New Journal of Chemistry Manuscript ID NJ-ART-11-2017-004349

Supporting information

Different self-assemblies, absorption and emission properties of picrate salts of aromatic amine or heterocycle linked oximes

Arup Tarai, Jubaraj B. Baruah*

Experimental Section:

Physical measurements: Infrared spectra of the solid samples were recorded on a Perkin-Elmer Spectrum-One FT-IR spectrophotometer in the region 4000-400 cm^{-1} by making KBr pellets. ^{1}H-NMR was recorded on a Varian 400 MHZ and BRUKER Ascend-600 MHz NMR spectrometer using TMS as internal standard. Solid state UV-visible spectra were recorded in PerkinElmer Lamda-750 spectrometer using the diffuse reflectance technique by taking the respective powdered sample in a solid sample holder. Fluorescence emissions were measured using Horiba Jobin Yvon Fluoromax-4 spectrofluorometer by taking definite amount of solutions and exciting at required wavelengths. Hirshfeld analyses are done by using CrystalExploer 3.1 software.

Crystallographic Study: X-ray single crystal diffraction data were collected at 298 K with MoKα radiation (λ = 0.71073 Å) on a Bruker Nonius SMART APEX CCD diffractometer equipped with a graphite monochromator and an Apex CCD camera. SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters. Data reduction and cell refinement were performed using SAINT and XPREP software. Structures were solved by direct methods using SHELXS-14 and were refined by full-matrix least-squares on F^2 using SHELXL-14. All non-hydrogen atoms were refined in anisotropic approximation against F^2 of all reflections. Hydrogen atoms of water could not be located by riding model in picrate salt of Indole-3-carbaldoxime; these were placed at their respective geometric positions, 'fixed' and refined in isotropic approximation, other hydrogen atoms were obtained by riding were refined in a similar manner.

Spectroscopic properties of the oximes and the salts:

Indole-3-carbaldoxime (*ico*): Isolated yield: 83%.^{1}H NMR (600 MHz, Acetone-d_6): 10.77 (s, -OH), 10.41 (s, -NH), 8.37 (s, 1H), 7.86 (d, J = 6 Hz, 1H), 7.76 (s, 1H), 7.49 (d, J = 6 Hz, 1H),

7.20 (t, J = 6 Hz, 1H), 7.15 (t, J = 6 Hz, 1H). IR (KBr, cm^{-1}): 3387 (br, s), 3156 (w), 3013 (w), 1679 (w), 1640 (s), 1612 (w), 1521 (s), 1489 (m), 1458 (s), 1414 (s), 1340 (s), 1234 (s), 1130 (m), 1098 (s), 1048 (w), 1008 (w), 930 (s), 905 (m), 866 (m), 840 (m), 747 (s), 659 (m), 612 (w), 588 (m) 551 (s).

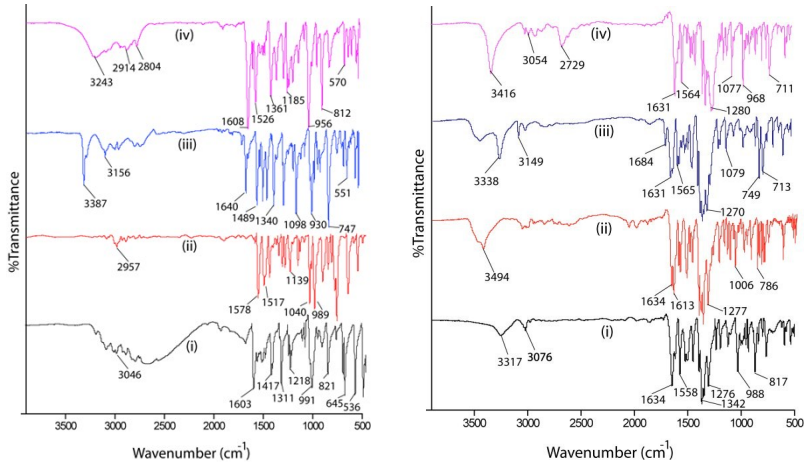
4-(N,N-dimethylaminophenyl)aldoxime (*dmo*): Isolated yield: 80%.^{1}H NMR (600 MHz, Acetone-d_6): 9.84 (s, 1H), 7.97 (s, 1H), 7.43 (d, J = 6 Hz, 2H), 6.72 (d, J = 8 Hz, 2H), 2.09 (-CH_3). IR (KBr, cm^{-1}): 3243 (br, w), 2914 (w), 1608 (s), 1556 (s), 1526 (s), 1565 (w), 1477 (w), 1444 (w), 1427 (w), 1361 (s), 1301 (s), 1224 (s), 1185 (m), 1169 (m), 1126 (s), 1065 (m), 1002 (m), 956 (s), 867 (s), 812 (s), 734 (s), 635 (w), 570 (s), 528 (s).

Hydrated picrate salt of quinoline-4-carbaldoxime (*Hqco*).(*tnp*).H_2O**:** Isolated yield: 64%. ^{1}H NMR (400 MHz, DMSO-d_6): 12.61 (s, 1H), 9.15 (d, J = 4 Hz, 1H), 9.04 (s, 1H), 8.80 (d, J = 8 Hz, 1H), 8.58 (s, 2H), 8.21 (d, J = 12 Hz, 1H), 8.10 (d, J = 4 Hz, 1H), 8.06 (t, J = 8 Hz, 1H), 7.90 (t, J = 8 Hz, 1H). IR (KBr, cm^{-1}): 3494 (br, s), 3112 (w), 1634 (m), 1613 (s), 1566 (S), 1549 (s), 1485 (s), 1454 (m), 1429 (s), 1366 (s), 1343 (m), 1323 (s), 1277 (s), 1226 (w), 1165 (s), 1114 (s), 1084 (s), 1055 (s), 1022 (w), 1006 (s), 940 (w), 917 (m), 891 (w), 786 (s), 766 (s), 744 (s), 725 (s), 712 (s), 677 (w), 544 (w), 532 (s).

