, a ground state sandwich configuration is promoted for DMABN-cyclam in toluene, fostering enhanced intramolecular exciplex formation despite

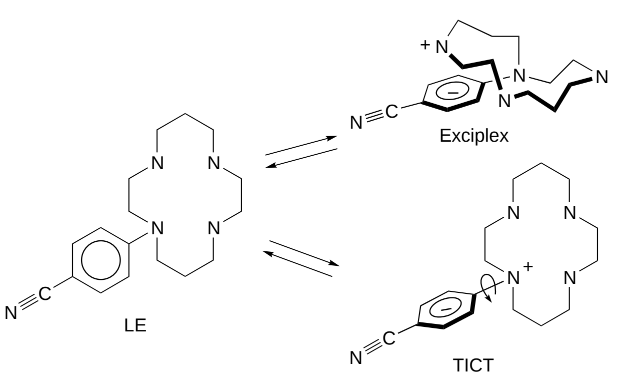

Fig. 1 Proposed structures and equilibria existing between the three excited state species, LE, TICT and E, generating the observed triple fluorescence

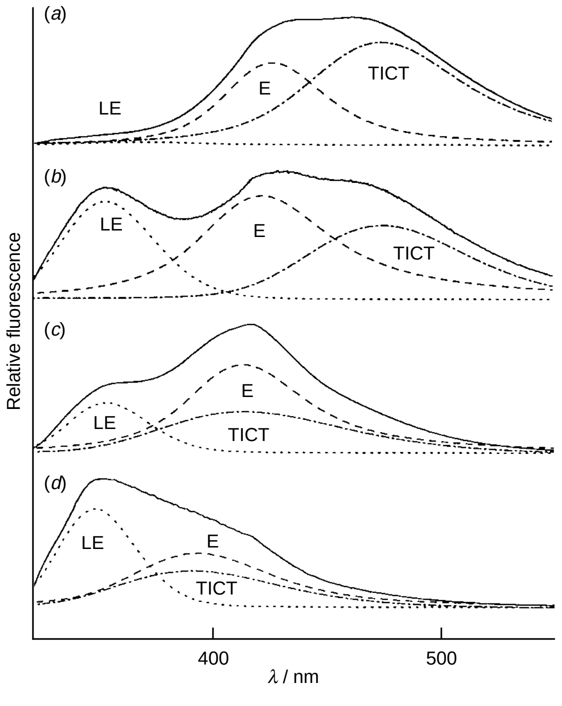

Fig. 2 Solvent effect on the triple fluorescence of DMABN-cyclam: (*a*) water, (*b*) EtOH, (*c*) toluene and (*d*) hexane

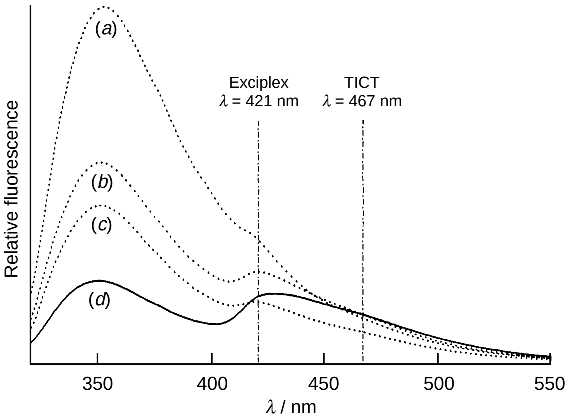

Fig. 3 Emission spectra of DMABN-cyclam in poly(vinyl alcohol) at (*a*) 20, (*b*) 40, (*c*) 60 and (*d*) 80 °C

the lower polarity of this solvent. The LE band exhibits an intensity minimum in water because of the high polarity of this solvent, and its capability for stabilizing the two charge transfer complexes.

Temperature studies of the fluorescence arising from thin films of DMABN-cyclam in poly(vinyl alcohol) (PVA) indicate the dependence of the two excited-state charge-transfer emission peaks (E and TICT) on the conformational mobility of the molecule.[9] PVA was chosen as a support material for DMABN-cyclam because it provides a solid matrix with similar polarity to EtOH. PVA is hydrophilic and absorbs moisture from the air, decreasing the glass transition temperature (T_g) and facilitating the conformational transitions in the excited state at higher temperatures. At room temperature, DMABN-cyclam in PVA shows only a single peak at 357 nm, with a slight shoulder evident at 421 nm (Fig. 3). As the temperature increases, the overall fluorescence intensity correspondingly decreases. However, as the temperature approaches 80 °C (above the T_g for PVA), the exciplex shoulder at 421 nm becomes a more prominent peak, and there is evidence for the formation of the TICT state at 467 nm. This result verifies the dependence of these excited-state charge transfer bands on the conformational mobility of DMABN-cyclam in PVA as it transitions from a glass to a rubbery state.

In conclusion, DMABN-cyclam is a unique molecule which exhibits triple fluorescence arising from the LE state and two excited state complexes, a TICT state and an intramolecular exciplex (E). All three emission bands are strongly perturbed by solvent polarity and conformational mobility.

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Notes and References

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