Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information: Incremental NH Stretching Downshift through Stepwise Nitrogen Complexation of Pyrrole: A Combined Jet Expansion and Matrix Isolation Study

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Table S1: Gaussian[1] keywords employed in the different calculations.

Level of approximation	Employed keywords
B3LYP-D3(BJ)/aVTZ	b3lyp, int=superfine, empiricaldispersion=gd3bj, aug-cc-pVTZ, fopt=verytight, freq=raman or freq=anharm
CCSD(T)/aVTZ	ccsd-t, aug-cc-pVTZ

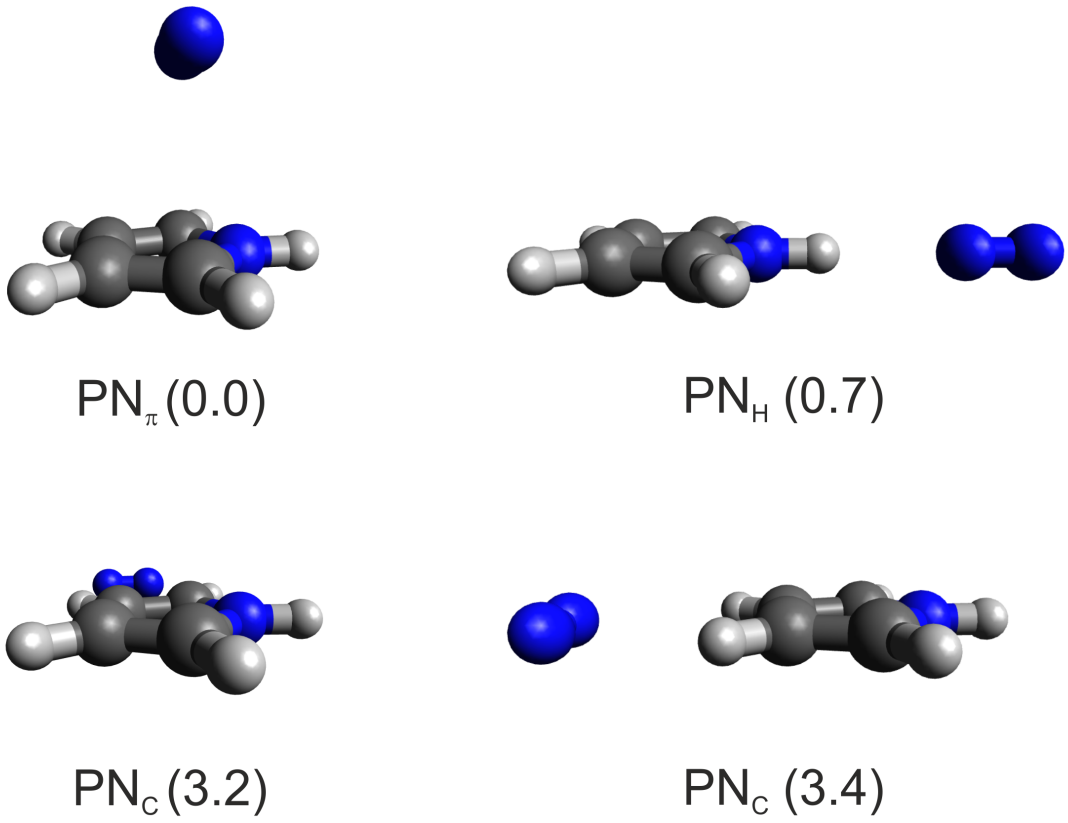

Figure S1: Stable structures found for the mixed dimer of pyrrole and nitrogen optimised at the B3LYP-D3(BJ)/aVTZ level. Relative energies in kJ mol^{-1} calculated from CCSD(T)/aVTZ single-point calculations and harmonic zero-point vibrational energy from B3LYP-D3(BJ)/aVTZ are given in parentheses.