Picrate salt of pyridine-4-carbaldoxime *(Hpco).(tnp)*: Isolated yield: 55%.^{1}H NMR (600 MHz, Acetone-d_6): 11.90 (s, 1H), 8.98 (d, J = 6 Hz, 2H), 8.76 (s, 2H), 8.46 (s, 1H), 8.27 (d, J = 6 Hz, 2H). IR (KBr, cm^{-1}): 3317 (br, m), 3076 (w), 1634 (s), 1604 (w), 1558 (s), 1505 (w), 1485 (w), 1459 (w), 1429 (s), 1369 (s), 1342 (m), 1321 (w), 1276 (s), 1201 (s), 1160 (s), 1084 (s), 988 (s), 957 (w), 907 (m), 884 (s), 817 (s), 786 (m), 745 (m), 708 (s), 528 (m).

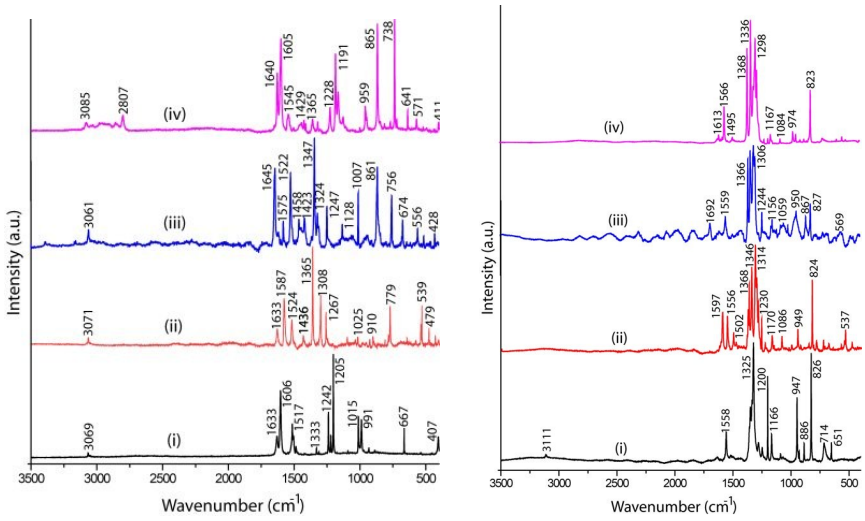
Picrate salt of 4-(N,N-dimethylaminophenyl)aldoxime *(Hdmo)(tnp)***:** Isolated yield: 52%. ^{1}H NMR (600 MHz, Acetone-d_6): 8.89 (s, 2H), 8.05 (s, 1H), 7.57 (d, J = 12 Hz, 2H), 7.12 (d, J = 6 Hz, 2H), 3.14 (s, 6H). IR (KBr, cm^{-1}): 3416 (br, s), 3088 (w), 2987 (w), 1631 (s), 1591 (w), 1564 (s), 1514 (w), 1480 (m), 1462 (m), 1435 (s), 1365 (s), 1335 (s), 1313 (w), 1280 (s), 1194 (m), 1184 (w), 1162 (s), 1127 (s), 1077 (s), 1057 (w), 988 (w), 968 (s), 947(w), 922 (m), 875 (w), 851 (s), 788 (s), 745 (s), 711 (s), 635 (w), 595 (w).

Hydrated picrate salt of indole-3-carbaldoxime *(Hico).(tnp).H_2O*: Isolated yield: 53%.^{1}H NMR (600 MHz, Acetone-d_6): 11.03 (s, -OH), 10.54 (s, -NH), 9.11 (s, 4H), 8.47 (s, 1H), 8.31 (s, 1H), 8.10 (d, J = 12 Hz, 1H), 7.99 (s, 1H), 7.90 (d, J = 6 Hz, 1H), 7.60 (s, 1H), 7.53 (d, J = 6Hz, 1H), 7.44 (d, J = 12 Hz, 1H), 7.24 (t, J = 6Hz, 1H), 7.20 (m, 2H), 7.10 (t, J = 6 Hz, 1H). IR (KBr, cm^{-1}): 3338 (br, s), 3149 (m), 3081 (w), 1684 (m), 1631 (w), 1610 (w), 1565 (w), 1521 (w), 1492 (w), 1459 (w), 1419 (s), 1362 (s), 1337 (w), 1315 (w), 1270 (m), 1240 (w), 1159 (w), 1138 (w), 1079 (s), 1006 (w), 910 (m), 788 (m), 749 (s), 713 (s), 669 (w), 612 (s), 558 (w).



(a) (b)

Figure S1: FT-IR spectra of ((a) i) pyridine-4-carbaldoxime, ii) quinoline-4-carbaldoxime, iii) indole-3-carbaldoxime, iv) 4-(N,N-dimethylaminophenyl)aldoxime; (b) picrate salts i) *(Hpco).(tnp),* ii) *(Hqco).(tnp).H_2O*, iii) *(Hico).(tnp).H_2O* and iv) *(Hdmo).(tnp)*.



