Pillar[6]pyridinium: a hexagonally-shaped molecular box that selectively recognizes multicharged anionic species

Sandra Kosiorek, Helena Butkiewicz, Oksana Danylyuk, and Volodymyr Sashuk*

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

E-mail: vsashuk@ichf.edu.pl Webpage: http://groups.ichf.edu.pl/sashuk

Supporting Information

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1. Materials, instrumentation and methods

All chemicals were purchased as reagent grade from commercial suppliers (Sigma-Aldrich, AlfaAesar, Fluorochem) and used without further purification. The solvents used *(Merck, ChemPur, PoCh)* were of analytical grade quality. Deionized water (18.3 MΩ·cm) was obtained from Milli-Q station. NMR solvents and tubes were purchased from Armar Chemicals. 4-(Bromomethyl)pyridine hydrobromide was synthesized according to literature procedure.[1]

NMR spectra were recorded on Bruker (400, 500 and 600 MHz) instruments. The chemical shifts (δ) are given in ppm relative to TMS, coupling constants are (J) in Hz. NMR data were analyzed using MestReNova Software. MS spectra were recorded on Maldi SYNAPT G2-S HDMS (Waters) spectrometer. Titrations were performed using MicroCal PEAQ-ITC from Malvern. Single crystals were grown by slow diffusion of the ethanol vapor into aqueous solution of P[6]P hexachloride salt. The suitable crystal was selected under Paratone-N oil, mounted on the nylon loop and positioned in the cold stream on the diffractometer. The X-ray data were collected at 100 K on the SuperNova Agilent diffractometer using Cu$K\alpha$ radiation (λ = 1.54184 Å). The data were processed with *CrysAlisPro*.[2] Solution, refinement and analysis of the structure was done using the programs integrated in the *WinGX* software system.[3] Structure was solved by direct methods and refined using *SHELXL-2013*.[4] The figures were prepared using the UCSF *Chimera* package.[5] Quantum chemical calculations were performed within the density functional theory (DFT) using the Gaussian 09 program suite.[6] The geometry was taken from the crystal structure of P[6]P and optimized with the B3LYP functional, using the 6-31+g(d) basis set. PCM (polarized continuum model) solvent effects were considered within the CPCM to model the interaction with the solvent. Molecular orbitals and electrostatic potential maps were displayed using the GaussView program.[7]

2. Synthesis

A suspension of 4-(bromomethyl)-pyridinium hydrobromide (4 g, 15.8 mmol) and $NaHCO_3$ (1.46 g, 17.4 mmol) in 160 mL of acetonitrile was prepared in a 500 mL round-bottom flask. The contents of the flask were heated to reflux and after 20 minutes NH_4PF_6 (2.58g, 15.8 mmol) was added. The reaction mixture was kept at reflux temperature for 48 hours. After this time, the content of the flask was cooled to room temperature, and the resulting precipitate was filtered and dried. The precipitate was next crystallized from 1M aqueous KBr (50 mL). The obtained white crystals of P[4]P were removed by centrifugation. The filtrate was concentrated under reduced pressure, and crystallization was carried out again with 1M aqueous KBr (10 mL). As a result, P[6]P contaminated with P[4]P was obtained. The solvent was distilled from the remaining mother liquor, and the precipitate was crystallized from water (3 mL) to give 13 mg of pure P[6]P. Another batch of P[6]P (97 mg) was isolated by recrystallization of the P[4]P-P[6]P mixture in the minimum volume of water. Then, the combined P[6]P fractions were dissolved in 12N HCl (5 mL) and refluxed for 2h. The cooled reaction mixture was poured into acetonitrile, and the resultant precipitate was centrifuged and dried in vacuo to yield P[6]P·$(Cl)_6$ as a white solid (59 mg, 3 %). ^{1}H NMR (400 MHz, D_2O): δ 9.11 (d, J = 6.2 Hz, 12H), 8.09 (d, J = 6.2 Hz, 12H), 6.38 (s, 12H). ^{13}C NMR (100 MHz, D_2O): δ 153.5, 146.4, 128.1, 62.0.

3. Characterization

3.1 NMR and MS spectra

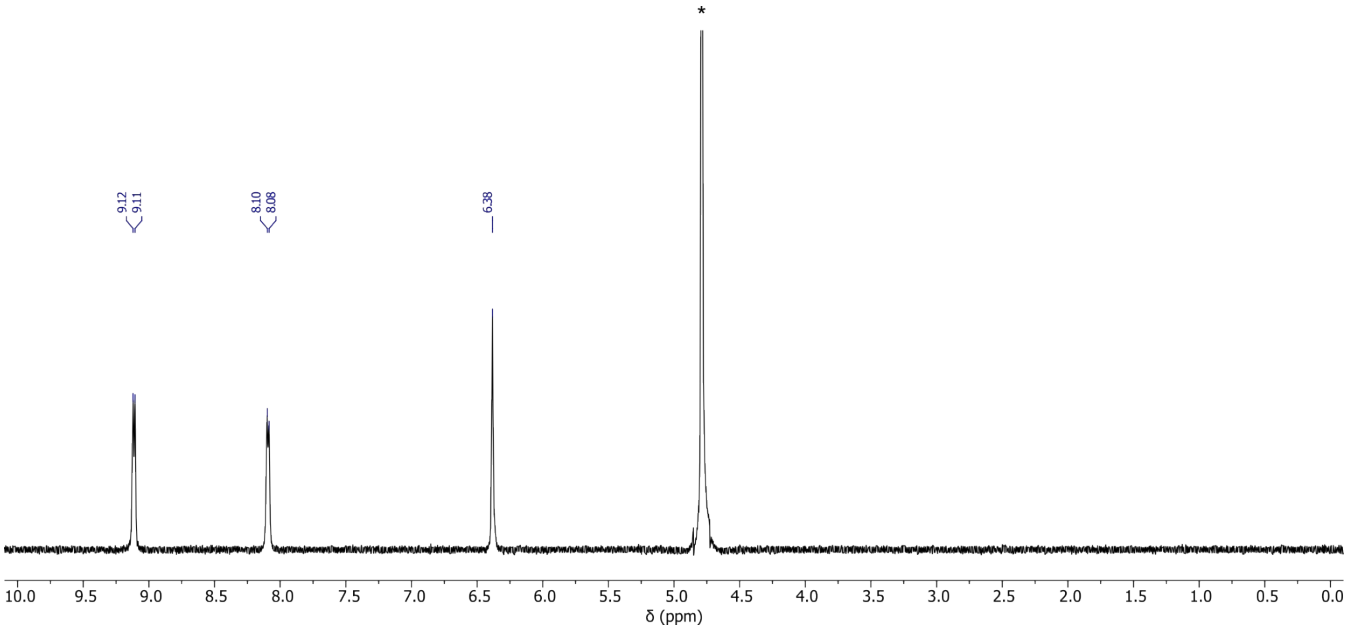

Figure S1. ^{1}H NMR spectrum of the crude P[6]P in D_2O at 298 K. Residual water is marked with an asterisk.