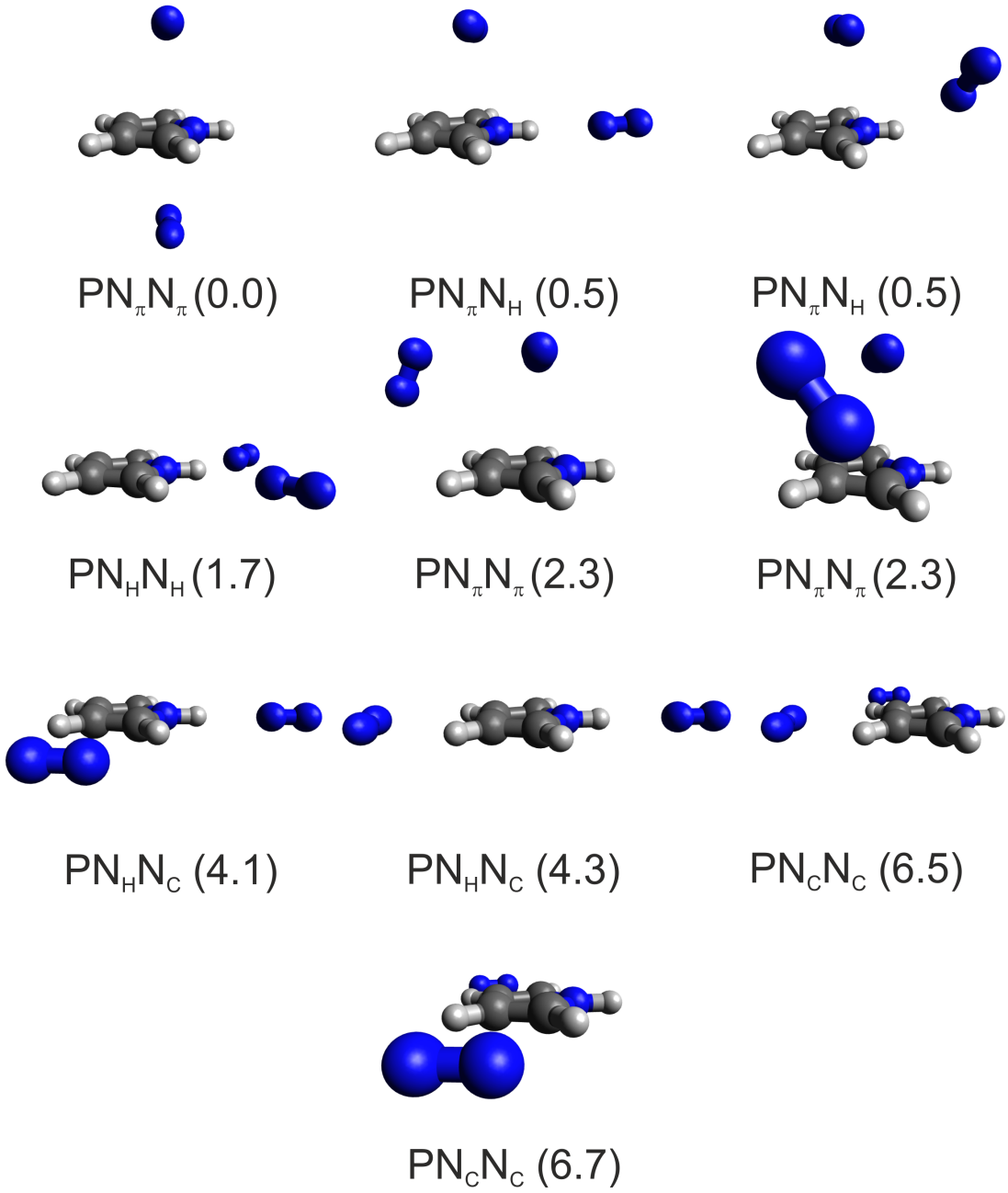

Figure S2: Stable structures found for the mixed trimer of pyrrole and two nitrogen molecules optimised at the B3LYP-D3(BJ)/aVTZ level. Relative energies in kJ mol^{-1} calculated from CCSD(T)/aVTZ single-point calculations and harmonic zero-point vibrational energy from B3LYP-D3(BJ)/aVTZ are given in parentheses.

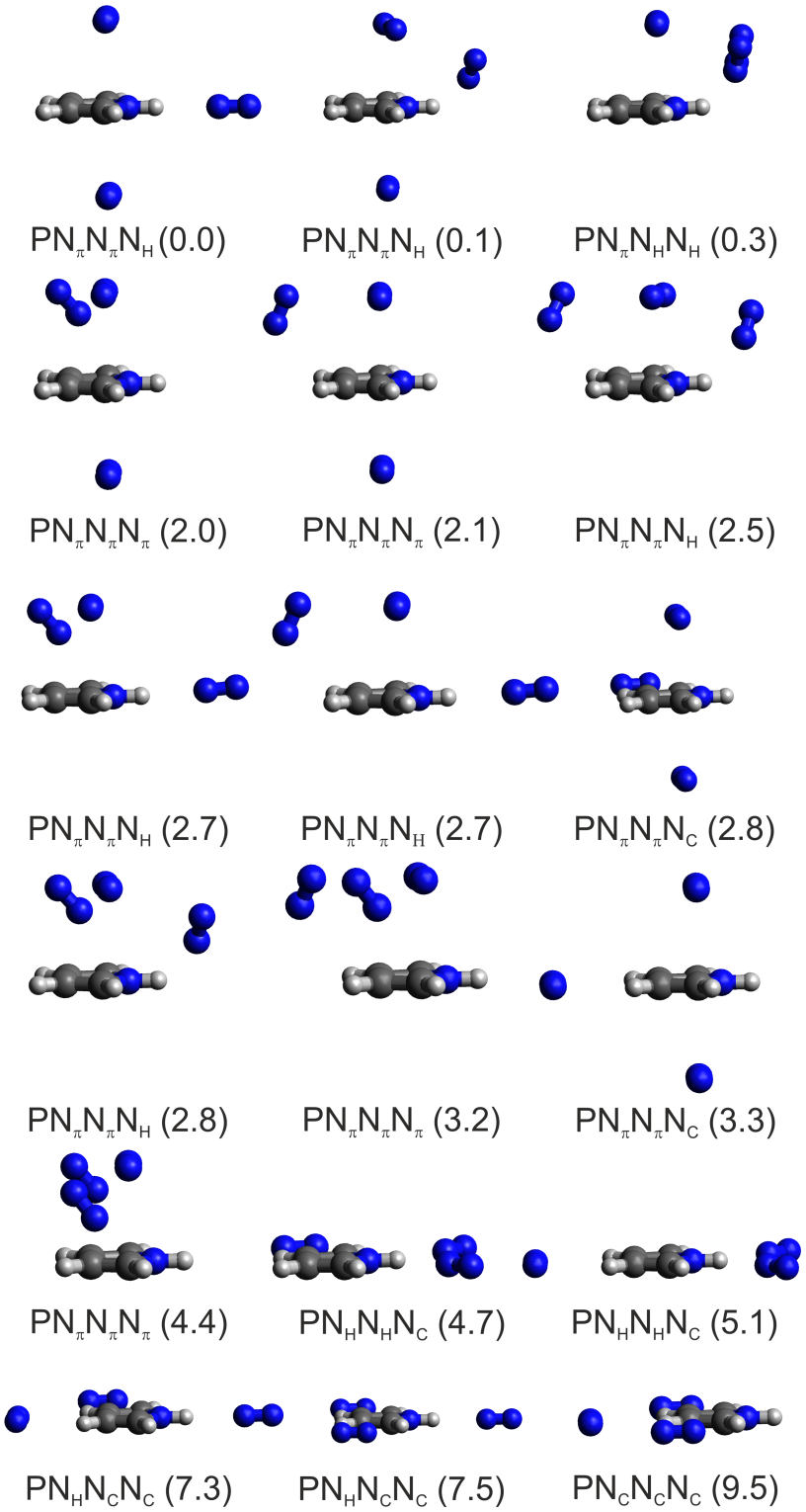

Figure S3: Stable structures found for the mixed tetramer of pyrrole and three nitrogen molecules optimised at the B3LYP-D3(BJ)/aVTZ level. Relative energies in kJ mol^{-1} calculated from CCSD(T)/aVTZ single-point calculations and harmonic zero-point vibrational energy from B3LYP-D3(BJ)/aVTZ are given in parentheses.