(a) (b)

Figure S2: Raman spectra of (a) i) pyridine-4-carbaldoxime, ii) quinoline-4-carbaldoxime, iii) indole-3-carbaldoxime, iv) 4-(N,N-dimethylaminophenyl)aldoxime and (b) picrate salt i) *(Hpco).(tnp)*, ii) *(Hqco).(tnp).H_2O*, iii) *(Hico).(tnp).H_2O* and iv) *(Hdmo).(tnp)*.

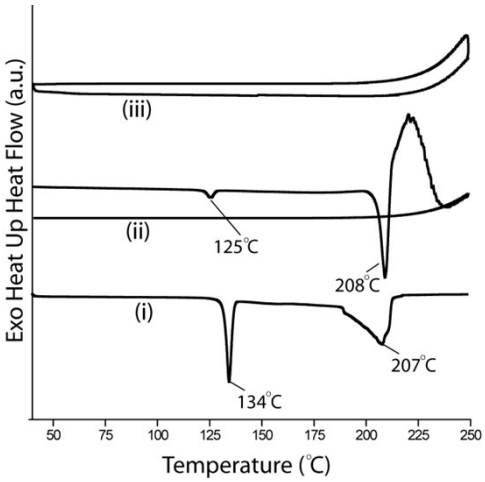


Figure S3: DSC plots of (i) pyridine-4-carbaldoxime and picrate salt *(Hpco).(tnp)* with (ii) 1st cycle heating and (iii) 2nd cycle heating.

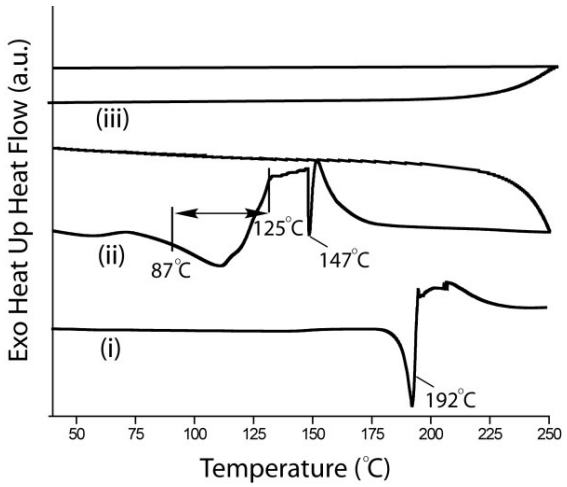


Figure S4: DSC plots of (i) Indole-3-carbaldoxime and hydrated picrate salt *(Hico).(tnp).H_2O* with (ii) 1st cycle heating and (iii) 2nd cycle heating.

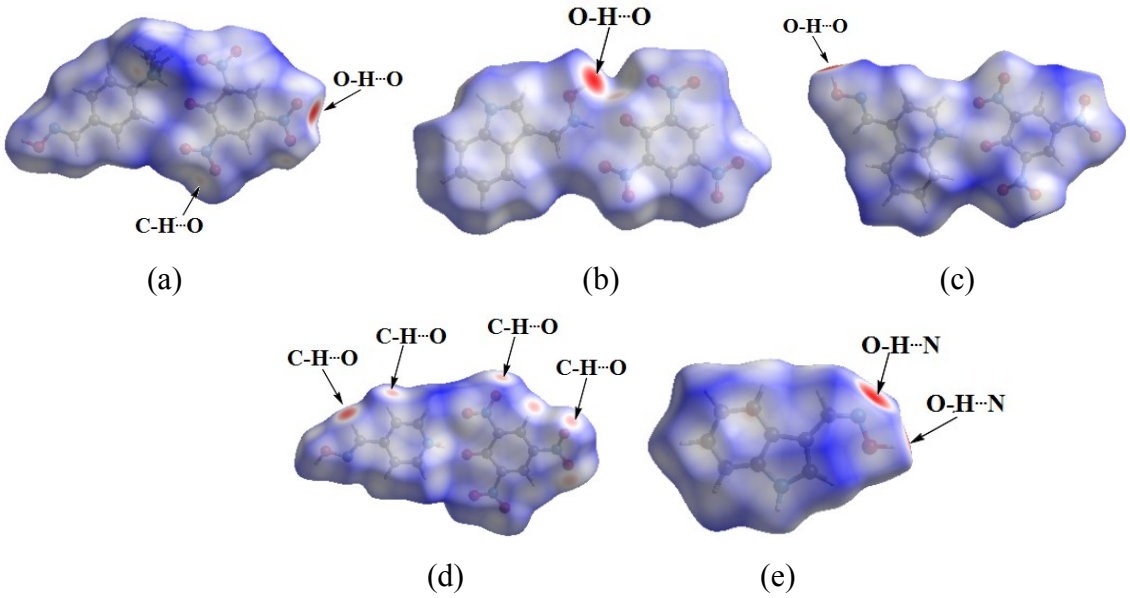


Figure S5: Hirshfeld surface of picrate salts (a) *(Hdmo).(tnp)*, (b) *(Hico).(tnp).H_2O*, (c) *(Hqco).(tnp).H_2O*, (d) *(Hpco).(tnp)* and (e) Indole-3-carbaldoxime.

