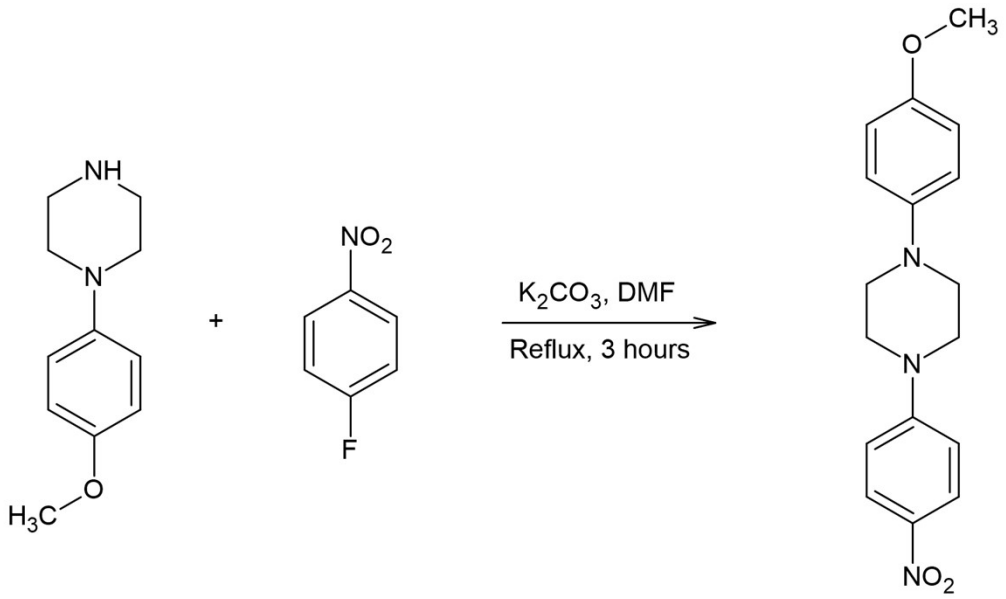
Supplementary Information

Mechanoluminescence and Nonlinear Optical Properties of a Self-Assembled Piperazine-Based Supramolecular System: Structural Insights and Computational Analysis



Scheme 1. Synthesis of 1-(4-methoxyphenyl)-4-(4-nitrophenyl)piperazine (MPNPP)

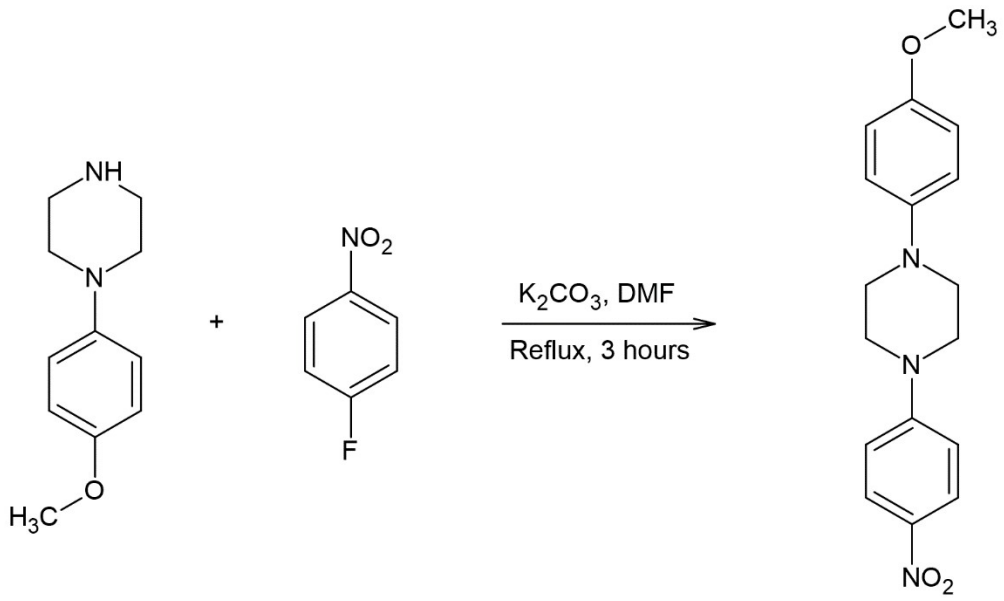


Figure S1. Synthetic scheme of 1-(4-methoxyphenyl)-4-(4-nitrophenyl)piperazine (MPNPP)

