# Solvent polarity controlled coupled intramolecular proton transfer and charge transfer dynamics

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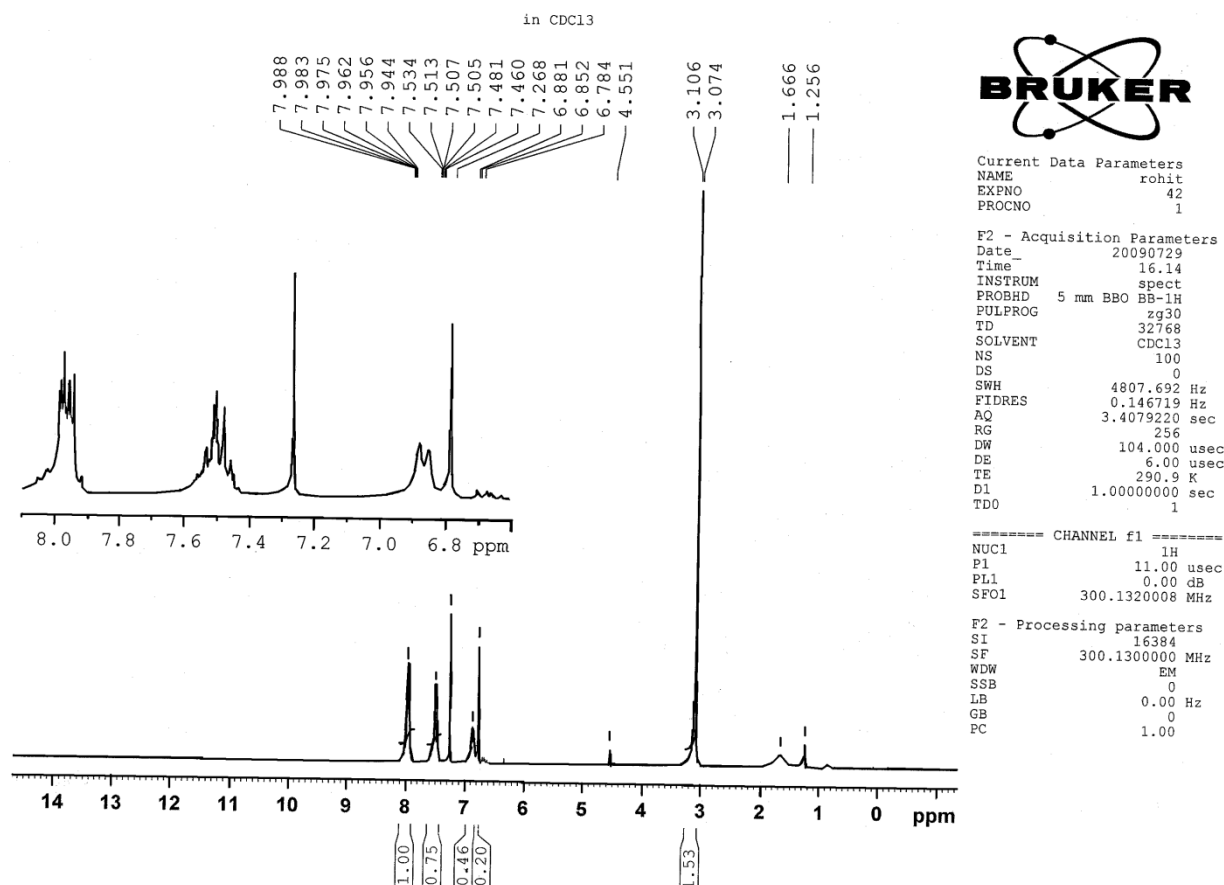## Electronic Supplimentary Information



Figure S1: NMR spectra of DMADK recorded in CDCl$_3$.

