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Preferential Solvation of *p*-Nitroaniline in Binary Mixture of Chloroform and Hydrogen Bond Acceptor Solvents: The Role of Specific Solute-Solvent Hydrogen Bonding

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Determination of relative percentage contribution (P(X) %) of the solvatochromic parameter (X)

Equation S1 represents a general linear multiparametric equation.

$$Q = Q_0 + \sum_{i=1}^{n} x_i X_i \qquad \text{(S1)}$$

Where Q represents physicochemical quantity with the parameters X_1,…, X_i,… X_n. Q_0 is the intercept of this linear model and x_1,..... x_i,…, x_n are the coefficients of the parameters X_1,…, X_i,… X_n, respectively. Q_0 and the coefficients and x_1,..... x_i,…, x_n are obtained through multiparametric regression analysis.

The relative percentage contribution of each parameter Xi [symbolized as P(Xi)%] to the quantity Q, can be calculated through Eq. S2 and S3.

$$P(X_i)\% = 100\,(x_i)' / \sum_{i=1}^{n} (x_i)' \qquad \text{(S2)}$$

Where
$$(x_i)' = |x_i| \left(\left(\sum_{j=1}^{m} (X_{ij} - \bar{X}_i)^2 \right) / \left(\sum_{j=1}^{m} (Q_j - \bar{Q})^2 \right) \right)^{\frac{1}{2}} \qquad \text{(S3)}$$

$\bar{X}_i$ *and* $\bar{Q}$ are the mean values of the parameter X_i and of the quantity Q, respectively. $|x_i|$ corresponds to the absolute regression value of x_i obtained from the regression analysis.

m is the number of series of data.

Table S1. Empirical solvent polarity parameters of the solvents used in this study.

Solvents	$E_T(30)$	E_T^N	α	β	π^*	A	B	DN	AN	δ (SP)	log$P$	μ	ε
n-Hexane	30.9	0.009	0	0	-0.08	0.01	-0.01	0	0	7.27	3.5	0.085	1.88
Cyclohexane	31.2	0.006	0	0	0	0.02	0.06	0	0	8.2	3.2	0	2.02
Toluene	33.9	0.099	0	0.11	0.49	0.13	0.54	0.1	3.3	8.9	2.69	0.31	2.38
Benzene	34.3	0.111	0	0.1	0.55	0.1	0.15	0.1	8.2	9.2	2.13	0	2.28
Chlorobenzene	37.5	0.188	0	0.07	0.71	0.2	0.65	3.3	7.9	9.5	0.84	1.54	5.62
DCM	40.7	0.309	0.13	0.1	0.82	0.33	0.8	1	20.4	10	1.15	1.14	8.93
Chloroform	39.1	0.259	0.2	0.1	0.58	0.42	0.73	4	23.1	9.3	1.94	1.15	4.81
Carbontetrachloride	32.4	0.052	0	0.1	0.21	0.09	0.34	0	8.6	8.6	0	0	2.24
Dioxane	36	0.164	0	0.37	0.49	0.19	0.67	14.8	10.8	9.8	-0.31	0.45	2.3
Diethyl ether	34.6	0.117	0	0.47	0.27	0.12	0.34	19.2	3.9	7.8	0.85	1.3	4.34
Ethyl acetate	38.1	0.288	0	0.45	0.45	0.21	0.59	17.1	9.3	8.9	0.73	1.78	6.02
Acetone	42.2	0.355	0.08	0.48	0.62	0.25	0.81	17	12.5	9.6	-0.24	2.88	21
THF	37.4	0.207	0	0.55	0.55	0.17	0.67	20	8	9.3	0.46	1.75	7.5
Pyridine	40.2	0.302	0	0.64	0.87	0.24	0.96	33.1	14.2	10.6	0.71	2.37	12.4
Triethylamine	33.3	0.043	0	0.71	0.14	0.08	0.19	61	1.4	7.45	1.56	0.87	2.42
DMF	43.2	0.386	0	0.69	0.88	0.3	0.93	26.6	16	11.8	-1.01	3.82	38
DMSO	45.1	0.444	0	0.76	1	0.34	1.08	29.8	19.3	13	-1.35	3.96	46.7
Dimethylacetamide	43.2	0.377	0	0.76	0.85	0.32	1.01	27.8	13.6	10.8	-0.77	3.72	37.78
Acetonitrile	45.6	0.46	0.19	0.4	0.66	0.37	0.86	14.1	18.9	11.7	-0.34	3.92	37.5
Methanol	55.4	0.762	0.98	0.66	0.6	0.75	0.5	19	41.5	14.3	-0.74	1.7	32.7