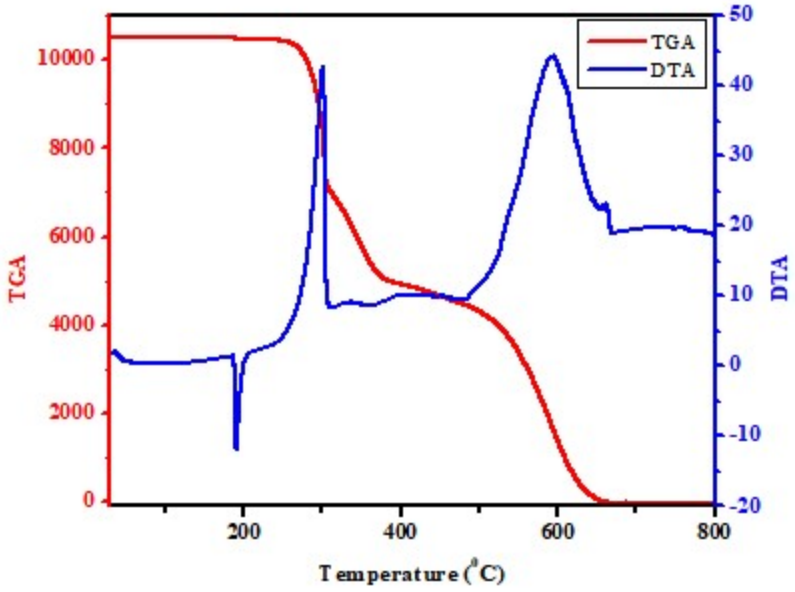


Figure S2. H-BDE (violet color) and BDE (light blue color) values for MPNPP molecule.

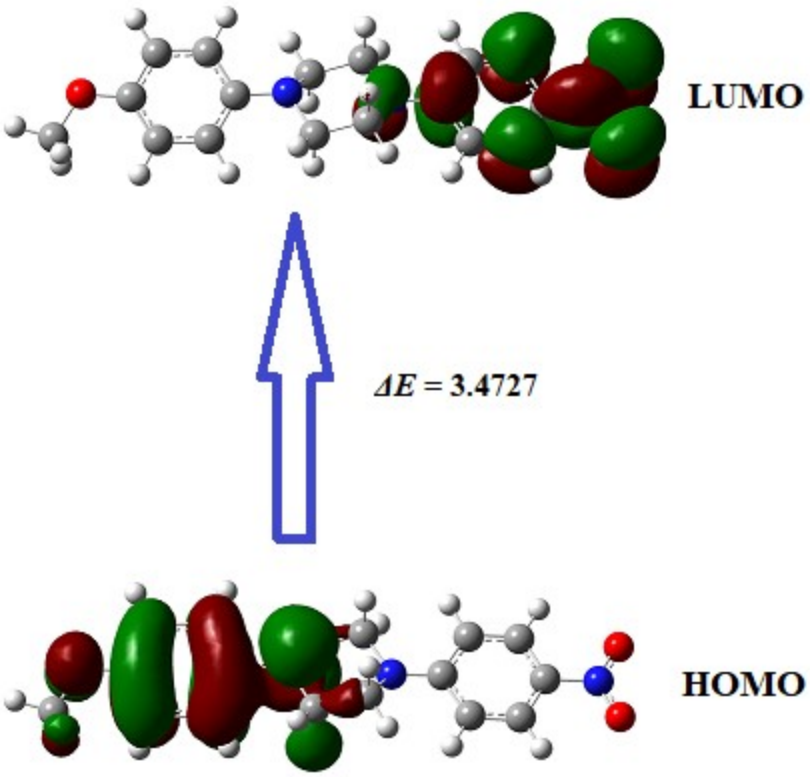


Figure S3. HOMO-LUMO plots of MPNPP molecule.

