Supplementary Material

Structural and reactivity analyses of nitrofurantoin–4-dimethylaminopyridine salt using spectroscopic and density functional theory calculations

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Theoretical details

It is to be mentioned that it is the Raman scattering amplitudes which are obtained by Density functional theory (DFT) calculations, which cannot be taken directly to be the Raman intensities. Raman scattering cross section, $\partial\sigma_j/\partial\Omega$, which are proportional to Raman intensities may be calculated from the Raman scattering amplitude and predicted wavenumbers for each normal mode using the formula [1]:

$$\frac{\partial\sigma_j}{\partial\Omega} = \left(\frac{2^4\pi^4}{45}\right)\left(\frac{(\nu_0 - \nu_j)^4}{1 - \exp\left[\frac{-hc\nu_j}{kT}\right]}\right)\left(\frac{h}{8\pi^2 c\nu_j}\right)S_j$$

where S_j and ν_j are the scattering activities and the predicted wavenumbers, respectively of the j^{th} normal mode, ν_0 is the wavenumber of the Raman excitation line and h, c and k are universal constants.

In analyzing gas-phase data using a newer functional, the only way to get the appropriate scaling factor is to find an experimental data set and simply scale the calculated values to the most intense peaks. So, we multiply the calculated data by an arbitrary number and just start visually adjusting from there to get the best match with the experimental one. For NF-DMAP

system, we found the scaling factor to be 0.980 and 0.991 for wB97X-D and B3LYP functionals, respectively.

In NBO study, for each donor (i) and acceptor (j), the stabilization energy $E^{(2)}$ associated with the delocalization i to j is taken from the second-order perturbation method [2] and is estimated as,

$$E^{(2)} = -q_i \left[\frac{(F_{ij})^2}{\epsilon_i - \varepsilon_j} \right]$$

where, q_i is the population of donor orbital or donor orbital occupancy; ε_i, ε_j are orbital energies of donor and acceptor NBO orbitals, respectively; F_{ij} is the off-diagonal Fock or Kohn-Sham matrix element between i and j NBO orbitals.

The relation between the energy of bond interaction and $\nabla^2\rho_{BCP}$ is given by the principle of the virial theorem.

$$1/4\ \nabla^2\rho_{BCP} = 2G_{BCP} + V_{BCP} = H_{BCP}$$

where $G(r_{BCP})$ is the kinetic energy density, V_{BCP} potential energy density and H_{BCP} total energy density at bond critical point BCP.

The relation between V_{BCP} and hydrogen bond energy (E_{HB}) at H···O contact is given by [3]:

$$E_{HB} = \frac{1}{2} V_{BCP}$$

DFT method gives definitions of significant universal concepts of molecular structure stability and reactivity [4]. HOMO energy can be used in combination with LUMO energy to give the global reactivity descriptors like the chemical potential (μ), hardness (η), softness (S), electronegativity (χ) and the electrophilicity index (ω) which may be used study the reactivity of the molecule [4].

Parr and Pearson introduced the formulas for these global reactivity descriptors which are given below:

$$\mu = -\chi = \frac{1}{2}(E_{HOMO} + E_{LUMO})$$

$$\eta = \frac{1}{2}(E_{LUMO} - E_{HOMO})$$

$$S = \frac{1}{2\eta}$$

$$\omega = \frac{\mu^2}{2\eta}$$

ω gives the propensity of a molecule to accept electrons. Electrophilicity based charge transfer (ECT) states the amount of charge transfer between the two molecules A and B and may be defined as [5]:

$$ECT = (\Delta N_{max})_A - (\Delta N_{max})_B$$

where $(\Delta N_{max})_A = \mu_A/\eta_A$ and $(\Delta N_{max})_B = \mu_B/\eta_B$,

is the maximum electronic charge that the electrophile may accept from the surroundings and is given by the expression:

$$\Delta N_{max} = -\frac{\mu}{\eta}$$

The hard and soft acids and bases (HSAB) principle can be very beneficial to calculate the reactivity of chemical systems (such as Fukui function (FF)) [6]. Fukui function (FF) is a local reactivity descriptor that specifies the best approach to alter the number of electrons in a molecule [7]. According to Parr and Yang [8], the greater the FF value of an atom more reactive it is. Fukui functions are calculated using the given expressions.

For nucleophilic attack, $f_k^+ = [q(N+1) - q(N)]$

For electrophilic attack, $f_k^- = [q(N) - q(N-1)]$

For radical attack, $f_k^0 = \frac{1}{2}[q(N+1) + q(N-1)]$

Molecular Electrostatic Potential at a point in space around a molecule gives information about the net electrostatic effect produced at that point by total charge distribution (electron +

proton) of the molecule and correlates with dipole moments, electro-negativity, partial charges and chemical reactivity of the molecules. The molecular electrostatic potential (MEP) at a point r in the space around a molecule (in atomic units) can be expressed as:

$$V(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')dr'}{|r' - r|} \quad ,$$

where Z_A is the charge on nucleus A, located at R_A and ρ (r′) is the electronic density function for the molecule. The first and second terms stand for the contributions to the potential due to nuclei and electrons, respectively. V(r) is the resultant at each point r, which is the net electrostatic effect produced at the point r by both the electrons and nuclei of the molecule.

Molar refractivity (MR) a substantial property is used to calculate the total polarizability of a material. MR value can be calculated by the Lorentz–Lorentz equation [9-10] which is:

$$MR = \left[\frac{n^2 - 1}{n^2 + 2}\right]\left(\frac{MW}{\rho}\right) = 1.333\ \pi N\alpha,$$

where n is the refractive index; (MW/ρ) is the molar volume; MW is the molecular weight; ρ is the density; N is the Avogadro number; α is the polarizability of the molecular system.

References

[1] G. A. Guirgis, P. Klaboe, S. Shen, D. L. Powell, A. Gruodis, V. Aleksa, C. J. Nielsen, J. Tao, C. Zheng, and J. R. Durig, *J. Raman Spectrosc*., 2003, **34**, 322.

[2] A.E. Reed, L.A. Curtiss and F. Weinhold, *Chem. Rev*., 1988, **88**, 899.

[3] E. Espinosa, E. Molins, and C. Lecomte, *ChemPhysLett.*, 1998, **285**, 170.

[4] P. Geerlings, F. De Proft and W. Langenaeker, *Chem. Rev*., 2003, **103**, 1793.

[5] R. G. Parr and R. G. Pearson, *J. Am. Chem. Soc*., 1983, **105**, 7512.

[6] R. G. Pearson, *J. Org. Chem.*, 1989, **54**, 1430.

[7] R. G. Parr and W. Yang, *Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989

[8] R. G. Parr and W. Yang, *J. Am. Chem. Soc*., 1984, **106**, 4049.

[9] J.A. Padron, R. Carasco and R.F. Pellon, *J. Pharm. Pharm. Sci*., 2002, **5**, 258.

[10] R.P. Verma, A. Kurup and C. Hansch, *Bioorg Med. Chem*., 2005, **13**, 237.

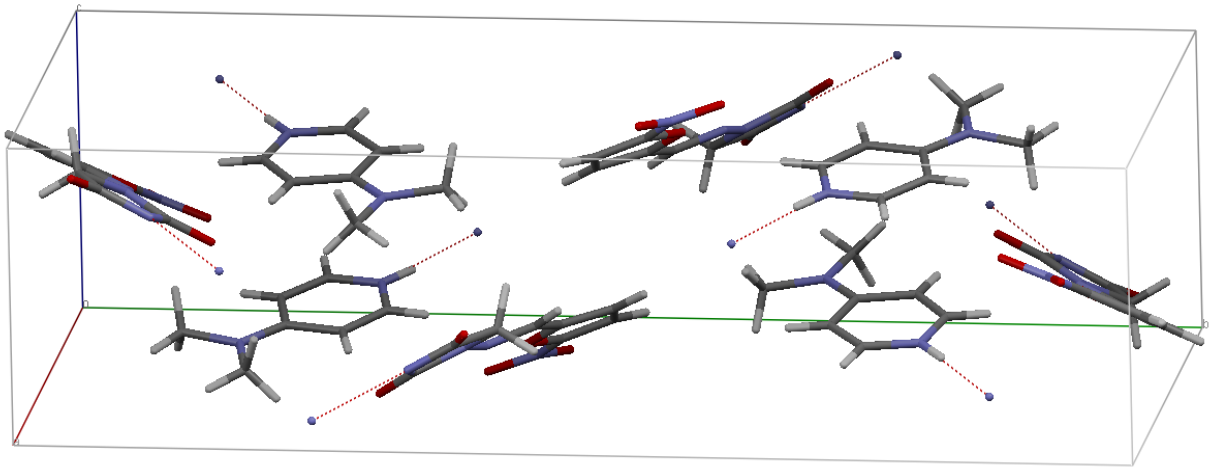

Figure S1. H-bond interactions within the unit cell of NF-DMAP.

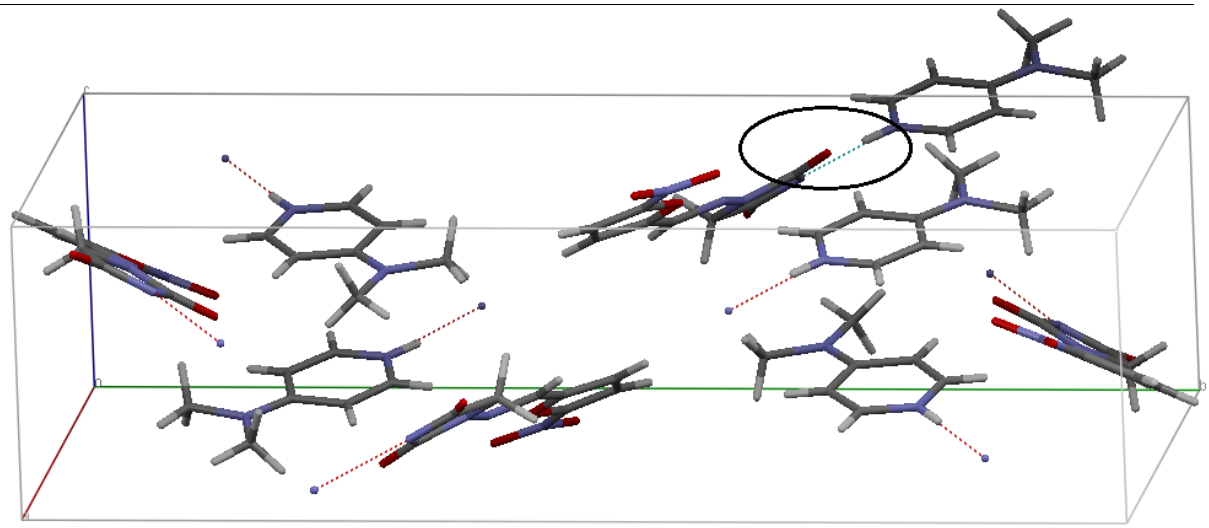

Figure S2. Intermolecular H-bond present within NF-DMAP.

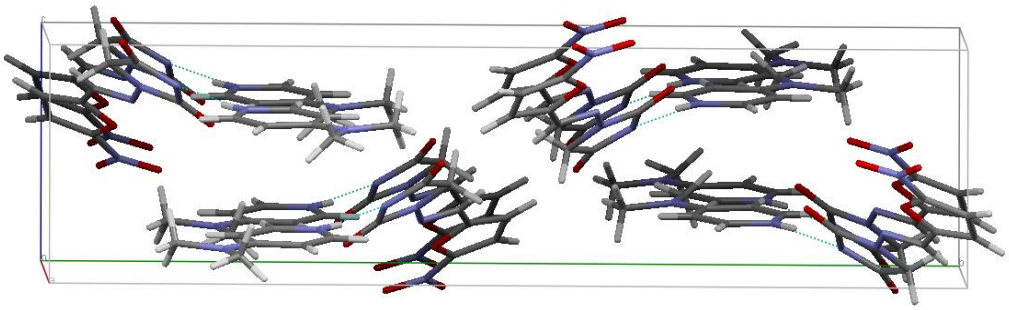

Figure S3. All the intermolecular H-bonds present within the unit cell.

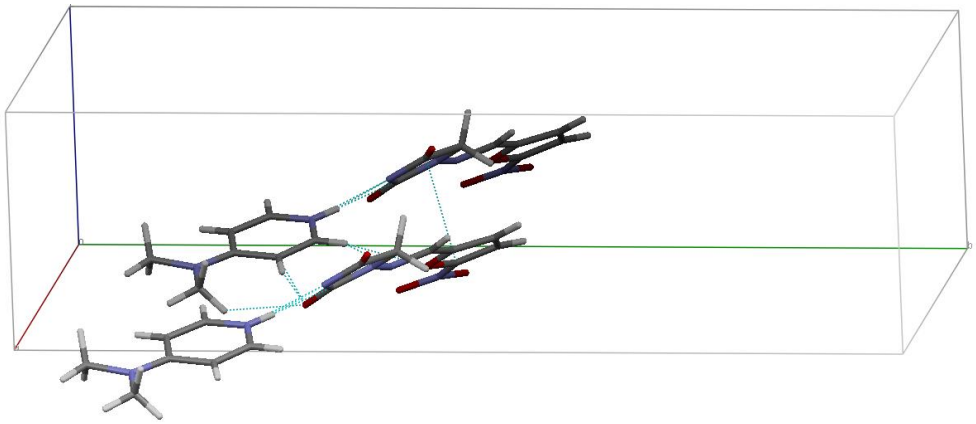

Figure S4. Short contacts present between two molecules (monomer) of NF-DMAP.

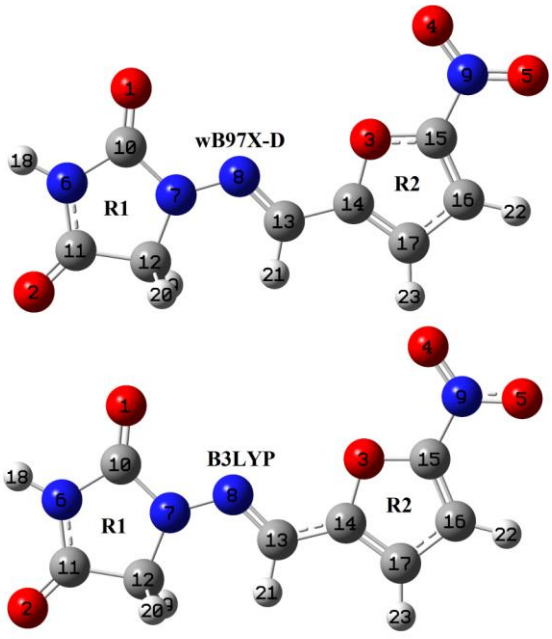

Figure S5. Optimized structure of NF using wB97X-D and B3LYP level of theories.

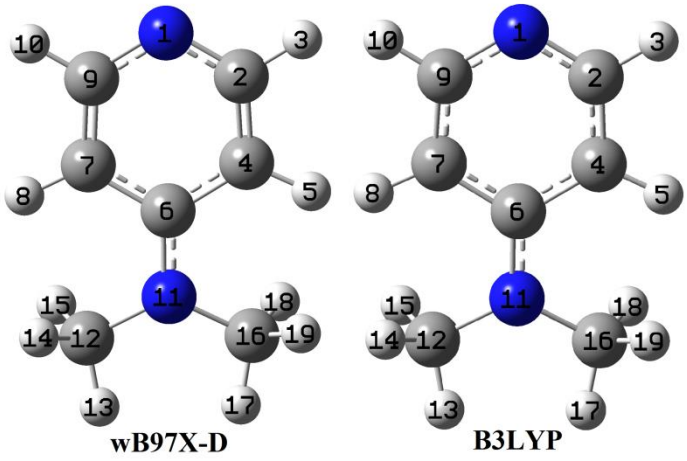

Figure S6. Optimized structure of DMAP using wB97X-D and B3LYP level of theories.