**Synthesis of DMADK:** A solution (10 mL) of 4-(N, N-dimethylamino)-acetophenone (9 mmol) and methylbenzoate (12 mmol) in tetrahydrofuran (THF) was added drop-wise to a boiling suspension of sodium hydride (12 mmol) in THF (10 mL) under argon atmosphere. After refluxing overnight, the reaction mixture was cooled and evaporated to dryness. The residue was dissolved in dichloromethane, and the solution was washed with dilute HCl. The dichloromethane solution was dried on sodium sulfate. The product was purified by a column chromatography and recrystallized from ethyl acetate (Yield: 30%). The product was identified by NMR spectroscopy. 'H NMR (CDC1$_3$, TMS): δ 3.12 (s, 6H), δ 6.73 (d, 2H), δ 6.79 (s, lH), δ 6.9(d, 2H, 8Hz), δ 7.6 (m, 3H), δ 6.9(d, 2H), δ 7.95 (m, 4H) (See Figure S1 in Supporting Information(SI)). Proton NMR spectrum indicates that the molecule mainly exists as keto-enol tautomeric forms.
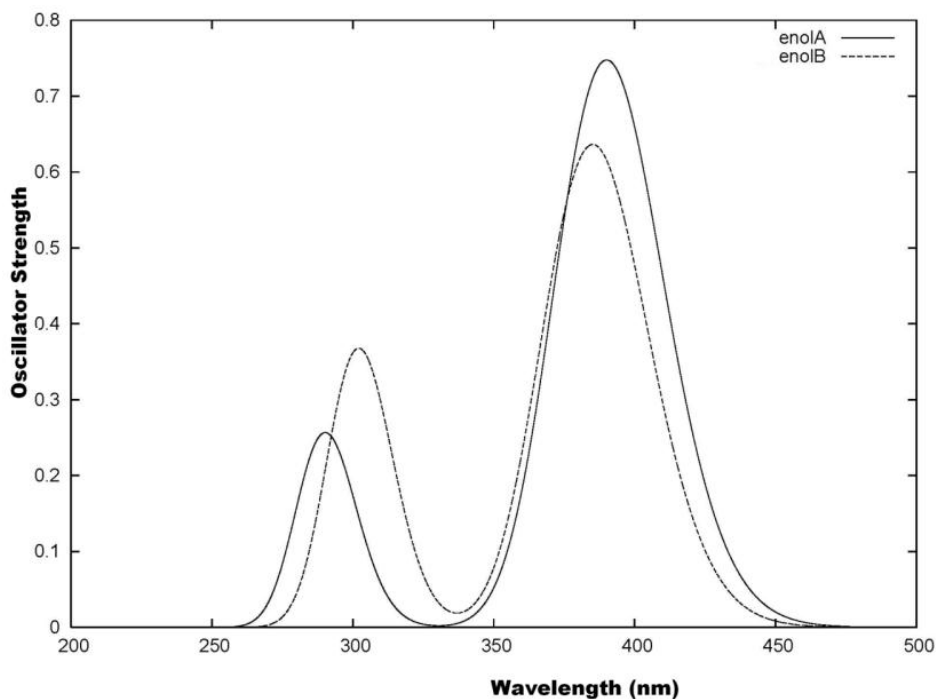
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Figure S2: TDDFT simulated absorption spectra of Enol-A and Enol-B in acetonitrile.

Table S1: Solvent Dependence of the Photophysical Parameters of DMADK.