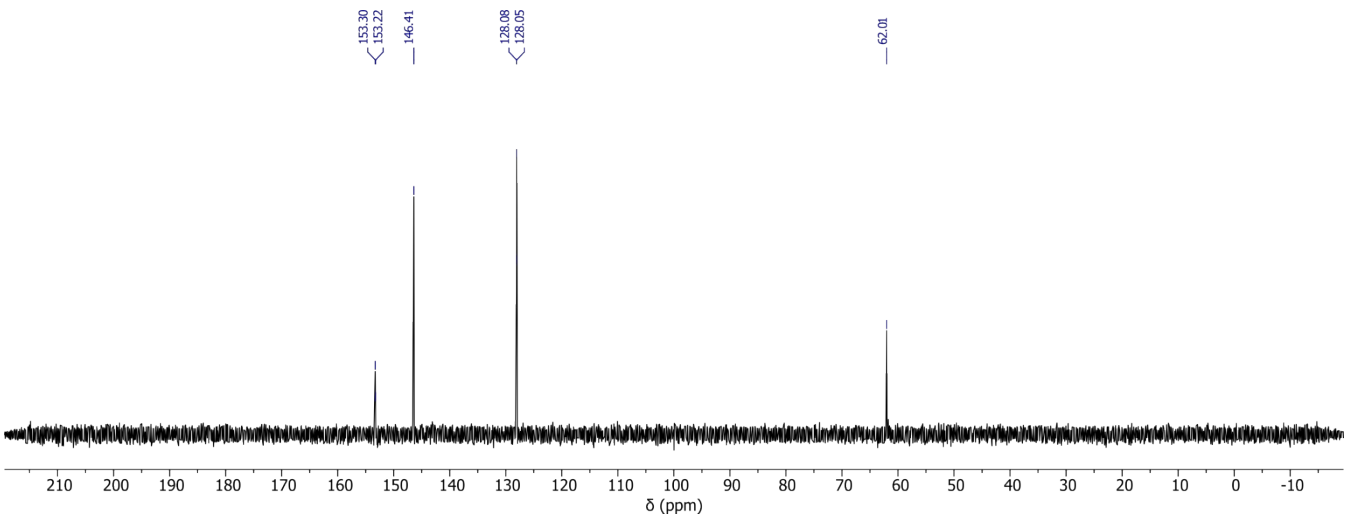

Figure S2. ^{13}C NMR spectrum of the crude P[6]P in D_2O at 298 K. Splitting of carbon atom signals indicates a through-space ^{13}C-^{19}F coupling with PF_6 ion which is probably located inside the macrocycle.

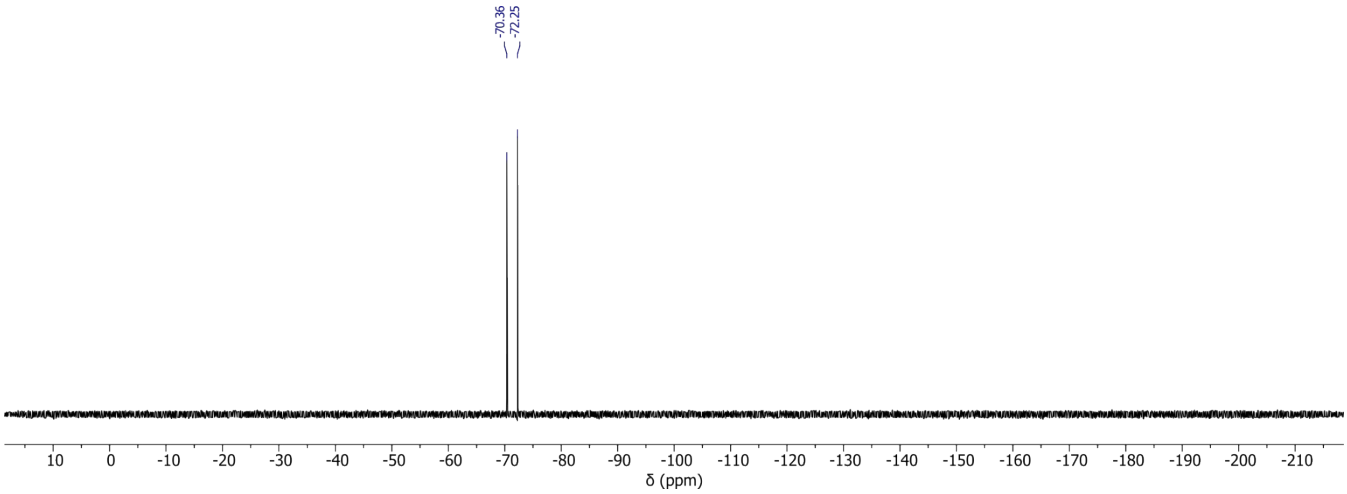

Figure S3. ^{19}F NMR spectrum of the crude P[6]P in D_2O at 298 K showing the presence of PF_6 ions.

