

Supporting information for

Modulation of ultrafast photoinduced electron transfer through H-bonding: PET from aniline to coumarin 153 in the presence of an inert cosolvent cyclohexane

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Table S1. Composition of the mixtures used in the MD simulations. Note that only one C153 was included at the centre of the box.

X_{AN}	$N_{Aniline}$	$N_{Cyclohexane}$
0.0	0	350
0.05	18	333
0.13	45	296
0.74	296	104
1.0	420	0

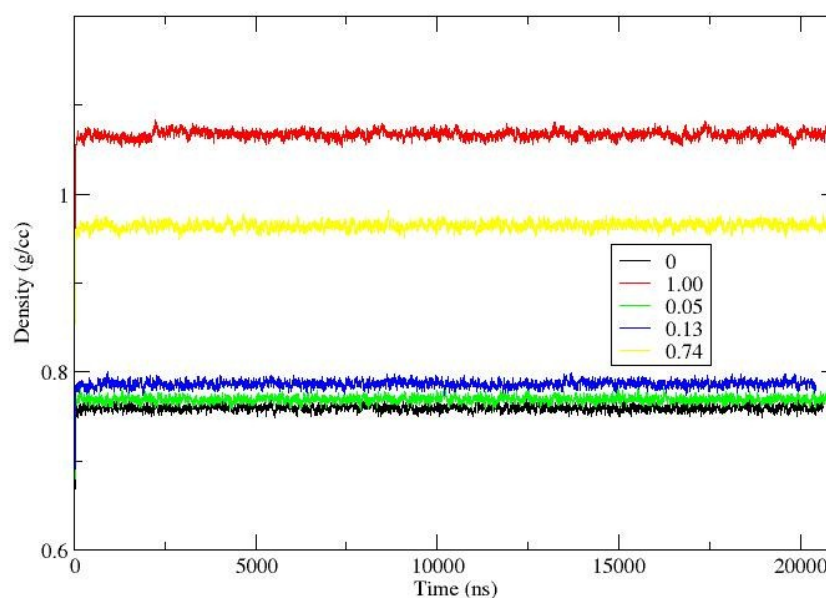


Fig. S1 The variation of density within the simulation period for different the systems at various mole fractions of aniline.

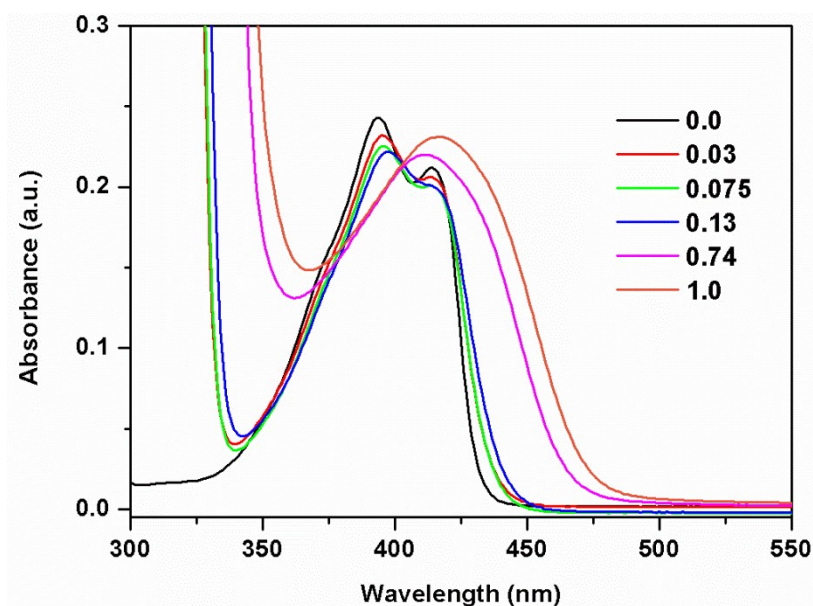


Fig. S2 Absorption spectra of C153 in cyclohexane-DMA mixtures at different mole fractions of DMA. Absorption spectra exhibit red-shift with increase of the mole fraction of donor but the extent of the shifting is less compared to cyclohexane-AN mixtures.