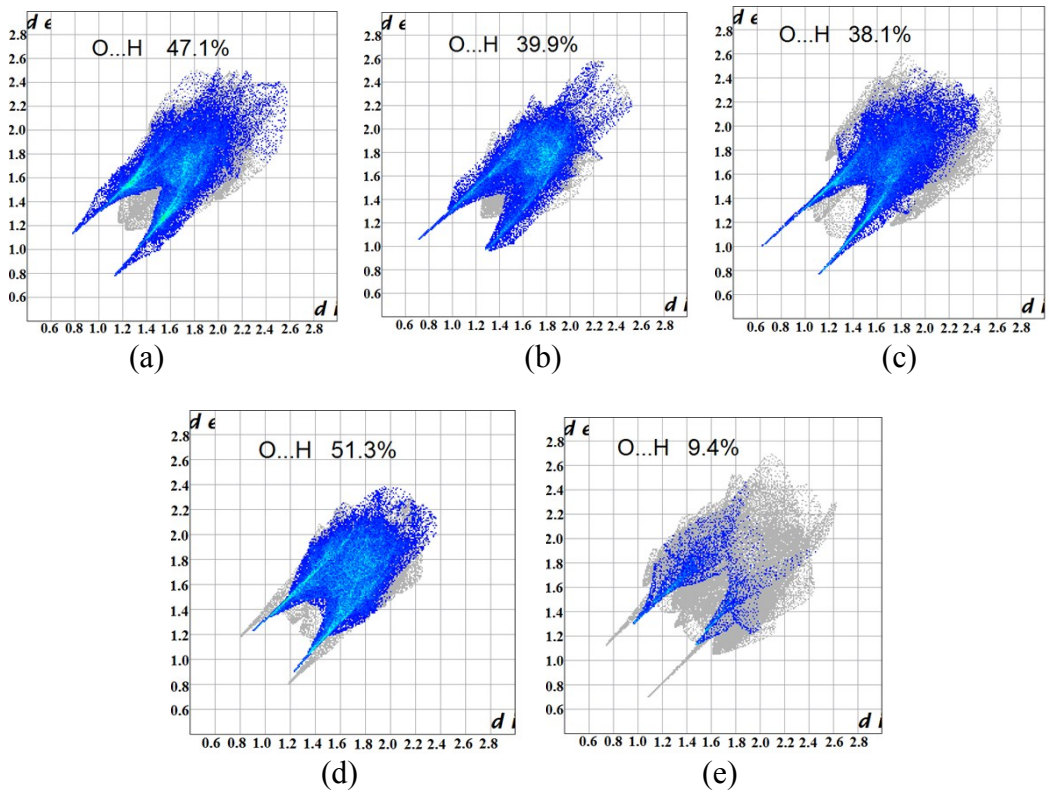


Figure S6: Fingerprint plots for (a) *(Hdmo).(tnp)*, (b) *(Hico).(tnp).H_2O*, (c) *(Hqco).(tnp).H_2O*, (d) *(Hpco).(tnp)* and (e) Indole-3-carbaldoxime with O···H interactions highlighted in colour.

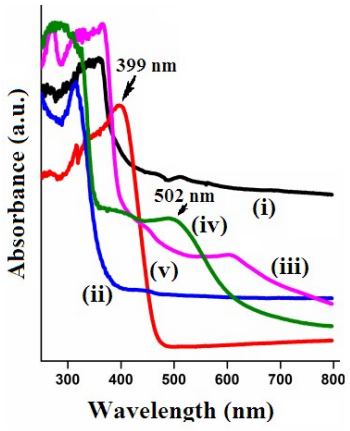


Figure S7: Solid-state UV-visible spectra of (i) quinoline-4-carbaldoxime, (ii) pyridine-4-carbaldoxime (iii) 4-(N,N-dimethylaminophenyl)aldoxime, (iv) indole-3-carbaldoxime and (v) picric acid.

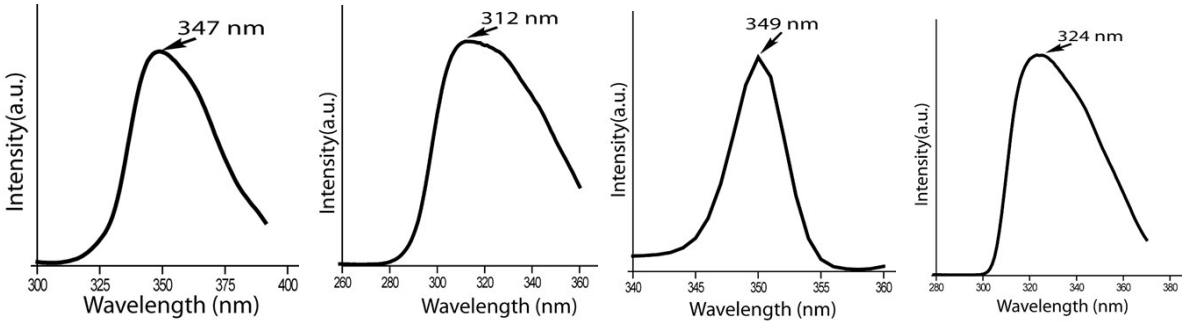


Figure S8: Fluorescence excitation spectra of (a) quinoline-4-carbaldoxime, (b) pyridine-4-carbaldoxime, (c) 4-(N,N-dimethylamino)benzaldoxime and (d) Indole-4-carbaldoxime.

