Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Faster Photoinduced Electron Transfer in a Diluted Mixture than in Neat Donor Solvent: Effect of Excited-State H-Bonding

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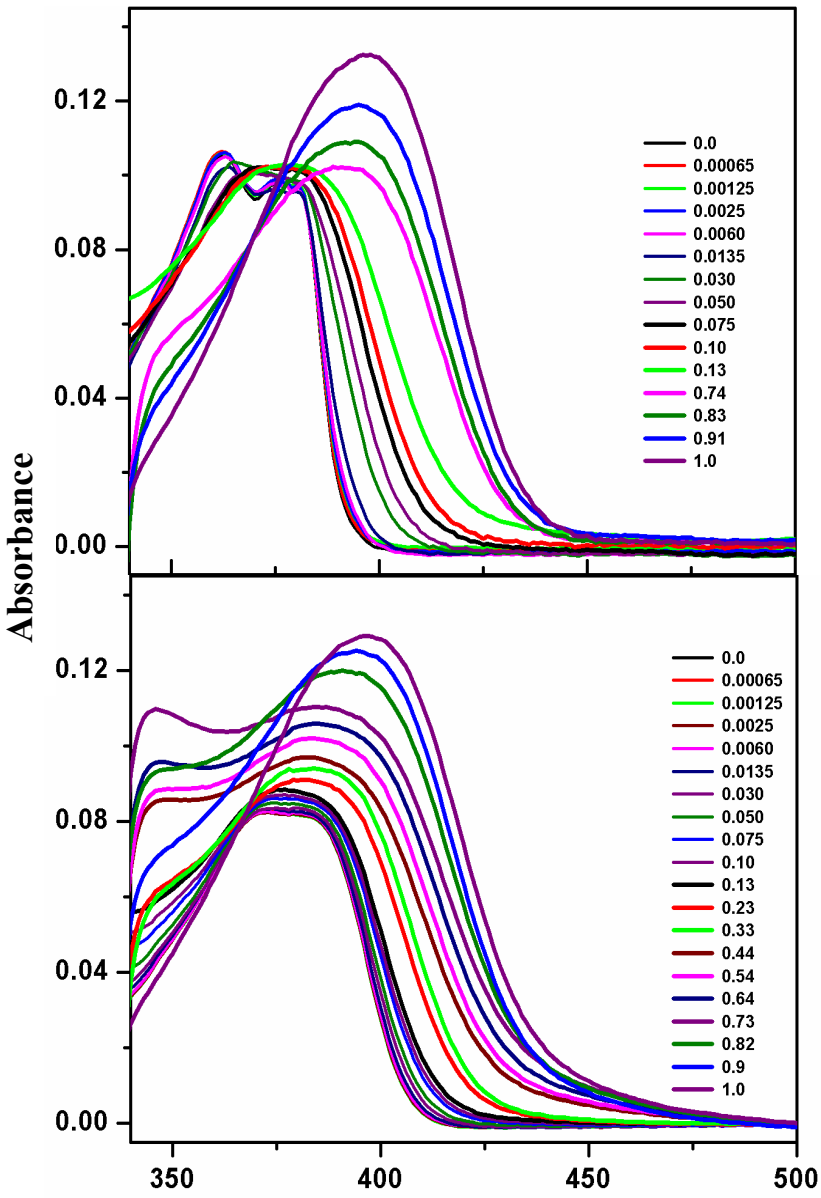

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Figure S1: Absorption spectra of C102 in the cyclohexane-aniline (top panel) and toluene-aniline (bottom panel) mixtures at different mole fraction of aniline, X_{AN}.