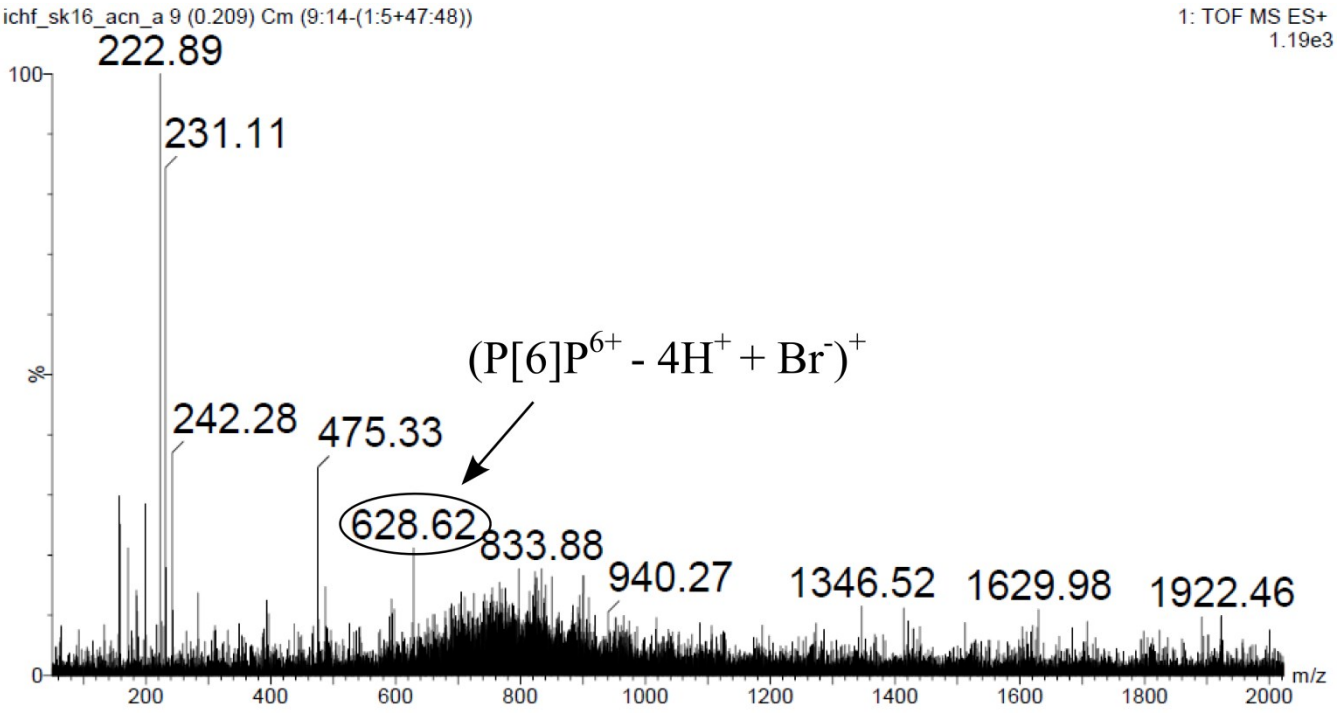

Figure S4. Mass spectrum of P[6]P under electrospray ionization showing the presence of Br ions in the crude product.

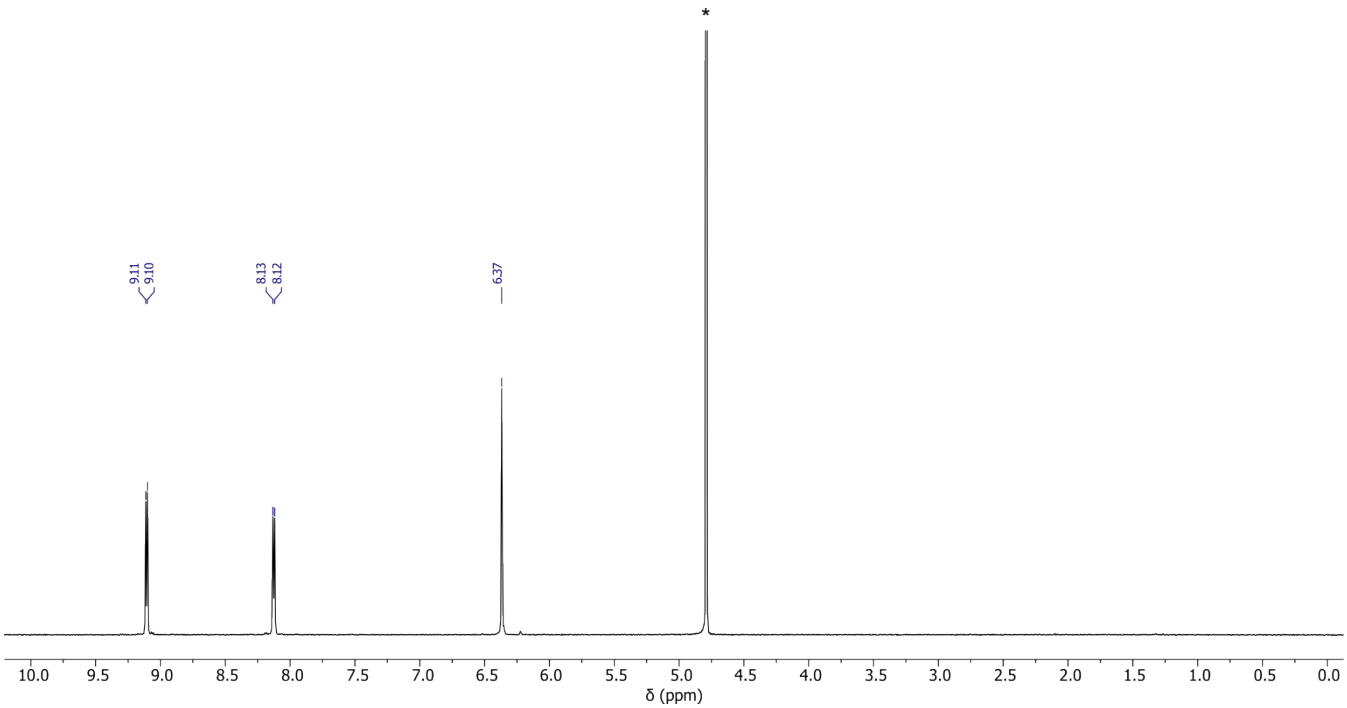

Figure S5. ^{1}H NMR spectrum of P[6]P·$(Cl)_6$ in D_2O at 298 K. Residual water is marked with an asterisk.