Ethanol	51.9	0.654	0.86	0.75	0.54	0.66	0.45	19.2	37.9	12.7	-0.3	1.88	24.55
1-Propanol	50.7	0.617	0.84	0.9	0.52	0.63	0.44	19.8	37.3	11.9	0.25	1.68	20.33
2-Propanol	48.4	0.546	0.76	0.84	0.48	0.59	0.44	21.1	33.8	11.5	0.05	1.66	19.92
1-Butanol	49.7	0.586	0.84	0.84	0.47	0.61	0.43	19.5	36.8	11.4	0.84	1.66	17.51
1-Pentanol	49.1	0.488	0.84	0.86	0.4	--	--	26.2	30.1	7.8	1.4	1.7	13.9
1-Octanol	47.7	0.537	0.7	0.82	0.45	--	--	32	44.9	7.7	3.15	1.68	10.3
Cyclohexanol	47.2	0.509	0.66	0.84	0.45	0.57	0.41	25	27.1	8.5	1.23	1.46	15
t-Butylalcohol	43.9	0.389	0.42	0.93	0.41	0.45	0.5	21.9	54.8	10.5	0.36	1.66	12.47
Ethyleneglycol	56.3	0.79	0.9	0.52	0.92	0.78	0.84	20	34.3	14.5	-2.27	2.2	37.7
Benzyl alcohol	50.8	0.608	0.43	0.5	0.98	--	--	23	33.1	12.2	1.1	1.67	13.1
Water	63	1	1.17	0.41	1.09	1	1	18	36.8	23.4	0	1.82	78.39

Table S2. Correlation Matrix for 8 Solvent Parameters for 30 Solvents Delineating Interrelationships of the Parameters.

	ET(30)	**α**	**β**	**π***	δ	**logP**	**μ**	**ε**
ET(30)	1							
α	0.891709	1						
β	0.564453	0.470357	1					
π*	0.615255	0.250166	0.254125	1				
δ	0.857551	0.702926	0.267273	0.677175	1			
logP	-0.63309	-0.34867	-0.55701	-0.66065	-0.53409	1		
μ	0.481074	0.084367	0.551032	0.679163	0.376762	-0.70683	1	
ε	0.814391	0.546557	0.39059	0.718308	0.898171	-0.64342	0.674101	1

Table S3. Transition energy of PNA in HBA solvents and their corresponding Solvent parameters.

Sl no	Solvents	$\mathcal{E}$	$E_T(30)$	μ	log*P*	β	π^*	δ	E_T	ΔE_T
1	Dioxane	2.3	36	0.45	-0.31	0.37	0.49	9.8	80.77	1.39
2	Acetonitrile	37.5	45.6	3.92	-0.34	0.4	0.66	11.7	78.54	3.62
3	Ethyl acetate	6.02	38.1	1.78	0.73	0.45	0.45	8.9	79.85	2.31
4	Diethyl ether	4.34	34.6	1.3	0.85	0.47	0.27	7.8	81.91	0.25
5	Acetone	21	42.2	2.88	-0.24	0.48	0.62	9.6	78.11	4.05
6	Tetrahydrofuran	7.5	37.4	1.75	0.46	0.55	0.55	9.3	78.76	3.40
7	Pyridine	12.4	40.2	2.37	0.71	0.64	0.87	10.6	75.53	6.63
8	Dimethylformamide	38	43.2	3.82	-1.01	0.69	0.88	11.8	74.85	7.31
9	Dimethyl sulfoxide	46.7	45.1	3.96	-1.35	0.76	1	13	73.50	8.66
10	Dimethylacetamide	37.78	43.2	3.72	-0.77	0.76	0.85	10.8	74.93	7.23

Table S4. Correlation Matrix of 7 solvent parameters for 10 HBA solvents delineating interrelationships of the parameters (DMSO, DMF, Acetonitrile, Acetone, THF, Dioxane, Ethyl acetate, diethylether, pyridine, DMA)