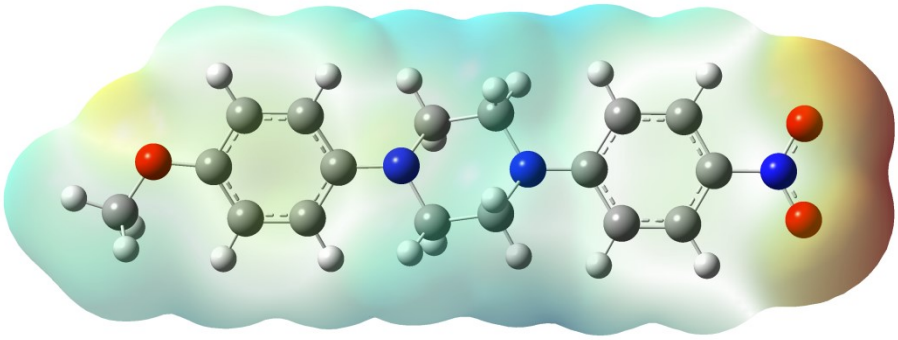
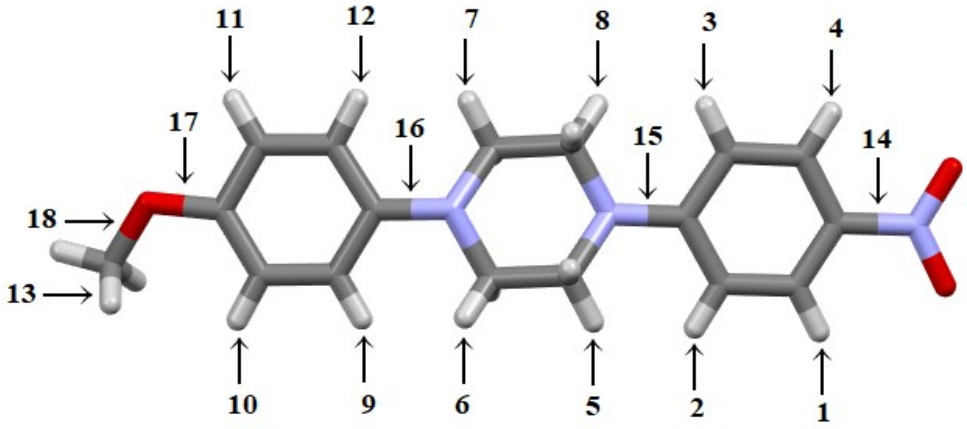


Figure S4. MEP plot of MPNPP molecule.



Bond	BDE [kcal/mol]
1.	112.29
2.	108.34
3.	108.39
4.	112.39
5.	96.42
6.	97.86
7.	96.78
8.	96.37
9.	108.98
10.	109.61
11.	112.20
12.	109.05
13.	94.33
14.	69.77
15.	87.40
16.	84.19
17.	90.35
18.	67.76

Figure S5. H-BDE (violet color) and BDE (light blue color) values for MPNPP molecule.

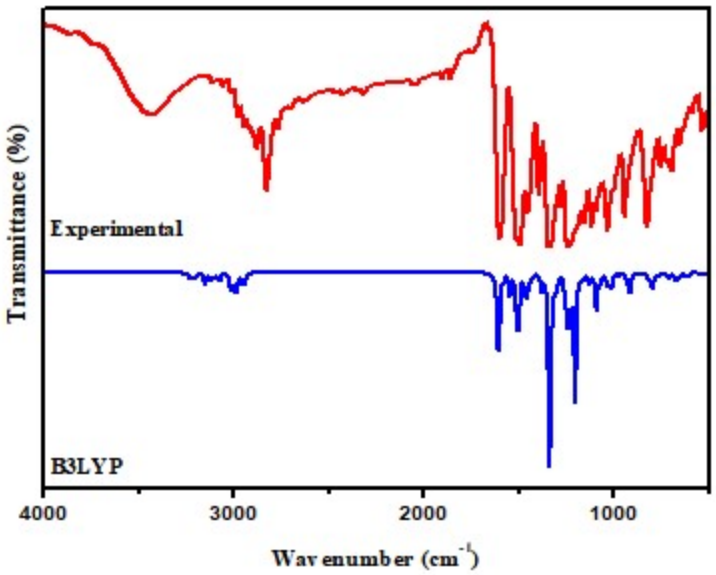


Figure S6. Infrared spectrum of MPNPP using (a) DFT/B3LYP/6–311 G (d,p) and (b) experimental data.

