Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Tailoring of Spectral Responses and Intramolecular Charge Transfer of β-enaminones through HOMO - LUMO Band Gap Tuning: Synthesis, Spectroscopic and Quantum Chemical Studies

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Figure Caption

Fig. S1: The ground state optimized structures of PACO in the (a) gas phase, (b) in SCRF of water (c) 1:3 microcluster with water and (d) PACO:3H_2O microcluster macrosolvated with water. The macroscopic solvation has been taken care of using Cramer and Truhler's SMD model.

Fig. S2: The ground state optimized structures of OACO in the (a) gas phase, (b) in SCRF of water (c) 1:4 microcluster with water and (d) OACO:4H_2O microcluster macrosolvated with water. The macroscopic solvation has been taken care of using Cramer and Truhler's SMD model.

Fig S3: The ground state optimized structures of NACO in the (a) gas phase, (b) in SCRF of water (c) 1:5 microcluster with water and (d) NACO:5H_2O microcluster macrosolvated with water. The macroscopic solvation has been taken care of using Cramer and Truhler's SMD model.

Fig S4: The room temperature emission spectra of NACO in cyclohexane (CYC), ethanol, methanol and water. The excitation wavelength (λ_{ex}) is 360 nm.

Table S1: All components of polarizability (α) and its average value (α_{av}) of PACO, OACO and NACO and their microhydrares, as calculated using B3LYP functional and aug-cc-pVDZ basis set. All values are in atomic unit (a.u.).

System	α_{xx}	α_{xy}	α_{yy}	α_{xz}	α_{yz}	α_{zz}	α_{av}
PACO	229.64	-6.71	159.47	-2.81	7.04	107.12	165.41
PACO.3H$_2$O	271.40	8.97	201.68	7.59	-7.71	127.96	200.35
OACO	257.97	-4.11	178.09	-1.02	6.13	121.85	185.97
OACO.4H$_2$O	318.06	0.68	231.88	-0.99	-9.63	147.89	232.62
NACO	300.16	-7.22	178.97	-1.14	7.30	109.09	196.07
NACO.5H$_2$O	389.07	-11.11	246.87	-1.13	-7.07	143.56	259.83

Table S2: All components of first hyper-polarizability and its total value (β_{total}) of PACO, OACO and NACO and their microhydrares, as calculated using B3LYP functional and aug-cc-pVDZ basis set. All values are in atomic unit (a.u.).

System	β_{xxx}	β_{yxx}	β_{xyy}	β_{yyy}	β_{zxx}	β_{xyz}	β_{zyy}	β_{xzz}	β_{yzz}	β_{zzz}	β_{total}
PACO	247.42	-16.23	-16.55	19.56	-373.71	36.03	22.76	172.79	6.40	79.25	486.68
PACO.3H_2O	991.27	50.07	-186.01	-19.85	-33.58	-11.46	-11.06	-44.98	0.78	-3.69	762.44
OACO	1094.94	18.25	-20.86	-37.19	-391.43	-37.55	36.39	214.84	15.27	43.86	1325.95
OACO.4H_2O	1589.83	-41.34	-20.62	-54.46	-514.57	-15.40	16.90	157.74	-7.18	54.63	1785.84
NACO	-3359.79	-192.76	62.73	18.78	-272.94	26.12	25.67	302.17	15.06	29.42	3007.01
NACO.5H_2O	3546.68	7.87	-48.64	20.62	-1981.47	-83.33	43.28	660.29	41.01	-53.69	4611.30

Table S3: The dominant contributions on vertical transition of first three excited sates (S_1, S_2 and S_3) of PACO, OACO and NACO and their 1:3, 1:4 and 1:5 molecular clusters, respectively with water in the gas phase, in SCRF of water, as calculated using TDDFT (CAM-B3LYP functional and aug-cc-pVTZ basis set).