	$\mathcal{E}$	$E_T(30)$	μ	log*P*	β	π^*	δ
$\mathcal{E}$	1						
$E_T(30)$	0.936578	1					
μ	0.956079	0.955204	1				
log*P*	-0.84656	-0.73607	-0.68369	1			
β	0.636054	0.494818	0.622986	-0.51677	1		
π^*	0.793074	0.798358	0.773129	-0.70256	0.809821	1	
δ	0.877281	0.868597	0.795073	-0.82611	0.575602	0.89326	1

Table S5. Optimization regression model by successive exclusion of variable

Model no.	No. of variables	R^2	F	RMS	t_{min}	Variable to be Excluded
1	4	0.995	267.54	0.067	0.836	log *P*
2	3	0.995	375.29	0.064	1.85	$E_T(30)$
3	2	0.992	416.8	0.085	4.85	β
4	1	0.964	212.28	0.326	14.57	-

Table S6. Transition energies and preferential solvation parameters of PNA at different solvent compositions in Chloroform–Dioxane binary solvent mixture. (Chloroform → solvent1; Dioxane →Solvent 2)

Chloroform: Dioxane (v/v %)	X_1	X_2	$E_T(12)$	$E_T(12)_{id}$	Δ	X_2^L	δ_2 (= X_2^L-X_2)
0:100	0.00	1.00	80.76	80.76	0.00	1.00	0.00
10:90	0.11	0.89	80.54	80.91	-0.37	1.16	0.27
20:80	0.21	0.79	80.31	81.05	-0.74	1.32	0.53
30:70	0.31	0.69	80.20	81.20	-1.00	1.40	0.71
40:60	0.41	0.59	80.08	81.34	-1.26	1.48	0.90
50:50	0.51	0.49	80.08	81.48	-1.40	1.48	1.00
60:40	0.61	0.39	80.20	81.62	-1.42	1.40	1.02
70:30	0.71	0.29	80.31	81.76	-1.45	1.32	1.03
80:20	0.81	0.19	80.54	81.89	-1.36	1.16	0.97
90:10	0.91	0.09	80.99	82.03	-1.04	0.83	0.74
100:0	1.00	0.00	82.16	82.16	0.00	0.00	0.00

Table S7. Transition energies and preferential solvation parameters of PNA at different solvent compositions in Chloroform–THF binary solvent mixture. (Chloroform → solvent1; THF →Solvent 2)

Chloroform: THF (v/v %)	X_1	X_2	$E_T(12)$	$E_T(12)_{id}$	Δ	X_2^L	δ_2 (= X_2^L-X_2)
0:100	0.00	1.00	78.76	78.76	0.00	1.00	0.00
10:90	0.10	0.90	78.65	79.10	-0.45	1.03	0.13
20:80	0.20	0.80	78.54	79.44	-0.90	1.06	0.26
30:70	0.30	0.70	78.54	79.79	-1.24	1.06	0.37
40:60	0.40	0.60	78.54	80.13	-1.58	1.06	0.47
50:50	0.50	0.50	78.54	80.47	-1.92	1.06	0.57
60:40	0.60	0.40	78.76	80.81	-2.05	1.00	0.60
70:30	0.70	0.30	79.20	81.15	-1.95	0.87	0.57
80:20	0.80	0.20	79.86	81.48	-1.62	0.68	0.48
90:10	0.90	0.10	80.76	81.82	-1.06	0.41	0.31
100:0	1.00	0.00	82.16	82.16	0.00	0.00	0.00

Table S8. Transition energies and preferential solvation parameters of PNA at different solvent compositions in Chloroform – DMSO binary solvent mixture. (Chloroform → solvent1; DMSO →Solvent 2)

Chloroform: DMSO (v/v %)	X_1	X_2	$E_T(12)$	$E_T(12)_{id}$	Δ	X_2^L	δ_2 (= X_2^L-X_2)
0:100	0.00	1.00	73.50	73.50	0.00	1.00	0.00
10:90	0.09	0.91	73.69	74.27	-0.59	0.98	0.07
20:80	0.18	0.82	73.88	75.06	-1.19	0.96	0.14
30:70	0.27	0.73	74.07	75.88	-1.81	0.93	0.21
40:60	0.37	0.63	74.26	76.71	-2.45	0.91	0.28
50:50	0.47	0.53	74.55	77.56	-3.01	0.88	0.35
60:40	0.57	0.43	74.94	78.43	-3.49	0.83	0.40
70:30	0.67	0.33	75.84	79.33	-3.49	0.73	0.40
80:20	0.78	0.22	76.96	80.25	-3.29	0.60	0.38
90:10	0.89	0.11	79.20	81.19	-1.99	0.34	0.23
100:0	1.00	0.00	82.16	82.16	0.00	0.00	0.00