| Solvents | $E_T(N)$, $\Delta F(\varepsilon_0, n)$ | Stokes shift, $\Delta \bar{\upsilon}$, cm$^{-1}$ | $\Phi_F$ | $\tau_F$, ps | $k_R$, $10^8$ s$^{-1}$ | $k_{NR}$, $10^{10}$ s$^{-1}$ |
|---|---|---|---|---|---|---|
| Cyclohexane | 0.006, 0.00 | 2759 | 0.014 | 25 | 5.6 | 3.9 |
| Toluene | 0.099, 0.02 | 2959 | 0.102 | 220 | 4.6 | 0.4 |
| 1,4-Dioxane | 0.164, 0.03 | 3718 | 0.20 | 570 | 3.5 | 0.14 |
| Ethylacetate | 0.228, 0.40 | 4085 | 0.136 | 250 | 5.4 | 0.3 |
| Acetone | 0.355, 0.65 | 4920 | 0.011 | 90 | 1.2 | 1.1 |
| Acetonitrile | 0.46, 0.71 | 5023 | 0.002 | 45 | 4.4 | 2.2 |
| Dimethylformamide | 0.41, 0.67 | 5283 | 0.005 | 100 | 4.8 | 1.0 |
| Dimethylsulfoxide | 0.444, 0.66 | 5056 | 0.007 | 65 | 1.1 | 1.5 |
| Methanol | 0.762 0.71 | 5096 | 0.003 | 30 | 0.8 | 3.3 |
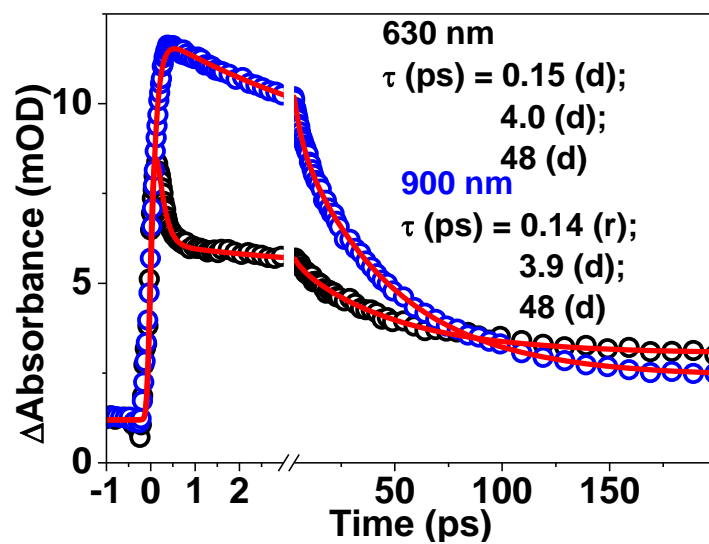
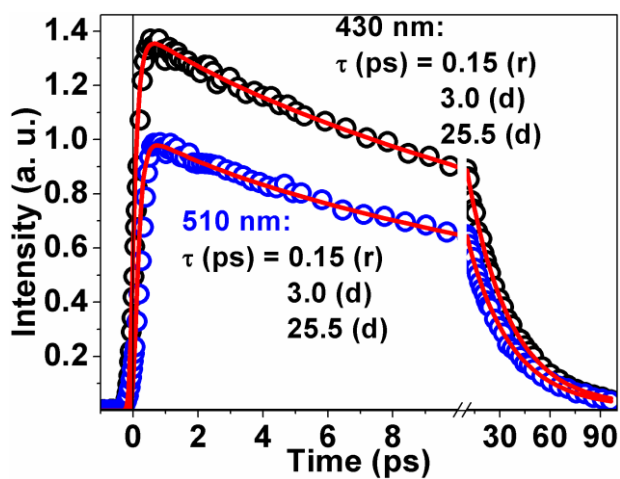Figure S3: Temporal TA profiles recorded in n-hexadecane.