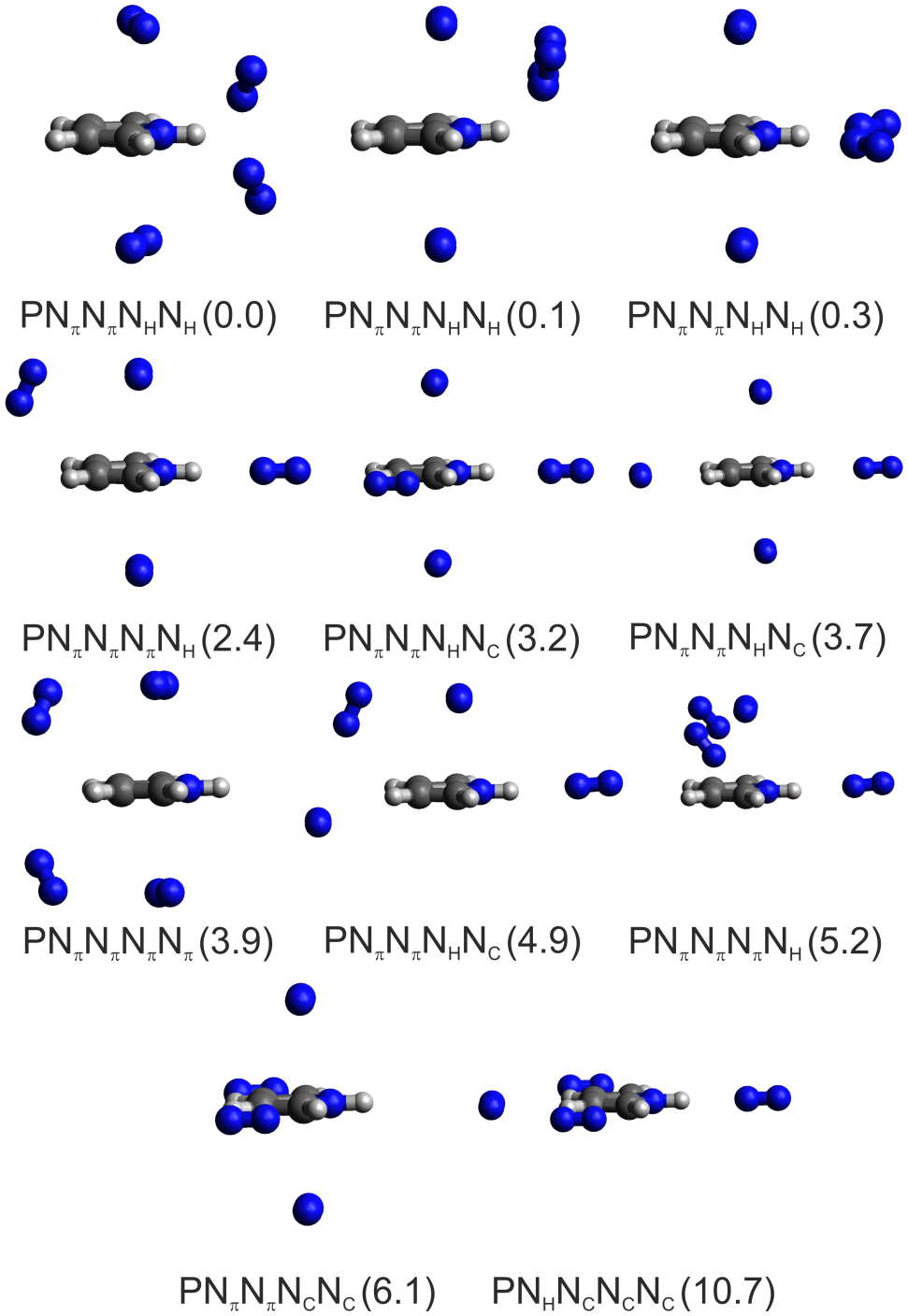

Figure S4: Stable structures found for the mixed pentamer of pyrrole and four nitrogen molecules optimised at the B3LYP-D3(BJ)/aVTZ level. Relative energies in kJ mol^{-1} calculated from CCSD(T)/aVTZ single-point calculations and harmonic zero-point vibrational energy from B3LYP-D3(BJ)/aVTZ are given in parentheses.