Molecule/Medium	PACO	OACO	NACO
Gas Phase			
S_1	(H-1) – (L+1) 0.46	(H-1) – (L+1) 0.55	(H-4) – L 0.62
S_2	H – L 0.62	H – (L+1) 0.44	H – L 0.37
S_3	-	H – (L+3) 0.52	H – L 0.51
		H – (L+1) 0.27	(H-1) – (L+1) 0.21
In SCRF			
S_1	(H-1) – L 0.49	(H-1) – (L+1) 0.52	(H-4) – L 0.64
S_2	H – L 0.65	H – L 0.46	(H-1) – L 0.33
		H – (L+3) 0.54	(H-1) – (L+1) 0.41
S_3	-		
		H – L 0.20	H – L 0.64
Cluster			
S_1	H – (L+1) 0.65	H – (L+1) 0.66	H – L 0.66
S_2	(H-1) – (L+1) 0.39	(H-2) – (L+1) 0.59	(H-8) – L 0.65
	(H-2) – (L+1) 0.39		
S_3	-	H – (L+3) 0.38	(H-2) – (L+2) 0.56
Cluster in SCRF			
S_1	H – (L+1) 0.62	H – (L+1) 0.64	H – L 0.64
	H-L 0.22		
S_2	(H-1) – (L+1) 0.56	(H-2) – (L+1) 0.60	(H-8) – L 0.60
S_3	-	H – (L+2) 0.43	(H-2) – (L+2) 0.54

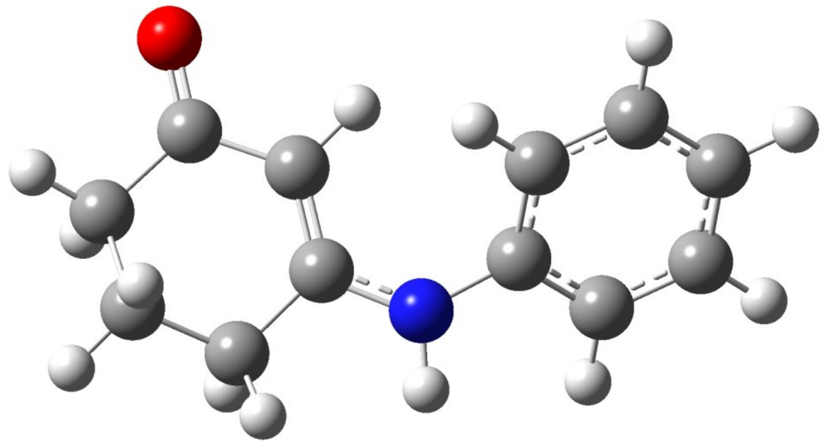


Fig. S1(a)

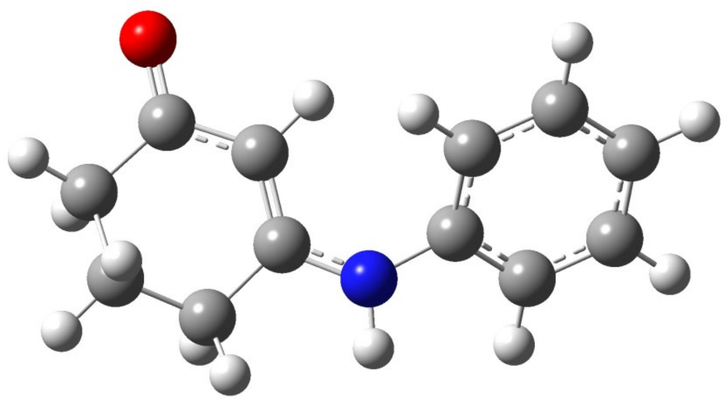


Fig. S1(b)

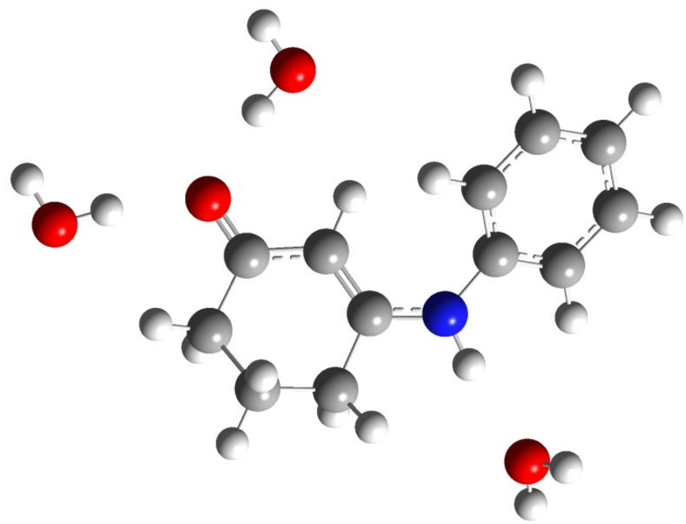


Fig. S1(c)