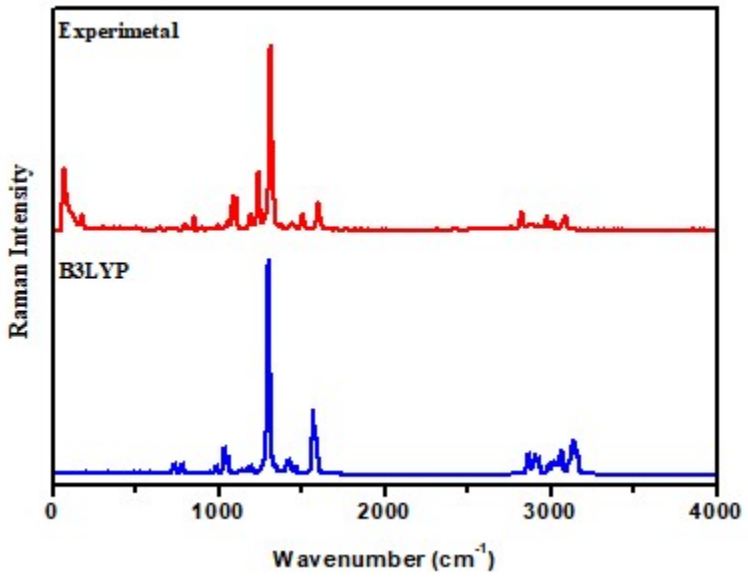


Figure S7. Raman spectrum of MPNPP using (a) DFT/B3LYP/6–311 G (d,p) and (b) experimental data.

Table S1.

Geometrical parameters of the MPNPP compound.

Bond length (Å) DFT/XRD			
C1-N37	1.460/1.443(5)	C6-N38	1.389/1.376(4)
N37-O40	1.229/1.231(5)	C23-N39	1.423/1.417(4)
N37-O41	1.229/1.206(4)	N38-C11	1.467/1.455(4)
C1-C2	1.395/1.377(5)	C17-N38	1.462/1.464(4)
C2-C4	1.381/1.368(5)	C11-C14	1.526/1.501(5)
C4-C6	1.416/1.405(4)	C14-N39	1.455/1.462(4)
C6-C7	1.414/1.401(5)	N39-C20	1.464/1.454(4)
C7-C9	1.385/1.363(5)	C20-C17	1.526/1.493(4)
C9-C1	1.391/1.363(5)	C28-C29	1.392/1.383(5)
C23-C24	1.407/1.391(4)	C29-C31	1.400/1.367(4)
C24-C26	1.382/1.377(5)	C31-C23	1.395/1.394(4)
C26-C28	1.401/1.375(4)	C28-O42	1.367/1.381(4)
		O42-C33	1.419/1.412(4)
Bond angle (º) DFT/XRD			
O40-N37-O41	124.12/122.1(4)	C14-N39-C23	117.44/115.0(3)
C1-N37-O40	117.95/117.8(4)	C20-N39-C23	115.75/116.1(2)
C1-N37-O41	117.91/120.1(4)	C28-O42-C33	118.33/117.3(3)
C2-C1-C9	120.42/119.4(3)	C29-C28-C26	119.03/118.2(3)
C17-N38-C11	112.43/110.8(3)	C6-N38-C11	119.87/120.8(3)
C20-N39-C14	110.19/109.9(3)	C20-N39-C14	110.19/115.0(3)
C6-N38-C17	119.79/120.8(3)	N38-C17-C20	110.94/111.6(3)
N-38-C11-C14	111.68/110.7(3)	N39-C20-C17	111.30/112.8(3)
N-39-C11-C14	110.19/112.9(3)	C26-C28-O42	115.90/126.2(3)
C29-C28-O42	125.05/126.2(3)	C9-C1-N37	119.80/121.0(4)
C2-C1-N37	119.77/119.5(4)		
Torsion angle (º) DFT/XRD			
C2-C1-N37-O40	178.97/176.4(4)	C2-C1-N37-O41	-0.99/-3.5(5)
C17-N38-C6-C7	1.65/33.6(5)	C11-N38-C6-C7	-145.07/-179.7(3)
C17-N38-C6-C4	-176.46/-149.3(3)	C11-N38-C6-C4	36.80/-2.6(5)
C20-N39-C23-C31	120.60/-172.5(3)	C20-N39-C23-C24	-61.19/9.5(4)
C14-N39-C23-C24	165.78/139.8(3)	C14-N39-C23-C31	-12.42/-42.3(4)
C26-C28-O42-C33	179.65/-11.6(5)	C14-N39-C20-C17	-58.83/53.4(4)
C11-N38-C17-C20	-52.0/55.2(4)	C20-N39-C14-C11	58.75/-54.1(4)
N38-C17-C20-N39	54.97/-54.9(4)		

Table S2.

