The Role of Cyclodextrin Cavity Size on the Normal and Twisted Intramolecular Charge Transfer (TICT) Fluorescence of N,N-Disubstituted p-Cyanoanilines in Aqueous Solutions.

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Abstract

p-Pyrrolidinobenzonitrile (PYRBN), and p-Piperidinobenzonitrile (PIPB) were utilized to probe the polarity and viscosity of cyclodextrins (CDs) interior. The dual fluorescence bands of PYRBN and PIPBN have been studied in α-, β-, and γ-CD aqueous solutions. The absorption and the fluorescence parameters (peak maxima, decay times, and the relative intensity) have been measured and were found to be consistent with the formation of complexes between probes and CDs.

It was found that the twisted intramolecular charge transfer (TICT) fluorescence band is enhanced and blue shifted upon complexation with cyclodextrins. The corresponding effect on the normal fluorescence band is small in both α-, and β-CD environments, while its obvious in the case of γ-CD environment.

Moreover, the steady state fluorescence spectra probably indicate for both PYRBN and PIPBN in both α-, and β-CD environments five different cases of complexes branched from two main positions called Type I and Type II. These environments may contain (1:1), (1:2), and (2:2) guest to CD inclusion complexes. In addition, the steady state fluorescence spectra probably indicate for both PYRBN and PIPBN in γ-CD environment five different cases of complexes. These environments may contain (1:1), (2:1), (2:2), and (3:1) guest
to CD inclusion complexes. Therefore, using the relation between the fluorescence intensity and the CD concentrations, the association constants for all these environments have been evaluated. We can conclude from the association constant values that (1:2) overcome (1:1) inclusion complexes, and (2:2) overcome both (1:1) and (1:1) inclusion complexes at specific wavelength.

All of these results emphasize that the motion of CD controls the motion of the guest molecules in CD environment, which enhance the ability to form the self-complex in excited state lifetime.