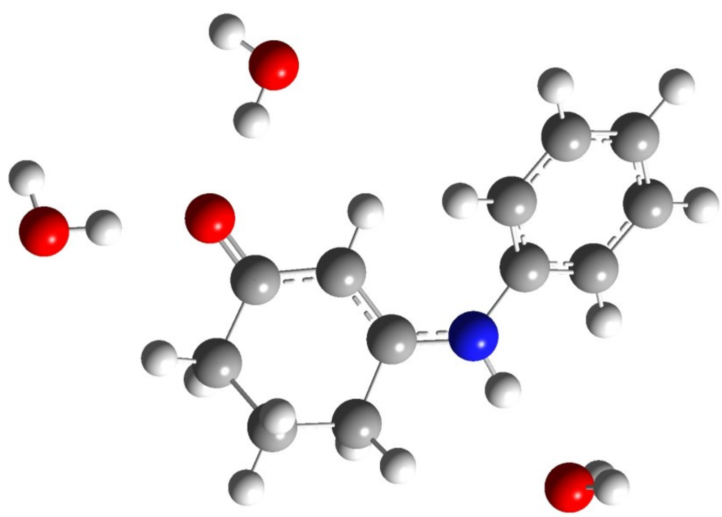
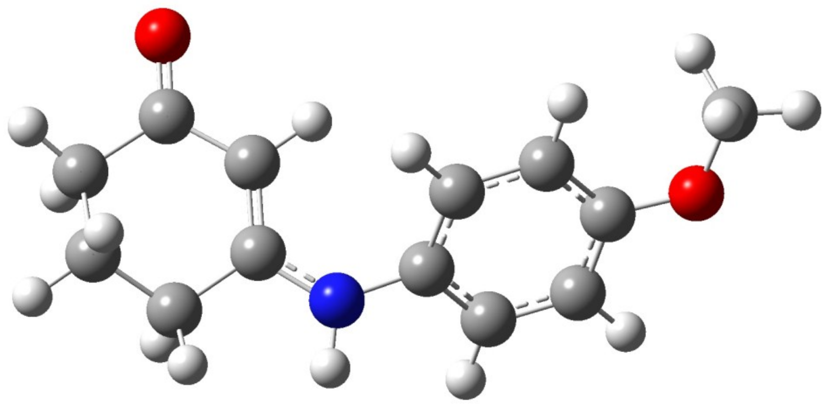


Fig. S1(d)



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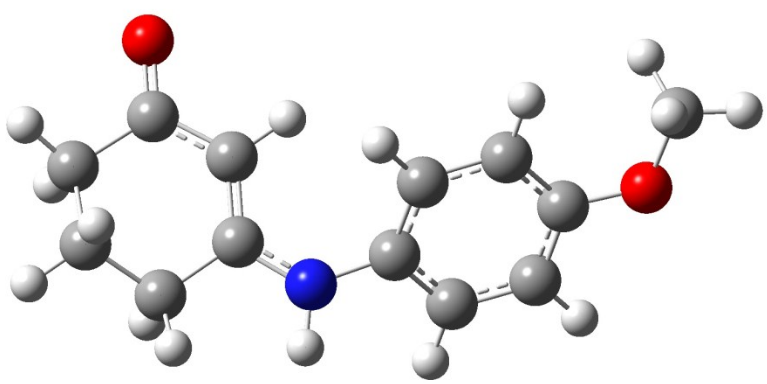