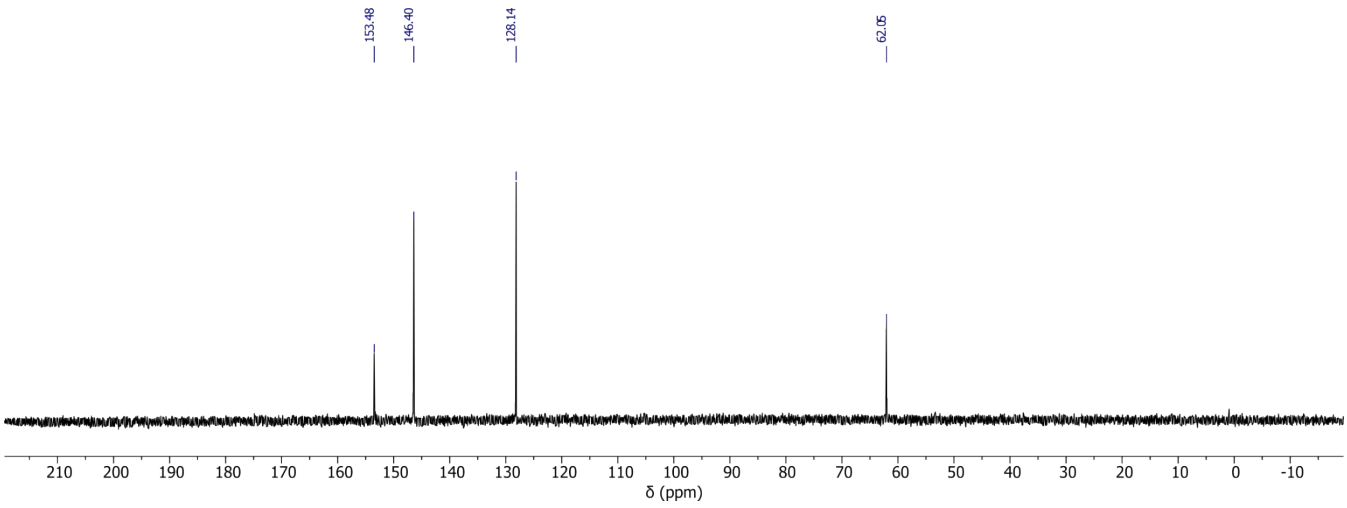

Figure S6. ^{13}C NMR spectrum of P[6]P·$(Cl)_6$ in D_2O at 298 K.

3.2 X-ray crystallography

P[6]P hexachloride salt crystallizes in the trigonal space group *R*-3. **Crystal data**: $C_{36}H_{36}N_6Cl_6O_{10}$, *Mr* =925.4, colourless, trigonal, space group *R*-3, *a* = 22.3483(4), *c* = 8.0031(1) Å, *V* = 3461.6(1) Å^3, *Z* = 3, ρ_{calc} = 1.332 g cm^{-3}, μ(Cu*Kα*) = 3.881 mm^{-1}, θ_{max} = 71.9°, 15744 reflections measured, 1507 unique, 172 parameters, 98 restraints, *R* = 0.040, *wR* = 0.109 (*R* = 0.040, *wR* = 0.110 for all data), GooF = 1.08. CCDC 1836980 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

The asymmetric unit comprises one sixth of the macrocycle, one chloride anion, water molecule disordered over two positions O1W and O1WA (refined with 0.5 site occupancy factors), and another water molecule residing in the macrocyclic cavity, refined as disordered over O2W and O2WA positions (refined with 0.33333 site occupancy factors because of their close position to the three-fold rotoinversion crystallographic axes).

The crystal structure is a peculiar example of the two types of the whole-molecule disorder. Firstly, the P[6]P macrocycle has two orientations (colored in blue and yellow, Figure S7) on the same site in the different unit cells. Moreover, the nitrogen atoms of the pyridinium rings cannot be reliably distinguished from the carbon atoms, therefore, the additional disorder has been introduced into the model. This substitutional disorder implies that the same site may be occupied by different atoms (carbon or nitrogen) in the different unit cells. As neither position has clear advantage over another, it is equally possible that nitrogen atoms might be found in the clockwise or anticlockwise directions around the macrocycle. The disorder model was built using PART instructions. The soft similarity restraints SIMU and DELU on anisotropic displacement parameters of P[6]P atoms have been applied during the refinement. The positional substitutional disorder of nitrogen and carbon atoms sharing the same site have been built using EXYZ (same position) and EADP (same thermal parameters) constraints.

All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. All components of the structure except one chloride anion are disordered.

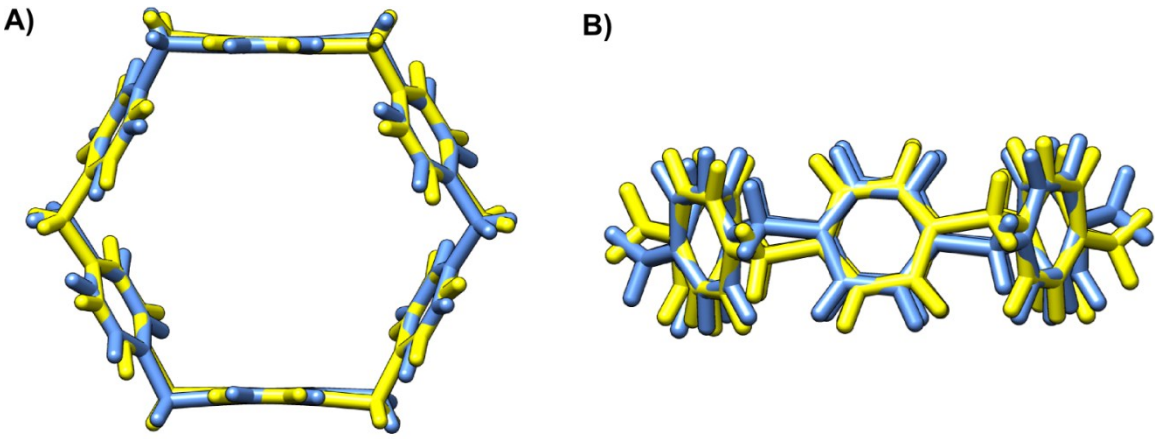

Figure S7. The whole-molecule disorder of the pillar[6]pyridinium macrocycle. The different orientations are colored in blue and yellow.