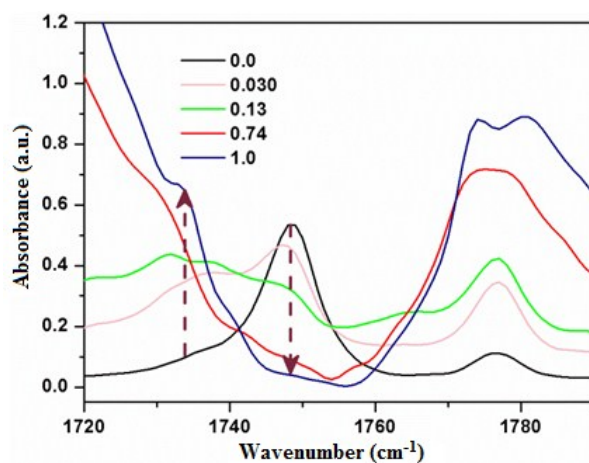


Fig. S3 The FTIR spectra of 20 mM coumarin 153 in the carbonyl stretching region in the cyclohexane-AN mixtures at different mole fractions of the electron donor (AN). Gradual disappearance of the free C=O stretching frequency (at 1748 cm^{-1}) and appearance of a new peak at 1736 cm^{-1} may be due to H-bonding.

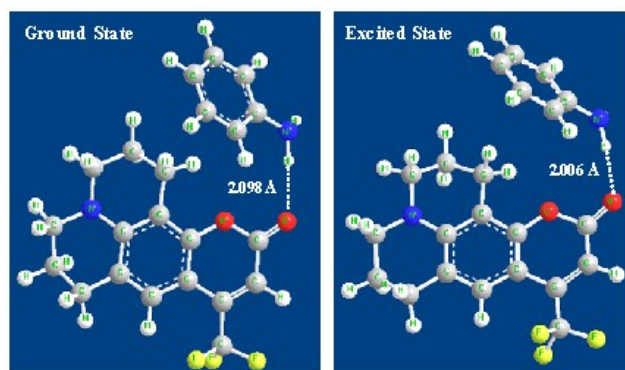


Fig. S4 Optimized ground-state (left) and excited-state (S2, right) structure of 1:1 C153-aniline hydrogen-bonded complex calculated using B3LYP/6-311+G(d,p).

Table S2 Excitation energies (in eV) of electronic transitions and corresponding oscillator strengths (in parentheses) of the low-lying electronically excited states.

transitions	C153	C153-AN
$S_0 \rightarrow S_1$	3.233 (0.3334)	2.40 (0.0011)
$S_0 \rightarrow S_2$	3.793 (0.0237)	3.134 (0.292)
$S_0 \rightarrow S_3$	4.378 (0.0371)	3.724 (0.025)
$S_0 \rightarrow S_4$	4.388 (0.0018)	3.812 (0.0046)

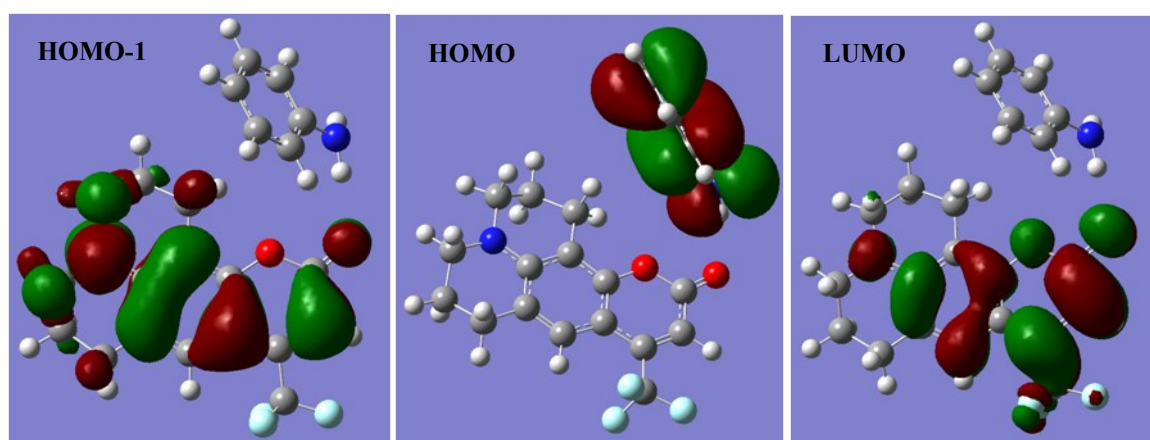


Fig. S5: Frontier molecular orbitals (MOs) for the hydrogen-bonded complex of C153 with aniline representing HOMO-1 (left), HOMO (middle) and LUMO (right). For $S_0 \rightarrow S_2$ transition (HOMO-1 to LUMO) electron remains on coumarin moiety but for $S_0 \rightarrow S_1$ transition (HOMO to LUMO) electron moves from the aniline to the coumarin unit. These MOs are generated by performing B3LYP/6-311+G(d,p) calculation in Gaussian 09.