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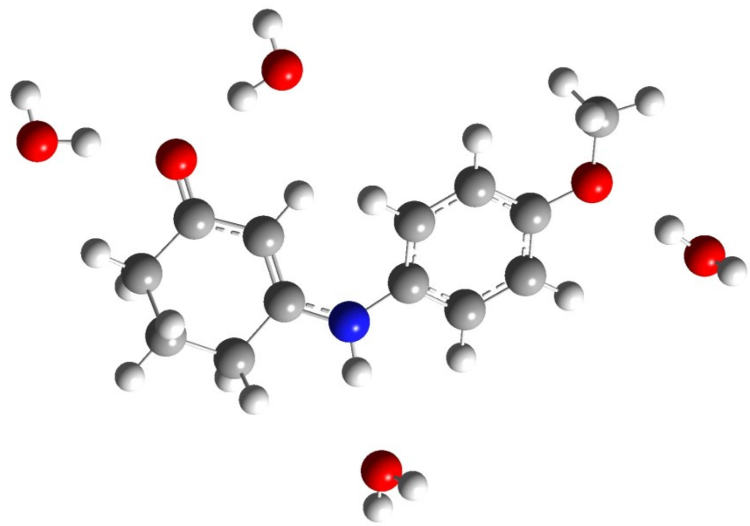

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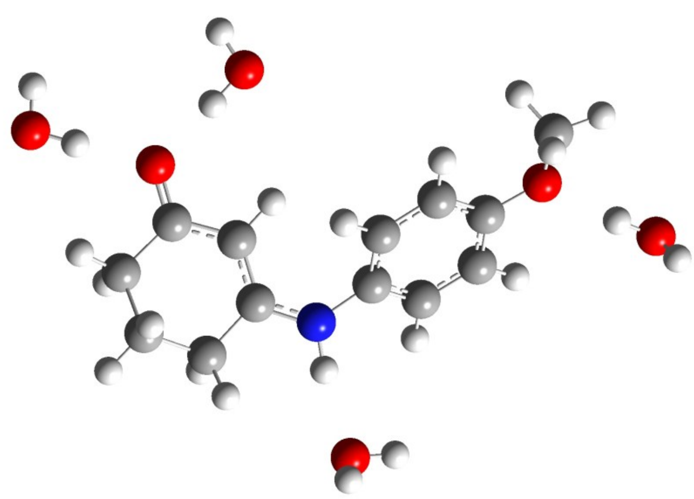

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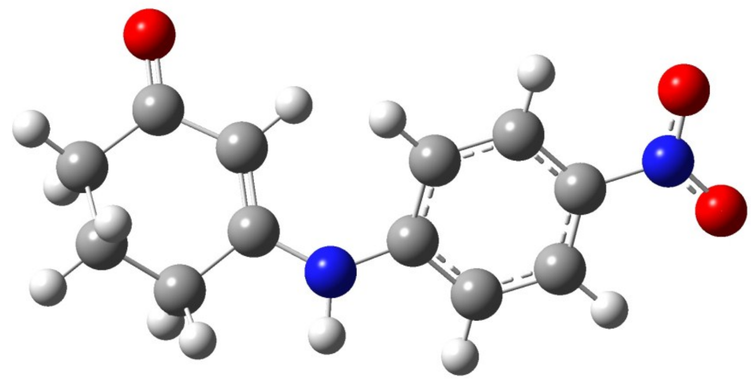

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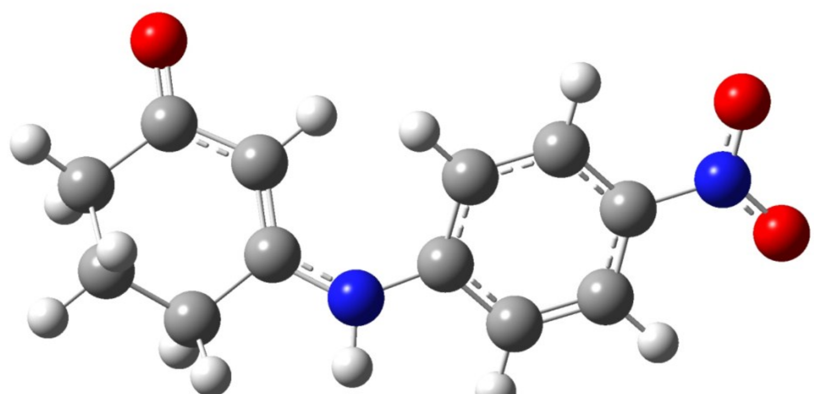