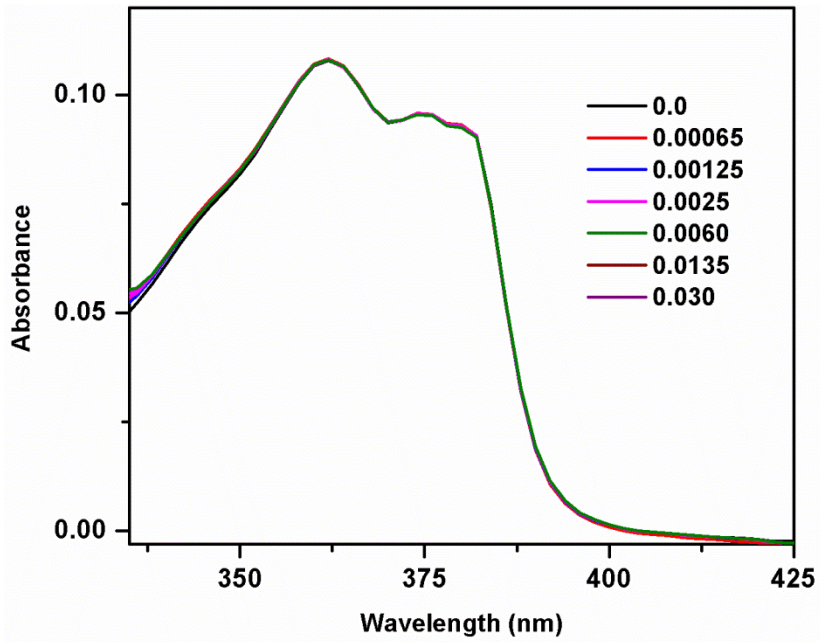

Figure S2: Absorption spectra of C102 in cyclohexane on gradual addition of DMA.

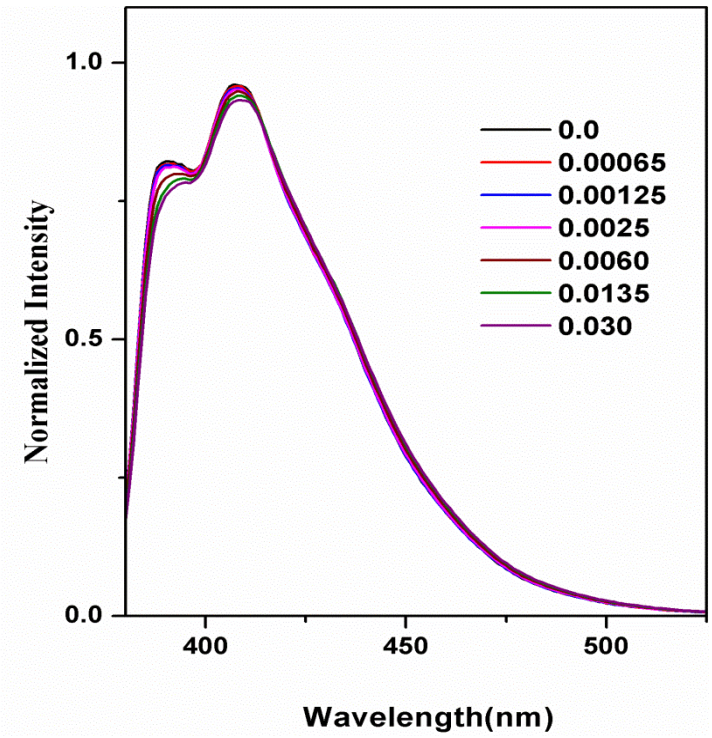

Figure S3: Emission spectra of C102 in cyclohexane on gradual addition of DMA.

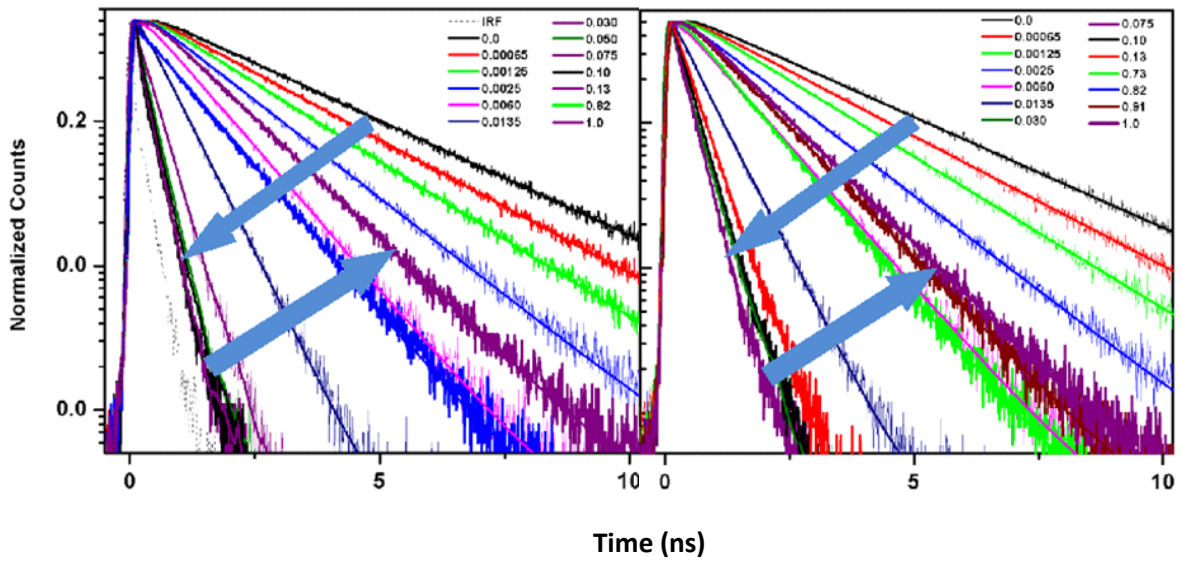

Figure S4: Fluorescence decays of C102 in the cyclohexane-aniline mixtures at different mole fraction of aniline, X_{AN}. Arrows indicate mode of the lifetime variation with increase in X_{AN}. The decays were measured at 410 nm (left panel) and 460 nm (right panel).