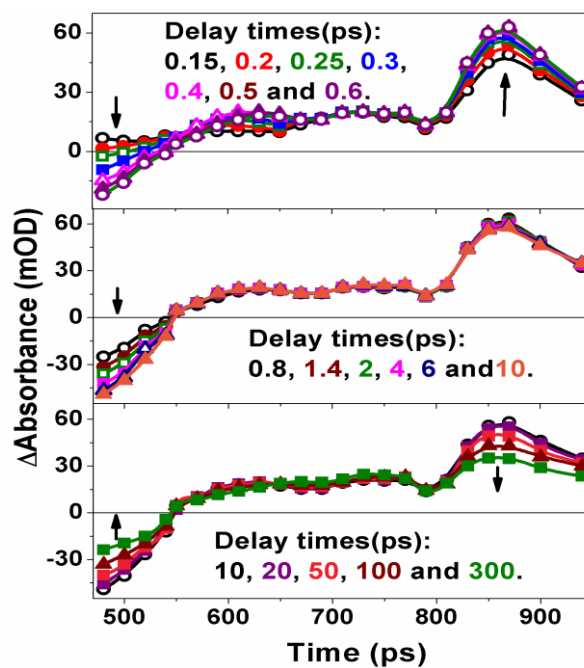Figure S4: Fluorescence temporal profiles of DMADK in cyclohexane

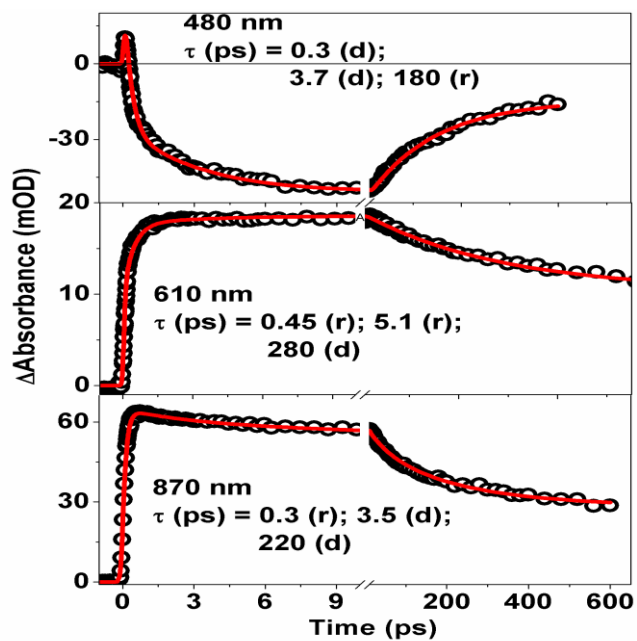Figure S5: Time-resolved TA spectra recorded in toluene following 400 nm photoexcitation.



Figure S6: Temporal dynamics recorded at a few selective wavelengths in toluene.
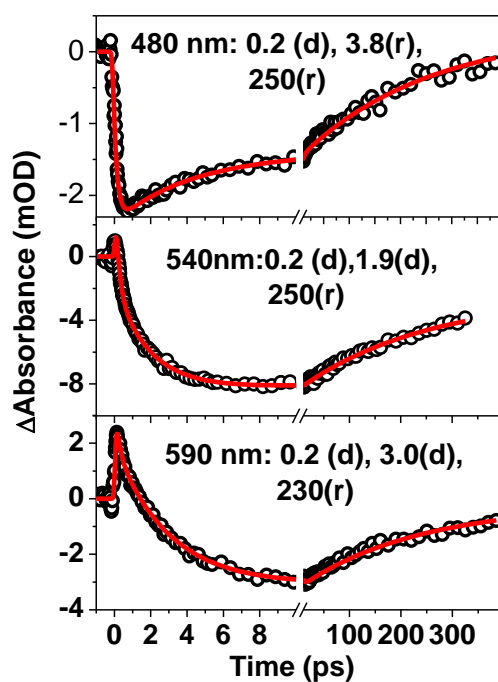
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**Figure S7:** Temporal profiles (circles) with fit functions (solid lines) recorded at a few selective wavelengths following photoexcitation of DMADK in ethyl acetate using 400 nm light. The lifetimes associated with the best fit function are given in the insets.