Table S9. Transition energies and preferential solvation parameters of PNA at different solvent compositions in Chloroform–DMF binary solvent mixture. (Chloroform → solvent1; DMF →Solvent 2)

Chloroform: DMF (v/v %)	X_1	X_2	$E_T(12)$	$E_T(12)_{id}$	Δ	X_2^L	δ_2 (= X_2^L-X_2)
0:100	0.00	1.00	74.84	74.84	0.00	1.00	0.00
10:90	0.10	0.90	75.04	75.55	-0.51	0.97	0.07
20:80	0.19	0.81	75.14	76.26	-1.12	0.96	0.15
30:70	0.29	0.71	75.24	76.98	-1.74	0.94	0.24
40:60	0.39	0.61	75.44	77.70	-2.26	0.92	0.31
50:50	0.49	0.51	75.74	78.43	-2.69	0.88	0.37
60:40	0.59	0.41	76.14	79.16	-3.02	0.82	0.41
70:30	0.69	0.31	76.96	79.90	-2.95	0.71	0.40
80:20	0.79	0.21	77.90	80.65	-2.75	0.58	0.37
90:10	0.90	0.10	79.53	81.40	-1.87	0.36	0.26
100:0	1.00	0.00	82.16	82.16	0.00	0.00	0.00

Table S10. Transition energies and preferential solvation parameters of PNA at different solvent compositions in Chloroform–Acetone binary solvent mixture. (Chloroform → solvent1; Acetone →Solvent 2)

Chloroform: Acetone (v/v %)	X_1	X_2	$E_T(12)$	$E_T(12)_{id}$	Δ	X_2^L	δ_2 (= X_2^L-X_2)
0:100	0.00	1.00	78.11	78.11	0.00	1.00	0.00
10:90	0.09	0.91	78.11	78.48	-0.37	1.00	0.09
20:80	0.19	0.81	78.11	78.86	-0.75	1.00	0.18
30:70	0.28	0.72	78.22	79.25	-1.03	0.97	0.25
40:60	0.38	0.62	78.33	79.64	-1.31	0.95	0.32
50:50	0.48	0.52	78.54	80.04	-1.50	0.89	0.37
60:40	0.58	0.42	78.76	80.45	-1.69	0.84	0.42
70:30	0.68	0.32	79.09	80.86	-1.78	0.76	0.44
80:20	0.78	0.22	79.64	81.29	-1.65	0.62	0.41
90:10	0.89	0.11	80.54	81.72	-1.18	0.40	0.29
100:0	1.00	0.00	82.16	82.16	0.00	0.00	0.00

Table S11. Transition energies and preferential solvation parameters of PNA at different solvent compositions in Chloroform–Ethyl acetate binary solvent mixture. (Chloroform → solvent1; Ethyl acetate →Solvent 2)

Chloroform: Ethyl acetate (v/v %)	X_1	X_2	$E_T(12)$	$E_T(12)_{id}$	Δ	X_2^L	$\delta_2 (= X_2^L - X_2)$
0:100	0.00	1.00	79.86	79.86	0.00	1.00	0.00
10:90	0.12	0.88	79.31	80.13	-0.83	1.24	0.36
20:80	0.23	0.77	79.20	80.40	-1.20	1.29	0.52
30:70	0.34	0.66	79.20	80.65	-1.45	1.29	0.63
40:60	0.45	0.55	79.20	80.89	-1.70	1.29	0.74
50:50	0.55	0.45	79.31	81.12	-1.82	1.24	0.79
60:40	0.65	0.35	79.42	81.35	-1.93	1.19	0.84
70:30	0.74	0.26	79.75	81.56	-1.81	1.05	0.79
80:20	0.83	0.17	80.20	81.77	-1.57	0.85	0.68
90:10	0.92	0.08	80.99	81.97	-0.98	0.51	0.42
100:0	1.00	0.00	82.16	82.16	0.00	0.00	0.00

Table S12. Transition energies and preferential solvation parameters of PNA at different solvent compositions in Chloroform– Acetonitrile binary solvent mixture. (Chloroform → solvent1; Acetonitrile →Solvent 2)