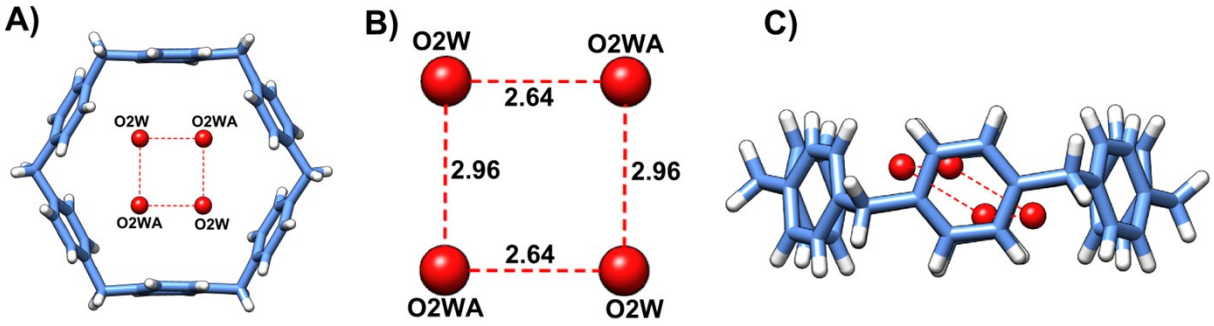

Figure S8. A) Top view of the tetrameric water cluster included into P[6]P inner cavity; B) Structure and hydrogen bonding of the rectangular tetrameric water cluster; C) Side view of the tetrameric water cluster included into P[6]P inner cavity.

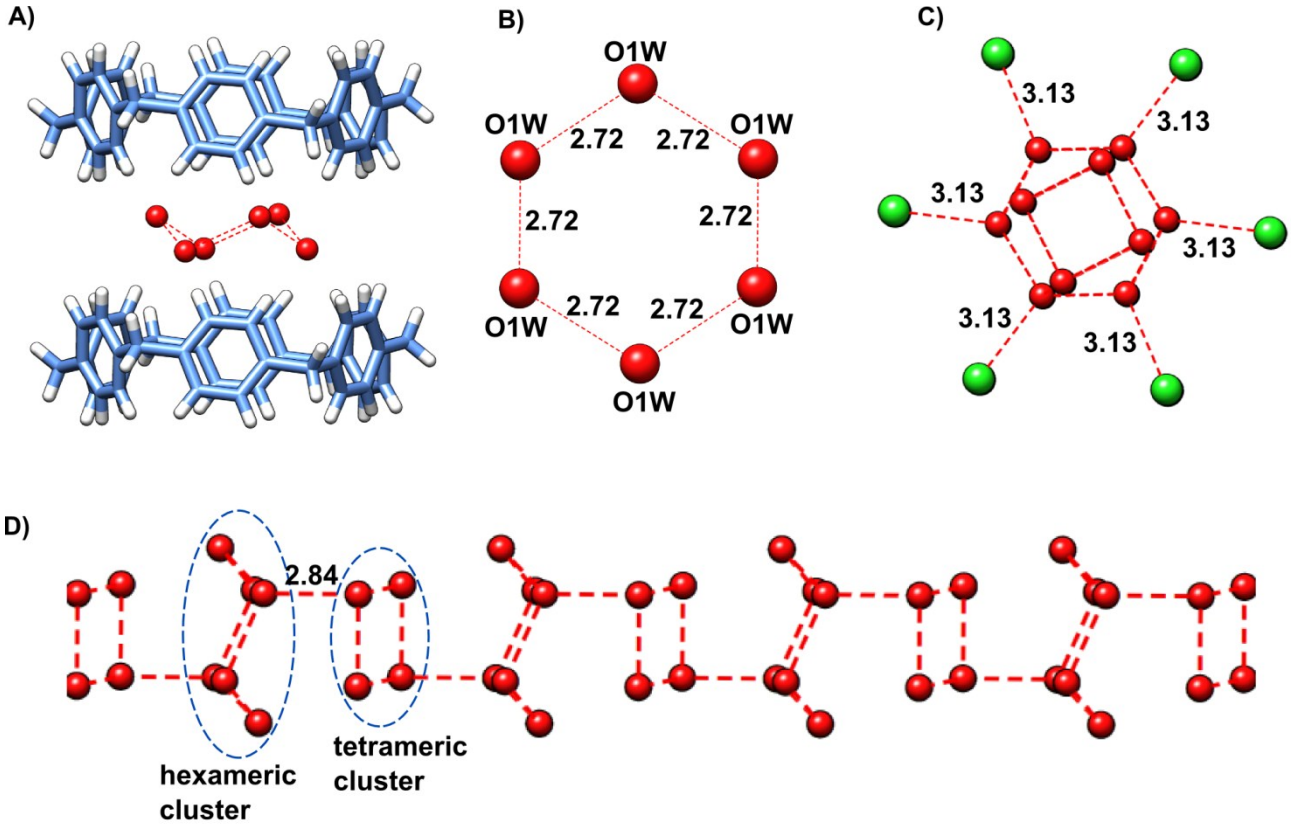

Figure S9. A) Side view of the hexameric water cluster in chair conformation sandwiched between adjacent P[6]P molecules in the crystal lattice; B) Structure and hydrogen bonding of the hexameric water cluster; C) Top view of the water tape surrounded by chloride anions; D) Structure of the water tape (polymeric cluster) consisting of hydrogen bonded alternating hexameric and tetrameric water clusters.

4. Binding studies

4.1 NMR

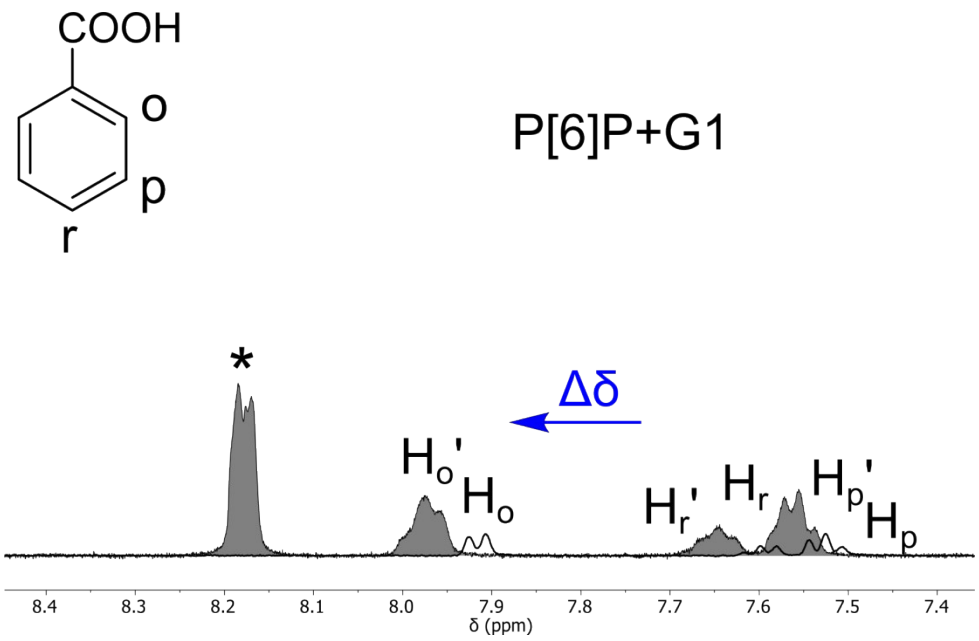

Figure S10. ^{1}H NMR spectra of **G1** before and after addition of P[6]P·$(Cl)_6$ in Tris buffer (pD=7.22) at 298 K.