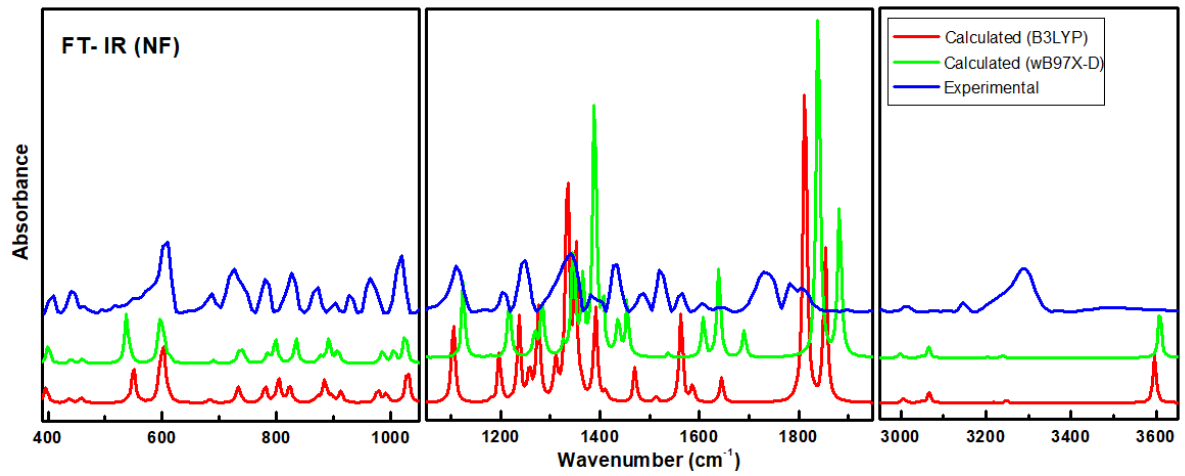

Figure S7. Comparison of experimental and calculated (scaled) IR spectra of NF.

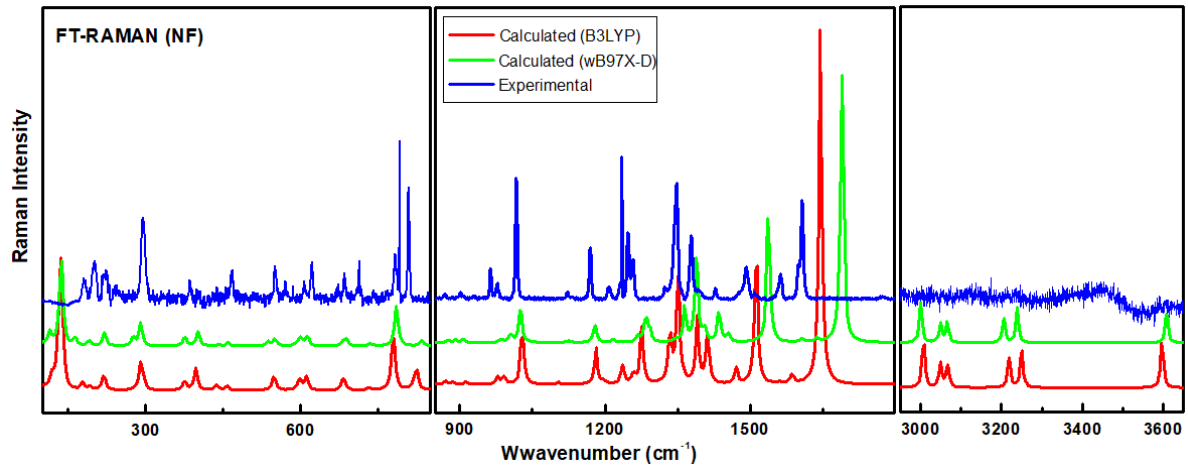

Figure S8. Comparison of experimental and calculated (scaled) Raman spectra of NF.

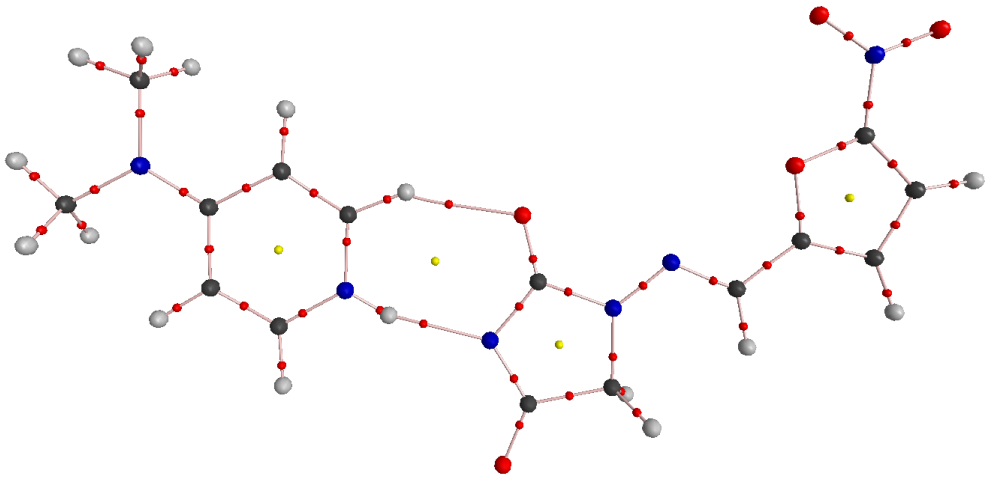

Figure S9. Molecular graph of the NF-DMAP using the B3LYP level of theory.

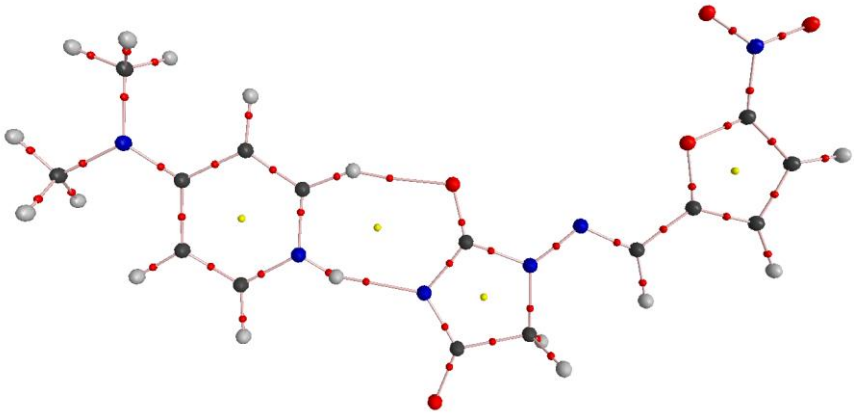

Figure S10. Molecular graph of the NF-DMAP using the wB97X-D level of theory.

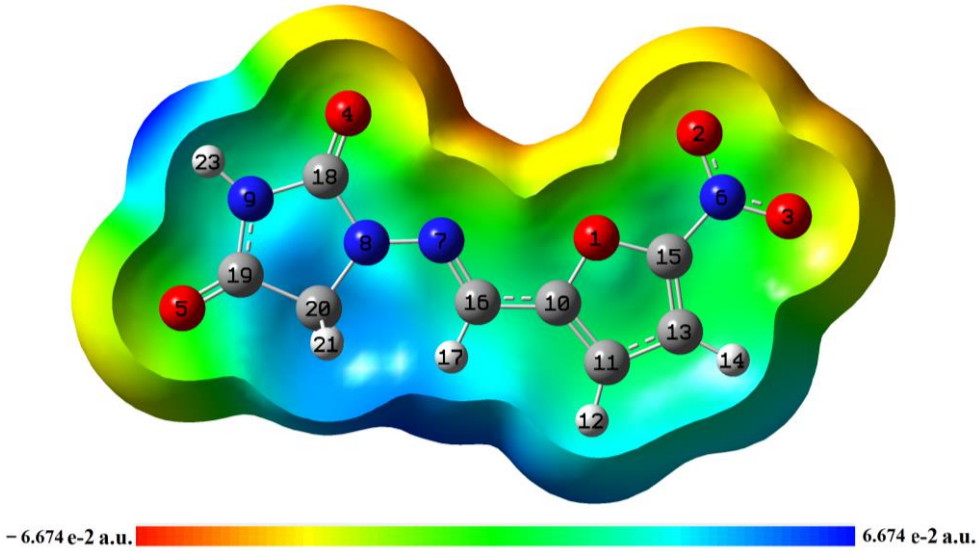

Figure S11. Molecular electrostatic potential (MEP) for NF using B3LYP level of theory.

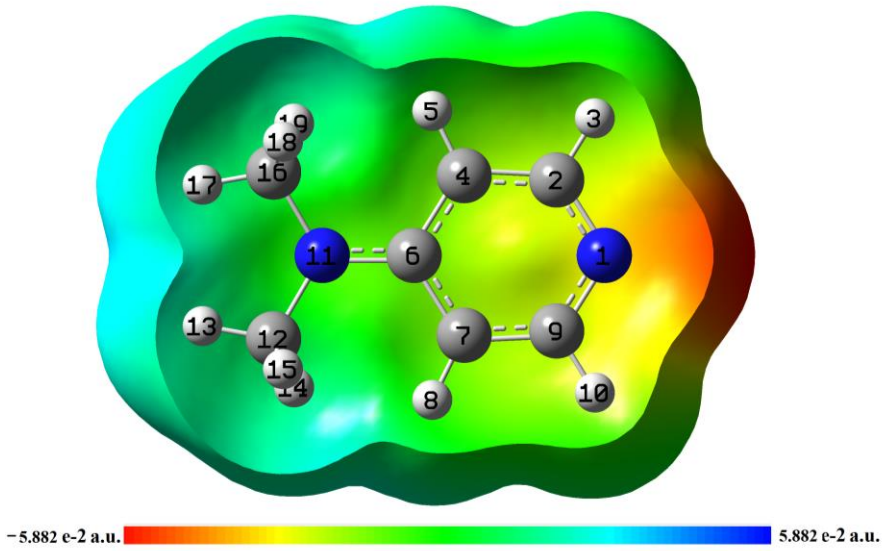

Figure S12. Molecular electrostatic potential (MEP) for DMAP using B3LYP level of theory.

	V(r) a.u.	Point charges (e)
9 N	-18.451430	-0.732496
5 O	-22.431331	-0.643079
4 O	-22.423541	-0.633632
3 O	-22.367614	-0.505667
2 O	-22.364757	-0.446531
7 N	-18.364842	-0.393062
31 C	-14.715636	-0.319669
28 C	-14.709550	-0.303747
11 C	-14.760281	-0.297837
20 C	-14.740612	-0.281558
25 N	-18.294522	-0.247381
1 O	-22.289251	-0.200833
13 C	-14.749815	-0.073720
23 N	-18.307551	-0.018130
39 C	-14.684293	0.016604
35 C	-14.686473	0.020456
26 C	-14.668470	0.028540
42 H	-1.054670	0.037270
40 H	-1.054504	0.037588
38 H	-1.057094	0.039819
36 H	-1.056931	0.040227
17 H	-1.087045	0.043342
33 C	-14.683665	0.066472
37 H	-1.049504	0.075855
41 H	-1.047674	0.078301
15 C	-14.676321	0.082408
16 C	-14.738158	0.082888
21 H	-1.100643	0.107085
22 H	-1.100567	0.107593
14 H	-1.076392	0.139738
27 H	-1.031918	0.153179
12 H	-1.079506	0.154648
29 H	-1.038522	0.156108
32 H	-1.046240	0.163485
34 H	-1.053087	0.193363
24 H	-0.993261	0.200061
8 N	-18.337123	0.223814
10 C	-14.696141	0.288829
30 C	-14.651059	0.428991
18 C	-14.676656	0.635204
19 C	-14.704534	0.730068
6 N	-18.172339	0.765403

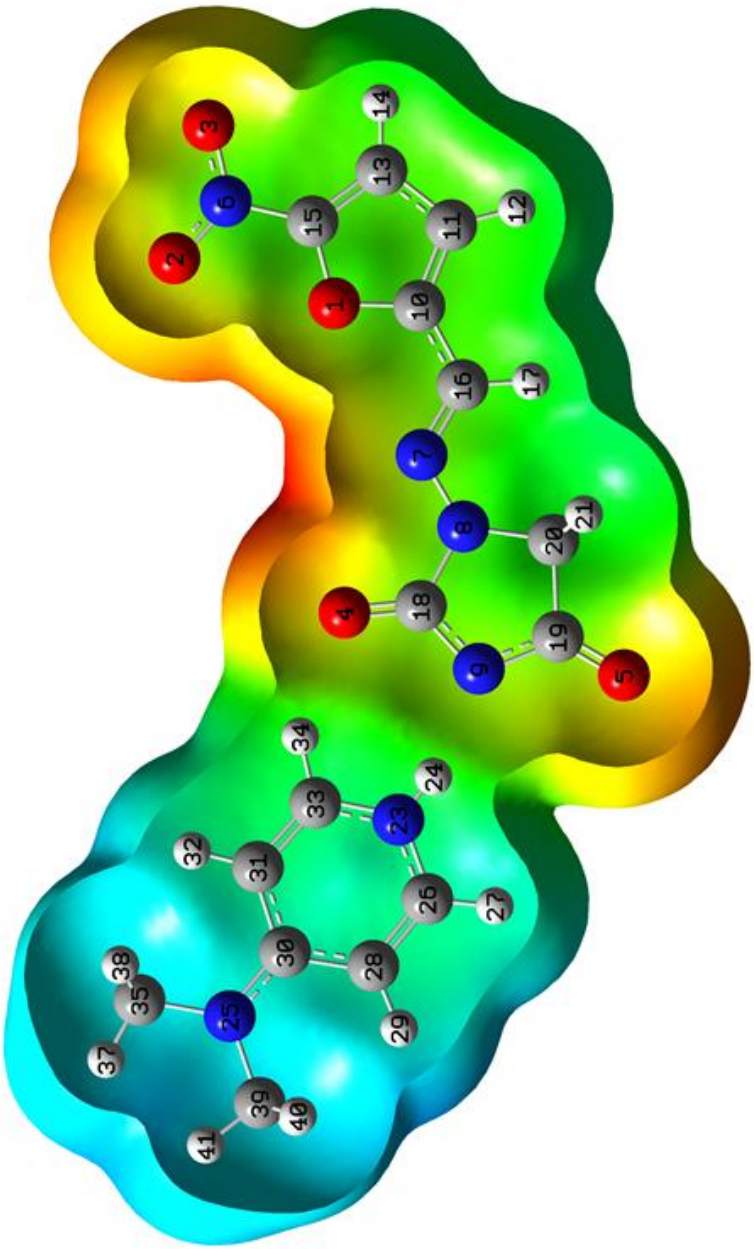

Figure S13. Molecular electrostatic potential (MEP) for NF-DMAP along with electrostatic potential V (r) and point charges using B3LYP level of theory.

Table S1. The experimental geometric parameters of NF-DMAP and NF and calculated geometric parameters of NF-DMAP and NF using B3LYP/6-311++g(d,p) and wB97X-D/6-311++g(d,p) theory.