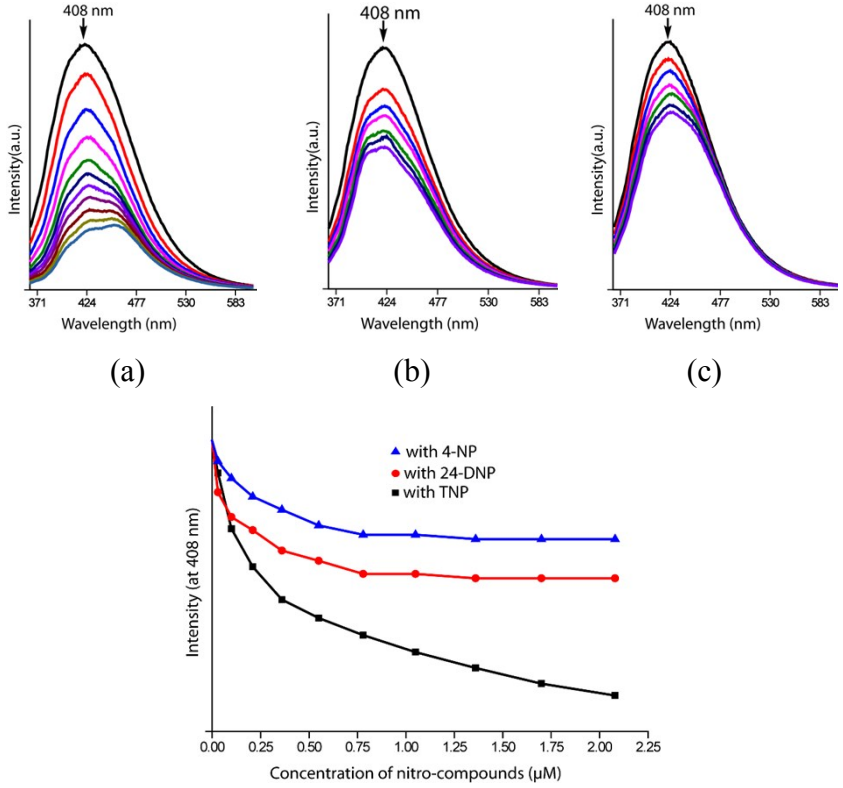
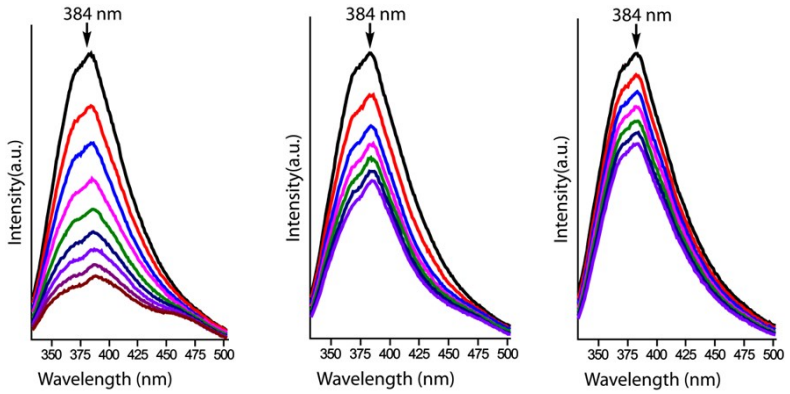
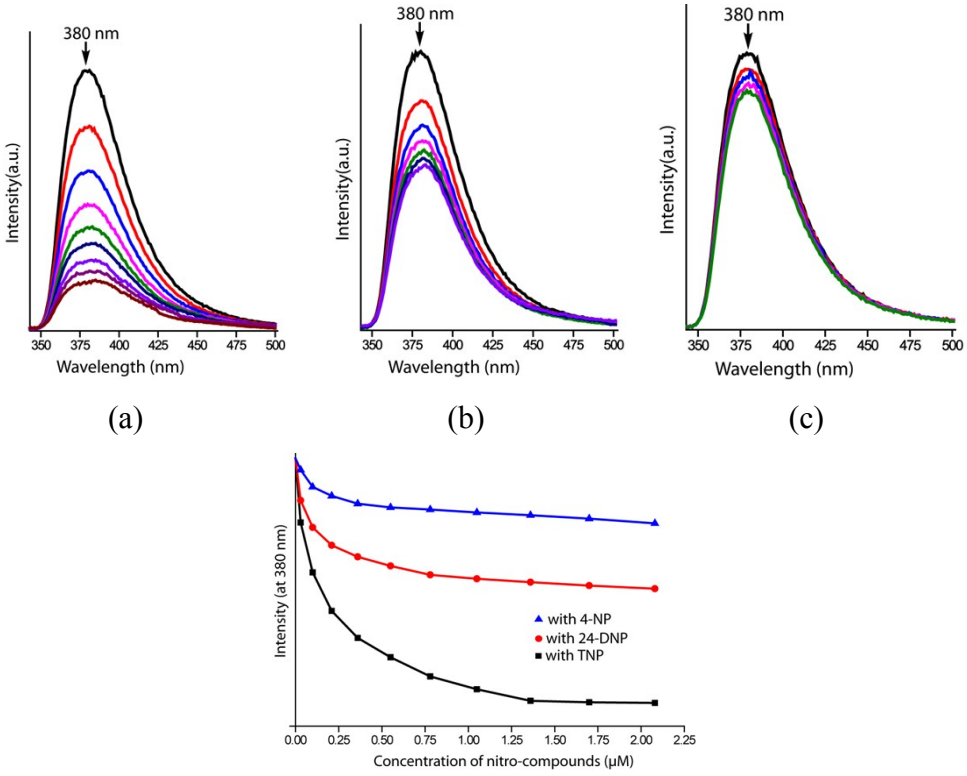


Figure S9: Changes in fluorescence emission of quinoline-4-carbaldoxime (10^{-4} M in acetonitrile) at 420 nm (excitation at 347 nm) upon addition (a) picric acid, (b) 2,4-dinitrophenol and (c) 4-nitrophenol (10 μl aliquots 10^{-5} M in acetonitrile in each case); (d) Plots of fluorescence intensity vs concentration with different nitro-compounds.