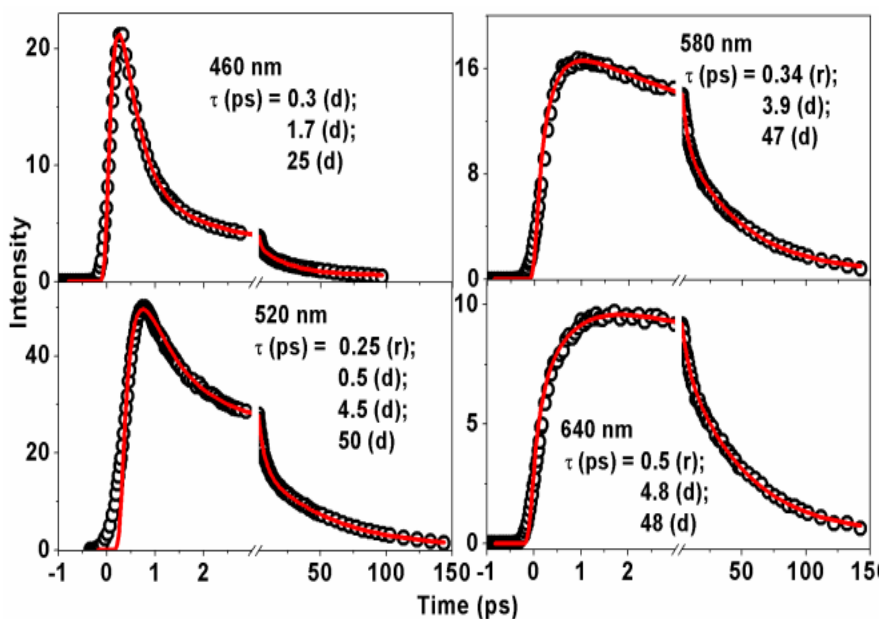


**Figure S8:** Fluorescence upconversion signals of DMADK in acetonitrile recorded at a few selective wavelengths along with the multi-exponential fit functions and the lifetimes associated with the different components given in the insets.
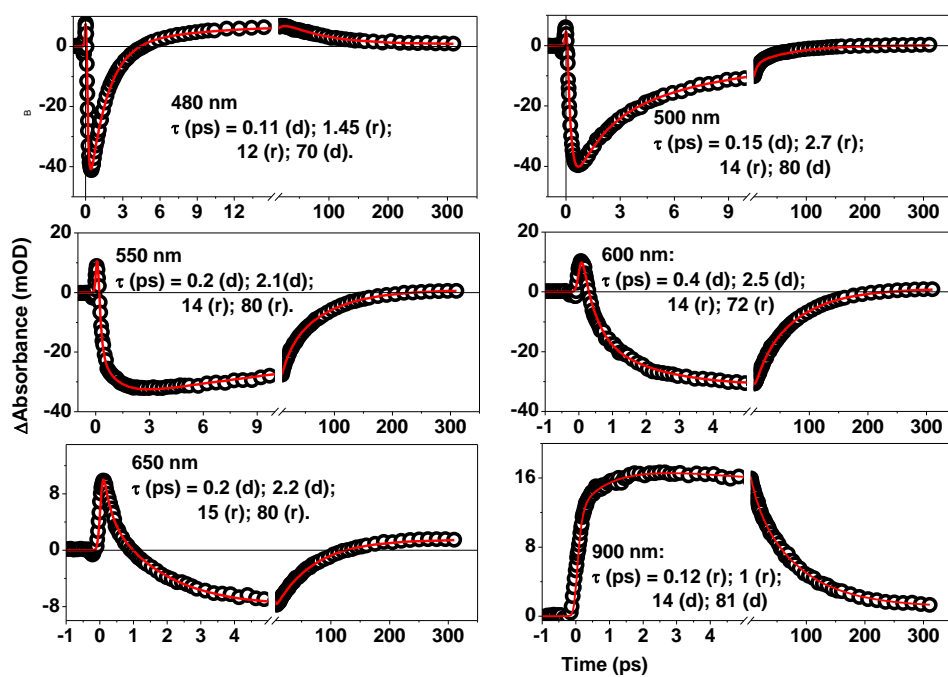
**Figure S9:** Temporal evolution of transient absorption monitored at different wavelengths following photo-excitation of DMADK in DMSO using 400 nm laser pulses of 50 fs duration. Solid lines represent the best multi-exponential fit-functions.