The energy values of global reactivity descriptors (E_{HOMO}, E_{LUMO}, E_{HOMO} - E_{LUMO}, Ionization potential (I), electron affinity (A), electro negativity (χ), global hardness (η), chemical softness (ν), chemical potential (μ), electrophilicity index (ω), electron donating capability (ω^-), electron accepting capability (ω^+), energy change (ΔE) and Maximal charge acceptance (ΔN_{max})) for MPNPP compound.

Parameter	Values (in eV)
SCF energy (a.u)	-1049.3224a.u.
E_{HOMO} (MO:83)	-5.6327
E_{LUMO} (MO:84)	-2.1600
E_{HOMO} - E_{LUMO} (eV)	3.4727
Ionization potential (I)	5.6327
Electron affinity (A)	2.1600
Electronegativity (χ)	3.8963
Global hardness (η)	1.7363
Chemical softness (ν)	0.5759
Chemical potential (μ)	-3.8963
Electrophilicity index (ω)	4.3716
Electron donating capability (ω^-)	6.5369
Electron accepting capability (ω^+)	2.6405
Energy change (ΔE)	-4.3716
Maximal charge acceptance (ΔN_{max})	-2.2440

Table S3.
Second-order perturbation theory analysis of Fock matrix in NBO basis corresponding to the intramolecular bonds of the title compound

Donor(i)	Type	ED/e	Acceptor(j)	Type	ED/e	E(2)[a]	E(j)-E(i)[b]	F(i,j)[c]
C1-N37	σ	1.98874	C1-C2	σ*	0.02276	0.71	1.36	0.028
			C1-C9	σ*	0.02252	0.74	1.37	0.029
			C2-C4	σ*	0.01306	1.37	1.40	0.039
C6-C7	σ	1.97212	C4-C6	σ*	0.02360	3.36	1.24	0.058
			C6-N38	σ*	0.03098	1.60	1.15	0.038
C6-C7	π	1.60191	C1-C9	π*	0.40836	27.94	0.28	0.079
			C2-C4	π*	0.28543	14.35	0.29	0.059
			C11-N38	σ*	0.02784	1.08	0.59	0.025
C11-C14	σ	1.98094	C6-N38	π*	0.03098	2.73	1.08	0.049
			C23-N39	π*	0.03237	2.83	1.05	0.049
C17-C20	σ	1.98068	C6-N38	σ*	0.03098	2.86	1.08	0.050
			C23-N39	σ*	0.03237	2.61	1.05	0.047
C23-C24	σ	1.97177	C14-N39	σ*	0.02338	2.58	1.04	0.046
			C23-C31	σ*	0.02670	3.83	1.27	0.062
			C23-N39	σ*	0.03237	1.24	1.11	0.033
C23-C31	σ	1.97343	C20-N39	σ*	0.02575	1.59	1.04	0.036
			C23-C24	σ*	0.02416	3.95	1.26	0.063
			C29-C31	σ*	0.01424	3.15	1.26	0.056
C23-C31	π	1.69251	C20-N39	σ*	0.02575	2.06	0.59	0.034
			C24-C26	π*	0.30950	18.99	0.29	0.066
			C28-C29	π*	0.38368	18.04	0.28	0.065
C28-C29	σ	1.97674	C26-C28	σ*	0.02310	4.18	1.27	0.065
			C29-C31	σ*	0.01424	3.74	1.26	0.061
C28-C29	π	1.68448	C23-C31	π*	0.37758	19.71	0.29	0.069
			C24-C26	π*	0.30950	17.63	0.30	0.064
N37-O40	σ	1.99572	C1-C2	σ*	0.02276	0.77	1.63	0.032
			C1-N37	σ*	0.09787	0.80	1.37	0.030
N37-O41	σ	1.99574	C1-C9	σ*	0.02252	0.76	1.63	0.032
			C1-N37	σ*	0.09787	0.80	1.37	0.030
N37-O41	π	1.98642	C1-C9	π*	0.40836	4.10	0.46	0.043
			N37-O41	π*	0.64756	7.94	0.31	0.054
N38	σ	1.73864	C6-C7	σ*	0.02440	1.30	0.80	0.031
			C6-C7	π*	0.41121	35.63	0.28	0.093
			C11-C14	σ*	0.01631	1.69	0.64	0.031
			C17-C20	σ*	0.01643	1.67	0.64	0.031
N39	σ	1.83014	C11-C14	σ*	0.01631	1.58	0.65	0.030
			C17-C20	σ*	0.01643	1.49	0.65	0.029
			C23-C24	σ*	0.02416	1.15	0.84	0.029
			C23-C31	σ*	0.02670	3.63	0.85	0.051
			C23-C31	π*	0.37758	16.35	0.31	0.067
O40	σ	1.98207	C1-N37	σ*	0.09787	4.25	1.09	0.062