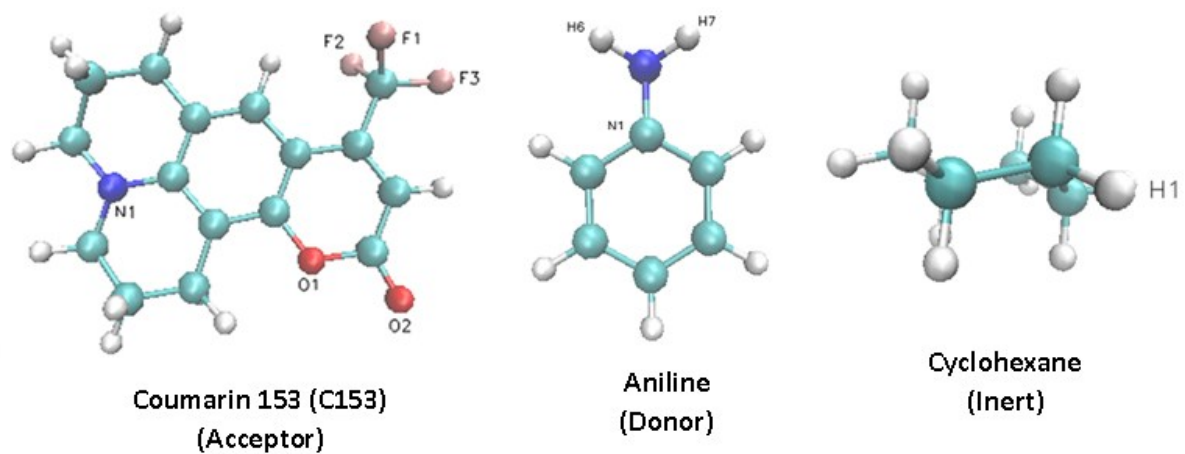


Fig. S6 Structures of the acceptor, donor and the inert solvent with the atom labels used in the rdf calculations.