Geometrical Parameters	Experimental		Calculated			
			Optimized parameters (monomer)			
	NF-DMAP (salt)	NF (API)	NF-DMAP	NF	NF-DMAP	NF
			B3LYP/6-311++g(d,p)		wB97X-D/6-311++g(d,p)	
Bond lengths (Å)						
O1-C10	1.380(5)	1.3582	1.3590	1.3588	1.3474	1.3478
O1-C15	1.356(5)	1.3476	1.3533	1.3486	1.3412	1.3377
O2-N6	1.241(5)	1.2200	1.2267	1.2226	1.2140	1.2114
O3-N6	1.243(5)	1.2276	1.2359	1.2311	1.2225	1.2193
O4-C18	1.220(5)	1.1954	1.2217	1.1965	1.2173	1.1922
O5-C19	1.243(6)	1.2023	1.2218	1.2041	1.2172	1.1995
N6-C15	1.409(6)	1.4317	1.4224	1.4338	1.4276	1.4358
N7-N8	1.350(5)	1.3376	1.3209	1.3406	1.3202	1.3383
N7-C16	1.302(6)	1.2824	1.2926	1.2850	1.2825	1.2763
N8-C18	1.416(6)	1.4012	1.4353	1.4044	1.4222	1.3958
N8-C20	1.445(6)	1.4560	1.4539	1.4608	1.4438	1.4502
N9-C18	1.376(6)	1.4041	1.3632	1.4078	1.3602	1.4021
N9-C19	1.350(5)	1.3744	1.3593	1.3771	1.3545	1.3731
C10-C11	1.366(6)	1.3751	1.3839	1.3788	1.3731	1.3695
C10-C16	1.419(6)	1.4388	1.4378	1.4423	1.4456	1.4481
C11-H12	0.9500	1.0763	1.0784	1.0786	1.0783	1.0786
C11-C13	1.410(7)	1.4141	1.4132	1.4173	1.4164	1.4190
C13-H14	0.9498	1.0743	1.0769	1.0768	1.077	1.0769
C13-C15	1.3501(6)	1.3617	1.368	1.3654	1.3591	1.3573
C16-H17	0.9493	1.0887	1.0904	1.0910	1.0906	1.0912
C19-C20	1.519(7)	1.5270	1.5436	1.5299	1.5377	1.5248
C20-H21	0.9899	1.0924	1.095	1.0946	1.0951	1.0945
C20-H22	0.9907	1.0925	1.0951	1.0946	1.095	1.0945
N23-H24	0.8857	-	0.8854	-	0.8854	-
N23-C26	1.342(6)	-	1.3469	-	1.3412	-
N23-C33	1.355(6)	-	1.351	-	1.3453	-
N25-C30	1.348(6)	-	1.3533	-	1.3477	-
N25-C35	1.460(6)	-	1.4637	-	1.4563	-
N25-C39	1.461(6)	-	1.4626	-	1.4551	-
C26-H27	0.9507	-	1.0823	-	1.0823	-
C26-C28	1.362(6)	-	1.3695	-	1.3656	-
C28-H29	0.9505	-	1.0789	-	1.0793	-
C28-C30	1.414(6)	-	1.4257	-	1.4219	-
C30-C31	1.419(7)	-	1.4228	-	1.4181	-
C31-H32	0.9500	-	1.0791	-	1.0794	-
C31-C33	1.362(7)	-	1.371	-	1.3675	-
C33-H34	0.9500	-	1.0894	-	1.0921	-
C35-H36	0.9800	-	1.0939	-	1.094	-
C35-H37	0.9800	-	1.0872	-	1.0875	-
C35-H38	0.9800	-	1.0941	-	1.0942	-
C39-H40	0.9800	-	1.0943	-	1.0939	-
C39-H41	0.9800	-	1.0872	-	1.0875	-
C39-H42	0.9800	-	1.0945	-	1.0947	-
Bond angle (°)						
C10-O1-C15	104.91	106.15	106.4334	106.19	106.3004	106.06
O2-N6-O3	124.09	126.20	125.3461	126.05	125.6573	126.23
O2-N6-C15	119.03	118.11	118.6103	118.28	118.4362	118.15
O3-N6-C15	116.88	115.69	116.0436	115.67	115.9065	115.62
N8-N7-C16	117.09	119.17	119.531	119.01	119.1523	118.70
N7-N8-C18	122.18	119.87	121.7006	119.75	121.8153	119.82
N7-N8-C20	127.16	127.73	128.6017	127.84	128.1229	127.46
C18-N8-C20	110.01	112.39	109.6966	112.41	110.0591	112.72

C18-N9-C19	109.22	114.50	110.5068	114.51	110.2078	114.27
O1-C10-C11	109.69	110.00	109.7787	110.05	110.2192	110.46
O1-C10-C16	118.82	119.82	120.22	119.78	119.7609	119.34
C11-C10-C16	131.46	130.18	130.0012	130.17	130.0198	130.20
C10-C11-H12	126.21	126.08	125.8628	126.13	125.9576	126.28
C10-C11-C13	107.54	106.70	106.7814	106.64	106.4655	106.33
H12-C11-C13	126.25	127.23	127.3557	127.23	127.5769	127.39
C11-C13-H14	127.50	128.94	128.957	128.96	129.1644	129.23
C11-C13-C15	104.97	105.06	105.2392	104.97	104.7423	104.58
H14-C13-C15	127.53	126.00	125.8038	126.06	126.0931	126.19
O1-C15-N6	117.05	117.69	117.9537	117.63	117.6108	117.45
O1-C15-C13	112.88	112.09	111.7672	112.15	112.2725	112.57
N6-C15-C13	130.07	130.22	130.2791	130.23	130.1167	129.98
N7-C16-C10	121.09	121.25	121.1616	121.19	120.6004	120.62
N7-C16-H17	119.41	123.79	123.5801	123.92	123.9927	124.22
C10-C16-H17	119.50	114.96	115.2582	114.89	115.4069	115.16
O4-C18-N8	123.68	128.63	123.1897	128.67	123.2699	128.63
O4-C18-N9	127.25	126.66	127.6106	126.65	127.4788	126.68
N8-C18-N9	109.07	104.71	109.1997	104.68	109.2513	104.69
O5-C19-N9	127.04	127.53	127.4579	127.59	127.3573	127.52
O5-C19-C20	122.20	126.90	122.9002	126.77	122.9612	126.78
N9-C19-C20	110.75	105.57	109.6419	105.63	109.6815	105.70
N8-C20-C19	100.76	102.83	100.9549	102.77	100.7992	102.62
N8-C20-H21	111.60	112.46	112.512	112.37	112.5035	112.46
N8-C20-H22	111.64	112.46	112.5066	112.37	112.6592	112.46
C19-C20-H21	111.63	110.09	110.8623	110.02	110.7154	109.89
C19-C20-H22	111.60	110.09	110.8437	110.02	110.7532	109.89
H21-C20-H22	109.41	108.79	108.9957	109.14	109.2061	109.34
H24-N23-C26	119.95	-	121.0225	-	121.6729	-
H24-N23-C33	121.25	-	117.5714	-	116.7877	-
C26-N23-C33	118.79	-	121.406	-	121.5393	-
C30-N25-C35	120.84	-	120.3323	-	120.1751	-
C30-N25-C39	121.59	-	120.4862	-	120.388	-
C35-N25-C39	117.27	-	119.1806	-	119.4333	-
N23-C26-H27	118.57	-	115.9621	-	115.9921	-
N23-C26-C28	122.84	-	121.0742	-	121.0863	-
H27-C26-C28	118.59	-	122.9637	-	122.9216	-
C26-C28-H29	120.30	-	118.5208	-	118.5785	-
C26-C28-C30	119.41	-	119.9246	-	119.7603	-
H29-C28-C30	120.29	-	121.5546	-	121.6609	-
N25-C30-C28	121.60	-	121.5475	-	121.4613	-
N25-C30-C31	121.29	-	121.7464	-	121.666	-
C28-C30-C31	117.11	-	116.7061	-	116.8727	-
C30-C31-H32	120.26	-	121.4754	-	121.6278	-
C30-C31-C33	119.41	-	120.3556	-	120.2076	-
H32-C31-C33	120.33	-	118.1689	-	118.1644	-
N23-C33-C31	122.38	-	120.5333	-	120.5331	-
N23-C33-H34	118.81	-	114.1907	-	114.3328	-
C31-C33-H34	118.81	-	125.276	-	125.1341	-
N25-C35-H36	109.52	-	111.279	-	111.2295	-
N25-C35-H37	109.40	-	108.9513	-	109.015	-
N25-C35-H38	109.41	-	111.3199	-	111.2923	-
H36-C35-H37	109.46	-	108.1658	-	108.0831	-
H36-C35-H38	109.49	-	108.8154	-	108.9041	-
H37-C35-H38	109.56	-	108.2094	-	108.2159	-
N25-C39-H40	109.45	-	111.331	-	111.2042	-
N25-C39-H41	109.49	-	108.9678	-	109.0459	-
N25-C39-H42	109.45	-	111.4079	-	111.4478	-
H40-C39-H41	109.51	-	108.0661	-	107.8824	-
H40-C39-H42	109.50	-	108.84	-	108.9847	-

H41-C39-H42	109.42	-	108.1179	-	108.1624	-
Dihedral angle(°)						
C15-O1-C10-C11	−0.33	0.00	−0.0014	−0.00	0.0304	0.00
C15-O1-C10-C16	−178.75	179.99	179.9785	179.99	−179.8977	179.99
C10-O1-C15-N6	−178.88	179.96	179.9899	179.99	−180.0005	179.99
C10-O1-C15-C13	0.95	0.00	−0.0049	0.00	−0.0274	0.00
O2-N6-C15-O1	0.63	−0.09	−0.064	−0.01	0.0591	−0.02
O2-N6-C15-C13	−179.17	179.86	179.9297	179.98	−179.9083	179.97
O3-N6-C15-O1	179.65	179.91	179.9325	179.97	−179.9568	179.98
O3-N6-C15-C13	−0.15	−0.14	−0.0738	−0.03	0.0758	−0.03
C16-N7-N8-C18	−173.50	−179.99	−179.7651	−179.99	179.7559	−179.98
C16-N7-N8-C20	−3.62	−0.03	−0.1989	−0.01	0.4255	−0.02
N8-N7-C16-C10	178.73	179.99	−179.9992	−180.00	179.8967	179.99
N7-N8-C18-O4	−5.19	−0.03	−0.353	−0.01	0.1716	−0.01
N7-N8-C18-N9	175.12	179.98	179.6591	179.99	−179.7908	179.97
C20-N8-C18-O4	−176.62	−179.99	−179.9929	179.99	179.6108	−179.98
C20-N8-C18-N9	3.70	0.01	0.0192	0.00	−0.3516	0.00
N7-N8-C20-C19	−175.13	−179.97	−179.6574	−179.97	179.6547	−179.98
C18-N8-C20-C19	−4.24	−0.01	−0.0494	0.00	0.2604	−0.01
C19-N9-C18-O4	179.10	179.99	−179.9609	179.99	−179.6766	−180.00
C19-N9-C18-N8	−1.23	−0.01	0.0263	−0.01	0.2838	0.01
C18-N9-C19-O5	179.36	−179.98	179.9423	179.97	179.8931	−179.97
C18-N9-C19-C20	−1.58	0.00	−0.0591	0.02	−0.1132	−0.02
O1-C10-C11-C13	−0.35	−0.01	0.0068	0.00	−0.0223	−0.00
C16-C10-C11-C13	177.79	−179.99	−179.9706	−179.99	179.8961	179.99
O1-C10-C16-N7	2.62	0.02	0.1569	−0.00	0.3819	−0.00
C11-C10-C16-N7	−175.39	−179.99	−179.8678	179.99	−179.53	179.99
C10-C11-C13-C15	0.89	0.01	−0.0094	−0.00	0.0053	0.00
C11-C13-C15-O1	−1.163	−0.01	0.009	0.00	0.0137	−0.00
C11-C13-C15-N6	178.64	−179.96	−179.985	−179.99	179.9825	−179.99
O5-C19-C20-N8	−177.30	179.99	−179.9354	−179.97	179.8993	179.97
N9-C19-C20-N8	3.59	0.00	0.0659	−0.01	−0.0947	0.023
C33-N23-C26-C28	1.46	-	−0.0387	-	−0.137	-
C26-N23-C33-C31	−1.29	-	0.034	-	0.1875	-
C35-N25-C30-C28	−174.77	-	−179.925	-	−178.872	-
C35-N25-C30-C31	5.08	-	0.1406	-	1.1804	-
C39-N25-C30-C28	−1.22	-	0.4141	-	0.4241	-
C39-N25-C30-C31	178.63	-	−179.5203	-	−179.5234	-
N23-C26-C28-C30	0.25	-	−0.0344	-	−0.0989	-
C26-C28-C30-N25	177.80	-	−179.8317	-	−179.6804	-
C26-C28-C30-C31	−2.05	-	0.1059	-	0.2696	-
N25-C30-C31-C33	−177.65	-	179.8267	-	179.7285	-
C28-C30-C31-C33	2.20	-	−0.1107	-	−0.2213	-

Table S2. Theoretical and experimental vibrational wavenumbers (cm^{-1}) of NF-DMAP with PED using B3LYP functional.

Unscaled DFT	Scaled DFT	Raman	IR	Assignment
3292	3263		3134	R3[υ(NH)](95)
3276	3246			R2[υ(CH14)(94)+υ(CH12)(5)]
3248	3218	3135		R2[υ(CH12)(94)+υ(CH14)(5)]
3240	3210	3122		R3[υ(CH29)](91)+υ(CH27)(8)]
3238	3209	3102		R3[υ(CH32)](99)
3216	3187	3094		R3[υ(CH27)(91)+υ(CH29)(8)]
3156	3128	3072		υ(CH37)(51)+υ(CH41)(41)
3144	3115	2992	3119	υ(CH41)(51)+υ(CH37)(41)
3122	3094	2966	3101	R3[υ(CH34)](99)
3099	3071	2938	3080	υ(CH17)(99)

3077	3049			υ(CH36)(51)+υ(CH38)(48)
3071	3044	2912	3053	υ(CH40)(51)+υ(CH42)(47)
3065	3037	2885	2987	R1[$\upsilon_a(CH_2)$](99)
3025	2998	2870	2930	$\upsilon_s(C35H_3)$(81)+$\upsilon_s(C39H_3)$(17)
3024	2997	2851	2905	R1[$\upsilon_s(CH_2)$](99)
3019	2991	2826	2847	$\upsilon_s(C39H_3)$(81)+$\upsilon_s(C35H_3)$(17)
1784	1768		1736	R1[υ(C=O5)(38)+υ(C=O4)(37)+δ'_{ring}(9)+υ(CN9)(9)]
1705	1690		1716	R1[υ(C=O5)(39)+υ(C=O4)(35)+δ_{ring}(7)+υ(CN9)(12)]
1698	1683		1643	R3[υ(CC)(46)+δ_a(9)+δ_{in}(CH34)(9)+δ_{in}(CH27)(8)+υ(CN)(15)]
1629	1614			υ(CN)(40)+R2[υ(CC)](33)+ρ(CH17)(15)
1586	1572	1596	1593	R2[υ(CC)(41)+δ_{in}(CH12)(6)]+υ(CN)(18)+$\upsilon(NO_2)$(11)
1577	1563	1553	1562	R3[υ(C30N)(35)+υ(C28C30)(9)+δ_{in}(CH29)(7)+δ_{in}(CH34)(5)]
1559	1545			R3[υ(C33N)(13)+υ(C26N)(13)+υ(CC)(29)+δ_{in}(CN)(9)+δ_{in}(CH34)(7)+δ'_a(7)+δ_{in}(CH27)(6)]
1555	1541		1558	$\upsilon_a(NO_2)$(41)+υ(NO3)(30)+R2[υ(C10C11)](7)+ρ(NO2)(6)+υ(CN)(4)
1535	1521			R3[υ(CC)(49)+δ_{in}(CH29)(13)+δ_{in}(CH34)(6)+δ_{in}(CH32)(5)+υ(C30C31)(5)]+ $\delta'_a(C39H_3)$(9)
1527	1513	1512	1508	$\delta'_a(C35H_3)$(27)+$\delta'_a(C39H_3)$(16)+R3[δ_{in}(CH32)(11)+υ(C30C31)(6)+δ_{in}(CH27)(5)]+$\delta_a(C35H_3)$(9)+ $\delta_a(C39H_3)$(6)
1523	1509	1483		R2[υ(C13C15)(49)+δ_{ring}(12)]+υ(NO_2)(13)+R1[υ(NN)](5)+υ(CN)(5)
1507	1493			$\delta'_a(C39H_3)$(31)+$\delta'_a(C35H_3)$(27)+$\delta_a(C39H_3)$(10)+$\delta_a(C35H_3)$(8)
1501	1488		1481	$\delta_a(C35H_3)$(35)+$\delta_a(C39H_3)$(33)+$\delta'_a(C39H_3)$(11)+$\delta'_a(C35H_3)$(11)
1490	1476	1469		$\delta_a(C39H_3)$(34)+$\delta_a(C35H_3)$(32)+$\delta'_a(C39H_3)$(13)+$\delta'_a(C35H_3)$(12)
1485	1471		1468	$\delta_s(C35H_3)$(36)+$\delta_s(C39H_3)$(34)+R3[δ_{in}(CH32)](6)
1480	1467	1450	1456	R1[$\delta(CH_2)$](91)
1453	1440	1431		$\delta_s(C39H_3)$(49)+$\delta_s(C35H_3)$(47)
1419	1407			R2[υ(CC)(28)+υ(CO)(20)+δ_{in}(CH14)(11)+δ_{in}(CH12)(7)+δ_{in}(CC)(5)]+ρ(CH17)(6)
1417	1404		1433	R3[υ(C30N)](30)+$\delta_s(C35H_3)$(8)+$\delta_s(C39H_3)$(7)+δ(NC2)(6)+υ(C35N)(5)+υ(C39N)(5)
1394	1382	1400	1400	$\upsilon(NO_2)$(21)+R2[υ(CN)(10)+υ(C10C11)(21)]+δ(NO2)(7)+R1[υ(NN)](7)+ρ(CH17)(7)
1371	1359	1361	1385	R3[δ_{in}(CH)(59)+δ_{in}(CN)(10)]+ρ(NC_2)(9)+υ(CN25)(10)
1355	1343	1346		ρ(CH17)(36)+υ(NO_2)(14)+R2[υ(CN)(11)+υ(C10C11)(6)]+δ(NO_2)(5)
1344	1332		1358	R3[υ(CN23)(48)+υ(CC)(25)+δ_{in}(CH27)(5)]
1321	1309	1323	1325	R1[υ(C19N9)(35)+δ_{in}(C=O5)(11)+δ_{in}(C=O4)(7)+ω(CH_2)(7)+δ'_{ring}(6)+υ(C18N8)(6)+υ(CC)(5)]
1311	1299	1294	1300	R1[υ(NN)(20)+ω(CH_2)(17)+δ_{ring}(10)+υ(C19N9)(8)+υ(CC)(7)+υ(C20N8)(7)]+ρ(CH17)(7)
1300	1288	1273		R1[ω(CH_2)(24)+υ(NN)(18)+υ(CN)(20)+δ_{in}(NN)(7)]+δ(NNC)(7)
1283	1271			R2[υ(C11C13)(23)+υ(C10C16)(11)+υ(C10O)(10)+δ_{in}(CH12)(6)]+υ(NO_2)(14)
1255	1244	1249	1269	υ(CN)(38)+R3[δ_{in}(CH32)(10)+υ(C30C31)(9)+υ(C28C30)(8)+δ_{in}(CH29)(7)]+$\rho'(C35H_3)$(6)+$\rho'(C39H_3)$(6)
1253	1241	1238	1246	R2[υ(CO)](38)+δ'_{ring}(11)+υ(CN)(6)+υ(C10C11)(5)]+R1[υ(C18N9)](14)
1245	1234			R3[δ_{in}(CH27)(13)+δ_{in}(CH34)(10)+δ_{in}(CH32)(10)+δ_{in}(CH29)(10)+υ(C31C33)(5)]+R1[υ(C18N9)](10)
1235	1224			R1[υ(CN)(35)+δ_{in}(C=O4)(6)]+R2[υ(C15O)](5)
1202	1191	1214		$\rho'(C39H_3)$(23)+$\rho'(C35H_3)$(22)+$\rho(C39H_3)$(8)+$\rho(C35H_3)$(8)+$\delta(NC_2)$(6)+R3[δ_{trig}(6)+υ(C30N)(5)]
1194	1183	1197	1205	R2[δ_{in}(CH12)(32)+δ_{in}(CH14)(22)+υ(C10C11)(6)+υ(CN)(5)]+ρ(CH17)(5)
1177	1166	1172	1171	R1[$\gamma(CH_2)$](93)
1165	1154	1155		R1[υ(CN8)(47)+ω(CH_2)(15)+δ_{in}(NN)(6)+υ(NN)(5)+δ'_{ring}(5)]
1147	1136		1151	R3[δ_{in}(CH29)(16)+δ_{in}(CH34)(12)+δ_{in}(CH27)(12)+υ(CN)(19)+υ(CC)(20)+δ_{in}(CH32)(8)]
1142	1132	1116	1113	$\rho(C35H_3)$(35)+$\rho(C39H_3)$(32)+$\rho'(C35H_3)$(12)+$\rho'(C39H_3)$(12)
1131	1121			$\rho(C39H_3)$(36)+$\rho(C35H_3)$(32)+$\rho'(C39H_3)$(13)+$\rho'(C35H_3)$(12)
1080	1070			R3[υ(CN)(58)+δ_{in}(CH32)(10)+δ_{in}(CH29)(7)+υ(C31C33)(6)]
1076	1067		1069	$\rho'(C35H_3)$(21)+$\rho'(C39H_3)$(21)+υ(CN25)(34)+$\rho(C35H_3)$(8)+$\rho(C39H_3)$(7)
1051	1041	1060	1051	R3[oop(CH34)(82)+oop(CH32)(10)]