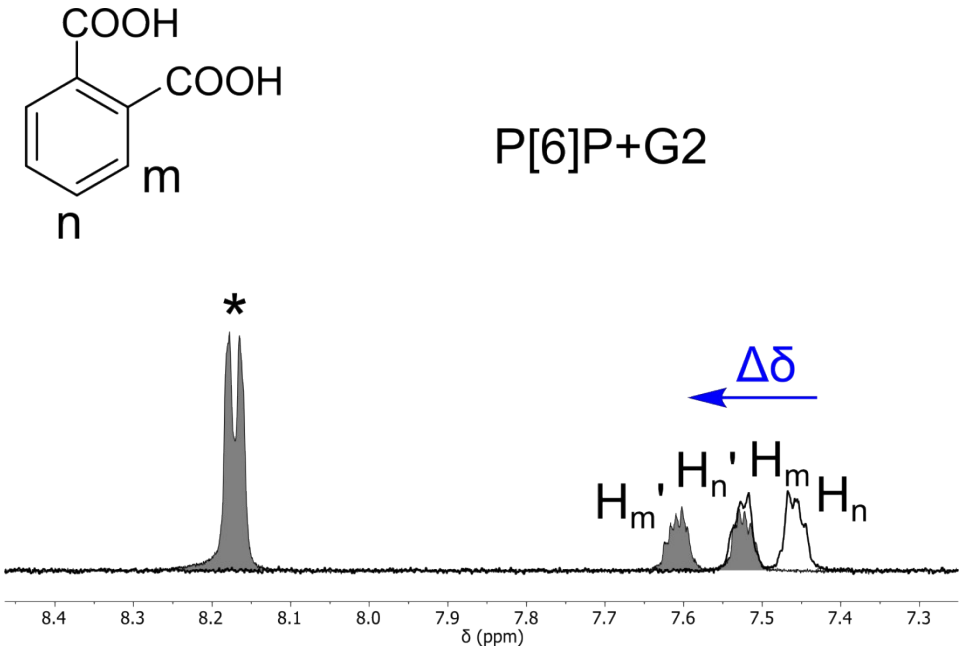

Figure S11. ^{1}H NMR spectra of **G2** before and after addition of P[6]P·$(Cl)_6$ in Tris buffer (pD=7.22) at 298 K.

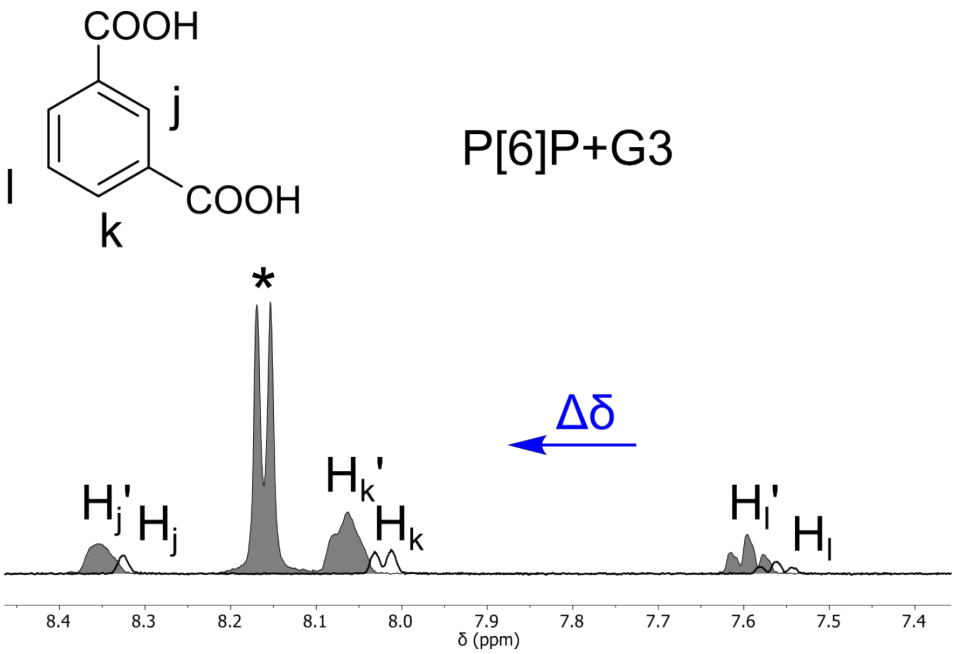

Figure S12. ^{1}H NMR spectra of **G3** before and after addition of P[6]P·$(Cl)_6$ in Tris buffer (pD=7.22) at 298 K.

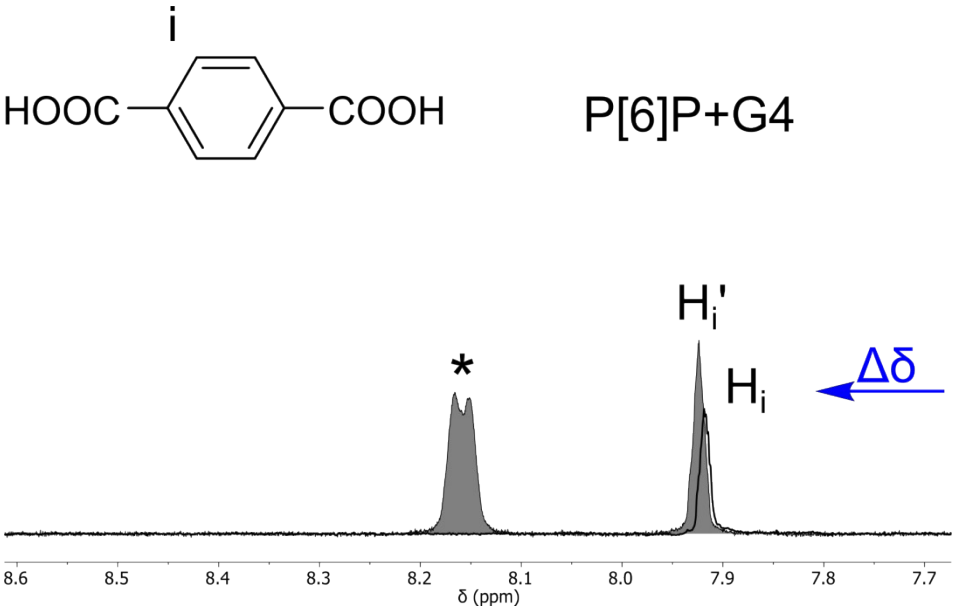

Figure S13. ^{1}H NMR spectra of **G4** before and after addition of P[6]P·$(Cl)_6$ in Tris buffer (pD=7.22) at 298 K.