Chloroform: Acetonitrile (v/v %)	X_1	X_2	$E_T(12)$	$E_T(12)_{id}$	Δ	X_2^L	$\delta_2 (= X_2^L - X_2)$
0:100	0.00	1.00	78.54	78.54	0.00	1.00	0.00
10:90	0.07	0.93	78.54	78.78	-0.24	1.00	0.07
20:80	0.14	0.86	78.54	79.05	-0.50	1.00	0.14
30:70	0.22	0.78	78.54	79.33	-0.78	1.00	0.22
40:60	0.30	0.70	78.54	79.63	-1.09	1.00	0.30
50:50	0.39	0.61	78.54	79.96	-1.42	1.00	0.39
60:40	0.49	0.51	78.65	80.33	-1.67	0.97	0.46
70:30	0.60	0.40	78.87	80.72	-1.85	0.91	0.51
80:20	0.72	0.28	79.42	81.15	-1.74	0.76	0.48
90:10	0.89	0.11	80.54	81.63	-1.10	0.45	0.30
100:0	1.00	0.00	82.16	82.16	0.00	0.00	0.00

Table S13. Computed Vertical Transitions and Their Oscillator Strengths and Configurations

Compound	State	f	λ_{max} nm	Energy (eV)	Configuration
PNA	Triplet	0	427.69	2.898	HOMO → LUMO (68.44%)
					HOMO → LUMO+2 (12.73%)
	S1	0.001	320.09	3.893	HOMO-2 → LUMO (69.71%)
	S2	0.312	304.99	4.065	HOMO → LUMO (69.79%)
	S3	0.0001	304.60	4.070	HOMO → LUMO (69.87%)
PNA+1Dioxane	Triplet	0	446.48	2.776	HOMO → LUMO (69.05%) HOMO → LUMO+3 (12.24%)
	S1	0.0003	319.99	3.874	HOMO-2 → LUMO (69.70%)
	S2	0.340	314.64	3.948	HOMO → LUMO (69.87%)
	S3	0.0001	309.48	4.006	HOMO-6 → LUMO (69.53%)
PNA+2Dioxane	Triplet	0	464.67	2.668	HOMO → LUMO (69.51%) HOMO → LUMO+4 (10.52%)
	S1	0.390	321.47	3.856	HOMO → LUMO (69.98%)
	S2	0.0003	319.83	3.865	HOMO-2 → LUMO (69.80%)
	S3	0.0001	278.47	4.452	HOMO-8→ LUMO (36.10%) HOMO-6→ LUMO (11.40%) HOMO-5→ LUMO (58.56%)
PNA+1$CHCl_3$	Triplet	0	452.74	2.738	HOMO → LUMO (69.16%) HOMO → LUMO+3 (11.56%)
	S1	0.0006	316.17	3.921	HOMO-4 → LUMO (26.15%) HOMO-3 → LUMO (64.11%)
	S2	0.3854	316.07	3.922	HOMO → LUMO (69.92%)
	S3	0.0001	300.73	4.122	HOMO-8 → LUMO (49.57%) HOMO-3 → LUMO (17.51%)
PNA+2$CHCl_3$	Triplet	0	474.56	2.612	HOMO-1→LUMO (69.58%) HOMO→LUMO+4 (10.30%)
	S1	0.3992	325.42	3.809	HOMO → LUMO (70.07%)
	S2	0.0001	317.07	3.910	HOMO-6 → LUMO (11.32%) HOMO-5 → LUMO (36.20%) HOMO-3 → LUMO (57.54%)
	S3	0.0001	313.78	3.951	HOMO-1 → LUMO (65.68%)
PNA+2Dioxane+ 1$CHCl_3$	Triplet	0	498.60	2.486	HOMO→LUMO (70.00%)
	S1	0.481	332.39	3.730	HOMO → LUMO (70.15%)
	S2	0.0002	320.46	3.869	HOMO-4 → LUMO (69.29%)
	S3	0.0002	315.88	3.925	HOMO-2 → LUMO (58.94%) HOMO → LUMO+2 (38.15%)
PNA+2Dioxane+	Triplet	0	528.24	2.347	HOMO→LUMO (70.26%)

$2CHCl_3$					
	S1	0.507	341.43	3.631	HOMO → LUMO (70.46%)
	S2	0.0001	317.37	3.906	HOMO-7 → LUMO (17.23%) HOMO-4 → LUMO (67.18%)
	S3	0.0004	285.20	4.347	HOMO-2 → LUMO (65.07%) HOMO → LUMO+3 (26.41%)