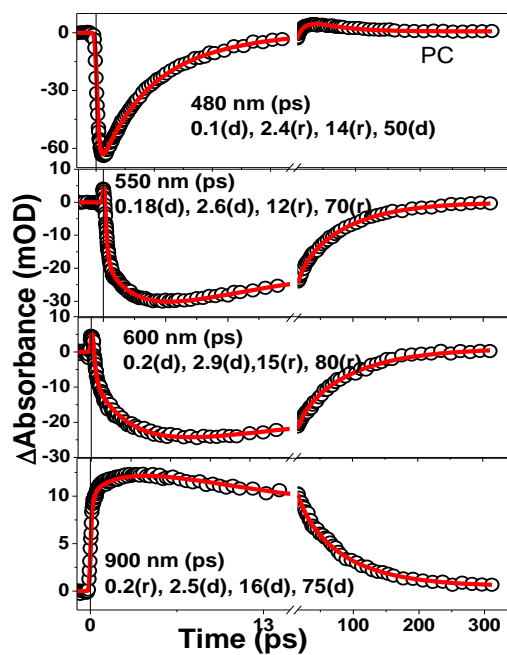
**Figure S10:** Temporal profiles (circles) with fit functions (solid lines) recorded at a few selective wavelengths following photoexcitation of DMADK in Propylene carbonate using 400 nm light. The lifetimes associated with the best fit function are given in the insets.
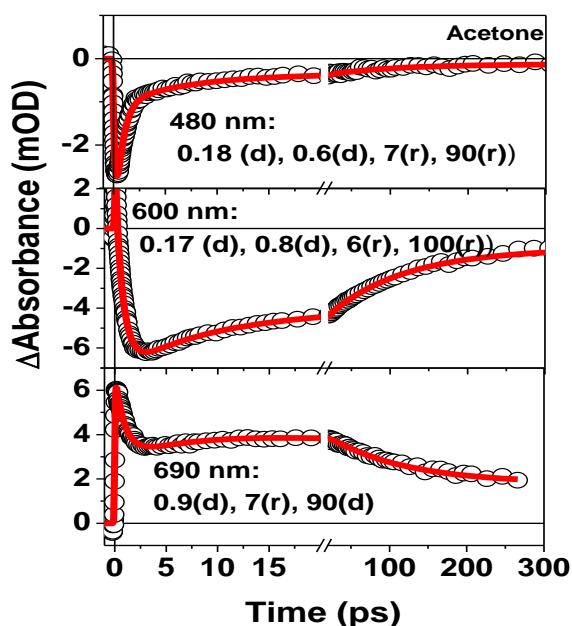


**Figure S11:** Temporal profiles (circles) with fit functions (solid lines) recorded at a few selective wavelengths following photoexcitation of DMADK in acetone using 400 nm light. The lifetimes associated with the best fit function are given in the insets.
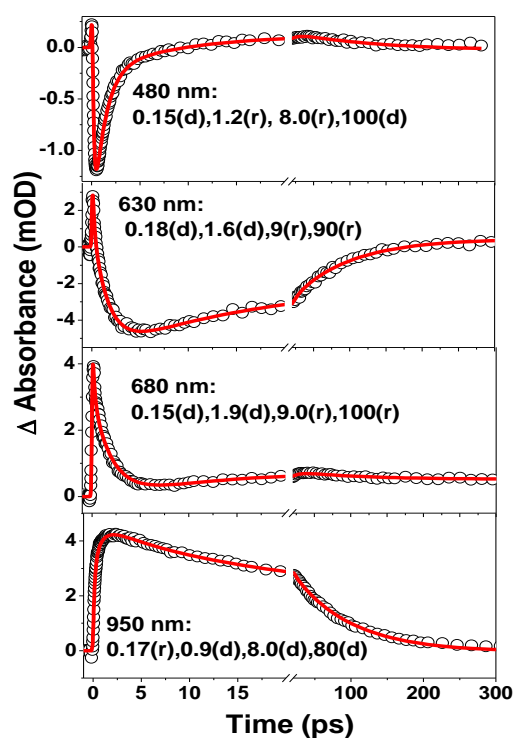
**Figure S12:** Temporal profiles (circles) with fit functions (solid lines) recorded at a few selective wavelengths following photoexcitation of DMADK in dimethyl formamide using 400 nm light. The lifetimes associated with the best fit function are given in the insets.