1037	1028	1028	1026	R2[δ_{in}(CH14)(35)+δ_{in}(CH12)(28)+υ(C11C13)(22)]
1022	1013	1000		R3[δ_{trig}(69)+υ(C28C30)(5)+υ(C30C31)(5)]
1008	998			R1[ρ(CH_2)(63)+oop(C=O5)(19)+τ(7)]
997	988	978		R2[υ(CO1)(54)+δ'$_{ring}$(12)+υ(C10C16)(7)+δ_{in}(CH14)(5)]
983	975		976	R2[δ_{ring}(40)+υ(CO1)(19)+υ(C13C15)(10)+υ(CN)(7)+υ(C10C11)](6)
977	968	964		R3[oop(CH27)(68)+oop(CH29)(20)+puck(7)]
957	948		962	υ(CN25)(46)+R3[υ(C28C30)(14)+υ(C30C31)(13)]+ρ'(C35H_3)(5)+ρ'(C39H_3)(5)
921	913	947	945	R1[υ(CC)(35)+δ_{in}(C=O4)(18)+υ(C20N8)(11)+δ_{in}(C=O5)(10)+ω(CH_2)(5)]
904	896	909	908	R2[oop(CH14)(61)+oop(CH12)(18)+τ(13)]
888	880	896	895	ω(CH17)(55)+τ(CN7)(28)+R2[oop(CH14)](8)
877	869			R2(δ'$_{ring}$)(16)+R1[υ(CC)(16)+δ'$_{ring}$(10)+υ(C18N8)(8)+υ(C20N8)(5)]+δ(NNC)(13)+δ_s(CH17)(9)
852	844		876	R3[oop(CH32)(73)+oop(CN)(10)+puck(7)+oop(CH34)(6)]
829	822	848	849	R3[oop(CH29)(64)+oop(CH27)(15)+oop(CN)(11)+puck(5)]
827	820	810	827	δ(NO_2)(52)+R2[δ'$_{ring}$(20)+δ_{ring}(6)]
813	806		816	R3(δ'$_a$)(39)+υ(N9H24)(13)+δ(NO_2)(8)+R2(δ_{ring})(5)
796	789			R2[oop(CH12)(72)+oop(CH14)(13)+τ'(5)]
784	777	786	783	R1[υ(C18N8)(23)+δ_{in}(C=O4)(9)+δ'$_{ring}$(5)]+R2[δ'$_{ring}$(11)+δ_{ring}(8)+υ(C10C16)(5)]+R3(δ'$_a$)(8)+δ(NO_2)(5)
767	760	770	770	R1[oop(C=O4)(73)+τ'(13)+τ(8)]
758	751	744	743	R3[δ_a(29)+υ(C28C30)(11)+υ(C30N)(10)+υ(C30C31)(7)]+υ(CN25)(29)
735	728	720	735	ω(CN6)(72)+R2[oop(CN)(13)+τ'(10)]
729	723	696		R3[puck(69)+oop(CN)(16)+oop(CH34)(7)+oop(CH27)(7)]
694	688			R1[δ_{ring}(20)+υ(C20N8)(15)+δ'$_{ring}$(15)+δ_{in}(C=O4)(9)+δ_{in}(NN)(7)+υ(C=O4)(5)]
694	688		692	R2[oop(CC)(35)+τ'(29)+τ(26)]
657	651	673		R1[δ_{ring}(19)+δ_{in}(C=O5)(18)+δ_{in}(C=O4)(16)+δ_{in}(NN)(8)+δ'$_{ring}$(6)]
626	620			R1[δ'$_{ring}$(37)+δ_{ring}(15)+υ(C18N9)(11)+υ(C=O5)(6)+δ_s(CH17)(5)]
593	587	645	644	R1[oop(C=O5)(51)+ρ(CH_2)(15)+τ(13)+γ(CH_2)(7)]+τ(C33NNC19)(9)
590	585	623	621	R2[τ(51)+τ'(26)+oop(CN)(17)]
557	552	582	602	ρ(NO_2)(36)+R2[δ_{in}(CN)(16)+δ_{in}(CC)(7)+R3(δ_a)(8)+δ(NC_2)(7)
554	549		581	R3(δ_a)(32)+δ(NC_2)(31)+ρ(NO_2)(8)
531	526	551		R3[oop(CN)(31)+puck(26)+τ_a(20)+oop(CH32)(8)+oop(CH29)(8)]
504	500	530	528	ρ(NC_2)(41)+R3[δ_{in}(CN)(27)+δ'$_a$(18)]
466	462	489	513	δ(NNC)(16)+R2[υ(CN)(14)+δ_{in}(CC)(11)+δ_{ring}(6)]+ρ(NO_2)(10)+R1[δ_{in}(C=O5)](7)+δ(NO_2)(6)
459	455		478	R1[δ_{in}(C=O5)(18)+δ_{in}(C=O4)(15)+υ(C18N9)(6)]+R2[δ_{in}(CC)](9)+δ_s(CH17)(7)+υ(N9H24)(6)+ρ(NO_2)(5)
436	433	468	465	R3[τ'$_a$(77)+oop(CH29)(7)+oop(CH34)(6)]
419	415	456	457	R2[υ(CN)(20)+δ_{ring}(7)]+R1[δ_{in}(C=O5)(17)+υ(CC)(6)]+δ(NO_2)(9)+υ(N9H24)(5)
395	391		424	δ(NC_2)(51)+R3[δ_a(18)+υ(C30N)(8)]+υ(N9H24)(5)
366	362		415	τ(CN7)(24)+R2[τ'(19)+τ(15)+oop(CC)(11)+oop(CN)(9)+oop(CH12)(5)]+ω(CH17)(9)
321	318	407	403	τ(NN)(50)+τ(CC)(12)+R1[oop(NN)(11)+τ'(10)]+τ(CN7)(7)
312	309	383		R3(δ'$_a$)(44)+ρ(NC_2)(34)+υ(N9H24)(12)
303	300		-	R1[δ_{in}(NN)(16)+δ_{in}(C=O4)(11)+υ(C18N8)(9)]+R2[δ_{in}(CC)(12)+δ_{in}(CN)(12)+υ(C10C16)(6)]+ρ(NO_2)(7)
286	284	315	-	R3[τ_a(45)+puck(7)]+ω(C30N)(31)+τ(C26NNC19)(7)
227	225	295	-	R2[δ_{in}(CN)(36)+υ(C10C16)(5)]+ρ(NO_2)(18)+δ_s(CH17)(12)
196	194		-	τ(C33NNC19)(32)+τ(C26NNC19)(20)+R1[τ'(17)+τ(16)]+R2[oop(CN)](8)
189	187	233	-	R1[τ'(31)+oop(NN)(8)]+R2[oop(CN)](26)+τ(CN7)(7)+τ(C33NNC19)(5)
178	177	203	-	τ(C35N)(35)+τ(C39N)(18)+τ(C26NNC19)(11)+τ(C30N)(9)+τ(C33NNC19)(8)
174	172		-	R1[τ'(41)+τ(30)+oop(NN)(8)]+τ(C33NNC19)(7)+τ(C26NNC19)(5)
157	156		-	R3[τ_a(40)+puck(7)]+τ(C26NNC19)(33)+ω(C30N)(13)+τ(C39N)(12)
148	147	150	-	R3[δ_{in}(CN)(52)+δ'$_a$(21)+υ(C26C28)(11)+υ(C31C33)(8)]+ρ(NC_2)(8)
143	141		-	δ(NNC)(22)+R1[δ_{in}(NN)](22)+R2[δ_{in}(CN)(15)+δ_{in}(CC)(10)]+δ(C19NN)(

				5)
123	122		-	τ(CN6)(20)+R2[oop(CN)(19)+oop(CC)(13)]+R1[oop(NN)](11)+ω(CH17)(6)+τ(CC)(5)
115	114		-	υ(N9H24)(84)
103	102	102	-	τ(C35N)(32)+ω(C30N)(27)+τ(C39N)(12)+τ(C26NNC19)(7)+τ(C33NNC19)(6)
94	93	92	-	τ(C33NNC19)(22)+τ(C39N)(18)+ω(C30N)(16)+τ(C26NNC19)(15)+τ(C18H24)(6)+τ(CN6)(6)
80	80		-	τ(C30N)(41)+τ(C39N)(31)+τ(C35N)(9)
65	65		-	τ(CN6)(33)+τ(C26NNC19)(16)+τ(C33NNC19)(9)+τ(C30N)(8)+R2[oop(CC)](7)
64	63	-	-	δ(C19NN)(61)+δ_s(CH17)(15)+R2[δ_{in}(CC)](15)+υ(N9H24)(13)+δ(NNC)(5)
39	38	-	-	τ(C33NNC19)(33)+τ(C26NNC19)(25)+R1[oop(NN)(13)+τ'(6)]+τ(C30N)(5)
37	36	-	-	τ(C33NNC19)(58)+τ(CC)(11)+τ(C18H24)(9)
28	28	-	-	τ(C33NNC19)(18)+ω(C30N)(16)+τ(CC)(15)+R3[puck(13)+τ_a(8)]+τ(C39N)(7)+τ(NN)(6)+τ(C18H24)(6)+τ(C35N)(5)
28	27	-	-	δ(C19NN)(20)+υ(N9H24)(17)+δ_s(CH17)(14)+R2[δ_{in}(CC)(11)+δ(NNC)(7)
19	19	-	-	R1[oop(NN)(67)+τ'(10)]+τ(NN)(5)
14	14	-	-	υ(N9H24)(76)+R3[δ'$_a$(33)+υ(C26C28)(9)+δ_{in}(CN)(9)+υ(C31C33)(8)+υ(C33N)(7)+υ(C26N)(5)]
10	10	-	-	τ(C18H24)(55)+R3[puck(20)+τ_a(8)+τ(C26NNC19)(5)]

Table S3. Theoretical and experimental vibrational wavenumbers (cm^{-1}) of NF-DMAP with PED using wB97X-D level of theory.

Unscaled DFT	Scaled DFT	Raman	IR	Assignment
3528	3458		3134	R3[υ(NH)](95)
3295	3229			R2[υ(CH14)](92)+R2[υ(CH12)](7)
3271	3206	3135		R2[υ(CH12)](92)+R2[υ(CH14)](7)
3266	3201	3122		R3[υ(CH29)](91)+R3[υ(CH27)](8)
3263	3198	3102		R3[υ(CH32)](99)
3241	3176			R3[υ(CH27)](91)+R3[υ(CH29)](8)
3183	3119	3094		υ(CH37)(60)+υ(CH41)(31)+υ(CH36)(3)+υ(CH38)(3)
3172	3108	3072	3119	υ(CH41)(59)+υ(CH37)(30)+υ(CH40)(4)
3131	3069	2992	3101	υ(CH17)(99)
3118	3055	2966	3080	R3[υ(CH34)](99)
3108	3046	2938		υ(CH36)(50)+υ(CH38)(47)
3105	3043	2912	3053	υ(CH40)(53)+υ(CH42)(43)
3096	3034	2885	2987	R1[$\upsilon_a(CH_2)$](100)
3048	2987	2870	2930	R1[$\upsilon_s(CH_2)$](99)
3046	2985	2851	2905	$\upsilon_s(C35H_3)$(75)+$\upsilon_s(C39H_3)$(23)
3041	2980	2862	2847	$\upsilon_s(C39H_3)$(75)+$\upsilon_a(C35H_3)$(22)
1833	1797		1736	R1[υ(C=O5)(38)+υ(C=O4)(37)+δ'$_{ring}$(9)+υ(C18N9)(5)]
1751	1716		1716	R1[υ(C=O5)(39)+υ(C=O4)(36)+δ_{ring}(6)+υ(C19N9)(6)+υ(C18N9)(6)]
1733	1698		1643	R3[υ(CC)(48)+δ_a(10)+δ_{in}(CH34)(10)+υ(CN23)(14)+δ_{in}(CH27)(8)]
1685	1652			υ(CN)(49)+R2[υ(C10C)](24)+ρ(CH17)(12)
1656	1623			$\upsilon_a(NO_2)$(69)+R2[υ(C13C15)](9)+$\rho(NO_2)$(8)
1628	1596			R2[υ(C13C15)(28)+υ(C10C11)(18)+δ_{in}(CH12)(6)]+$\upsilon(NO_2)$(23)+υ(CN)(12)
1605	1573	1596	1593	R3[υ(C30N)(36)+υ(C28C30)(15)+δ_{in}(CH29)(10)+υ(C26N)(7)]
1601	1569		1562	R3[υ(C30C31)(17)+υ(CN23)(29)+υ(C28C30)(9)+δ_{in}(CH34)(8)+δ_{in}(CN)(8)+δ'$_a$(8)]
1567	1535	1553	1558	R2[υ(CC)(58)+δ_{ring}(13)]+υ(CN)(6)+R1[υ(NN)](6)
1556	1525			R3[υ(CC)(56)+δ_{in}(CH29)(10)+δ_{in}(CH34)(8)+δ_{in}(CH32)(5)+δ_{in}(CH27)(5)]
1534	1504	1512	1508	δ'$_a(C35H_3)$(21)+δ'$_a(C39H_3)$(20)+$\delta_a(C39H_3)$(13)+$\delta_a(C35H_3)$(9)+R3[δ_{in}(CH