			N37-O41	σ*	0.05509	2.24	1.23	0.047
O40	π	1.90196	C1-N37	σ*	0.09787	11.39	0.58	0.073
			N37-O41	σ*	0.05509	18.93	0.72	0.105
O40	n	1.46643	N37-O41	π*	0.64756	159.34	0.14	0.137
O41	σ	1.98208	C1-N37	σ*	0.09787	4.25	1.09	0.062
			N37-O40	σ*	0.05503	2.23	1.23	0.047
O41	π	1.90220	C1-N37	σ*	0.09787	11.37	0.58	0.073
			N37-O40	σ*	0.05503	18.92	0.72	0.105
O42	σ	1.96332	C28-C29	σ*	0.02957	6.88	1.09	0.077
O42	π	1.84856	C28-C29	π*	0.38368	29.03	0.34	0.094

[a]E(2) means energy of hyper-conjugative interactions (stabilization energy in kJ/mol)

[b] Energy difference (a.u) between donor and acceptor i and j NBO orbitals

[c] F(i,j) is the Fock matrix elements (a.u) between i and j NBO orbitals

Table S4.

NBO results showing the formation of Lewis and non-Lewis orbitals.

Bond(A-B)	ED/e[a]	EDA%	EDB%	NBO	s%	p%
σC1-N37	1.98874	37.13	62.87	$0.6093(sp^{3.09})C+$	24.40	75.48
	-0.81676			$0.7929(sp^{1.74})C$	36.50	63.47
σC6-C7	1.97212	50.96	49.04	$0.7139(sp^{1.80})C+$	35.69	64.27
-	-0.71395	-	-	$0.7003(sp^{1.88})C$	34.71	65.22
πC6-C7	1.60191	44.69	55.31	$0.6685(sp^{99.99})C+$	0.01	99.94
	-0.27160			$0.7437(sp^{1.00})C$	0.00	99.96
σC11-C14	1.98094	50.19	49.81	$0.7084(sp^{2.40})C+$	29.41	70.55
	-0.64168			$0.7058(sp^{2.50})C$	28.52	71.43
σC17-C20	1.98068	50.58	49.42	$0.7112(sp^{2.42})C+$	29.21	70.74
	-0.64133			$0.7030(sp^{2.48})C$	28.71	71.24
σC23-C24	1.97177	50.68	49.32	$0.7119(sp^{1.83})C+$	35.71	64.59
	-0.69771			$0.7023(sp^{1.82})C$	35.41	64.54
σC23-C31	1.97343	50.53	49.47	$0.7108(sp^{1.73})C+$	36.65	63.32
	-0.70949			$0.7034(sp^{1.80})C$	35.72	64.24
πC23-C31	1.69251	49.57	50.43	$0.7040(sp^{1.00})C+$	0.01	99.95
	-0.26285			$0.7102(sp^{1.00})C$	0.00	99.95
σC28-C29	1.97674	50.66	49.34	$0.7118(sp^{1.60})C+$	38.51	61.47
	-0.71618			$0.7024(sp^{1.86})C$	34.94	64.98
πC28-C29	1.68448	47.20	52.80	$0.6870(sp^{1.00})C+$	0.00	99.95
	-0.26706			$0.7267(sp^{1.00})C$	0.00	99.96
σN37-O40	1.99572	49.20	50.80	$0.7014(sp^{2.15})N+$	31.65	68.21
	-1.08180			$0.7128(sp^{3.06})O$	24.59	75.27
σN37-O41	1.99574	49.19	50.81	$0.7014(sp^{2.16})N+$	31.64	68.23
	-1.08172			$0.7128(sp^{3.06})O$	24.59	75.27
πN37-O41	1.98642	38.90	61.10	$0.6237(sp^{1.00})N+$	0.00	99.74
	-0.44958			$0.7817(sp^{1.00})O$	0.00	99.86
n1N38	1.73864	-	-	$sp^{18.24}$	5.20	94.78
	-0.27880					
n1 N39	1.83014	-	-	$sp^{8.91}$	10.09	89.88
	-0.28041					
n1 O40	1.98207	-	-	$sp^{0.33}$	75.34	24.66
	-0.80097					
n2 O40	1.90196	-	-	$sp^{99.99}$	0.16	99.77
	-0.29277					
n3 O40	1.46643	-	-	$sp^{1.00}$	0.00	99.88
	-0.27657					
n1 O41	1.98208	-	-	$sp^{0.33}$	75.34	24.66
	-0.80107					
n2 O41	1.90220	-	-	$sp^{99.99}$	0.17	99.77
	-0.29288					
n1 O42	1.96332	-	-	$sp^{1.63}$	38.05	61.91
	-0.54986					
n2 O42	1.84856	-	-	$sp^{1.00}$	0.00	99.96