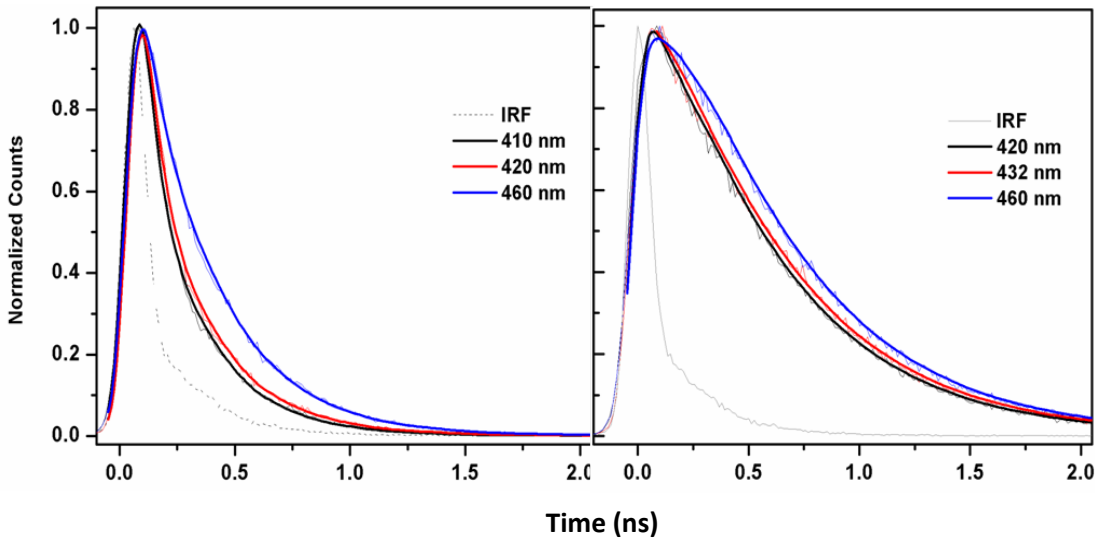

Figure S5: Fluorescence decays of C102 in the cyclohexane-aniline (left panel) and toluene-aniline (right panel) mixtures at three different emission wavelengths. Mole fractions of aniline, X_{AN} in cyclohexane-aniline and toluene-aniline mixtures are 0.075 and 0.13, respectively.

Calculation of the solvation energy correction (ΔE_{sol}):

ΔE_{sol} can be calculated by using the following equation[1]

$$\Delta E_{sol} = \Delta G_s^0(-) + \Delta G_s^0(+) \quad (1)$$

where $\Delta G_s^0(-)$ and $\Delta G_s^0(+)$ are the free energies of solvation of anion and cation respectively. Free energy of solvation can be calculated by using the following equations.[1]

$$G_{s(-)}^0 = -\left(\frac{N_0 z_i^2 e^2}{8\pi\varepsilon_0}\right)\left(1-\frac{1}{\varepsilon_s}\right)\left(\frac{1}{\frac{1}{Ap}+r_i}\right) \quad (3)$$

$$G_{s(+)}^0 = -\left(\frac{N_0 z_i^2 e^2}{8\pi\varepsilon_0}\right)\left(1-\frac{1}{\varepsilon_s}\right)\left(\frac{1}{\frac{1}{Bp}+r_i}\right) \quad (4)$$

where N_0 is the Avogadro's number, z_i is the ionic charge, e is the electronic charge, ε_0 is the permittivity of the free space, ε_s the dielectric constant of the solvent, r_i is the ionic radius, and Ap and Bp are the Fawcett's parameters of acidity and basicity, respectively. Ap and Bp are defined by the following equations[1]

$$Ap = 1.29E_T(30) - 33.3 \quad (5)$$

$$Bp = 10.14 + 0.108D_n \quad (6)$$

where $E_T(30)$ is the polarity scale and Dn is the donor number.

References

1. Shirota, H.; Pal, H.; Tominaga, K.; Yoshihara, K., Substituent Effect and Deuterium Isotope Effect of Ultrafast Intermolecular Electron Transfer: Coumarin in Electron-Donating Solvent. *J. Phys. Chem. A* **1998,** *102*, 3089-3102.