				32)(7)+δ_{in}(CH27)(5)]
1513	1483	1483	1481	δ_a(C39H$_3$)(24)+δ'_a(C35H$_3$)(22)+δ_a(C35H$_3$)(21)+δ'_a(C39H$_3$)(14)+ρ'(C35H$_3$)(5)
1509	1479	1469		δ'_a(C39H$_3$)(35)+δ_a(C39H$_3$)(30)+δ'_a(C35H$_3$)(12)+δ_a(C35H$_3$)(9)+ρ(C39H$_3$)(8)
1496	1466			δ_a(C35H$_3$)(40)+δ'_a(C35H$_3$)(26)+δ_a(C39H$_3$)(11)+δ'_a(C39H$_3$)(7)+ρ(C35H$_3$)(6)+δ_s(C39H$_3$)(5)
1491	1461		1456	R1[δ(CH$_2$)](80)
1490	1460	1450		δ_s(C39H$_3$)(39)+δ_s(C35H$_3$)(24)+δ_a(C35H$_3$)(7)+δ_a(C39H$_3$)(6)
1460	1431			R2[υ(CO1)(29)+υ(CN)(9)+υ(C10C11)(16)]+R1[δ(CH$_2$)](6)+υ(NO$_2$)(12)
1457	1428	1431	1433	δ_s(C35H$_3$)(51)+δ_s(C39H$_3$)(41)
1441	1412			R3[υ(C30N)(25)+δ_{in}(CH34)(6)+δ_{in}(CH27)(6)]+δ_s(C35H$_3$)(14)+υ(CN25)(10)+δ(NC2)(5)
1436	1408			υ(NO$_2$)(31)+R2[υ(C11C13)(19)+υ(CN)(9)+δ_{in}(CH14)(5)]+δ(NO$_2$)(9)+R1[υ(NN)](5)
1391	1363	1400	1400	R3[δ_{in}(CH34)(16)+δ_{in}(CH29)(12)+δ_{in}(CN)(11)+δ_{in}(CH27)(8)+δ_{in}(CH32)(7)]+υ(C39N)(7)+ρ(NC$_2$)(11)+υ(C35N)(8)
1380	1353	1361	1358	ρ(CH17)(20)+R1[υ(NN)(13)+υ(C18N8)(5)]+R2[υ(C10C11)(8)+δ_{in}(CH12)(5)]+υ(NO3)(6)
1368	1340	1346		R3[υ(CN23)](28)+R1[υ(C19N9)](13)+R3[υ(CC)](11)
1362	1335	1323	1325	R1[υ(C19N9)(23)+δ_{in}(C=O5)(7)+δ_{in}(C=O4)(5)+υ(CC)(5)+υ(C18N8)(3)]+R3[υ(C33N)(9)+υ(C26N)(8)+δ_{in}(CH27)(5)]
1349	1322	1294	1300	R1[υ(NN)(24)+υ(C20N8)(18)+δ_{ring}(6)+ω(CH$_2$)(5)]+ρ(CH17)(14)+δ(NNC)(7)+υ(CN)(5)
1334	1307	1273		R1[ω(CH$_2$)(28)+υ(C18N)(23)+υ(CC)(7)+υ(C19N9)(6)+υ(C20N8)(5)]
1306	1280			R2[υ(C11C13)(28)+υ(C10O)(19)+υ(C10C16)(10)+δ_{in}(CH14)(8)]+ρ(CH17)(8)
1300	1274		1269	R2[υ(CO1)(46)+δ'_{ring}(10)+υ(CN)(10)+υ(C11C)(11)]
1283	1258			υ(CN25)(34)+R3[δ_{in}(CH29)(14)+υ(CC30)(22)+υ(C26N)(5)]
1274	1248	1249	1246	R1[υ(CN9)](44)+ω(CH$_2$)(17)+δ_{in}(C=O4)(6)]
1251	1226	1238		R3[δ_{in}(CH27)(24)+δ_{in}(CH32)(24)+δ_{in}(CH34)(9)+υ(C33N)(6)+υ(C31C33)(6)]
1214	1190	1214	1205	R1[υ(CN8)(34)+ω(CH$_2$)(13)+υ(NN)(5)]+ρ(CH17)(8)+R2[δ_{in}(CH12)(6)+δ_{in}(CH14)(5)]
1210	1186	1197		ρ'(C35H$_3$)(19)+ρ'(C39H$_3$)(18)+ρ(C39H$_3$)(9)+ρ(C35H$_3$)(7)+δ(NC$_2$)(6)+R3(δ_{trig})(6)
1202	1178	1172	1171	R2[δ_{in}(CH12)(29)+δ_{in}(CH14)(17)+υ(C10C16)(5)+υ(CN)(5)]+R1[υ(CN8)(11)+ω(CH$_2$)(5)
1195	1171	1155		R1[γ(CH$_2$)](88)
1172	1148			R3[δ_{in}(CH29)(18)+υ(C26N)(16)+δ_{in}(CH34)(11)+δ_{in}(CH32)(11)+υ(C26C28)(19)+δ_{in}(CH27)(9)]
1153	1130		1151	ρ(C39H$_3$)(51)+ρ'(C39H$_3$)(22)+ρ(C35H$_3$)(14)+δ_a(C39H$_3$)(5)
1138	1116	1116	1113	ρ(C35H$_3$)(53)+ρ'(C35H$_3$)(22)+ρ(C39H$_3$)(11)+δ_a(C35H$_3$)(5)+ρ'(C39H$_3$)(5)
1095	1074			R3[υ(CN23)(45)+δ_{in}(CH32)(15)+υ(C31C33)(8)]+ρ'(C39H$_3$)(5)
1091	1069		1069	ρ'(C35H$_3$)(22)+ρ'(C39H$_3$)(21)+υ(CN25)(22)+ρ(C35H$_3$)(9)+ρ(C39H$_3$)(7)+R3[υ(C33N)](6)
1078	1057	1060	1051	R3[oop(CH34)(84)+oop(CH32)(8)]
1045	1024	1028	1026	R2[δ_{in}(CH14)(31)+δ_{in}(CH12)(27)+υ(C11C13)(21)+υ(C10O)(5)]
1031	1011	1000		R3[δ_{trig}(70)+υ(C28C30)(5)]
1023	1002			R2[υ(CO1)(42)+δ'_{ring}(15)+δ_{in}(CH14)(9)+υ(C10C16)(9)]
1021	1000			R1[ρ(CH$_2$)(63)+oop(C=O5)(19)+τ(7)]
1006	986	978		R2[δ_{ring}(40)+υ(CN)(9)+υ(CO1)(14)+υ(C13C15)(7)+δ_{in}(CH12)(6)]
1001	981		976	R3[oop(CH27)(72)+oop(CH29)(16)+puck(7)]
979	960	964	962	υ(CN25)(45)+R3[υ(C28C30)(14)+υ(C30C31)(13)]+ρ'(C35H$_3$)(5)
944	925	947	945	R1[υ(CC)(33)+δ_{in}(C=O4)(17)+δ_{in}(C=O5)(10)+υ(C20N8)(10)+ω(CH$_2$)(6)+υ(C18N8)(5)+υ(NN)(5)]
925	907	909	908	R2[oop(CH14)(63)+oop(CH12)(18)+τ(14)]
903	885	896	895	ω(CH17)(55)+τ(CN7)(30)+R2[oop(CH14)](5)
895	877		876	R1[υ(CC)(17)+δ'_{ring}(11)+υ(C18N8)(10)+υ(C20N8)(6)]+R2(δ'_{ring})(12)+δ(

				NNC)(12)+δ_s(CH17)(7)
859	842	848	849	R3[oop(CH32)(74)+oop(CN)(10)+puck(8)]
850	833			$\delta(NO_2)$(58)+R2[δ'_{ring}(20)+δ_{ring}(8)]
837	820	810	827	R3[oop(CH29)(65)+oop(CN)(12)+oop(CH27)(11)+puck(7)]
823	807		816	R2[oop(CH12)(73)+oop(CH14)(13)]
820	803			R3(δ'_a)(22)+υ(N9H24)(16)+R1[υ(C18N8)](7)+R2[δ'_{ring}(7)+δ_{ring}(6)]
800	784	786	783	R3(δ'_a)(16)+R1[υ(C18N8)(16)+δ_{in}(C=O4)(7)]+R2[δ'_{ring}(11)+δ_{ring}(7)+υ(C10C16)(5)]
781	765	770	770	R1[oop(C=O4)(72)+τ'(13)+τ(8)]
774	758			R3[δ_a(27)+υ(C28C30)(12)+υ(C30N)(10)+υ(C30C31)(6)]+υ(C35N)(13)+υ(C39N)(11)
752	737	744	743	ω(CN6)(71)+R2[oop(CN)(14)+τ'(11)]
739	724	720	735	R3[puck(68)+oop(CN)(16)+oop(CH34)(7)+oop(CH27)(7)]
709	695			R1[δ_{ring}(19)+δ'_{ring}(16)+υ(C20N8)(14)+δ_{in}(C=O4)(12)+δ_{in}(NN)(9)+δ_{in}(C=O5)(5)+υ(C=O4)(5)]
707	692	696		R2[oop(CC)(35)+τ'(33)+τ(24)]
666	653	673	692	R1[δ_{ring}(21)+δ_{in}(C=O5)(17)+δ_{in}(C=O4)(16)+δ'_{ring}(7)+δ_{in}(NN)(7)]
634	621	645		R1[δ'_{ring}(39)+δ_{ring}(15)+υ(C18N9)(11)+υ(C=O5)(6)]
607	595		644	R1[oop(C=O5)(51)+ρ(CH_2)(15)+τ(13)]+τ(C33NNC19)(10)
601	589	623	621	R2[τ(53)+τ'(25)+oop(CN)(17)]
565	554		602	ρ(NO_2)(44)+R2[δ_{in}(CN)(20)+δ_{in}(CC)(8)]
560	549	582	581	R3(δ_a)(39)+δ(NC=)(34)
539	528			R3[oop(CN)(29)+puck(26)+τ_a(20)+oop(CH32)(8)+oop(CH29)(8)]
512	502	551		ρ(NC_2)(41)+R3[δ_{in}(CN)(27)+δ'_a(16)]
474	464		513	R2[υ(CN)(17)+δ_{in}(CC)(8)+δ_{ring}(6)]+δ(NNC)(16)+R1[δin(C=O5)](11)+ρ(NO_2)(8)+δ(NO_2)(7)
467	457	489	478	R1[δ_{in}(C=O4)(17)+δ_{in}(C=O5)(14)+υ(C18N9)(5)]+R2[δ_{in}(CC)](12)+δ_s(CH17)(8)+ρ(NO_2)(6)+υ(N9H24)(6)
441	432	468	465	R3[τ'_a(75)+oop(CH29)(7)+oop(CH34)(6)]
427	419	456	457	R2[υ(CN)(21)+δ_{ring}(7)]+R1[δ_{in}(C=O5)(16)+υ(CC)(6)]+δ(NO_2)(8)+υ(N9H24)(5)
407	398			δ(NC_2)(48)+R3[δ_a(17)+υ(C30N)(7)]
372	364		424	τ(CN7)(24)+R2[τ'(19)+τ(15)+oop(CC)(12)+oop(CN)(9)+oop(CH12)(6)]+ω(CH17)(9)
319	312	407	403	R3[δ'_a(30)+δ_{in}(CN)(5)]+ρ(NC_2)(27)+υ(N9H24)(18)
310	304	383		R1[δ_{in}(NN)(16)+δ_{in}(C=O4)(10)+υ(C18N8)(7)]+R2[δ_{in}(CC)(12)+δ_{in}(CN)(11)+υ(C10C16)(7)]+ρ(NO_2)(6)
306	300		-	τ(NN)(51)+R1[oop(NN)(11)+τ'(10)]+τ(CC)(10)+ τ(CN7)(7)
294	288	315	-	R3[τ_a(38)+puck(6)]+ω(C30N)(25)+τ(C26NNC19)(6)+τ(C39N)(6)
231	226	295	-	R2[δ_{in}(CN)(37)+υ(C10C16)(5)]+ρ(NO_2)(17)+δ_s(CH17)(11)+υ(N9H24)(5)
200	196		-	τ(C39N)(45)+τ(C35N)(24)+τ(C30N)(7)+τ(C33NNC19)(6)+R3(τ'_a)(5)
197	193		-	τ(C33NNC19)(27)+R1[τ'(23)+oop(CN)(15)+τ(10)]+τ(C26NNC19)(14)
189	185		-	R2[oop(CN)](20)+R1[τ'(20)+τ(14)]+τ(C33NNC19)(18)+τ(C26NNC19)(8)+τ(CN7)(5)
169	166	233	-	R1[τ'(44)+τ(29)+oop(NN)(8)]+τ(C33NNC19)(8)+τ(C26NNC19)(5)
162	159		-	R3[τ_a(33)+puck(7)]+τ(C26NNC19)(30)+τ(C35N)(14)+τ(C39N)(8)
151	148	203	-	R3[δ_{in}(CN)(38)+δ'_a(15)+υ(C26C28)(9)+υ(C31C33)(6)+τ_a(5)]+τ(C26NNC19)(7)+ω(C30N)(7)+ρ(NC2)(6)
147	144		-	δ(NNC)(25)+R1[δ_{in}(NN)](20)+R2[δ_{in}(CN)(14)+δ_{in}(CC)(9)+δ(C19NN)(9)
121	119		-	υ(N9H24)(34)+ω(C30N)(20)+τ(C35N)(13)+τ(C39N)(12)
120	117		-	R1[oop(NN)](14)+τ(CN6)(13)+R2[oop(CC)(10)+oop(CN)(9)]+υ(N9H24)(10)+ω(CH17)(6)+τ(C18H24)(5)+τ(CN7)(5)
117	114	150	-	ω(C30N)(27)+υ(N9H24)(23)+τ(C39N)(20)+τ(C35N)(15)
95.7	93.8		-	τ(C33NNC19)(31)+τ(C26NNC19)(20)+τ(C30N)(17)+τ(C35N)(10)+τ(C39N)(7)
82.6	81		-	τ(C30N)(34)+τ(C35N)(19)+τ(C39N)(9)+τ(C18H24)(8)+R1[oop(NN)(6)+τ'(6)]
64.7	63.4		-	δ(C19NN)(58)+R2[δ_{in}(CC)](9)+δ_s(CH17)(8)+δ(C26NN)(8)+υ(N9H24)(7)
64.1	62.8	102	-	τ(CN6)(38)+R1[oop(NN)(11)+τ'(6)]+τ(C26NNC19)(10)+R2[oop(CC)](8)

39.6	38.8	92	-	τ(C33NNC19)(45)+τ(C26NNC19)(16)+R1[oop(NN)(15)+τ'(12)]
35.7	35		-	τ(C33NNC19)(29)+τ(C18H24)(19)+R1[oop(NN)(13)+τ'(12)]+τ(CC)(11)
29.7	29.1	-	-	τ(CC)(22)+τ(C18H24)(14)+R3[puck(8)+τ_a(6)]+R1(τ')(6)+τ(NN)(6)+ω(C30N)(6)+τ(C39N)(5)
28.6	28	-	-	δ(C19NN)(45)+δ(C26NN)(28)+υ(N9H24)(15)
18.3	17.9	-	-	R1[oop(NN)(49)+τ'(26)]+τ(C33NNC19)(17)
11.1	10.8	-	-	υ(N9H24)(85)+R3[δ'_a(17)+υ(C26C28)(5)]
9.05	8.87	-	-	τ(C18H24)(170)+R3(puck)(8)

Table S4. Theoretical and experimental vibrational wavenumbers (cm^{-1}) of NF with PED using B3LYP level of theory.