	-0.31948

[a]ED/e is expressed in a.u.

Table S5.

The calculated (scaled) wavenumbers, experimental IR, Raman bands and assignments of the MPNPP compound.

B3LYP/6-311G++(d,p)			IR	Raman	Assignments[a]
ν (cm^{-1})	IRI	RA	(cm^{-1})	(cm^{-1})	
3120	7.4432	138.0048	-	-	νCHI(87)
3118	3.3294	69.167	-	-	νCHI(83)
3111	2.8115	46.5499	3110	-	νCHI(91)
3100	5.2673	27.7899	-	-	νCHI(91)
3097	6.3418	126.2675	3094	3095	νCHI(91)
3088	4.7908	166.8335	-	-	νCHI(85)
3083	14.4646	31.7147	-	-	νCHI(90)
3072	12.863	47.1623	3070	3071	νCHI(87)
3028	10.5678	42.9177	-	-	νCH2(96)
3014	25.2688	166.7014	3010	3013	νCH3(97)
2977	19.7512	81.9756	2976	2977	νCH2(97)
2953	39.778	63.8508	2949	2951	νCH3()
2896	64.561	199.0731	2895	2896	νCH3()
2876	96.507	143.9606	2874	2872	νCH2(94)
2826	37.8789	61.4247	-	2825	νCH2(93)
1606	5.7143	201.9261	1602	1600	νPhII(53)
					δCHI(16)
					νCO(53)
1589	95.0168	8.9637	1587	1588	νPhI(64),
					νasy NO2 (64)
1556	18.7221	2.6053	1551	1554	νPhII(70)
					δCHI(11)
					δCH3(15)
1534	191.8004	19.2118	1533	1533	νPhI(82)
					νasy NO2 (82)
1499	217.6768	1.3704	1498	1495	δCHI(29)
					δCH3(29)
					νCO(13)
1490	220.8905	54.2258	1489	1490	νPhII(22)
					δCHI(37
1457	31.5975	5.26	1454	1452	δCH2(74)
1448	104.3893	4.513	-	-	δCH2(83)
1446	9.341	15.5661	1443	1444	δCH3(83)
1443	2.1117	2.9775	-	1442	δCH2(81)
1438	4.1139	11.2897	-	-	δCH2(80)
1431	19.2801	3.624	1437	1425	δCHI(11)
					δCH3(15)
1417	5.4122	5.185	-	-	νPhI(46)

					δCHI(28)
1381	67.2172	2.5398	1381	1380	δCH2(19)
					δCHI(19)
1371	21.627	5.5737	-	1370	δCH2(19)
1354	11.2146	0.9689	-	-	δCH2(28)
1351	4.8589	2.5405	-	-	δCH2(30)
					δCHI(30)
1334	3.5318	0.6891	1333	1334	νsy NO2 (52)
1329	5.9897	202.351	1327		δCH2(36)
					δCHI(36)
1321	721.9003	1188.473	1319	1320	δCHI(10)
1311	89.8241	207.8429	-	1313	δCH2(12)
					νPhI(50)
					δCHI(12)
1300	75.2559	38.1699	-	-	νPhII(27)
1293	4.3914	1.6846	-	1293	δCHI(54)
1286	41.276	34.601	-	-	δCHI(66)
1254	47.4459	7.2529	-	1250	δCH2(15)
1240	201.0994	91.3162	1239	1240	νPhII(55)
					νCO(55)
1197	378.2032	7.449	1193	1195	δCH3(12)
1190	120.6349	8.4309	1187	1189	δCH2(65)
1180	11.644	1.6348	-	-	NO2 (20)
1174	29.5033	1.8186	-	-	νNC(39)
1160	9.2469	15.7901	1155	1158	δCHI(35)
1134	47.7615	10.609	1131	1130	δCHI(45)
					δCH3(14)
1131	0.5937	2.6394	1128	1129	νCC(55)
					νNC(55)
1102	2.9615	0.2484	-	-	δCHI(51)
1091	76.3451	115.2528	1091	1090	νPhI(25)
1076	93.3072	185.1679	-	1073	δCH2(12)
					δCHI(12)
1043	0.4813	0.4287	-	-	δCH2(12)
					δCHI(12)
1039	21.9538	47.0248	1036	1037	νCO(59)
1029	101.5301	3.7216	1027	1028	νNC(12)
985	2.2109	1.1034	983	982	δPhII(52)
					δCHI(52)
					νCO(13)
980	12.3125	23.165	-	-	νPhII(48)
					δCHI(47)
948	2.1437	0.2875	-	-	τCHI(69)