[a]Orbital contributions below 10% are omitted

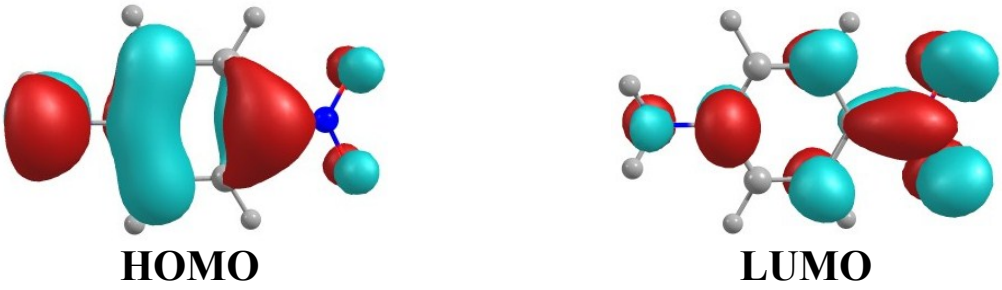

Figure S1. Contour plots for the frontier molecular orbitals of PNA in gas phase

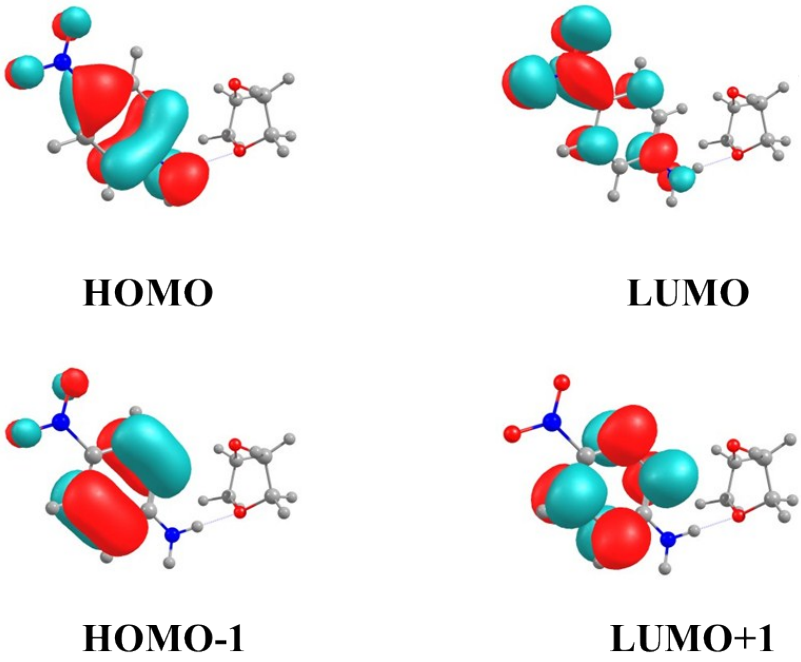

Figure S2. Contour plots for the frontier molecular orbitals of PNA hydrogen bonded to one dioxane.

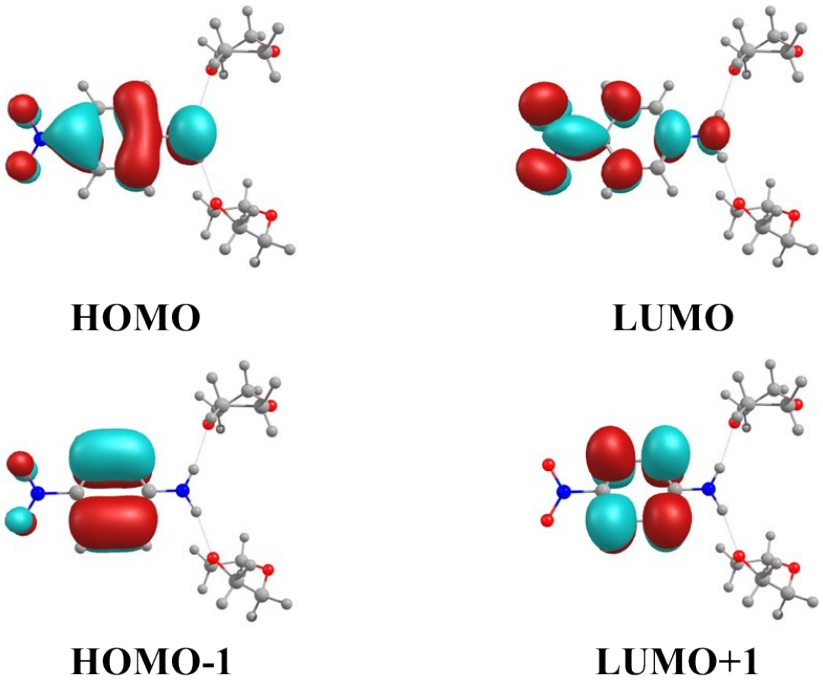

Figure S3. Contour plots for the frontier molecular orbitals of PNA hydrogen bonded to two numbers of dioxane.