(a) (b) (c)

Figure S10: Changes in fluorescence emission of pyridine-4-carbaldoxime (10^{-4} M in acetonitrile) at 384 nm (λ_{em} at 312 nm) upon addition of different aliquots of (a) picric acid, (b) 2,4-dinitrophenol and (c) 4-nitrophenol (10 µl aliquots 10^{-5} M in acetonitrile in each case).



(a) (b) (c)

(d)

Figure S11: Changes in intensity of fluorescence emission at 380 nm of 4-(dimethylamino)benzaldehyde oxime (10^{-4} M in acetonitrile) (excitation at 349 nm) upon addition (a) picric acid, (b) 2,4-dinitrophenol and (c) 4-nitrophenol (10 µl aliquots 10^{-5} M in

acetonitrile in each case); (d) Plots of fluorescence intensity vs concentration with different nitro-compounds.

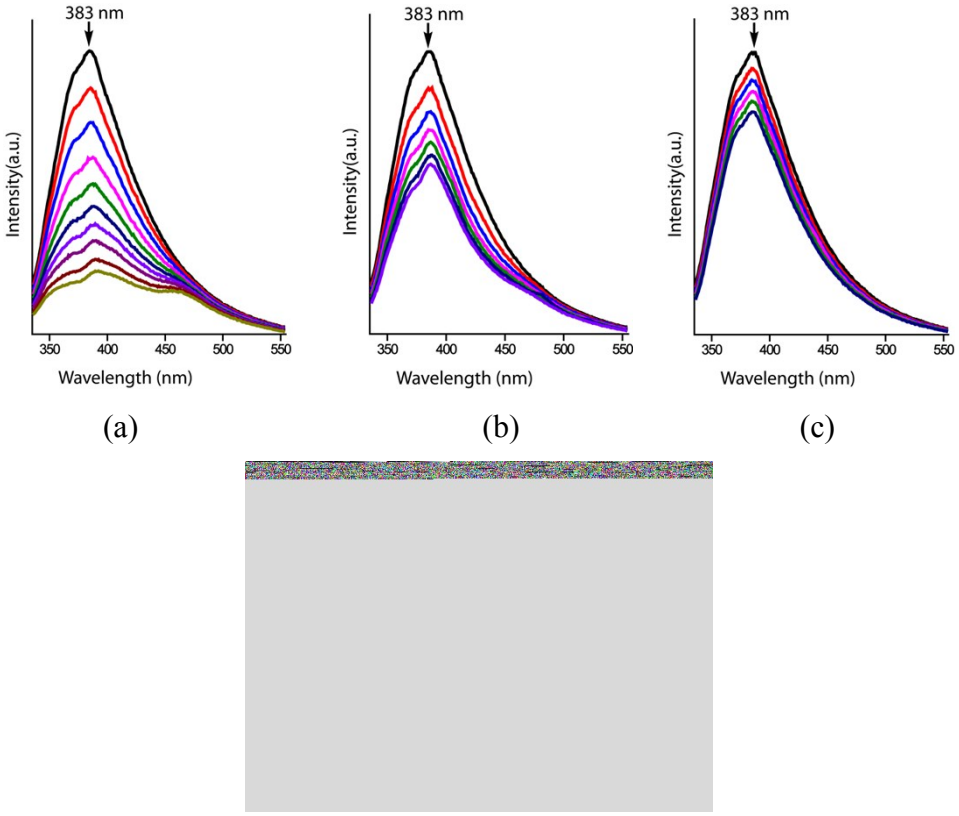


Figure S12: Changes in fluorescence emission of indole-3-carbaldoxime (10^{-4} M in acetonitrile) at 383 nm (excitation at 324 nm) upon addition (a) picric acid, (b) 2,4-dinitrophenol and (c) 4-nitrophenol (10 µl aliquots 10^{-5} M in acetonitrile in each case); (d) Plots of fluorescence intensity vs concentration at different nitro-compounds.

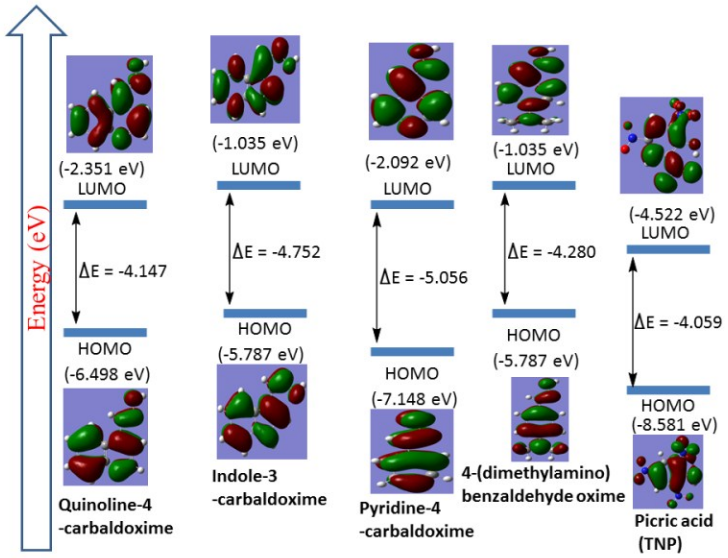


Figure S13: HOMO-LUMO of oxime derivatives and picric acid calculated by DFT using B3LYP/6-31+G (d,p) functional.