938	2.7773	0.2146	936	935	τCHI(86)
929	42.0818	0.6742	925	928	νCC(18)
					τCHI(11)
920	89.0949	1.3881	-	918	τCHI(69)
889	0.4092	0.1311	-	-	τCHI(78)
882	2.8032	9.3882	-	-	νCO(42)
					νNC(42)
836	21.5435	58.2084	833	829	νNC(12)
					τCH2()
					τCHI(40)
832	11.1615	1.8763	-	831	νPhII(12)
					NO2 (34)
822	59.2309	2.873	821	822	NO2 (18)
801	31.4783	0.4558		799	τCHI(47)
793	5.0819	16.7328	789	791	νPhII(12)
					τCHI(16)
787	3.0381	29.7392	-	-	τCHI(40)
782	6.2678	9.4216	-	-	τCHI(12)
731	1.6471	5.3695	-	731	NO2 (31)
725	12.1403	3.0172	723	724	NO2 (16)
700	6.26	2.1783	-	-	τPhII(37)
691	49.1534	3.8943	-	-	νNC(13)
678	17.0996	1.1885	-	675	τPhII(72)
627	0.9491	5.3036	-	-	νPhII(10)
620	0.6973	6.3037	-	-	νPhII(58)
567	11.8191	1.882	-	-	δPhII(36)
533	11.5626	2.2238	532	536	τCHI(36)
506	10.8113	15.9033	505	-	τCHI(16)
470	2.5951	0.8121	-	468	δCH2(35)
460	0.0722	6.4579	-	-	δCH2(18)
413	1.1463	0.8466	-	413	τPhII(76)
					τCHI(76)
411	3.3873	1.5125	-	-	τPhI(70)
					τCHI(70)
319	0.7395	2.4982	-	-	τCHI(16)
308	15.787	9.5747	-	308	τPhII(13)
					τCHI(13)
272	14.2273	4.7674	-	-	τCHI(12)
247	5.8592	0.8615	-	-	τCHI(11)
16	0.8937	1.2872	-	-	δCH2(10)

a ν-stretching; δ-in-plane deformation and out-of-plane deformation; τ-torsion; 4-Nitrophenyl and 4-methoxyphenyl rings are designated as PhI and PhII; potential energy distribution is given in brackets (%) in the assignment column.

Table S6.

Hydrogen bonding and molecular docking, statistical mechanical analysis of anticancer protein targets with MPNPP molecule and standard anticancer drugs.

Ligands	Protein (PDB ID)	Bonded residues	No. of hydrogen bond	Bond distance (Å)	Estimated Inhibition Constant (μm)	Binding energy (kcal/mol)	Reference RMSD (Å)	Statistical mechanical analysis [Temperature = 298.15 K]		
								Free energy (A)kcal/mol	Internal energy (U)kcal/mol	Entropy(S) kcal/mol/K
MPNPP (This work)	2YJR	LYS 1101	2	1.6	2.42	-7.66	56.09	-2324.29	-6.49	7.77
		LYS 1173		2.0						
	IUSN	LYS 1702	2	2.0	12.98	-6.67	86.04	-2323.59	-5.79	7.77
		GLY 1656		2.0						
Lorlatinib	2YJR	ASP 1203	3	2.5	41.03	-5.98	55.30	-2323.09	-5.29	7.77
		ALA 1200		2.2						
		MET 1199		1.8						
Doxorubicin	IUSN	THR 215	4	2.2	26.62	-6.24	91.617	-1910.98	-3.85	6.40
		THR 215		2.5						
		ARG 233		3.2						
		ASP 228		1.6						