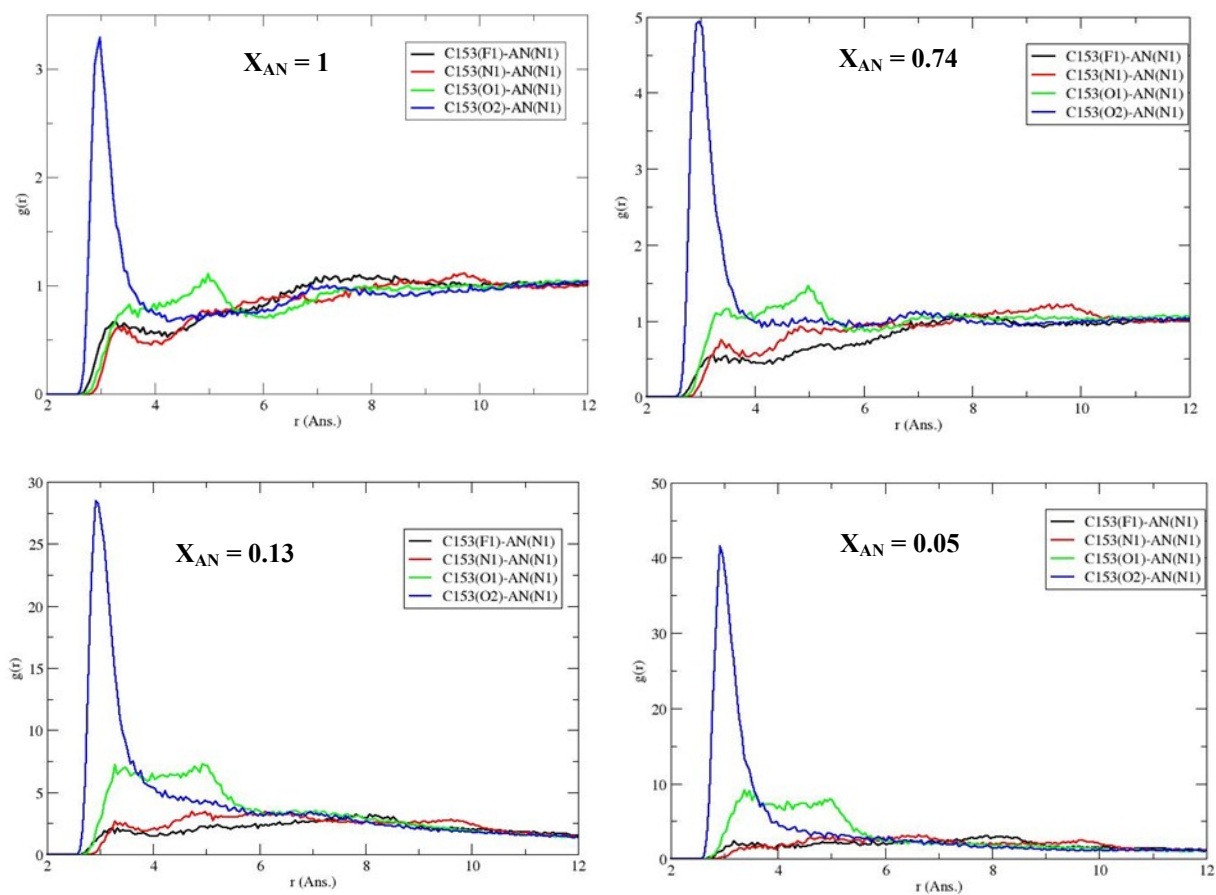


Fig. S7 Comparison of distribution functions, $g(r)$ of the distance between different H-bonding accepting sites of C153 (carbonyl oxygen (O2), ring oxygen (O1), tertiary nitrogen (N1) and fluorine (F1)) and the nitrogen atom of aniline. It is clear the extent of interaction for the O2 site is much s=dominant compared to the any other possible sites.

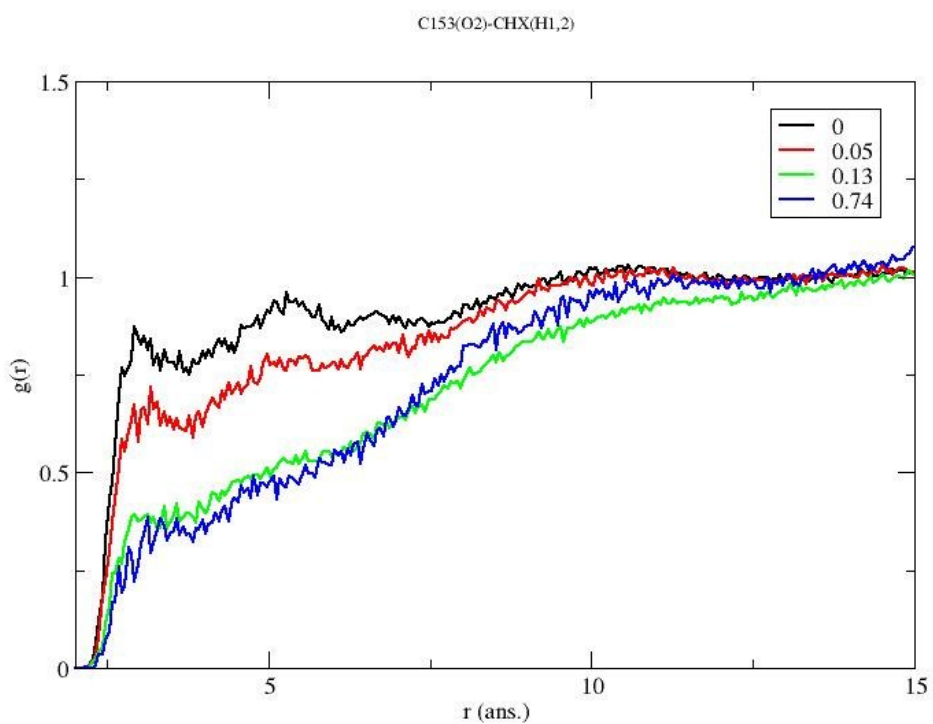


Fig. S8 The radial distribution of the distance between the carbonyl oxygen (O2) of C153 and the one of the H atoms of cyclohexane. The local density of cyclohexane (within ~ 8 Å of C153) is lower than the average number density and the deviation increases with increase of X_{AN} .