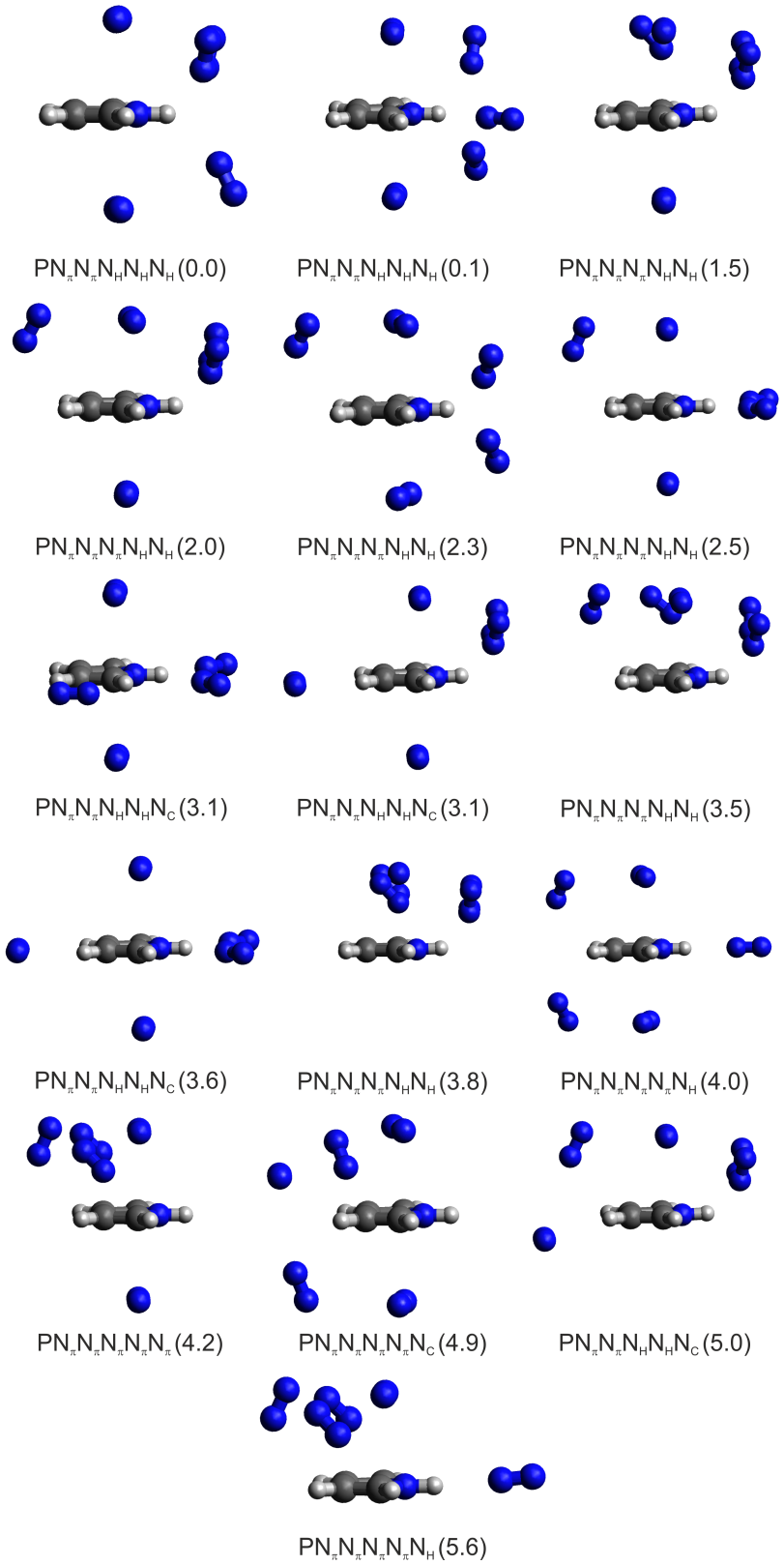

Figure S5: Stable structures found for the mixed hexamer of pyrrole and five nitrogen molecules optimised at the B3LYP-D3(BJ)/aVTZ level. Relative energies in kJ mol^{-1} including harmonic zero-point vibrational energy are given in parentheses.

Table S2: Theoretically predicted properties of stable P and N_2 aggregates such as harmonic (ω_{NH}) and anharmonic ($\tilde{\nu}_{NH}$) NH stretching wavenumbers, lowest predicted harmonic (ω_L) and anharmonic ($\tilde{\nu}_L$) wavenumbers in cm^{-1}, harmonic (S_ω) and anharmonic (S_ν) infrared band strengths in $km\,mol^{-1}$, spectroscopic shifts ($\Delta\omega_{NH}$, $\Delta\tilde{\nu}_{NH}$) relative to the pyrrole monomer in cm^{-1}, as well as relative electronic and harmonically zero-point corrected energies ΔE_e and ΔE_0 compared to the most stable cluster conformation in $kJ\,mol^{-1}$. All properties were calculated at the B3LYP-D3(BJ)/aVTZ level. Only the electronic energy was taken from CCSD(T)/aVTZ single-point calculations for all clusters except hexamers.