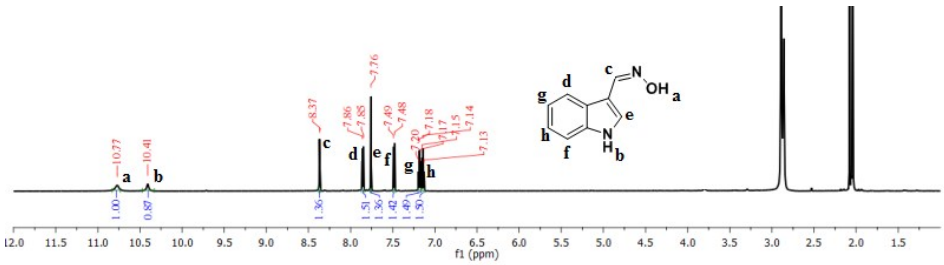


Figure S14: ^{1}H NMR (600 MHz, Acetone-d_6) spectra of indole-3-carbaldoxime.

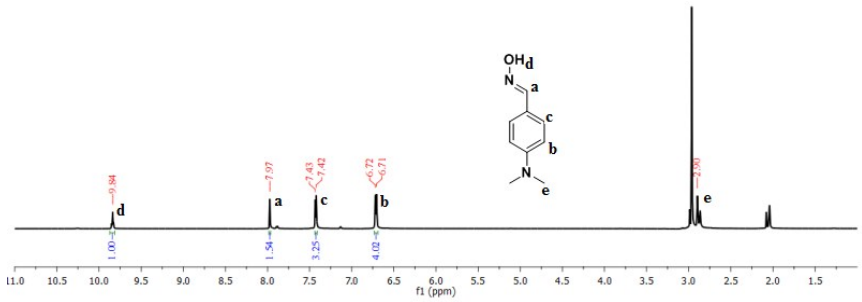


Figure S15: ^{1}H NMR (600 MHz, Acetone-d_6) spectra of 4-(N,N-dimethylaminophenyl) aldoxime.

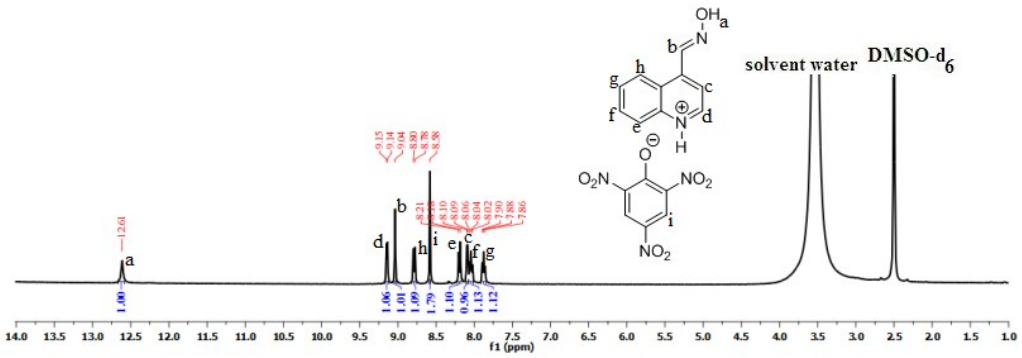


Figure S16: ^{1}H NMR (600 MHz, DMSO-d_6) spectra of salt *(Hqco).(tnp).H_2O*.

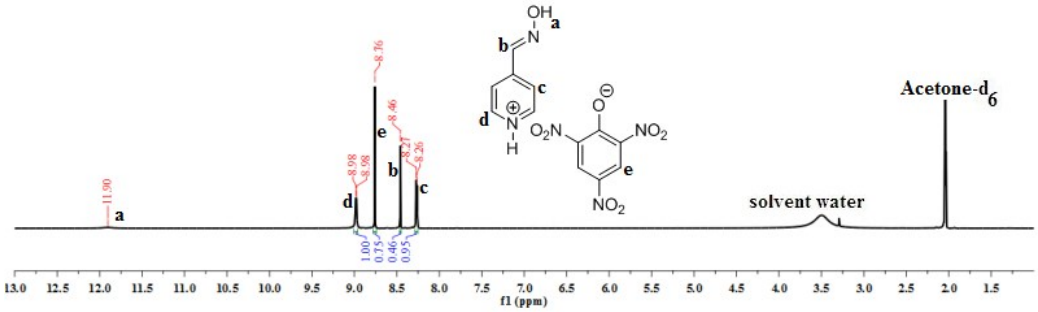


Figure S17: ^{1}H NMR (600 MHz, Acetone-d_6) spectra of salt *(Hpco).(tnp)*.

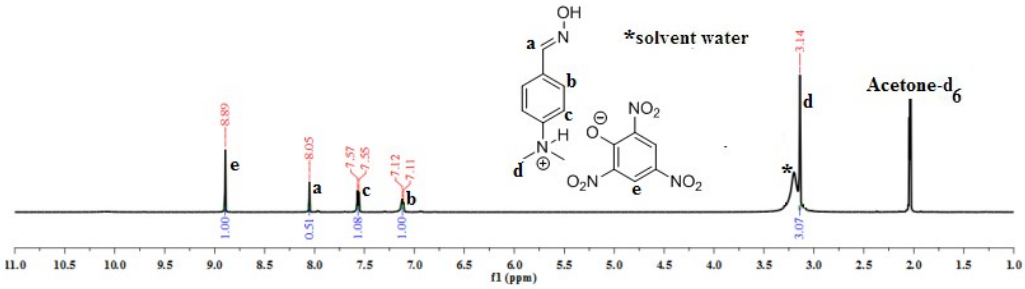


Figure S18: ^{1}H NMR (600 MHz, Acetone-d_6) spectra of salt (Hdmo).(tnp).