**Table S2:** Important Bond Lengths, Bond Angles and Dipole Moments of Enol-A and Enol-B in $S_0$ (opt) and $S_1$(opt) state.

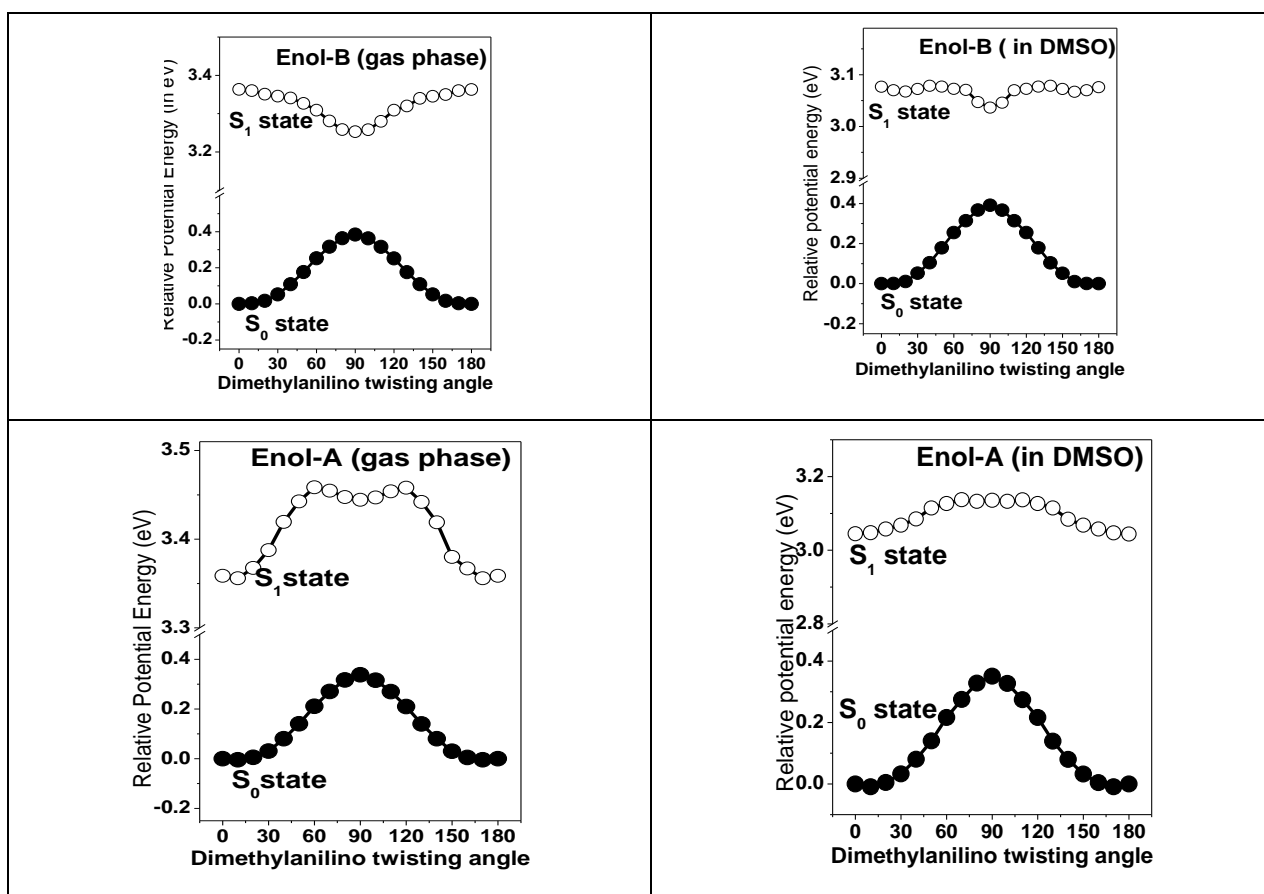| Bond Parameters (Bond lengths are in A°). | Enol-A | | Enol-B | |
|---|---|---|---|---|
|  | | | | |
| | $S_0$ | $S_1$ | $S_0$ | $S_1$ |
| $^1C=O^1$ | 1.265 | 1.299 | 1.226 | 1.292 |
| $^3C-O^2$ | 1.326 | 1.350 | 1.326 | 1.371 |
| $^2O-H^1$ | 1.025 | 1.037 | 1.026 | 0.982 |
| $^1O{\ldots}H^1$ | 1.514 | 1.492 | 1.509 | 1.711 |
| $^2C=C^3$ | 1.389 | 1.379 | 1.380 | 1.430 |
| $^7C-N^1$ | 1.379 | 1.367 | 1.379 | 1.365 |
| $\Phi(^8C-^7C-^1N-^{11}C)$ | $5.5^0$ | $1.1^0$ | $4.6^0$ | $7.1^0$ |