Structure	ω_{NH}	S_ω	$\Delta\omega_{NH}$	ω_L	$\tilde{\nu}_{NH}$	S_ν	$\Delta\tilde{\nu}_{NH}$	$\tilde{\nu}_L$	ΔE_e	ΔE_0
P	3674	65	-	496	3508	51	-	492	-	-
PP	3669	72	−5	17	-	-	-	-	-	-
	3598	324	−76							
PPP	3553	631	−121	22	-	-	-	-	-	-
	3553	631	−121							
	3536	0	−138							
PN_π	3674	65	0	21	3507	51	−1	18810	0.0	0.0
PN_H	3669	206	−5	11	3506	133	−2	20	0.8	0.7
PN_C	3674	65	0	19	3510	52	2	−58	4.1	3.2
PN_C	3674	67	0	16	3517	52	9	−24	4.3	3.4
$PN_\pi N_\pi$	3673	65	−1	18	3517	52	9	132	0.0	0.0
$PN_\pi N_H$	3668	210	−6	10	3505	131	−3	−22	0.4	0.5
$PN_\pi N_H$	3675	94	1	8	3508	69	0	23	0.7	0.5
$PN_H N_H$	3679	166	5	16	3530	121	22	137	2.2	1.7
$PN_\pi N_\pi$	3674	67	0	7	3517	54	9	−667	3.0	2.3
$PN_\pi N_\pi$	3673	65	−1	17	3513	51	5	−13	2.9	2.3
$PN_H N_C$	3669	207	−5	6	3510	123	2	−146	4.9	4.1
$PN_H N_C$	3669	213	−5	7	3514	139	6	−92	5.1	4.3
$PN_C N_C$	3674	67	0	10	3521	53	13	−11	8.2	6.5
$PN_C N_C$	3674	65	0	11	3526	49	18	25	8.4	6.7
$PN_\pi N_\pi N_H$	3667	214	−7	9	-	-	-	-	0.0	0.0
$PN_\pi N_\pi N_H$	3674	98	0	12	-	-	-	-	0.5	0.1
$PN_\pi N_H N_H$	3677	100	3	11	-	-	-	-	0.8	0.3
$PN_\pi N_\pi N_\pi$	3672	65	−2	15	-	-	-	-	2.9	2.0
$PN_\pi N_\pi N_\pi$	3673	67	−1	7	-	-	-	-	3.0	2.1
$PN_\pi N_\pi N_H$	3675	97	1	10	-	-	-	-	3.6	2.5
$PN_\pi N_\pi N_H$	3668	209	−6	6	-	-	-	-	3.4	2.7
$PN_\pi N_\pi N_H$	3668	214	−6	7	-	-	-	-	3.5	2.7
$PN_\pi N_\pi N_C$	3672	65	−2	1	-	-	-	-	3.7	2.8

$PN_{\pi}N_{\pi}N_{H}$	3675	92	1	10	-	-	-	-	3.8	2.8
$PN_{\pi}N_{\pi}N_{\pi}$	3673	67	−1	17	-	-	-	-	4.4	3.2
$PN_{\pi}N_{\pi}N_{C}$	3672	67	−2	4	-	-	-	-	4.3	3.3
$PN_{\pi}N_{\pi}N_{\pi}$	3673	65	−1	13	-	-	-	-	5.9	4.4
$PN_{H}N_{H}N_{C}$	3678	165	4	8	-	-	-	-	6.1	4.7
$PN_{H}N_{H}N_{C}$	3679	172	5	7	-	-	-	-	6.7	5.1
$PN_{H}N_{C}N_{C}$	3668	214	−6	6	-	-	-	-	9.1	7.3
$PN_{H}N_{C}N_{C}$	3668	208	−6	5	-	-	-	-	9.1	7.5
$PN_{C}N_{C}N_{C}$	3673	67	−1	5	-	-	-	-	12.2	9.5
$PN_{\pi}N_{\pi}N_{H}N_{H}$	3676	122	2	10	-	-	-	-	0.1	0.0
$PN_{\pi}N_{\pi}N_{H}N_{H}$	3676	104	2	9	-	-	-	-	0.0	0.1
$PN_{\pi}N_{\pi}N_{H}N_{H}$	3678	168	4	4	-	-	-	-	0.1	0.3
$PN_{\pi}N_{\pi}N_{\pi}N_{H}$	3667	219	−7	7	-	-	-	-	2.5	2.4
$PN_{\pi}N_{\pi}N_{H}N_{C}$	3666	214	−8	2	-	-	-	-	3.3	3.2
$PN_{\pi}N_{\pi}N_{H}N_{C}$	3666	221	−8	5	-	-	-	-	3.9	3.7
$PN_{\pi}N_{\pi}N_{\pi}N_{\pi}$	3673	69	−1	6	-	-	-	-	4.9	3.9
$PN_{\pi}N_{\pi}N_{H}N_{C}$	3668	221	−6	6	-	-	-	-	5.7	4.9
$PN_{\pi}N_{\pi}N_{\pi}N_{H}$	3667	211	−7	5	-	-	-	-	5.9	5.2
$PN_{\pi}N_{\pi}N_{C}N_{C}$	3672	65	−2	1	-	-	-	-	7.2	6.1
$PN_{H}N_{C}N_{C}N_{C}$	3668	215	−6	5	-	-	-	-	12.6	10.7
$PN_{\pi}N_{\pi}N_{H}N_{H}N_{H}$	3674	142	0	3	-	-	-	-	0.0	0.0
$PN_{\pi}N_{\pi}N_{H}N_{H}N_{H}$	3674	174	0	8	-	-	-	-	0.1	0.1
$PN_{\pi}N_{\pi}N_{\pi}N_{H}N_{H}$	3675	98	1	9	-	-	-	-	1.5	1.5
$PN_{\pi}N_{\pi}N_{\pi}N_{H}N_{H}$	3676	106	2	4	-	-	-	-	2.2	2.0
$PN_{\pi}N_{\pi}N_{\pi}N_{H}N_{H}$	3676	126	2	10	-	-	-	-	2.6	2.3
$PN_{\pi}N_{\pi}N_{\pi}N_{H}N_{H}$	3678	171	4	1	-	-	-	-	2.7	2.5
$PN_{\pi}N_{\pi}N_{H}N_{H}N_{C}$	3677	166	3	4	-	-	-	-	3.2	3.1
$PN_{\pi}N_{\pi}N_{H}N_{H}N_{C}$	3676	107	2	4	-	-	-	-	3.4	3.1
$PN_{\pi}N_{\pi}N_{\pi}N_{H}N_{H}$	3675	100	1	11	-	-	-	-	3.9	3.5
$PN_{\pi}N_{\pi}N_{H}N_{H}N_{C}$	3678	173	4	5	-	-	-	-	3.8	3.6
$PN_{\pi}N_{\pi}N_{\pi}N_{H}N_{H}$	3675	91	1	8	-	-	-	-	4.3	3.8
$PN_{\pi}N_{\pi}N_{\pi}N_{\pi}N_{H}$	3666	224	−8	6	-	-	-	-	4.4	4.0
$PN_{\pi}N_{\pi}N_{\pi}N_{\pi}N_{\pi}$	3672	67	−2	14	-	-	-	-	4.9	4.2
$PN_{\pi}N_{\pi}N_{\pi}N_{\pi}N_{C}$	3672	69	−2	7	-	-	-	-	5.9	4.9
$PN_{\pi}N_{\pi}N_{H}N_{H}N_{C}$	3677	107	3	1	-	-	-	-	5.7	5.0
$PN_{\pi}N_{\pi}N_{\pi}N_{\pi}N_{H}$	3667	215	−7	5	-	-	-	-	6.2	5.6

Table S3: Cartesian coordinates (in Å) of computed P monomer from B3LYP-D3(BJ)/aVTZ geometry optimisations in Gaussian 09 Revision E.01.

