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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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 ($\Delta E_{\text{sol}}$):

$\Delta E_{\text{sol}}$ can be calculated by using the following equation:1

$$\Delta E_{\text{sol}} = \Delta G^0_{\text{s}(-)} + \Delta G^0_{\text{s}(+)}$$  \hspace{1cm} (1)

where $\Delta G^0_{\text{s}(-)}$ and $\Delta G^0_{\text{s}(+)}$ are the free energies of solvation of anion and cation respectively. Free energy of solvation can be calculated by using the following equations:1

$$\Delta G^0_{\text{s}(-)} = -\left( \frac{N_0 z_i^2 e^2}{8 \pi \varepsilon_0} \right) \left( 1 - \frac{1}{\varepsilon_s} \right) \frac{1}{(A_p + r_i)}$$  \hspace{1cm} (3)

$$\Delta G^0_{\text{s}(+)} = -\left( \frac{N_0 z_i^2 e^2}{8 \pi \varepsilon_0} \right) \left( 1 - \frac{1}{\varepsilon_s} \right) \frac{1}{(B_p + r_i)}$$  \hspace{1cm} (4)

where $N_0$ is the Avogadro’s number, $z_i$ is the ionic charge, $e$ is the electronic charge, $\varepsilon_0$ is the permittivity of the free space, $\varepsilon_s$ the dielectric constant of the solvent, $r_i$ is the ionic radius, and $A_p$ and $B_p$ are the Fawcett’s parameters of acidity and basicity, respectively. $A_p$ and $B_p$ are defined by the following equations:1

$$A_p = 1.29E_T(30) - 33.3$$  \hspace{1cm} (5)

$$B_p = 10.14 + 0.108D_n$$  \hspace{1cm} (6)

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

References