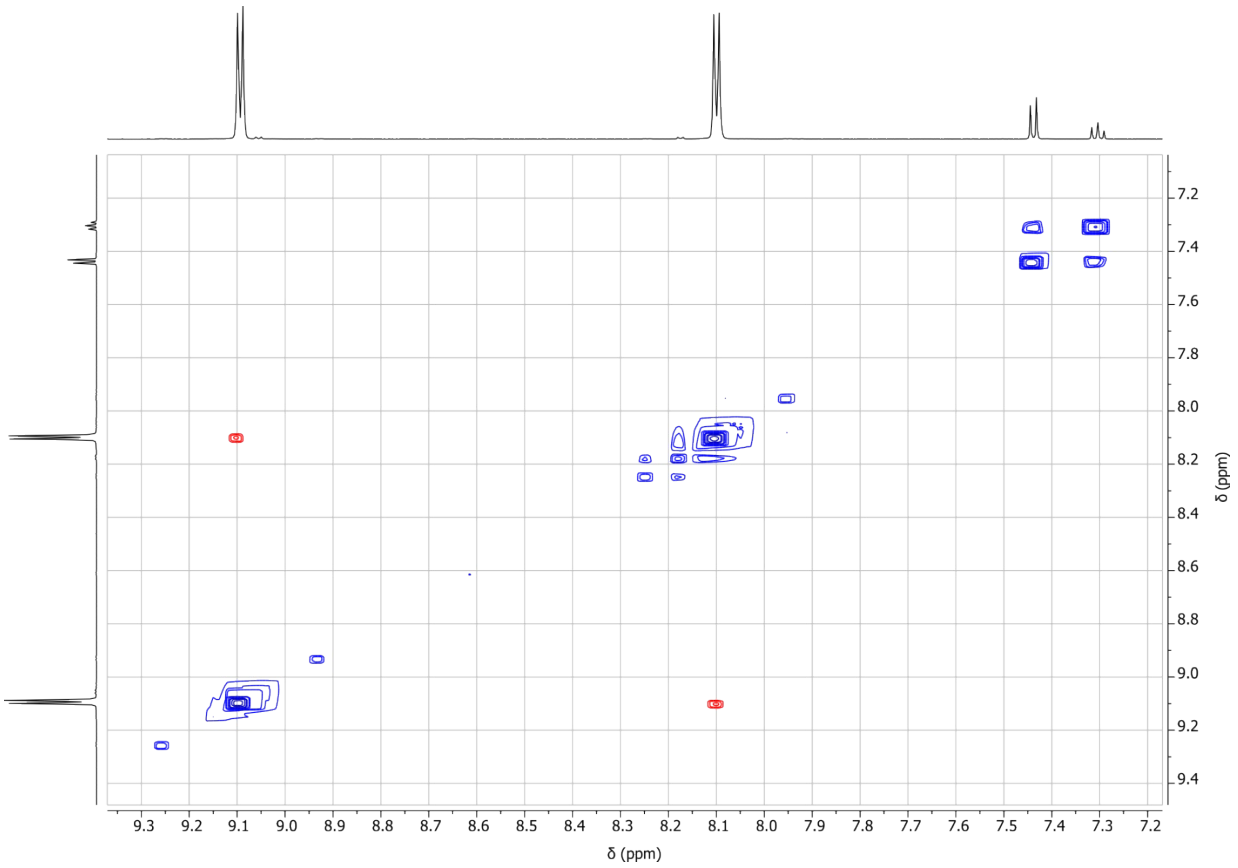

Figure S14. ^{1}H 2D ROESY NMR spectra of a mixture of P[6]P·$(Cl)_6$ and **G5** at 1:1 ratio in Tris buffer (pD=6.40) at 298 K.