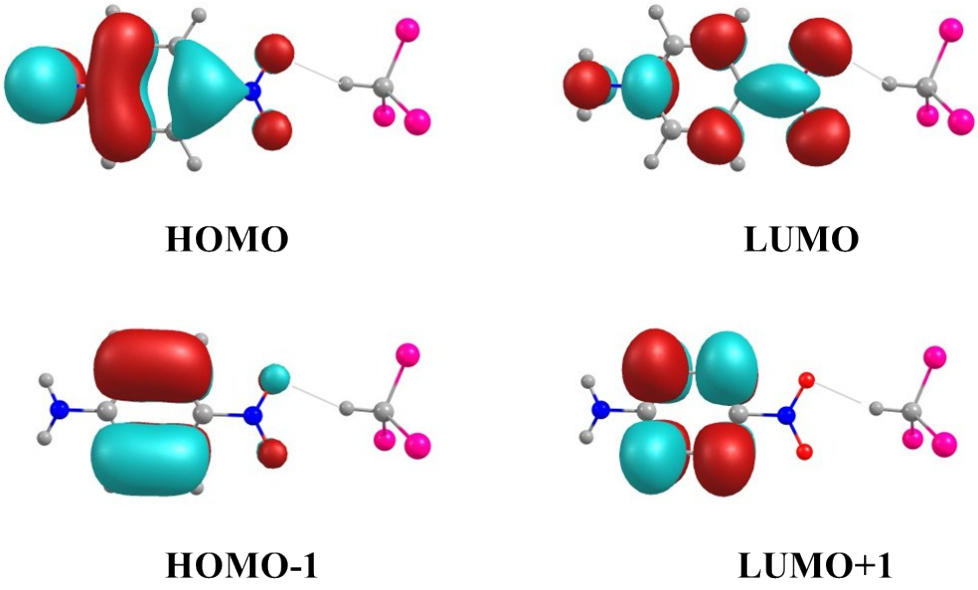

Figure S4. Contour plots for the frontier molecular orbitals of PNA hydrogen bonded to one chloroform.

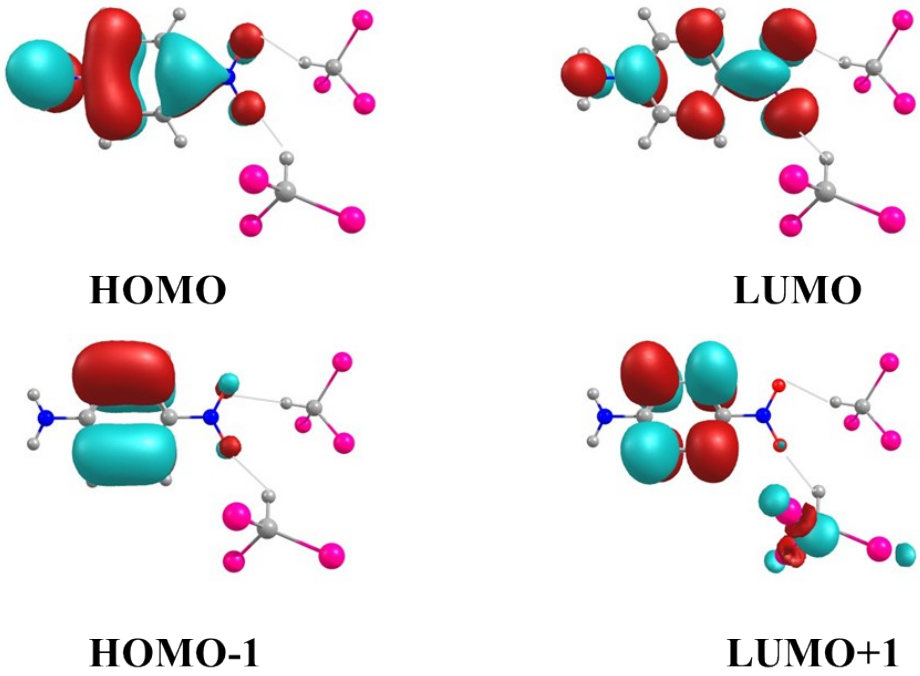

Figure S5. Contour plots for the frontier molecular orbitals of PNA hydrogen bonded to two numbers of chloroform.