	P		
C	0.33057	1.12258	0.00005
C	−0.98003	0.71094	0.00008
C	−0.98004	−0.71093	0.00000
C	0.33056	−1.12258	−0.00008
N	1.11865	−0.00001	−0.00005
H	2.12156	−0.00001	−0.00009
H	0.7621	2.10731	0.00009
H	−1.8413	1.3561	0.00015
H	−1.84132	−1.35608	0.00000
H	0.76207	−2.10732	−0.00015

Table S4: Cartesian coordinates (in Å) of computed PP dimer from B3LYP-D3(BJ)/aVTZ geometry optimisations in Gaussian 09 Revision E.01.

	PP		
C	−0.71416	−1.89023	1.12198
C	0.48597	−2.42219	0.71210
C	0.48597	−2.42219	−0.71210
C	−0.71416	−1.89023	−1.12198
N	−1.43493	−1.57833	0.00000
H	−2.32343	−1.11178	0.00000
H	−1.10650	−1.70755	2.10585
H	1.26893	−2.78068	1.35740
H	1.26893	−2.78068	−1.35740
H	−1.10650	−1.70755	−2.10585
C	0.48597	1.70142	1.11946
C	0.18765	2.98101	0.71090
C	0.18765	2.98101	−0.71090
C	0.48597	1.70142	−1.11946
N	0.66923	0.93630	0.00000
H	0.85518	−0.05357	0.00000
H	0.58351	1.27748	2.10266
H	−0.00443	3.82041	1.35666
H	−0.00443	3.82041	−1.35666
H	0.58351	1.27748	−2.10266

Table S5: Cartesian coordinates (in Å) of computed PPP trimer from B3LYP-D3(BJ)/aVTZ geometry optimisations in Gaussian 09 Revision E.01.

	PPP		
C	−2.18953	−0.23303	1.11855
C	−2.74811	−1.42552	0.71223
C	−2.74811	−1.42552	−0.71223
C	−2.18953	−0.23303	−1.11855
N	−1.86135	0.47884	0.00000
H	−1.37888	1.36646	0.00000
H	−1.99895	0.16023	2.10057
H	−3.12508	−2.19956	1.35811
H	−3.12508	−2.19956	−1.35811
H	−1.99895	0.16023	−2.10057
C	1.29658	−1.77967	1.11855
C	2.60859	−1.66718	0.71223
C	2.60859	−1.66718	−0.71223
C	1.29658	−1.77967	−1.11855
N	0.51599	−1.85139	0.00000
H	−0.49395	−1.87738	0.00000
H	0.86071	−1.81125	2.10057
H	3.46742	−1.60662	1.35811
H	3.46742	−1.60662	−1.35811
H	0.86071	−1.81125	−2.10057
C	0.89295	2.01271	1.11855
C	0.13952	3.09269	0.71223
C	0.13952	3.09269	−0.71223
C	0.89295	2.01271	−1.11855
N	1.34536	1.37255	0.00000
H	1.87283	0.51091	0.00000
H	1.13824	1.65102	2.10057
H	−0.34234	3.80618	1.35811
H	−0.34234	3.80618	−1.35811
H	1.13824	1.65102	−2.10057

Table S6: Cartesian coordinates (in Å) of computed PN_π dimer from B3LYP-D3(BJ)/aVTZ geometry optimisations in Gaussian 09 Revision E.01.

	PN_π		
C	−0.86230	−1.12240	0.37035
C	−1.06372	−0.71013	−0.92505
C	−1.06371	0.71049	−0.92478
C	−0.86229	1.12226	0.37078
N	−0.74482	−0.00022	1.14939
H	−0.58723	−0.00040	2.13989
H	−0.79300	−2.10717	0.79573
H	−1.19241	−1.35548	−1.77643
H	−1.19239	1.35616	−1.77592
H	−0.79297	2.10687	0.79653
N	2.34884	−0.54579	−0.11238
N	2.34885	0.54582	−0.11239

Table S7: Cartesian coordinates (in Å) of computed PN_H dimer from B3LYP-D3(BJ)/aVTZ geometry optimisations in Gaussian 09 Revision E.01.

	PN_H		
C	1.08023	1.12154	0.00000
C	2.39165	0.71090	−0.00001
C	2.39168	−0.71086	−0.00001
C	1.08027	−1.12156	0.00000
N	0.29171	−0.00002	0.00001
H	−0.71166	−0.00004	0.00002
H	0.64878	2.10643	0.00001
H	3.25285	1.35623	−0.00001
H	3.25290	−1.35615	−0.00001
H	0.64886	−2.10646	0.00001
N	−3.08307	−0.00001	0.00001
N	−4.17360	0.00001	−0.00001

Table S8: Cartesian coordinates (in Å) of computed $PN_{\pi}N_{\pi}$ trimer from B3LYP-D3(BJ)/aVTZ geometry optimisations in Gaussian 09 Revision E.01.

