Solvation and hydrogen bonding aided efficient non-

radiative deactivation of polar excited state of 5-

Aminoquinoline

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Figure S1. Absorption and emission peak maxima of 5AQ plotted against orientation polarizability.



(A)



(B)

Figure S2. (A) Kohn sham contours of HOMO and LUMO of 3AQ and 5AQ in gas phase as indicated (B) Absorption spectra of 3AQ and 5AQ in i) n-hexane and ii) Ethanol, normalized at the peak position. The experimental spectra are in good agreement with calculated absorption spectra



Figure S3. Variation of log k_{NR} with empirical polarity parameter $E_T(30)$ for 5AQ in nonalcoholic (blue) and alcoholic (red) solvents.



Figure S4. Variation of log k_{NR} with solvent viscosity (cP) for non-polar (blue), polar-aprotic (green), and alcoholic (red) solvents.



Figure S5. Lippert Mataga plot for 5AQ

Note S1. Difference in the ground and excited state dipole moment was determined using Lippert – Mataga equation¹ :

$$\Delta \bar{\nu} = \bar{\nu}_A - \bar{\nu}_F = \frac{2\Delta f}{hca^3} (\mu_E - \mu_G)^2 + constant$$

Where, v_A and v_F are absorption and emission peak frequency in cm⁻¹. *h* is the Planck's constant, Δf is the solvent orientation polarizability, a is the Onsager cavity radius (calculated using the expression given by Suppan)². μ_E and μ_G are dipole moments in the ground and excited state respectively. The orientation polarizability is defined as

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

Where, ε and *n* are the dielectric constant and refractive index of the solvent respectively.

For solvent mixtures, dielectric constant and refractive index was calculated using the following relations³

$$\varepsilon = f_A \varepsilon_A + f_B \varepsilon_B$$
$$\eta^2 = f_A \eta_A^2 + f_B \eta_B^2$$

Where ε_A , ε_B are the dielectric constants for the cosolvents A and B, η_A and η_B are the refractive indices for the cosolvents A and B, f_A and f_B are the corresponding volume fractions of the cosovents.

Note S2. Calculation of quantum yield (ϕ_f)

Fluorescence quantum yield was calculated using the following relation

$$\phi_f = \frac{I_S}{I_R} \times \frac{(1 - 10^{-A_R})}{(1 - 10^{-A_S})} \times \frac{\eta_S^2}{\eta_R^2} \times \phi_f^{ref}$$

Where, I_S and I_R are the integrated emission intensity of sample and reference respectively. A_R and A_S are absorbance of reference and sample respectively. η is the refractive index of the solvents used for the measurements. ϕ_f^{ref} is the quantum yield of the reference. Absorbance of the samples was kept around 0.05 for all measurements.

Note S3. Calculation of non-radiative rate constant (k_{NR}) and radiative rate constant (k_R)

Non radiative rate constant was calculated using the following relation

$$k_{NR} = \frac{1 - \phi_f}{\tau}$$

Radiative rate constant was calculated using the relation

$$k_R = \frac{\phi_f}{\tau}$$

Where ϕ_f and τ are fluorescence quantum yield and fluorescence lifetime respectively.

	π*	β	α
Methanol	0.60	0.62	0.93
Ethanol	0.54	0.77	0.83
1-propanol	0.52	0.84	0.78
2-propanol	0.48	0.95	0.76
tert-butanol	0.41	1.01	0.68

Table S1 : Kamlet-Taft parameters of alcohols used in present study^{4,5}

The following equation also known as Kamlet-Taft linear solvation energy relationship, relates the absorption and emission peak frequency to the solvent parameters like polarity, hydrogen bond accepting ability and hydrogen bond donating ability.

$$\nu = p\pi^* + b\beta + a\alpha + \nu_0$$

Where, v and v_0 represent peak frequencies in presence and absence of solvent respectively. π^* , β and α are indices of polarity, hydrogen bond accepting ability and hydrogen bond donating ability of the solvent. *p*, *b* and *a* are coefficients for π^* , β and α , respectively

Kamlet-Taft analysis has been performed using absorption and emission peak frequencies on by multiple regression fitting using OriginPro 8.0 software.

