Relaxation processes in TICT chromophores containing acetyl and cyano acceptor groups

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The term twisted intramolecular charge transfer (TICT) refers to a certain class of compounds composed of an electron donor and acceptor part separated by a single bond that exhibit dual fluorescence. The origin of the long-wavelength band has been under discussion for many years^[1] and is now commonly accepted to occur from a TICT state where the electron donor part is twisted with respect to the acceptor part.

Research on TICT chromophores that were initially considered good candidates for fluorescence enhancement experiments in plasmonic nanostructures revealed unusual differences in their photophysical properties. Two series of compounds have been studied: containing acetyl and nitrile electron acceptor groups (Fig. 1).

Surprisingly, band positions, relative emission intensities, quantum yields, and excited state lifetimes change in a different manner with consecutive extensions of the electron donor part. This manifests itself in, e.g., unexpectedly weak CT emission band in 4-piperazinoacetophenone. Efforts to explain these deviations, including quantum chemical calculations, have been undertaken.

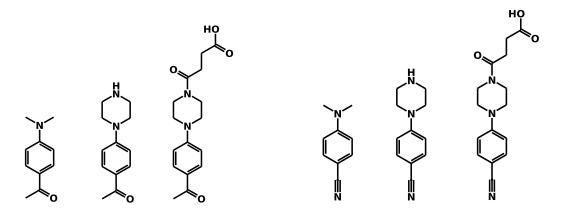


Figure 1: Two series of TICT chromophores under investigation: containing acetyl and nitrile electron acceptor groups.

References:

[1] Z.R. Grabowski, K. Rotkiewicz, W. Rettig, Chem. Rev., 2003, 103, 3899