	$PN_{\pi}N_{\pi}$		
C	0.00000	1.12203	−0.17929
C	0.00001	0.71016	1.13230
C	0.00000	−0.70932	1.13285
C	−0.00001	−1.12218	−0.17843
N	−0.00001	−0.00038	−0.96606
H	0.00000	−0.00076	−1.96906
H	0.00001	2.10652	−0.61050
H	0.00002	1.35634	1.99268
H	0.00000	−1.35483	1.99371
H	−0.00002	−2.10700	−0.60889
N	3.25331	0.54572	−0.19570
N	3.25323	−0.54585	−0.19574
N	−3.25326	−0.54584	−0.19560
N	−3.25328	0.54573	−0.19583

Table S9: Cartesian coordinates (in Å) of computed $PN_{\pi}N_{H}$ trimer from B3LYP-D3(BJ)/aVTZ geometry optimisations in Gaussian 09 Revision E.01.

	$PN_{\pi}N_{H}$		
C	−0.74846	−0.85340	−1.12119
C	−2.04945	−1.02260	−0.71023
C	−2.04953	−1.02248	0.71026
C	−0.74859	−0.85321	1.12134
N	0.03344	−0.75584	0.00011
H	1.02708	−0.61606	0.00015
H	−0.32137	−0.79443	−2.10601
H	−2.90349	−1.13052	−1.35594
H	−2.90364	−1.13029	1.35590
H	−0.32160	−0.79408	2.10619
N	−1.10837	2.36424	−0.54605
N	−1.10842	2.36433	0.54559
N	4.41081	0.05314	0.00006
N	3.34384	−0.17221	0.00010

Table S10: Cartesian coordinates (in Å) of computed $PN_{\pi}N_{H}$ trimer from B3LYP-D3(BJ)/aVTZ geometry optimisations in Gaussian 09 Revision E.01.

	$PN_{\pi}N_{H}$		
C	1.56993	−0.38600	1.14364
C	2.45976	−0.06484	0.14588
C	1.88020	−0.46866	−1.08676
C	0.65421	−1.02144	−0.80305
N	0.47974	−0.97127	0.55555
H	−0.34514	−1.27895	1.03610
H	1.62271	−0.24656	2.20828
H	3.41639	0.40768	0.28547
H	2.31083	−0.36421	−2.06739
H	−0.09736	−1.44172	−1.44636
N	−0.70082	1.92819	−0.44995
N	−0.04884	2.39165	0.29273
N	−3.58200	−0.38311	−0.20034
N	−2.76124	−0.88412	0.31425

Table S11: Cartesian coordinates (in Å) of computed $PN_{\pi}N_{\pi}N_{H}$ tetramer from B3LYP-D3(BJ)/aVTZ geometry optimisations in Gaussian 09 Revision E.01.

	$PN_{\pi}N_{\pi}N_{H}$		
C	0.70719	0.00009	−1.12099
C	2.01954	0.00010	−0.70963
C	2.01954	0.00001	0.70969
C	0.70718	−0.00005	1.12104
N	−0.08034	0.00000	0.00003
H	−1.08382	−0.00003	0.00002
H	0.27643	0.00014	−2.10579
H	2.88011	0.00016	−1.35562
H	2.88010	−0.00001	1.35569
H	0.27642	−0.00013	2.10584
N	0.65240	−3.24418	−0.54596
N	0.65241	−3.24425	0.54562
N	0.65225	3.24422	0.54602
N	0.65223	3.24428	−0.54556
N	−4.52042	−0.00011	−0.00017
N	−3.42995	−0.00009	−0.00010

Table S12: Cartesian coordinates (in Å) of computed $PN_{\pi}N_{\pi}N_{H}$ tetramer from B3LYP-D3(BJ)/aVTZ geometry optimisations in Gaussian 09 Revision E.01.

	$PN_{\pi}N_{\pi}N_{H}$		
C	0.82753	−0.83261	−1.04611
C	1.30473	−1.65796	−0.05475
C	0.98191	−1.05719	1.19042
C	0.31544	0.11473	0.92117
N	0.23014	0.24069	−0.44066
H	−0.23258	0.99354	−0.91523
H	0.86381	−0.92165	−2.11669
H	1.82790	−2.58565	−0.20802
H	1.21262	−1.43779	2.17011
H	−0.09740	0.85942	1.57690
N	−2.48555	−1.44042	0.23814
N	−2.14846	−2.25295	−0.40789
N	−3.40350	2.20407	0.16858
N	−2.41840	2.10568	−0.28889
N	3.26287	1.49328	0.37508
N	3.51262	1.03399	−0.58314

Table S13: Cartesian coordinates (in Å) of computed $PN_{\pi}N_{H}N_{H}$ tetramer from B3LYP-D3(BJ)/aVTZ geometry optimisations in Gaussian 09 Revision E.01.

	$PN_{\pi}N_{H}N_{H}$		
C	1.52112	−1.12105	−0.65255
C	2.67580	−0.71028	−0.02890
C	2.67584	0.71019	−0.02878
C	1.52119	1.12112	−0.65237
N	0.83208	0.00009	−1.03274
H	−0.06895	0.00015	−1.47341
H	1.13968	−2.10528	−0.85489
H	3.43238	−1.35611	0.38160
H	3.43246	1.35590	0.38182
H	1.13980	2.10540	−0.85455
N	−0.15787	0.54566	2.09226
N	−0.15800	−0.54594	2.09209
N	−2.55854	2.23043	−0.04630
N	−1.94514	1.69542	−0.77231
N	−1.94520	−1.69523	−0.77265
N	−2.55863	−2.23040	−0.04680

Table S14: Cartesian coordinates (in Å) of computed $PN_{\pi}N_{\pi}N_{H}N_{H}$ pentamer from B3LYP-D3(BJ)/aVTZ geometry optimisations in Gaussian 09 Revision E.01.