| $\Phi(^6C-^7C-^1N-^{10}C)$ | $6.3^0$ | $1.9^0$ | $3.1^0$ | $7.9^0$ |
| $\Phi(^2C-^3C-^4C-^9C)$ | $9.1^0$ | $19.5^0$ | $1.5^0$ | $91.1^0$ |
| $\Phi(^2C-^{1/3}C-^{12}C-^{13}C)$ | $13.1^0$ | $2.1^0$ | $15^0$ | $0.6^0$ |
| Dipole Moment | 6.5 D | 15 D (LE) 18.5 D (ICT) | 5.2 D | 16 D (LE) 21.5 D (TICT) |

**Figure S13**: Potential energies of Enol-A and Enol-B in the ground (solid symbols) and the excited (open symbols) states in the gas phase and DMSO at different twist angles of N, N-dimethylaniline group varying in the range 0 to 180°.
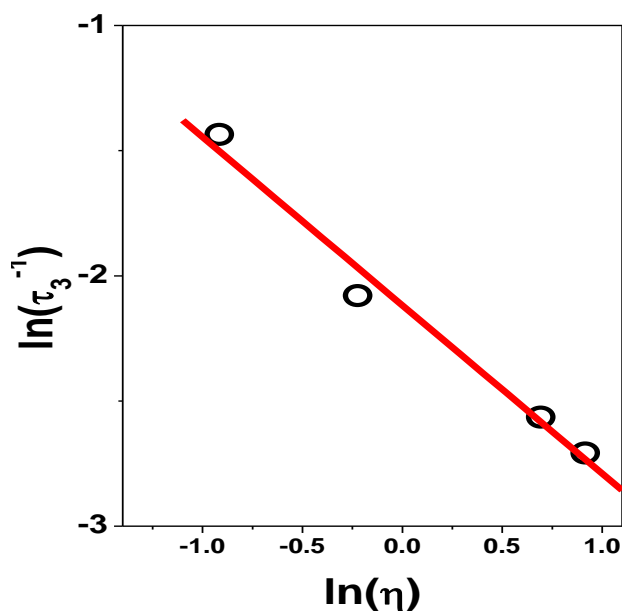


**Figure S14**: Plot of $\ln[(\tau_3)^{-1}]$ vs $\ln(\eta)$