Unscaled DFT	Scaled DFT	Raman	IR	Assignment
3629	3560		3287	R1[υ(NH)](100)
3279	3216		3148	R2[υ(CH)](99)
3248	3186		3109	R2[υ(CH)](99)
3095	3036		3017	υ(CH)(99)
3076	3018			R1[$\upsilon_a(CH_2)$](100)
3034	2977			R1[$\upsilon_s(CH_2)$](98)
1871	1836		1805	R1[υ(C=O)(79)+δ'_{ring}(6)+υ(C10N)(9)]
1829	1795		1782	R1[υ(C=O)(78)+υ(C11N6)(7)]
1660	1629	1608	1728	υ(CN)(55)+ρ(CH)(15)+R2[υ(CC13)(15)+υ(C14C17)(6)]
1601	1571			R2[υ(CC)](46)+$\upsilon(NO_2)$(18)+υ(CN)(8)+$\rho(NO_2)$(5)
1577	1547	1563	1566	$\upsilon(NO_2)$(74)+R2[υ(C14C17)](8)
1526	1497	1492	1489	R2[υ(CC)(41)+δ_{ring}(13)+υ(CC13)(12)+υ(CN)(5)+υ(CN)(5)
1484	1456	1428	1435	R1[$\delta(CH_2)$](92)
1425	1398	1393	1381	R2[υ(CC)(23)+υ(CO)(27)+δ_{in}(CH)(15)+δ_{in}(CC)(5)]+ρ(CH)(6)
1403	1377	1378		ρ(CH)(12)+R1[υ(C10N7)(11)+$\omega(CH_2)$(8)+υ(NN)(6)]+R2[υ(CC)(18)+δ_{in}(CH23)(5)]
1375	1349	1348	1342	R1[δ_{in}(NH)(36)+υ(C11N6)(17)]+ρ(CH)(7)+$\upsilon(NO_2)$(7)
1363	1337			ρ(CH)(22)+$\upsilon(NO_2)$(30)+R2[υ(CN)(14)+υ(CC)(10)+δ_{in}(CH22)(5)]+$\delta(NO_2)$(10)
1346	1321	1323		R1[$\omega(CH_2)$(21)+δ_{in}(NH)(20)+υ(C10N)(23)]+ρ(CH)(5)
1323	1298			R1[υ(CN6)(26)+υ(CC)(19)+$\omega(CH_2)$(16)+δ_{in}(C=O)(14)+δ_{ring}(6)]
1287	1263	1258	1250	R2[υ(C16C17)(28)+υ(CC13)(11)+υ(C14O)(10)+δ_{in}(CH23)(7)]+$\upsilon(NO_2)$(15)+ρ(CH)(6)
1270	1246	1247		R1[υ(NN)(26)+υ(C12N7)(13)]+R2[υ(C15O)(11)+υ(C14O)(8)+δ_{in}(CH22)(5)+δ'_{ring}(5)]+δ(NNC)(6)
1248	1224	1235	1203	R2[υ(C15O)(34)+δ'_{ring}(10)+υ(CN)(8)+υ(C14C17)(5)+R1[υ(C12N7)(5)+υ(NN)(16)]
1209	1186			R1[$\omega(CH_2)$(23)+υ(CN7)(42)+υ(C11N6)(5)]
1192	1169	1169		R2[δ_{in}(CH)(52)+υ(CN)(9)+δ'_{ring}(7)+υ(C15O)(6)+υ(CC13)(5)]
1191	1169		1111	R1[$\gamma(CH_2)$](96)
1115	1093			R1[υ(CN6)(54)+δ_{in}(C=O1)(10)+δ_{in}(NH)(10)+υ(C12N7)(7)+υ(CC)(5)]
1038	1018	1017	1018	R2[δ_{in}(CH)(64)+υ(C16C17)(24)]
1015	995	993		R1[$\rho(CH_2)$(71)+oop(C=O2)(15)+τ(6)]
1000	981	977		R2[υ(CO)(53)+δ'_{ring}(13)+υ(C15O)(9)+υ(CC13)(8)]
986	968	963	964	R2[δ_{ring}(42)+υ(CO)(17)+υ(C15C16)(9)+υ(CN)(8)+υ(C14C17)(5)]
921	903	900	903	ω(CH)(54)+τ(CC)(24)+R2[oop(CH)](11)
904	887			R2[oop(CH)(78)+τ(12)]+ω(CH)(5)
892	875	870	872	R1[υ(CC)(54)+υ(C11N6)(18)]
879	862			R2[δ'_{ring}(17)+υ(CN7)](19)+δ'_{ring}(9)+υ(NN)(8)]+δ(NNC)(17)+δ_s(CH)(14)
830	815	809	825	$\delta(NO_2)$(59)+R2[δ'_{ring}(17)+δ_{ring}(7)]+$\upsilon(NO_2)$(9)
811	795	791		R2[oop(CH)](88)
786	771	783	779	R1[υ(C10N7)(22)+δ_{in}(C=O1)(5)]+R2[δ'_{ring}(15)+δ_{ring}(12)+δ'_{ring}(8)+υ(CC13)(7)]+$\delta(NO_2)$(5)
741	727		725	R1[oop(C=O1)(70)+τ'(13)+τ(8)]
738	724	713		ω(CN9)(65)+R2[oop(CN)(15)+τ'(10)]
690	677	685	687	R1(δ_{ring})(26)+υ(C12N7)(16)+δ_{in}(C=O)(17)+δ'_{ring}(10)+δ_{in}(NN)(10)+υ(CC

				)(5)]
688	675	673		R2[τ'(35)+oop(CC)(33)+τ(24)]
616	604	606	609	R1[δ_{in}(C=O)(32)+δ'_{ring}(15)+δ_{ring}(11)+δ_{in}(NN)(9)+υ(CN6)(8)]+δ(NNC)(6)
608	596	585		R1[oop(C=O2)(40)+oop(NH)(38)+τ(12)+ρ(CH_2)(7)]
602	591			R1[δ'_{ring}(25)+δ_{ring}(19)+υ(C10N6)(10)]+R2[υ(CC13)](5)
594	583	571		R2[τ(53)+τ'(24)+oop(CN)(17)]
555	544	551	548	R1[oop(NH)(53)+oop(C=O2)(27)+ρ(CH_2)(10)+γ(CH_2)(5)]
553	542			ρ(NO_2)(43)+R2[δ_{in}(CN)(20)+δ_{in}(CC)(10)+υ(C15C16)(5)+δ_{in}(C=O)(8)]
463	454	468	440	δ(NNC)(17)+R2[δ_{in}(CC)(15)+υ(CN)(11)+δ_{ring}(6)]+δ_s(CH)(6)+ρ(NO_2)(12)+R1[δ_{in}(NN)(5)+δ_{in}(C=O)(9)]
441	433		409	R2[υ(CN)(19)+δ_{in}(CC)(6)+δ'_{ring}(5)]+R1[δ_{in}(C=O)(19)+υ(C10N6)(5)+δ_{ring}(5)]+δ(NO_2)(8)+δ_s(CH)(6)
400	393	386		R1[δ_{in}(C=O)(43)+δ_{in}(C=O1)(10)+υ(C10N6)(6)+υ(CC)(6)+υ(C12N7)(5)]+R2[υ(CN)(11)+δ_{ring}(6)]
378	371		-	τ(CC)(28)+R2[τ'(17)+τ(13)+oop(CC)(10)+oop(CN)(8)]+ω(CH)(9)+R1[oop(NN)](6)
299	293	295	-	τ(NN)(41)+R1[oop(NN)(20)+τ(CC)(12)+τ'(9)]+τ(CC)(8)
293	287		-	R1[δ_{in}(NN)(18)+δ_{in}(C=O1)(17)+υ(C10N7)(6)]+R2[δ_{in}(CN)(13)+δ_{in}(CC)(12)+υ(CC13)(6)]+ρ(NO_2)(7)
222	217	202	-	R2[δ_{in}(CN)(33)+υ(CC13)(6)+δ_{ring}(5)]+ρ(NO_2)(17)+δ_s(CH)(12)
194	191	181	-	R2[oop(CN)(56)+oop(CC)(6)]+τ(NN)(13)+τ(CC)(7)
179	175		-	R1[τ'(77)+oop(NN)(16)]
142	139	-	-	R1[τ(54)+oop(NH)(36)]
137	134	-	-	R1[δ_{in}(NN)](30)+δ(NNC)(21)+R2[δ_{in}(CN)(18)+δ_{in}(CC)(13)]
121	118	-	-	R1[τ(34)+oop(NH)(21)+τ(CN)(10)+oop(NN)(5)]+R2[oop(CC)(10)+oop(CN)(9)]
75.8	74.3	-	-	R1[τ(CN)(43)+oop(NN)(31)+τ'(9)]
50.7	49.7	-	-	δ_s(CH)(36)+R2[δ_{in}(CC)(29)+δ_{in}(CN)(5)]+δ(NNC)(17)+R1[δ_{in}(NN)](6)
44.8	43.9	-	-	R1[oop(NN](30)+τ(CN)(20)+τ(CC)(18)+τ'(11)]+R2[oop(CC)](8)
24.7	24.2	-	-	R1[oop(NN)(37)+τ(CC)(19)+τ(5)]+τ(NN)(19)+τ(CC)(8)

Table S5. Theoretical and experimental vibrational wavenumbers (cm^{-1}) of NF with PED using wB97X-D level of theory.

Unscaled DFT	Scaled DFT	Raman	IR	Assignment
3682	3608		3287	R1[υ(NH)](100)
3305	3239			R2[υ(CH)](98)
3271	3205		3148	R2[υ(CH)](99)
3128	3066			υ(CH)(99)
3111	3049		3017	R1[υ_a(CH_2)](100)
3061	3000			R1[υ_s(CH_2)](100)
1921	1883		1805	R1[υ(C=O)(79)+δ'_{ring}(6)+υ(C10N)](9)
1877	1840		1782	R1[υ(C=O)(78)+υ(C11N6)(7)]
1724	1690		1728	υ(CN)(61)+R2[υ(CC13)](13)+ρ(CH)(12)
1673	1639		1566	υ(NO_2)(77)+ρ(NO_2)(8)+R2[υ(C15C16)](7)
1641	1608	1608	1520	R2[υ(CC)(55)+δ_{in}(CH)(10)]+υ(NO_2)(15)+υ(CN)(8)
1569	1538	1563	1489	R2[υ(CC)(45)+δ_{ring}(13)+υ(CC13)(12)+υ(CN)(5)]+υ(CN)(5)
1485	1455	1492		R1[δ(CH_2)](79)
1465	1436	1428	1435	R2[υ(CO)(28)+υ(CN)(8)+υ(CC)(12)+δ_{in}(CH22)(5)]+υ(NO_2)(10)+R1[δ(CH_2)](8)
1435	1406			υ(NO_2)(27)+R2[υ(CC)(15)+δ_{in}(CH)(9)]+δ(NO_2)(7)+ρ(CH)(7)+R1[υ(C10N7)](5)
1417	1389	1378	1381	R1[υ(C10N7)(13)+υ(C11N6)(8)+δ_{in}(NH)(7)+ω(CH_2)(7)]+υ(NO_2)(22)+R2[υ(CN)](7)+δ(NO_2)(6)
1393	1365	1348		R1[δ_{in}(NH)(21)+υ(C11N6)(19)]+ρ(CH)(20)+R2[υ(C14C17)](5)
1374	1346		1342	R1[δ_{in}(NH)(25)+υ(CN6)(27)+ω(CH_2)(7)]+ρ(CH)(15)
1353	1326	1323		R1[ω(CH_2)(21)+υ(CC)(17)+υ(CN6)(16)+δ_{ring}(7)+δ_{in}(C=O2)(7)+δ_{in}(NH)(5)]+ρ(CH)(10)
1319	1293			R2[υ(CO)(29)+δ'_{ring}(7)+δ_{in}(CH22)(6)]+R1[υ(C12N7)(12)+υ(NN)(12)]+δ(NN

				C)(5)
1310	1284			R2[υ(C16C17)(27)+υ(C14O)(11)+υ(CC13)(9)+δ_{in}(CH)(9)]+R1[υ(NN)(9)+υ(C12N7)(6)+ω(CH_2)(5)]+ρ(CH)(5)
1294	1269	1258	1250	R2[υ(CO)(33)+υ(C16C17)(10)+υ(CN)(7)+δ'_{ring}(7)]+R1[υ(NN)(12)+υ(C12N7)(11)]
1242	1217	1235	1203	R1[ω(CH_2)(33)+υ(C10N7)(18)+υ(C12N7)(13)+υ(NN)(7)+δ_{ring}(5)+υ(C11N6)(5)]
1203	1179	1169		R2[δ_{in}(CH)(60)+υ(CN)(9)+υ(CC13)(5)+δ'_{ring}(5)]
1201	1177			R1[γ(CH_2)](96)
1148	1125	1123	1111	R1[υ(CN6)(51)+δ_{in}(NH)(13)+δ_{in}(C=O1)(10)+υ(C12N7)(6)+υ(CC)(5)]
1046	1025	1017	1018	R2[δ_{in}(CH)(61)+υ(C16C17)(23)+υ(C15O)(6)]
1025	1005			R2[υ(CO)(42)+δ'_{ring}(15)+υ(CC13)(11)+δ_{in}(CH22)(5)]
1017	997	977		R1[ρ(CH_2)(71)+oop(C=O2)(16)+τ(6)]
1006	986		964	R2[δ_{ring}(38)+υ(CN)(10)+υ(CO)(13)+δ_{in}(CH)(11)+υ(C15C16)(12)]
926	907	-	903	ω(CH)(54)+τ(CC)(24)+R2[oop(CH)](11)
909	891	-		R1[υ(CC)(52)+υ(C11N6)(17)+δ_{in}(NH)(8)+δ_{in}(C=O)(6)]
909	891	-		R2[oop(CH)(76)+τ(13)]+ω(CH)(5)
895	877	-	872	δ(NNC)(17)+R2(δ'_{ring})(14)+δ_s(CH)(13)+R1[υ(CN7)(21)+δ'_{ring}(10)+υ(NN)(8)]
851	834	-	825	δ(NO_2)(61)+R2[δ'_{ring}(18)+δ_{ring}(9)]+υ(NO_2)(7)
815	798	-	779	R2[oop(CH)(85)+τ'(5)]
801	785	-		R1[υ(C10N7)(19)+δ'_{ring}(7)]+R2[δ'_{ring}(19)+δ_{ring}(11)+υ(CC13)(7)]+δ_s(CH)(5)
756	741	-		R1[oop(C=O1)(75)+τ'(12)+τ(8)]
749	734	-	725	ω(CN9)(68)+R2[oop(CN)(15)+τ'(10)]
704	690	-	687	R1[δ_{ring}(26)+υ(C12N7)(14)+δ_{in}(C=O1)(12)+δ'_{ring}(12)+δ_{in}(NN)(10)+δ_{in}(C=O2)(6)]
697	683	-		R2[τ'(39)+oop(CC)(32)+τ(22)]
626	613	-	609	R1[δ_{in}(C=O)(33)+δ'_{ring}(15)+δ_{ring}(11)+δ_{in}(NN)(10)+υ(CN6)(6)]+δ(NNC)(6)
613	601	-		R1[δ'_{ring}(26)+δ_{ring}(20)+υ(C10N6)(10)+υ(CC13)(5)]
607	595	-	548	R1[oop(C=O2)(46)+oop(NH)(27)+τ(12)+ρ(CH_2)(9)]
602	590	-		R2[τ(55)+τ'(22)+oop(CN)(17)]
561	550	-		ρ(NO_2)(44)+R2[δ_{in}(CN)(20)+δ_{in}(CC)(9)+υ(C15C16)(5)]+R1[δ_{in}(C=O)](8)
548	538	-		R1[oop(NH)(69)+oop(C=O2)(17)+ρ(CH_2)(8)]
469	460	-		δ(NNC)(17)+R2[δ_{in}(CC)(13)+υ(CN)(13)+δ_{ring}(7)]+ρ(NO_2)(11)+δ_s(CH)(5)+δ(NO_2)(5)+R1[δ_{in}(NN)(5)+δ_{in}(C=O)(9)]
449	440	-	440	R2[υ(CN)(17)+δ_{in}(CC)(9)+δ'_{ring}(5)]+R1[δ_{in}(C=O)](17)+δ_s(CH)(7)+δ(NO_2)(7)+ρ(NO_2)(5)
409	401	-	409	R1[δ_{in}(C=O)(45)+υ(CN6)(10)+υ(CC)(6)+υ(C12N7)(5)]+R2[υ(CN)(11)+δ_{ring}(6)]
383	375	-		τ(CC)(29)+R2[τ'(17)+τ(14)+oop(CC)(11)+oop(CN)(8)]+ω(CH)(9)
297	291	-	-	R1[δ_{in}(NN)(19)+δ_{in}(C=O1)(17)+υ(C10N7)(6)]+R2[δ_{in}(CN)(13)+δin(CC)(12)+υ(CC13)(6)]+ρ(NO_2)(7)
282	276	-	-	τ(NN)(45)+R1[oop(NN)(14)+τ(CC)(9)]+τ'(9)]+τ(CC)(8)+R2[oop(CC)](5)
225	220	-	-	R2[δ_{in}(CN)(33)+υ(CC13)(7)+δ_{ring}(5)]+ρ(NO_2)(17)+δ_s(CH)(12)
195	191	-	-	R2[oop(CN)(57)+oop(CC)(5)]+τ(NN)(14)+τ(CC)(6)
166	163	-	-	R1[τ'(77)+oop(NN)(10)+oop(NH)(7)]
139	136	-	-	R1[δ_{in}(NN)](30)+δ(NNC)(21)+R2[δ_{in}(CN)(18)+δ_{in}(CC)(13)]
137	135	-	-	R1[τ(54)+oop(NH)(32)+τ'(5)+oop(NN)(5)]
116	114	-	-	R1[τ(28)+oop(NH)(19)+τ(CN)(11)+oop(NN)(5)]+R2[oop(CC)(14)+oop(CN)(9)]+ω(CH)(5)
68.2	66.8	-	-	R1[τ(CN)(48)+oop(NN)(23)+τ'(12)]
51.1	50.1	-	-	δ_s(CH)(36)+R2[δ_{in}(CC)(30)+δ_{in}(CN)(5)]+δ(NNC)(16)+R1[δ_{in}(NN)](5)
34.5	33.8	-	-	R1[oop(NN)(35)+τ(CC)(19)+τ'(17)+τ(CN)(10)]+R2[oop(CC)](5)
13.12	12.9	-	-	R1[τ(24)+τ'(23)+τ(CC)(21)+oop(NH)(11)+ρ(CH_2)(7)]+τ(NN)(5)

Table S6. Geometrical parameters for intermolecular hydrogen bond in NF-DMAP.