Table S2. Kamlet-Taft analysis for 5AQ

Solvent class	Parameter	Fractional contribution of			$v_0 (cm^{-1})$	R^{a}
		π^*	β	α		
All solvents	Absorption	0.29	0.64	0.07	30221	0.92
	Emission	0.42	0.29	0.29	23302	0.95
Protic	Absorption	-0.10	0.38	0.72	31418	0.36
	Emission	0.58	0.19	0.23	21997	0.94

	τ_1 (ps)	$\tau_2 (ps)$	τ_3 (ps)	a ₁	a ₂	a ₃
Methanol	0.8	8.2	38.5	0.22	0.42	0.36
Ethanol	3.38	27.3	240	0.15	0.40	0.45
1-propanol	6.04	43.15	342.4	0.14	0.38	0.48
2-propanol	3.99	47.00	2600	0.29	0.45	0.26

Table S3: Comparison of Temporal parameters of 5AQ in alcohols. $\lambda_{ex} = 400$ nm, $\lambda_{em} = 470$ nm.



Figure S6. Fluorescence decays of 5AQ at different emission wavelengths in methanol

$\lambda_{em}(nm)$	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	a ₁	a ₂	a ₃
445	0.60	7.2	60	0.54	0.37	0.09
455	0.77	8.2	60	0.46	0.43	0.10
470	0.80	8.0	40	0.31	0.49	0.20
480	0.76	7.6	35	0.26	0.41	0.33
490	0.99	9.1	39	0.22	0.42	0.36
500	1.50	11.0	44	0.14	0.46	0.40
510	4.50	20.0	54	0.17	0.52	0.31
520	1	25.0	66	0	0.72	0.28
530	0.67	15.8	47	-0.14	0.40	0.74
540	0.58	23.0	55	-0.18	0.60	0.56
550	1.57	33.0	64	-0.20	0.82	0.38
560	1.10	-	43	-0.27	-	1.27
570	1.30	-	48	-0.27	-	1.27
580	2.78	-	52	-0.42	-	1.42
590	0.68	7.1	52	-0.31	-0.44	1.75
600	0.55	9.2	54	-0.42	-0.69	2.11
610	0.79	10.8	58	-0.39	-0.93	2.31
630	1.15	18.4	57	-0.47	-1.99	3.47
650	0.91	18.6	61	-0.74	-4.22	5.96

Table S4. Temporal parameters of 5AQ at different emission wavelengths in methanol obtained by fitting of data obtained by femtosecond optical gating. ($\lambda_{ex} = 400 \text{ nm}$)

Emission decay traces were fitted in an unconstrained way employing iterative reconvolution method using a homebuilt program on IGOR 6.3 platform.



Figure S7. Fluorescence decays of 5AQ at different emission wavelengths in 2-propanol

$\lambda_{em}(nm)$	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	a ₁	a ₂	a ₃
430	0.96	14.76	2600	0.55	0.41	0.04
435	0.79	14.3	2600	0.53	0.42	0.05
440	1.23	21.9	2600	0.51	0.42	0.07
445	1.30	23.50	2600	0.48	0.45	0.08
450	1.10	23.49	2600	0.41	0.49	0.10
455	3.40	48.10	2600	0.49	0.39	0.12
465	3.74	47.18	2600	0.37	0.43	0.20
470	3.99	47.00	2600	0.29	0.45	0.26
480	5.10	50	2600	0.21	0.39	0.40
490	-	43.07	2600	-	0.45	0.55
500	-	53.26	2600	-	0.31	0.69
510	1.61	55.10	2600	-0.12	0.17	0.95
520	1.34	-	2600	-0.20	-	1.20
530	4.04	-	2600	-0.18	-	1.18
540	2.78	75.05	2600	-0.16	-0.14	1.31
550	5.05	153.72	2600	-0.27	-0.25	1.52
560	1.68	42.48	2600	-0.25	-0.41	1.66
570	9.52	97.23	2600	-0.30	-0.33	1.63
580	4.75	84.50	2600	-0.27	-0.50	1.77
590	4.62	81.84	2600	-0.35	-0.61	1.97
600	1.31	50	2600	-0.25	-0.95	2.20
610	_	50.87	2600	0	-0.81	1.81
630	_	52.36	2600	0	-1.19	2.19