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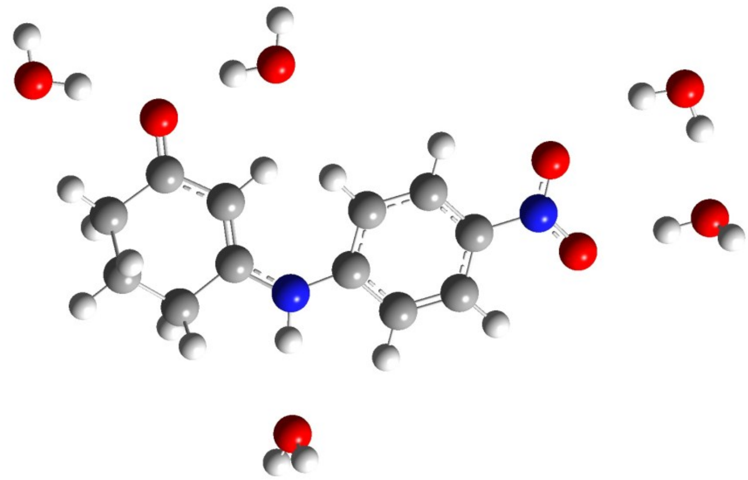

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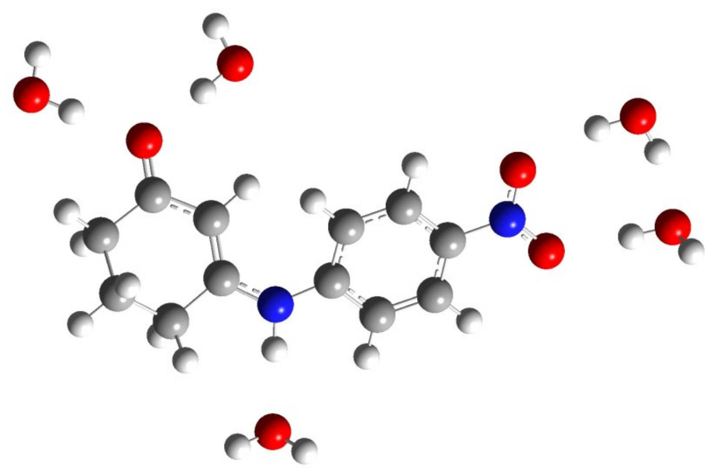

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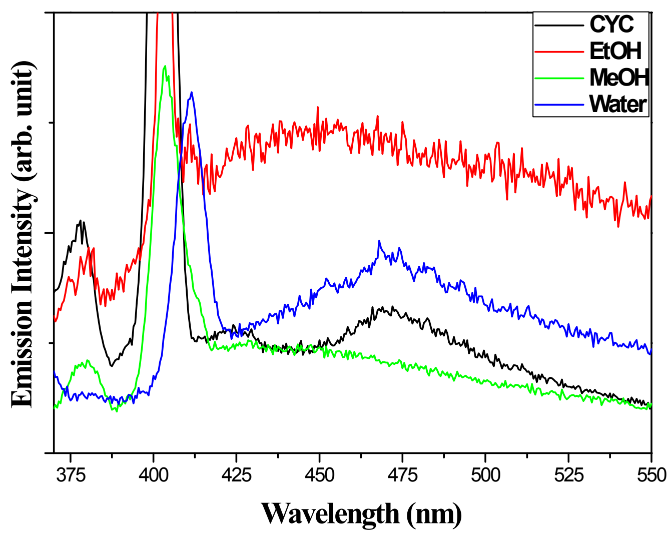

CYC
EtOH
MeOH
Water
Emission Intensity (arb. unit)
375
400
425
450
475
500
525
550
Wavelength (nm)

Fig. S4