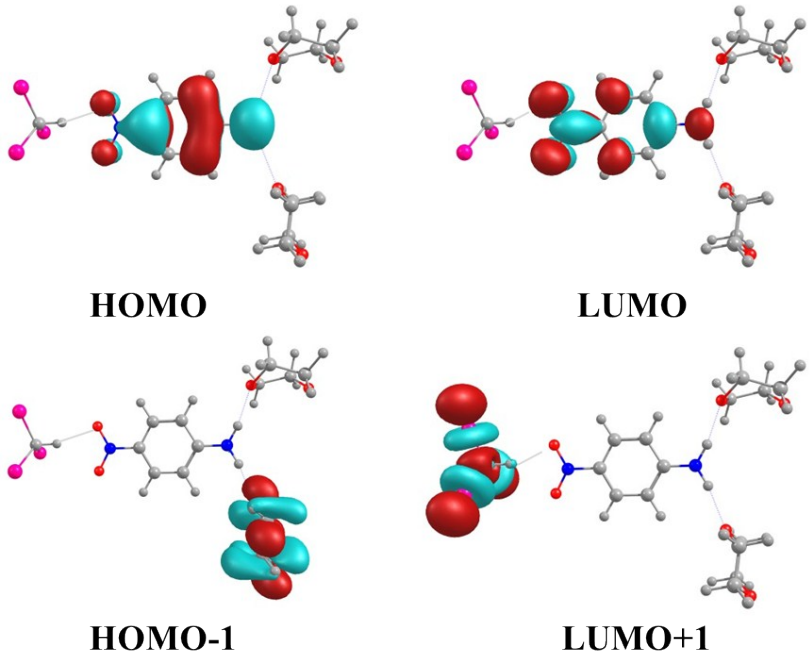

Figure S6. Contour plots for the frontier molecular orbitals of PNA hydrogen bonded to two numbers of dioxane and one chloroform.

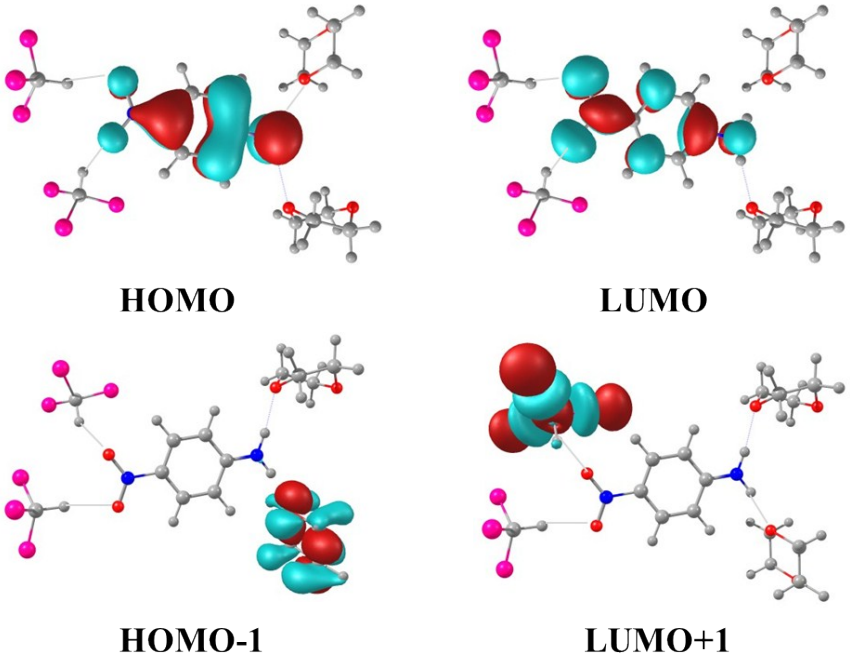

Figure S7. Contour plots for the frontier molecular orbitals of PNA hydrogen bonded to two numbers of dioxane and two numbers of chloroform.