D-H•••A	D-H (Å)	H•••A (Å) (Experimental)	H•••A (Å)	D-H•••A ( )	(r_H+ r_A) (Å)
			B3LYP		

N23-H24···N9	0.88540	1.881	1.86713	163.84932	2.75
C33-H34···O4	1.08944	3.483	2.09574	147.53862	2.72
			wB97X-D		
N23-H24···N9	0.88540	1.881	1.84679	159.65588	2.75
C33-H34···O4	1.09207	3.483	2.05102	152.06889	2.72

Table S7. Bond contributions to atomic net charges for NF-DMAP using QTAIM approach.

Atom	Net charge (B3LYP)	Net charge (wB97X-D)
O1	-1.0221	-1.0663
O2	-0.4450	-0.4492
O3	-0.4804	-0.4847
O4	-1.1818	-1.2144
O5	-1.1707	-1.2043
N6	0.33087	0.3652
N7	-0.6123	-0.6428
N8	-0.6597	-0.7273
N9	-1.1585	-1.2238
C10	0.4727	0.4895
C11	-0.0083	-0.0133
H12	0.0530	0.0614
C13	0.0422	0.0383
H14	0.0932	0.1023
C15	0.7960	0.8139
C16	0.5944	0.6227
H17	0.0238	0.0328
C18	1.6661	1.7524
C19	1.3889	1.4506
C20	0.2881	0.2964
H21	0.0368	0.0414
H22	0.0367	0.0418
N23	-1.2391	-1.3008
H24	0.5476	0.5632
N25	-1.1040	-1.1761
C26	0.4821	0.5009
H27	0.1040	0.1111
C28	-0.0017	-0.0099
H29	0.0515	0.0591
C30	0.4798	0.5049
C31	-0.0037	-0.0122
H32	0.0574	0.0659
C33	0.4504	0.4631
H34	0.2060	0.2242
C35	0.3423	0.3459
H36	0.0336	0.0388
H37	0.0359	0.0412
H38	0.0333	0.0383
C39	0.3441	0.3480
H40	0.0296	0.0344
H41	0.0374	0.0428
H42	0.0295	0.0337

Table S8. Second order perturbation theory analysis of Fock matrix in NBO Basis for NF-DMAP using B3LYP level of theory.

Donor NBO (i)	ED(i)/e	Acceptor NBO (j)	ED(j)/e	E(2)[a] (kcal mol^{-1})	E(j)-E(i)[b]	F(i,j)[c]
Within unit 1						

πO2-N6	1.98285	n(3) O3	1.49443	10.82	0.18	0.076
	1.98285	π*O2-N6	0.66923	7.99	0.31	0.055
πO4-C18	1.98661	n(2) N9	1.45527	6.07	0.18	0.055
πO5-C19	1.98618	n(2) N9	1.45527	7.04	0.17	0.058
πN7-C16	1.89113	π*C10-C11	0.34552	14.15	0.34	0.065
σN9-C19	1.98438	σ*O4-C18	0.01607	5.34	1.41	0.077
πC10-C11	1.73541	π*N7-C16	0.28629	16.03	0.28	0.060
	1.73541	π*C13-C15	0.33715	20.77	0.28	0.070
σC11-C13	1.96810	σ*N6-C15	0.09612	7.73	1.01	0.080
πC13-C15	1.77164	π*O2-N6	0.66923	26.22	0.17	0.067
	1.77164	π*C10-C11	0.34552	13.58	0.30	0.059
σC16-H17	1.97798	σ*O1-C10	0.02842	6.30	0.89	0.067
σC19-C20	1.97819	σ*N7-N8	0.02796	5.62	1.05	0.069
n(2) O1	1.70092	π*C10-C11	0.34552	30.45	0.35	0.094
	1.70092	π*C13-C15	0.33715	27.86	0.35	0.089
n(2) O2	1.89445	σ*O3-N6	0.05735	18.92	0.70	0.104
	1.89445	σ*N6-C15	0.09612	12.33	0.60	0.077
n(2) O3	1.89776	σ*O2-N6	0.05446	18.11	0.72	0.103
	1.89776	σ*N6-C15	0.09612	10.39	0.61	0.071
n(3) O3	1.49443	π*O2-N6	0.66923	148.50	0.14	0.134
n(2) O4	1.84683	σ*N8-C18	0.12005	30.80	0.61	0.123
	1.84683	σ*N9-C18	0.05551	18.12	0.75	0.107
n(2) O5	1.86694	σ*N9-C19	0.06213	20.98	0.75	0.114
	1.86694	σ*C19-C20	0.08917	23.05	0.59	0.105
n(1) N7	1.90957	σ*N8-C20	0.04237	12.85	0.71	0.086
	1.90957	σ*C16-H17	0.03258	10.71	0.76	0.082
n(1) N8	1.61375	π*O4-C18	0.37760	44.72	0.29	0.101
	1.61375	π*N7-C16	0.28629	47.36	0.26	0.102
	1.61375	σ*C20-H21	0.01935	5.52	0.65	0.059
	1.61375	σ*C20-H22	0.01938	5.51	0.65	0.059
n(1) N9	1.89294	σ*N8-C18	0.12005	7.92	0.73	0.068
	1.89294	σ*C19-C20	0.08917	8.18	0.72	0.069
n(2) N9	1.45527	π*O4-C18	0.37760	84.89	0.20	0.123
	1.45527	π*O5-C19	0.30419	76.95	0.22	0.123
From unit 1 to unit 2						
σC19-C20	1.97819	σ*N23-H24	0.04673	0.22	1.32	0.015
n(1) O4	1.97361	σ*C33-H34	0.02537	2.01	1.08	0.042
n(2) O4	1.84683	σ*C33-H34	0.02537	4.24	0.65	0.048
n(1) N9	1.89294	σ*N23-H24	0.04673	18.66	1.08	0.128
	1.89294	σ*N23-C26	0.02270	0.29	0.79	0.014
From unit 2 to unit 1						
σN23-C33	1.98544	σ*N9-C19	0.06213	0.06	1.40	0.008
n(1) N23	1.46730	n(2) N9	1.45527	0.33	0.14	0.008
Within unit 2						
σC26-H27	1.98021	σ*N23-C33	0.02138	4.85	1.03	0.063
πC26-C28	1.74299	n(1) N23	1.46730	175.49	0.02	0.081
	1.74299	π*N25-C30	0.60852	32.04	0.25	0.087
πC31-C33	1.71140	π*N25-C30	0.60852	35.87	0.24	0.090
σC33-H34	1.97733	σ*N23-C26	0.02270	5.38	1.00	0.066
n(1) N23	1.46730	π*C26-C28	0.24642	47.06	0.28	0.110
	1.46730	π*C31-C33	0.22656	44.58	0.29	0.110

[a]E(2) means the energy of hyper conjugative interaction (stabilization energy).
[b]Energy difference between donor (i) and acceptor (j) NBOorbitals.
[c]F(i, j) is the Fock matrix element between i and j NBOorbitals.

Table S9. Second order perturbation theory analysis of Fock matrix in NBO Basis for NF-DMAP using wB97X-D level of theory

Donor NBO (i)	**ED(i)/e**	**Acceptor NBO (j)**	**ED(j)/e**	**E(2) (kcal mol^{-1})**	**E(j)-E(i)**	**F(i,j)**

Within unit 1						
πO2-N6	1.98530	n(3) O3	1.48474	10.15	0.23	0.083
	1.98530	π*O2-N6	0.63129	6.44	0.44	0.057
πO5-C19	1.98898	n(2) N9	1.47983	6.43	0.21	0.064
πN7-C16	1.91512	π*C10-C11	0.31785	17.82	0.47	0.087
πC10-C11	1.77161	π*N7-C16	0.25016	18.32	0.42	0.078
	1.77161	π*C13-C15	0.31835	33.32	0.41	0.106
σC11-C13	1.96708	σ*N6-C15	0.09879	9.11	1.17	0.094
	1.96708	σ*C10-C16	0.03031	6.29	1.34	0.082
πC13-C15	1.80156	π*O2-N6	0.63129	31.36	0.27	0.092
	1.80156	π*C10-C11	0.31785	20.80	0.43	0.087
σC16-H17	1.97961	σ*O1-C10	0.02669	6.81	1.08	0.077
σC19-C20	1.97855	σ*N7-N8	0.02754	6.64	1.23	0.081
n(2) O1	1.69852	π*C10-C11	0.31785	46.46	0.48	0.134
	1.69852	π*C13-C15	0.31835	43.16	0.47	0.128
n(2) O2	1.89523	σ*O3-N6	0.05551	24.42	0.89	0.133
	1.89523	σ*N6-C15	0.09879	16.65	0.76	0.100
n(2) O3	1.89937	σ*O2-N6	0.05288	23.39	0.91	0.132
	1.89937	σ*N6-C15	0.09879	13.90	0.76	0.092
n(3) O3	1.48474	π*O2-N6	0.63129	227.86	0.22	0.205
n(2) O4	1.85021	σ*N8-C18	0.11312	37.83	0.78	0.155
	1.85021	σ*N9-C18	0.05497	22.71	0.91	0.132
n(2) O5	1.87078	σ*N9-C19	0.06078	26.32	0.92	0.141
	1.87078	σ*C19-C20	0.08618	28.89	0.75	0.133
n(1) N7	1.91476	σ*N8-C20	0.03824	14.80	0.89	0.104
	1.91476	σ*C16-H17	0.03071	13.13	0.92	0.100
n(1) N8	1.64528	π*O4-C18	0.36214	59.48	0.40	0.138
	1.64528	π*N7-C16	0.25016	64.40	0.38	0.143
	1.64528	σ*C20-H21	0.01898	6.90	0.79	0.072
	1.64528	σ*C20-H22	0.01895	6.88	0.79	0.072
n(1) N9	1.89543	σ*N8-C18	0.11312	9.62	0.90	0.083
	1.89543	σ*C19-C20	0.08618	10.00	0.89	0.084
n(2) N9	1.47983	π*O4-C18	0.36214	108.90	0.30	0.169
	1.47983	π*O5-C19	0.29508	105.07	0.32	0.173
From unit 1 to unit 2						
n(1) O4	1.97344	σ*C33-H34	0.02779	2.76	1.25	0.052
n(2) O4	1.85021	σ*C33-H34	0.02779	6.28	0.81	0.066
n(1) N9	1.89543	σ*N23-H24	0.04703	22.72	1.23	0.152
	1.89543	σ*N23-C26	0.02278	0.49	0.96	0.020
From unit 2 to unit 1						
σN23-C33	1.98514	σ*N9-C19	0.06078	0.07	1.59	0.010
n(1) N23	1.47046	n(2) N9	1.47983	0.51	0.14	0.010
Within unit 2						
πC26-C28	1.74641	n(1) N23	1.47046	134.80	0.04	0.104
	1.74641	n*(1) C30	0.88177	67.64	0.22	0.133
σC31-H32	1.97577	σ*N23-C33	0.02120	5.14	1.19	0.070
πC31-C33	1.71146	n(1) N23	1.47046	225.80	0.02	0.104
	1.71146	n*(1) C30	0.88177	79.94	0.21	0.138
σC33-H34	1.97770	σ*N23-C26	0.02278	6.19	1.18	0.076
n(1) N23	1.47046	π*C26-C28	0.24561	67.45	0.38	0.154
	1.47046	π*C31-C33	0.22544	63.30	0.39	0.153
n(1) N25	1.66604	σ*C35-H36	0.01339	6.01	0.79	0.067
	1.66604	σ*C35-H38	0.01374	6.28	0.79	0.069
	1.66604	σ*C39-H40	0.01331	5.84	0.79	0.066
	1.66604	σ*C39-H42	0.01446	6.67	0.79	0.071

Table S10. Calculated local reactivity properties of atoms of NF-DMAP by Hirshfeld derived charges.