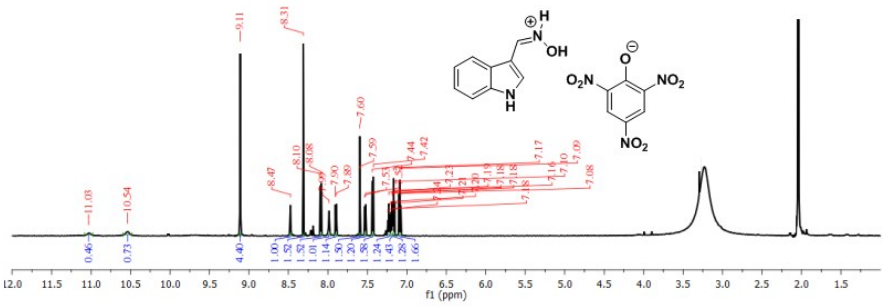


Figure S19: ^{1}H NMR (600 MHz, Acetone-d_6) spectra of salt (Hico).(tnp).H_2O.

Table S1: Some of the selective bond distance

Compound	C=N (oxime)	Length (Å)	N-O (oxime)	Length (Å)
Indole-3-carbaldoxime	C10-N3	1.276(4)	N3-O2	1.396(3)
(Hico).(tnp).H_2O	C8-N1	1.294(6)	N1-O1	1.357(5)
(Hqco).(tnp).H_2O	C1-N1	1.277(4)	N1-O1	1.374(3)
(Hpco).(tnp)	C1-N1	1.274(6)	N1-O1	1.391(5)
(Hdmo).(tnp)	C1-N1	1.270(2)	N1-O1	1.394(2)

Table S2: Hydrogen bond parameters of the salts and indole-3-carbaldoxime

Salts/oxime	D-H…A	d_{D-H} (Å)	$d_{H...A}$ (Å)	$d_{D...A}$ (Å)	∠D-H…A (°)
(Hqco).(tnp).H_2O	O(1)-H(1A)…O(9) [-x,-y,-z]	0.82(4)	1.81(3)	2.632(4)	176(4)
	N(2)-H(2)…O(4) [1/2-x,1/2+y,1/2-z]	0.90(3)	2.50(4)	2.962(4)	113(3)
	N(2)-H(2)…O(8) [1/2-x,1/2+y,1/2-z]	0.90(3)	1.83(3)	2.718(3)	170(3)
	O(9)-H(9A)…O (6) [1-x,2-y,-z]	0.87(5)	2.06(5)	2.923(4)	176(3)
	O(9)-H(9B)…O(2) [x,-1+y,z]	0.86(3)	2.01(3)	2.858(4)	172(3)
(Hpco).(tnp)	O(1)-H(1)…N(1) [1-x,2-y,-z]	0.82(6)	2.12(4)	2.843(6)	146(6)
	N(2)-H(2)…O(3) [1+x,y,z]	0.87(7)	2.57(9)	3.020(6)	114(7)
	N(2)-H(2)…O(8) [1+x,y,z]	0.87(7)	1.77(7)	2.630(6)	172(10)
(Hdmo).(tnp)	O(1)-H(1A)…O(5) [2-x,-y,1-z]	0.82(3)	2.08(4)	2.896(2)	171(4)
	N(2)-H(2)…O(2) [1-x,1-y,-z]	0.94(2)	1.82(2)	2.738(2)	165(2)
	N(2)-H(2)…O(3) [1-x,1-y,-z]	0.94(2)	2.55(2)	3.066(3)	114(15)
Indole-3-carbaldoxime	O(1)-H(1A)…N(3) [1-x,1-y,1/2+z]	0.82(4)	2.02(4)	2.824(2)	166(5)
	N(2)-H(2)…O(2) [1+x,y,z]	0.88(2)	2.39(2)	3.227(3)	159.(19)
	O(2)-H(2A)…N(1) [1/2-x,-1/2+y,-1/2+z]	0.82(2)	1.94(4)	2.759(2)	172(4)
(Hico).(tnp).H_2O	N(1)-H(1A)…O(3) [1-x,1-y,-z]	0.94(6)	2.24(7)	2.888(5)	125(5)
	N(1)-H(1A)…O(8) [1-x,1-y,-z]	0.94(6)	1.83(6)	2.705(6)	153(6)

Table S3: Melting point and decomposition temperature of the oximes and picrate salts

Compound	*qco*	*pco*	*dmo*	*ico*	Picric acid	Picrate salt of			
						Quinoline-4-carbaloxime	Pyridine-4-carbaloxime	4-(N,N-Dimethyl aminophenyl)aldoxime	Indole-3-carbal doxime
Melting point (°C)	180	134	147	192	122	199	125	176	147
Decomposition Temperature (°C)	>250	207	201	>250	>250	>225	208	209	> 250

Table S4: Relative contributions from various interactions from Hirshfeld analysis.

	(Hqco).(tnp).H_2O	*(Hpco).(tnp)*	*(Hdmo).(tnp)*	*(Hico).(tnp).H_2O*	*ico*
O···O	5.4	6.4	3.7	11.9	0.0
N···O	5.3	6.2	2.0	2.8	0.0
C···O	8.5	4.1	4.0	3.6	0.6
H···O	38.1	51.3	47.1	39.9	9.4
C···N	3.6	2.5	4.6	4.6	0.8
N···H	2.5	6.2	3.2	2.8	14.2
C···H	17.3	8.9	7.9	3.8	35.9
C···C	3.2	8.1	5.7	12.4	0.0
H···H	15.8	6.3	20.9	18.1	39.0