Table S5. Temporal parameters of 5AQ at different emission wavelengths in 2-propanol obtained by fitting of data obtained by femtosecond optical gating. ($\lambda_{ex} = 390$ nm)

Emission traces were fitted keeping the longest component fixed at 2600 ps which was obtained from TCSPC experiment.



Figure S8: Fluorescence decay of 5-AQ (a) in ethanol at 298K (red, $\lambda_{em} = 510$ nm), 180 K (blue, $\lambda_{em} = 570$ nm), 180 K (green, $\lambda_{em} = 570$ nm) and in (b) 3-Methylpentane (red) and ethanol (blue) at 77K.

$\lambda_{em}(nm)$	τ_1 (ps)	$\tau_2 (ps)$	\mathbf{a}_1	a_2
460	209	1070	0.56	0.44
465	343	1109	0.41	0.59
470	213	1121	0.43	0.57
475	366	1180	0.27	0.73
480	267	1134	0.15	0.85
490	236	1188	0.17	0.83
500	-	1200	0	1
510	-	1233	0	1
520	858.	1096	-0.54	1.54
530	738	1044	-1.50	2.50
540	545	1044	-0.61	1.61
550	336	1193	-0.74	1.74
560	493	1177	-0.62	1.62
570	299	1242	-0.84	1.84
580	392	1211	-0.89	1.89
590	393	1229	-0.84	1.84

Table S6. Temporal parameters of 5AQ at different emission wavelengths in ethanol at 180 K obtained by fitting of data obtained by TCSPC experiment. ($\lambda_{ex} = 374$ nm)



Figure S9. Fluorescence decays at 470 nm (red) and 550 nm (blue) for 5AQ at 77 K in ethanol ($\lambda_{ex} = 336$ nm)

	Molecule	$S_1 E (eV)$	E(nm)	f	$T_1_E(eV)$	E(nm)	f
	3AQ	3.9577	313.27	0.0700	2.6646	465.31	0.0
_	540	2 7210	222.10	0.0570	0.5500	405 70	0.0
	5AQ	3.7219	333.12	0.0570	2.5523	485.78	0.0
-	840	2 5022	252.01	0.0401	2 4212	500.07	0.0
	ðAQ	5.3032	555.91	0.0491	2.4312	309.97	0.0

Table S7. S_1 and T_1 state energies from Franck-Condon state (ground state geometry) at B3LYP/6-31G* level of theory.

References

- (1) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 3rd ed.; Springer: New York, 2006.
- (2) Suppan, P. Excited-State Dipole Moments from Absorption/fluorescence Solvatochromic Ratios. *Chem. Phys. Lett.* **1983**, *94*, 272–275.
- (3) Panda, D.; Datta, A. The Role of the Ring Nitrogen and the Amino Group in the Solvent Dependence of the Excited-State Dynamics of 3-Aminoquinoline. J. Chem. Phys. 2006, 125, 054513.
- (4) Kamlet, M. J.; Abboud, J. L. M.; Abraham, M. H.; Taft, R. W. Linear Solvation Energy Relationships. 23. A Comprehensive Collection of the Solvatochromic Parameters, .pi.*, .alpha., and .beta., and Some Methods for Simplifying the Generalized Solvatochromic Equation. J. Org. Chem. 1983, 48, 2877–2887.
- (5) Das, K.; Jain, B.; Patel, H. S. Hydrogen Bonding Properties of Coumarin 151, 500, and 35: The Effect of Substitution at the 7-Amino Position. J. Phys. Chem. A 2006, 110, 1698–1704.