Atom No.		f_k^+	S_k^+	ω_k^+	f_k^-	S_k^-	ω_k^-	f_k^0	S_k^0	ω_k^0	f_k^+/f_k^-	f_k^-/f_k^+
B3LYP												
O	1	0.0112	0.0035	0.0574	0.0373	−0.1455	0.1918	0.0243	0.0076	0.1246	0.2994	3.3399
O	2	0.0587	0.0184	0.3016	0.0883	−0.1440	0.4538	0.0735	0.0231	0.3777	0.6646	1.5046
O	3	0.0721	0.0226	0.3703	0.0956	−0.1591	0.4911	0.0838	0.0263	0.4307	0.7539	1.3264
O	4	0.0594	0.0187	0.3053	0.0051	−0.2097	0.0260	0.0323	0.0101	0.1657	11.7239	0.0853
O	5	0.1148	0.0360	0.5897	0.0283	−0.2092	0.1452	0.0715	0.0225	0.3674	4.0619	0.2462
N	6	−0.0109	−0.0034	−0.0563	0.0467	0.1247	0.2397	0.0179	0.0056	0.0917	−0.2347	−4.2612
N	7	0.0104	0.0033	0.0537	0.0456	−0.0620	0.2341	0.0280	0.0088	0.1439	0.2293	4.3617
N	8	0.1500	0.0471	0.7707	0.0174	−0.0985	0.0894	0.0837	0.0263	0.4301	8.6180	0.1160
N	9	0.1474	0.0463	0.7573	−0.0044	−0.2412	−0.0228	0.0715	0.0224	0.3672	−33.2030	−0.0301
C	10	−0.0205	−0.0064	−0.1054	−0.0496	0.0775	−0.2548	−0.0351	−0.0110	−0.1801	0.4137	2.4172
C	11	0.1057	0.0332	0.5431	0.0220	0.1944	0.1131	0.0639	0.0200	0.3281	4.8033	0.2082
H	12	0.0292	0.0092	0.1500	0.0249	−0.1097	0.1282	0.0271	0.0085	0.1391	1.1707	0.8542
C	13	0.0034	0.0011	0.0174	0.0683	−0.1784	0.3510	0.0359	0.0113	0.1842	0.0495	20.2160
H	14	0.0267	0.0084	0.1370	0.0161	0.0704	0.0826	0.0214	0.0067	0.1098	1.6575	0.6033
C	15	0.0936	0.0294	0.4807	0.0021	0.1139	0.0110	0.0479	0.0150	0.2458	43.5209	0.0230
C	16	0.1205	0.0378	0.6188	0.0600	−0.0452	0.3085	0.0903	0.0283	0.4636	2.0060	0.4985
H	17	0.0183	0.0058	0.0942	0.0166	0.0523	0.0851	0.0174	0.0055	0.0896	1.1075	0.9029
C	18	−0.0357	−0.0112	−0.1836	0.0033	0.2494	0.0168	−0.0162	−0.0050	−0.0834	−10.9330	−0.0915
C	19	−0.0178	−0.0056	−0.0914	0.0029	0.2052	0.0148	−0.0075	−0.0020	−0.0383	−6.1557	−0.1625
C	20	−0.0188	−0.0059	−0.0967	−0.0035	−0.0917	−0.0179	−0.0112	−0.0040	−0.0573	5.4109	0.1848
H	21	0.0292	0.0092	0.1502	0.0118	0.0633	0.0605	0.0205	0.0064	0.1053	2.4834	0.4027
H	22	0.0292	0.0092	0.1497	0.0117	0.0633	0.0602	0.0204	0.0064	0.1050	2.4872	0.4021
N	23	−0.0113	−0.0035	−0.0578	0.0528	−0.1540	0.2715	0.0208	0.0065	0.1068	−0.2131	−4.6936
H	24	−0.0140	−0.0044	−0.0719	0.0077	0.1336	0.0397	−0.0031	−1E−03	−0.0161	−1.8122	−0.5518
N	25	0.0167	0.0052	0.0856	0.0349	−0.1495	0.1793	0.0258	0.0081	0.1324	0.4776	2.0936
C	26	−0.0050	−0.0016	−0.0257	0.0806	0.0083	0.4140	0.0378	0.0119	0.1942	−0.0620	−16.1180
H	27	0.0002	5.3E−05	0.0009	0.0206	0.0654	0.1059	0.0104	0.0033	0.0534	0.0082	121.2940
C	28	0.0122	0.0038	0.0628	−0.0022	−0.0912	−0.0111	0.0050	0.0016	0.0259	−5.6620	−0.1766
H	29	0.0083	0.0026	0.0427	0.0204	0.0658	0.1046	0.0143	0.0045	0.0737	0.4079	2.4513
C	30	0.0050	0.0016	0.0258	0.0996	0.0511	0.5118	0.0523	0.0164	0.2688	0.0505	19.8091
C	31	0.0087	0.0027	0.0445	0.0154	−0.0968	0.0790	0.0120	0.0038	0.0617	0.5631	1.7760
H	32	0.0055	0.0017	0.0281	0.0213	0.0675	0.1097	0.0134	0.0042	0.0689	0.2562	3.9031
C	33	−0.0103	−0.0032	−0.0532	0.0353	0.0225	0.1812	0.0125	0.0039	0.0640	−0.2934	−3.4087
H	34	−0.0148	−0.0046	−0.0761	0.0134	0.0835	0.0690	−0.0007	−2E−04	−0.0035	−1.1028	−0.9068
C	35	−0.0033	−0.0010	−0.0171	−0.0092	−0.1093	−0.0471	−0.0062	−0.0020	−0.0321	0.3631	2.7537
H	36	0.0025	0.0008	0.0129	0.0133	0.0597	0.0685	0.0079	0.0025	0.0407	0.1882	5.3147
H	37	0.0080	0.0025	0.0410	0.0170	0.0604	0.0875	0.0125	0.0039	0.0643	0.4692	2.1314
H	38	0.0026	0.0008	0.0136	0.0138	0.0595	0.0707	0.0082	0.0026	0.0422	0.1926	5.1924
C	39	−0.0038	−0.0012	−0.0197	−0.0093	−0.1092	−0.0476	−0.0066	−0.0020	−0.0336	0.4132	2.4204
H	40	0.0043	0.0014	0.0221	0.0157	0.0582	0.0806	0.0100	0.0031	0.0513	0.2741	3.6488
H	41	0.0073	0.0023	0.0377	0.0169	0.0608	0.0871	0.0122	0.0038	0.0624	0.4330	2.3093
H	42	0.0045	0.0014	0.0232	0.0160	0.0581	0.0824	0.0103	0.0032	0.0528	0.2816	3.5509
wB97X-D												
O	1	0.2359	0.0341	0.5482	0.1668	−0.1169	0.3878	0.2014	0.0291	0.4680	1.4137	0.7074
O	2	0.0457	0.0066	0.1062	0.2443	−0.0876	0.5678	0.1450	0.0209	0.3370	0.1870	5.3488
O	3	0.0694	0.0100	0.1613	0.6639	−0.1556	1.5430	0.3666	0.0530	0.8521	0.1045	9.5685
O	4	0.0649	0.0094	0.1509	0.0245	−0.1009	0.0570	0.0447	0.0065	0.1039	2.6461	0.3779
O	5	0.0984	0.0142	0.2286	0.0378	−0.0995	0.0878	0.0681	0.0098	0.1582	2.6042	0.3840
N	6	0.3546	0.0512	0.8243	0.3679	−0.0379	0.8551	0.3613	0.0522	0.8397	0.9639	1.0374
N	7	0.0421	0.0061	0.0979	0.0812	−0.0398	0.1887	0.0616	0.0089	0.1433	0.5187	1.9278
N	8	0.2147	0.0310	0.4989	0.0232	−0.0504	0.0538	0.1189	0.0172	0.2764	9.2681	0.1079
N	9	0.1291	0.0186	0.3000	0.0240	−0.1199	0.0557	0.0765	0.0111	0.1778	5.3865	0.1857
C	10	−0.6214	−0.0900	−1.4442	0.1350	0.1080	0.3138	−0.2432	−0.0350	−0.5652	−4.6026	−0.2173
C	11	−0.4357	−0.0630	−1.0127	−0.2399	0.0750	−0.5577	−0.3378	−0.0490	−0.7852	1.8158	0.5507

H	12	0.5737	0.0829	1.3334	0.0549	−0.0546	0.1277	0.3143	0.0454	0.7305	10.4437	0.0958
C	13	0.5114	0.0739	1.1885	−0.0100	−0.1083	−0.0232	0.2507	0.0362	0.5827	−51.2370	−0.0195
H	14	0.0332	0.0048	0.0771	0.0429	0.0289	0.0998	0.0381	0.0055	0.0885	0.7728	1.2941
C	15	−0.4588	−0.0660	−1.0663	0.6887	0.0351	1.6007	0.1150	0.0166	0.2672	−0.6661	−1.5012
C	16	0.7930	0.1146	1.8432	−0.4633	−0.0342	−1.0768	0.1649	0.0238	0.3832	−1.7117	−0.5842
H	17	0.0309	0.0045	0.0719	0.0238	0.0220	0.0554	0.0274	0.0040	0.0636	1.2981	0.7704
C	18	−0.0274	−0.0040	−0.0636	−0.0136	0.1176	−0.0315	−0.0205	−0.0030	−0.0476	2.0199	0.4951
C	19	−0.0147	−0.0020	−0.0342	−0.0037	0.0975	−0.0087	−0.0092	−0.0010	−0.0214	3.9305	0.2544
C	20	−0.0007	−1E−04	−0.0016	−0.0321	−0.0430	−0.0745	−0.0164	−0.0020	−0.0380	0.0209	47.8507
H	21	0.0358	0.0052	0.0831	0.0094	0.0295	0.0218	0.0226	0.0033	0.0525	3.8043	0.2629
H	22	0.0357	0.0052	0.0831	0.0096	0.0295	0.0222	0.0226	0.0033	0.0526	3.7385	0.2675
N	23	−0.0108	−0.0020	−0.0251	−0.0044	−0.0640	−0.0101	−0.0076	−0.0010	−0.0176	2.4851	0.4024
H	24	−0.0121	−0.0020	−0.0281	−0.0064	0.0643	−0.0149	−0.0092	−0.0010	−0.0215	1.8889	0.5294
N	25	0.0153	0.0022	0.0355	0.0088	−0.0667	0.0204	0.0120	0.0017	0.0279	1.7412	0.5743
C	26	−0.0038	−6E−04	−0.0089	−0.0015	0.0167	−0.0035	−0.0027	−4E−04	−0.0062	2.5638	0.3901
H	27	0.0009	0.0001	0.0022	0.0015	0.0332	0.0035	0.0012	0.0002	0.0028	0.6267	1.5957
C	28	0.0117	0.0017	0.0272	0.0071	−0.0459	0.0164	0.0094	0.0014	0.0218	1.6535	0.6048
H	29	0.0084	0.0012	0.0195	0.0060	0.0330	0.0139	0.0072	0.0010	0.0167	1.4007	0.7139
C	30	0.0064	0.0009	0.0148	0.0039	0.0401	0.0091	0.0051	0.0007	0.0119	1.6224	0.6164
C	31	0.0084	0.0012	0.0196	0.0026	−0.0455	0.0060	0.0055	0.0008	0.0128	3.2462	0.3081
H	32	0.0051	0.0007	0.0120	0.0015	0.0346	0.0035	0.0033	0.0005	0.0077	3.3882	0.2951
C	33	−0.0090	−0.0010	−0.0210	−0.0083	0.0174	−0.0193	−0.0087	−0.0010	−0.0201	1.0880	0.9192
H	34	−0.0158	−0.0020	−0.0367	−0.0119	0.0428	−0.0277	−0.0138	−0.0020	−0.0322	1.3230	0.7559
C	35	−0.0034	−5E−04	−0.0080	−0.0018	−0.0521	−0.0042	−0.0026	−4E−04	−0.0061	1.9056	0.5248
H	36	0.0019	0.0003	0.0045	0.0002	0.0296	0.0005	0.0011	0.0002	0.0025	8.7727	0.1140
H	37	0.0080	0.0012	0.0185	0.0057	0.0297	0.0133	0.0068	0.0010	0.0159	1.3892	0.7198
H	38	0.0022	0.0003	0.0051	0.0004	0.0295	0.0010	0.0013	0.0002	0.0031	5.0227	0.1991
C	39	−0.0041	−6E−04	−0.0094	−0.0027	−0.0519	−0.0062	−0.0034	−5E−04	−0.0078	1.5321	0.6527
H	40	0.0038	0.0005	0.0088	0.0027	0.0289	0.0064	0.0033	0.0005	0.0075	1.3759	0.7268
H	41	0.0072	0.0010	0.0167	0.0048	0.0300	0.0112	0.0060	0.0009	0.0139	1.4875	0.6722
H	42	0.0045	0.0006	0.0104	0.0032	0.0287	0.0074	0.0038	0.0006	0.0089	1.4119	0.7082

Table S11. Calculated local reactivity properties of the atoms of NF using Hirshfeld derived charges.

Atom No.	f_k^+	S_k^+	ω_k^+	f_k^-	S_k^-	ω_k^-	f_k^0	S_k^0	ω_k^0	f_k^+/f_k^-	f_k^-/f_k^+
B3LYP											
1 O	0.0664	0.0179	0.4767	0.0436	0.0118	0.3128	0.0550	0.0148	0.3947	1.5242	0.6561
2 O	0.0558	0.0150	0.4004	0.0428	0.0115	0.3068	0.0493	0.0133	0.3536	1.3051	0.7662
3 O	0.0240	0.0065	0.1723	0.0351	0.0095	0.2520	0.0296	0.0080	0.2121	0.6839	1.4622
4 O	0.0580	0.0156	0.4165	0.1272	0.0343	0.9131	0.0926	0.0250	0.6648	0.4561	2.1927
5 O	0.0696	0.0188	0.4993	0.1322	0.0356	0.9484	0.1009	0.0272	0.7239	0.5265	1.8993
6 N	0.0248	0.0067	0.1783	0.0137	0.0037	0.0986	0.0193	0.0052	0.1385	1.8078	0.5532
7 N	0.0830	0.0224	0.5954	0.0166	0.0045	0.1192	0.0498	0.0134	0.3573	4.9968	0.2001
8 N	0.0588	0.0158	0.4217	0.0731	0.0197	0.5242	0.0659	0.0178	0.4730	0.8043	1.2433
9 N	0.0154	0.0041	0.1102	0.0693	0.0187	0.4975	0.0423	0.0114	0.3038	0.2215	4.5150
10 C	0.0260	0.0070	0.1864	0.0312	0.0084	0.2239	0.0286	0.0077	0.2052	0.8326	1.2011
11 C	0.0139	0.0037	0.0995	0.0160	0.0043	0.1145	0.0149	0.0040	0.1070	0.8690	1.1507
12 C	0.0172	0.0046	0.1236	0.0094	0.0025	0.0672	0.0133	0.0036	0.0954	1.8391	0.5437
13 C	0.0621	0.0168	0.4459	0.0510	0.0137	0.3658	0.0566	0.0152	0.4058	1.2190	0.8203
14 C	0.0486	0.0131	0.3485	0.0540	0.0146	0.3874	0.0513	0.0138	0.3679	0.8996	1.1117
15 C	0.0830	0.0224	0.5954	0.0375	0.0101	0.2693	0.0603	0.0162	0.4324	2.2108	0.4523
16 C	0.0494	0.0133	0.3546	0.0646	0.0174	0.4639	0.0570	0.0154	0.4092	0.7644	1.3082
17 C	0.0806	0.0217	0.5782	0.0482	0.0130	0.3456	0.0644	0.0174	0.4619	1.6730	0.5977
18 H	0.0240	0.0065	0.1720	0.0180	0.0049	0.1295	0.0210	0.0057	0.1508	1.3288	0.7526
19 H	0.0233	0.0063	0.1669	0.0110	0.0030	0.0793	0.0172	0.0046	0.1231	2.1064	0.4747
20 H	0.0233	0.0063	0.1670	0.0111	0.0030	0.0793	0.0172	0.0046	0.1231	2.1061	0.4748
21 H	0.0268	0.0072	0.1924	0.0283	0.0076	0.2034	0.0276	0.0074	0.1979	0.9459	1.0572
22 H	0.0307	0.0083	0.2202	0.0346	0.0093	0.2486	0.0327	0.0088	0.2344	0.8857	1.1290

23	H	0.0356	0.0096	0.2554	0.0315	0.0085	0.2261	0.0336	0.0090	0.2408	1.1295	0.8854
						wB97X-D						
1	O	0.0685	0.0091	0.2365	0.0349	0.0046	0.1206	0.0517	0.0069	0.1785	1.9618	0.5097
2	O	0.0529	0.0070	0.1828	0.0363	0.0048	0.1253	0.0446	0.0059	0.1541	1.4594	0.6852
3	O	0.0233	0.0031	0.0804	0.0385	0.0051	0.1330	0.0309	0.0041	0.1067	0.6044	1.6546
4	O	0.0530	0.0071	0.1831	0.1391	0.0185	0.4806	0.0961	0.0128	0.3319	0.3810	2.6248
5	O	0.0631	0.0084	0.2178	0.1437	0.0191	0.4964	0.1034	0.0137	0.3571	0.4388	2.2790
6	N	0.0218	0.0029	0.0754	0.0120	0.0016	0.0414	0.0169	0.0023	0.0584	1.8217	0.5489
7	N	0.0887	0.0118	0.3065	0.0148	0.0020	0.0511	0.0518	0.0069	0.1788	5.9989	0.1667
8	N	0.0628	0.0084	0.2170	0.0756	0.0100	0.2610	0.0692	0.0092	0.2390	0.8315	1.2026
9	N	0.0121	0.0016	0.0419	0.0775	0.0103	0.2676	0.0448	0.0060	0.1548	0.1566	6.3869
10	C	0.0250	0.0033	0.0864	0.0238	0.0032	0.0822	0.0244	0.0032	0.0843	1.0510	0.9515
11	C	0.0123	0.0016	0.0426	0.0109	0.0015	0.0376	0.0116	0.0015	0.0401	1.1353	0.8808
12	C	0.0166	0.0022	0.0574	0.0078	0.0010	0.0269	0.0122	0.0016	0.0421	2.1361	0.4681
13	C	0.0606	0.0081	0.2092	0.0454	0.0060	0.1567	0.0530	0.0070	0.1830	1.3346	0.7493
14	C	0.0500	0.0066	0.1726	0.0599	0.0080	0.2070	0.0550	0.0073	0.1898	0.8339	1.1993
15	C	0.0875	0.0116	0.3023	0.0371	0.0049	0.1283	0.0623	0.0083	0.2153	2.3562	0.4244
16	C	0.0470	0.0063	0.1623	0.0691	0.0092	0.2388	0.0581	0.0077	0.2006	0.6798	1.4710
17	C	0.0902	0.0120	0.3115	0.0445	0.0059	0.1537	0.0673	0.0090	0.2326	2.0266	0.4934
18	H	0.0230	0.0031	0.0794	0.0160	0.0021	0.0554	0.0195	0.0026	0.0674	1.4324	0.6981
19	H	0.0233	0.0031	0.0804	0.0094	0.0013	0.0325	0.0164	0.0022	0.0565	2.4723	0.4045
20	H	0.0233	0.0031	0.0805	0.0094	0.0013	0.0326	0.0164	0.0022	0.0565	2.4712	0.4047
21	H	0.0266	0.0035	0.0918	0.0269	0.0036	0.0930	0.0267	0.0036	0.0924	0.9875	1.0127
22	H	0.0308	0.0041	0.1065	0.0359	0.0048	0.1239	0.0334	0.0044	0.1152	0.8592	1.1639
23	H	0.0376	0.0050	0.1300	0.0314	0.0042	0.1085	0.0345	0.0046	0.1192	1.1981	0.8347