	$PN_{\pi}N_{\pi}N_{H}N_{H}$		
C	−0.36548	0.96362	−1.05942
C	−0.22992	2.27636	−0.67154
C	0.23020	2.27627	0.67165
C	0.36558	0.96348	1.05942
N	−0.00001	0.17729	−0.00003
H	−0.00008	−0.82576	−0.00007
H	−0.68515	0.53201	−1.99035
H	−0.43796	3.13706	−1.28295
H	0.43837	3.13688	1.28313
H	0.68518	0.53174	1.99032
N	2.94141	1.00252	−1.54036
N	3.18894	0.60824	−0.55317
N	−2.94124	1.00268	1.54044
N	−3.18889	0.60862	0.55319
N	2.77694	−2.62138	1.34371
N	1.77780	−2.32064	1.02636
N	−1.77810	−2.32043	−1.02645
N	−2.77722	−2.62126	−1.34377

Table S15: Cartesian coordinates (in Å) of computed $PN_{\pi}N_{\pi}N_{H}N_{H}$ pentamer from B3LYP-D3(BJ)/aVTZ geometry optimisations in Gaussian 09 Revision E.01.

	$PN_{\pi}N_{\pi}N_{H}N_{H}$		
C	−0.98587	0.41115	−1.12148
C	−1.71392	1.50417	−0.71211
C	−1.71391	1.50649	0.70726
C	−0.98585	0.41482	1.12019
N	−0.55265	−0.24346	0.00043
H	0.03377	−1.05722	0.00175
H	−0.74653	0.05065	−2.10511
H	−2.19279	2.21806	−1.35936
H	−2.19277	2.22250	1.35218
H	−0.74650	0.05754	2.10500
N	1.80449	2.02981	0.54248
N	1.80471	2.02744	−0.54907
N	2.87944	−1.02524	2.24654
N	1.99445	−1.35128	1.69878
N	1.99417	−1.35730	−1.69437
N	2.87904	−1.03337	−2.24356
N	−3.67027	−1.41784	−0.54337
N	−3.67021	−1.41610	0.54818

Table S16: Cartesian coordinates (in Å) of computed $PN_{\pi}N_{\pi}N_{H}N_{H}$ pentamer from B3LYP-D3(BJ)/aVTZ geometry optimisations in Gaussian 09 Revision E.01.

	$PN_{\pi}N_{\pi}N_{H}N_{H}$		
C	1.08498	0.00040	1.12033
C	2.39808	0.00030	0.70966
C	2.39810	−0.00017	−0.70962
C	1.08501	−0.00035	−1.12033
N	0.29838	0.00001	−0.00001
H	−0.70464	−0.00002	−0.00003
H	0.65378	0.00072	2.10472
H	3.25857	0.00054	1.35579
H	3.25861	−0.00036	−1.35573
H	0.65384	−0.00069	−2.10473
N	−3.15849	−0.00166	−2.59289
N	−2.45174	−0.00106	−1.76230
N	−2.45175	0.00093	1.76227
N	−3.15842	0.00151	2.59294
N	0.98350	−3.23479	−0.54474
N	0.98363	−3.23445	0.54684
N	0.98323	3.23482	0.54473
N	0.98349	3.23451	−0.54686

Table S17: Cartesian coordinates (in Å) of computed $PN_{\pi}N_{\pi}N_{H}N_{H}N_{H}$ hexamer from B3LYP-D3(BJ)/aVTZ geometry optimisations in Gaussian 09 Revision E.01.

	$PN_{\pi}N_{\pi}N_{H}N_{H}N_{H}$		
C	0.53978	−1.14580	−1.13093
C	0.82954	−2.44185	−0.77044
C	0.81282	−2.50088	0.64746
C	0.51249	−1.23914	1.10751
N	0.34875	−0.42731	0.01809
H	0.13053	0.55119	0.05588
H	0.45604	−0.68390	−2.09761
H	1.02942	−3.25307	−1.44861
H	0.99772	−3.36577	1.26041
H	0.40480	−0.85945	2.10707
N	−2.63994	−1.77170	−0.61757
N	−2.65454	−1.75354	0.47371
N	3.65012	−0.37691	0.60845
N	3.61645	−0.22743	−0.47229
N	−2.65350	1.41374	2.23380
N	−1.67008	1.43537	1.76265
N	1.39105	2.69176	−0.01876
N	2.23196	3.38180	−0.09703
N	−2.67358	1.48752	−2.10676
N	−1.68759	1.51484	−1.64126

Table S18: Cartesian coordinates (in Å) of computed $PN_{\pi}N_{\pi}N_{H}N_{H}N_{H}$ hexamer from B3LYP-D3(BJ)/aVTZ geometry optimisations in Gaussian 09 Revision E.01.

	$PN_{\pi}N_{\pi}N_{H}N_{H}N_{H}$		
C	0.12705	−1.48055	1.22278
C	0.23150	−2.71807	0.62996
C	0.22444	−2.51636	−0.77474
C	0.11624	−1.16227	−0.99469
N	0.05767	−0.54571	0.22569
H	−0.02073	0.44397	0.37023
H	0.09705	−1.19400	2.25827
H	0.30414	−3.65879	1.14735
H	0.29061	−3.27344	−1.53658
H	0.07654	−0.59711	−1.90784
N	2.37483	2.32263	−1.74192
N	1.62395	2.10189	−0.98228
N	−0.22694	2.22065	1.97144
N	−0.30793	3.12260	2.57895
N	−3.10684	−1.44659	−0.43765
N	−3.10197	−1.56765	0.64716
N	3.34156	−1.06861	0.69319
N	3.32655	−0.88170	−0.38212
N	−2.81699	1.88956	−1.61134
N	−1.87001	1.78765	−1.07986

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