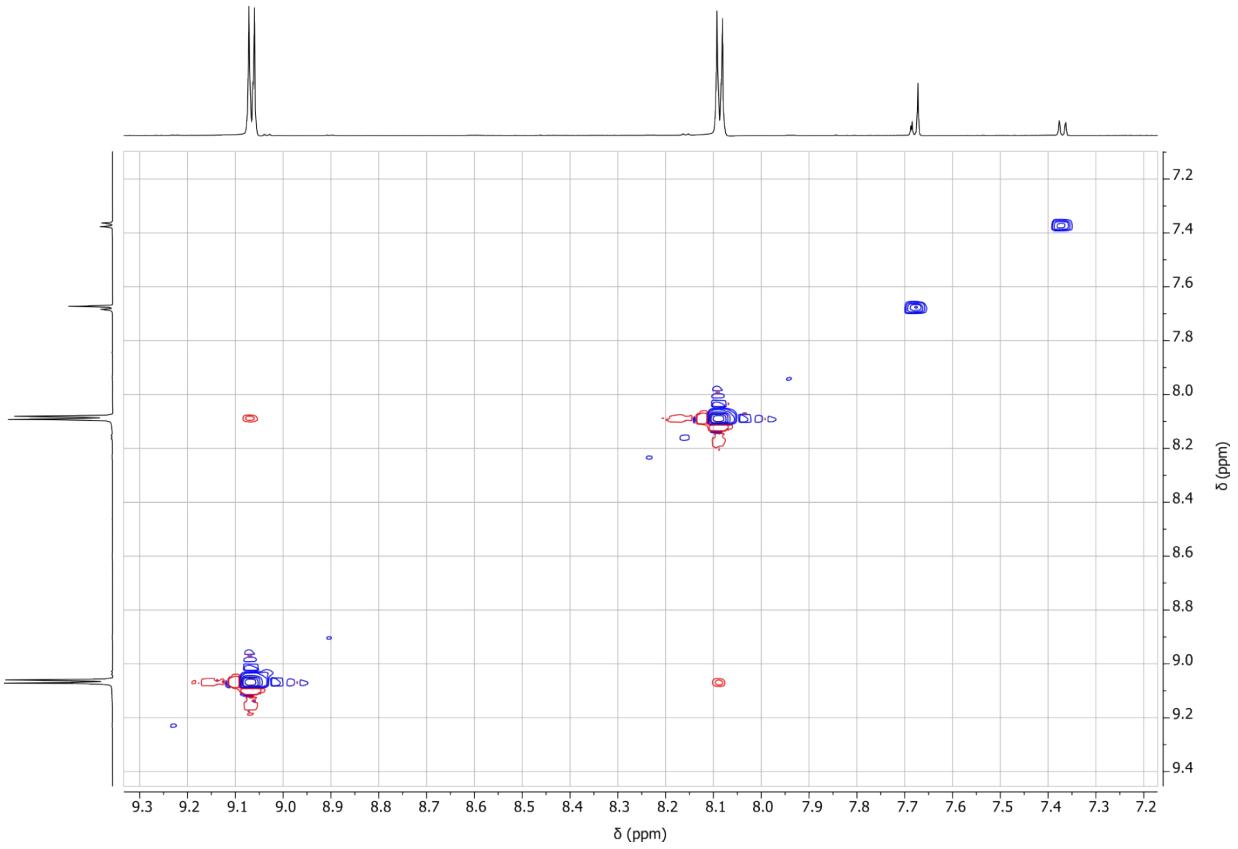

Figure S15. ^{1}H 2D ROESY NMR spectra of a mixture of P[6]P·$(Cl)_6$ and **G6** at 1:1 ratio in Tris buffer (pD=6.40) at 298 K.

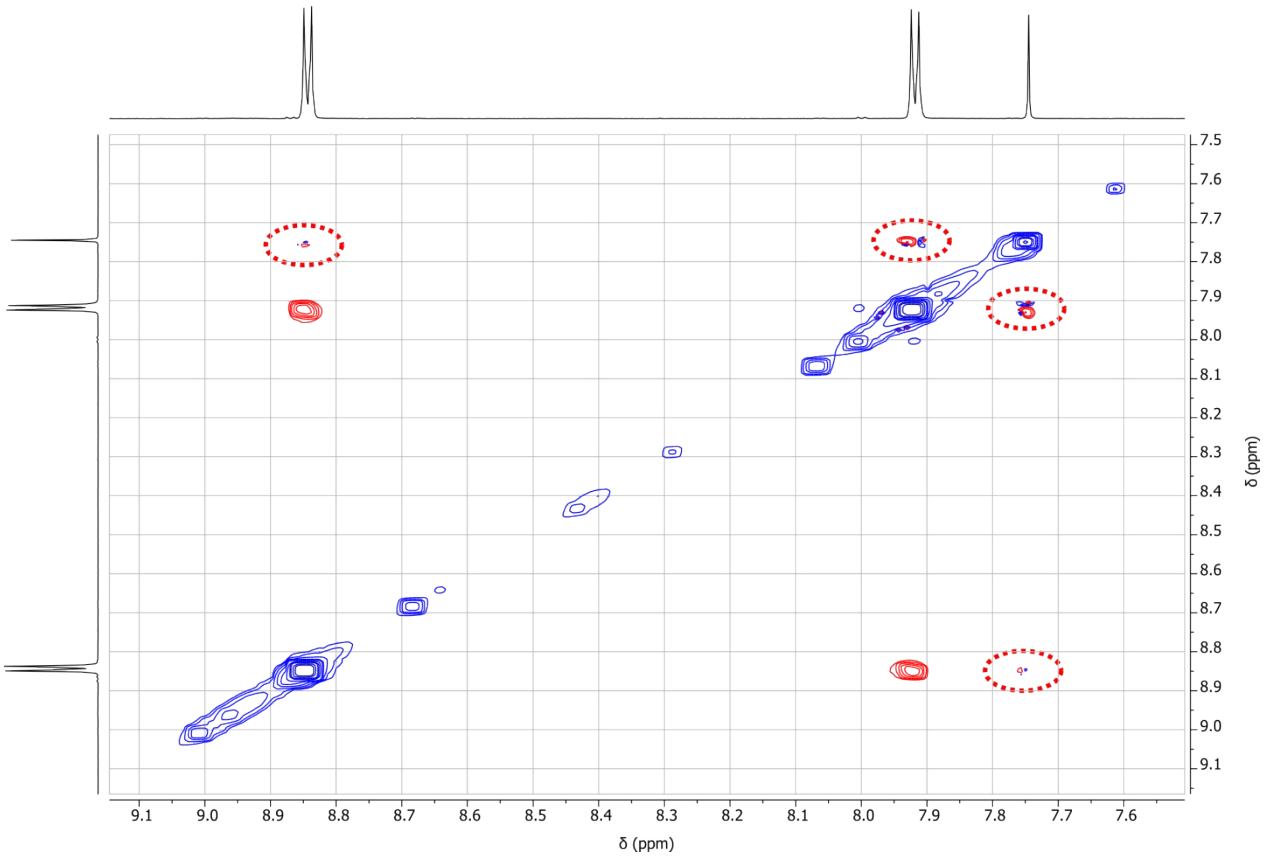

Figure S16. ^{1}H 2D ROESY NMR spectra of a mixture of P[6]P·$(Cl)_6$ and **G7** at 1:1 ratio in Tris buffer (pD=6.40) at 298 K.

4.2 ITC

Each solution used in titration experiment was prepared in 0.05M TRIS (tris (hydroxymethyl) aminomethane/HCl; pH =7.22 or 8.08), 0.05M phosphate (KH_2PO_4/NaOH; pH = 6.97) or 0.1M acetate (AcOH/AcONa; pH = 4.11, 4.86 or 5.85) buffer. Guest compounds were used as sodium salts in order to increase their solubility in water.

All calorimetric titrations were carried out at 298 K. In a typical ITC measurement 300 µL of P[6]P·$(Cl)_6$ solution was placed in a cell and titrated by 36,4 µl of guest solution (18 injections of 2 µl each preceded by one 0,4 µl injection which was excluded during data analysis). Concentration of titrant was 10-20 times higher than concentration of P[6]P in the cell. Control experiment for each titration was performed by injecting guest solution into buffer. Experimental data were analysed using MicroCal PEAQ-ITC Analysis software.

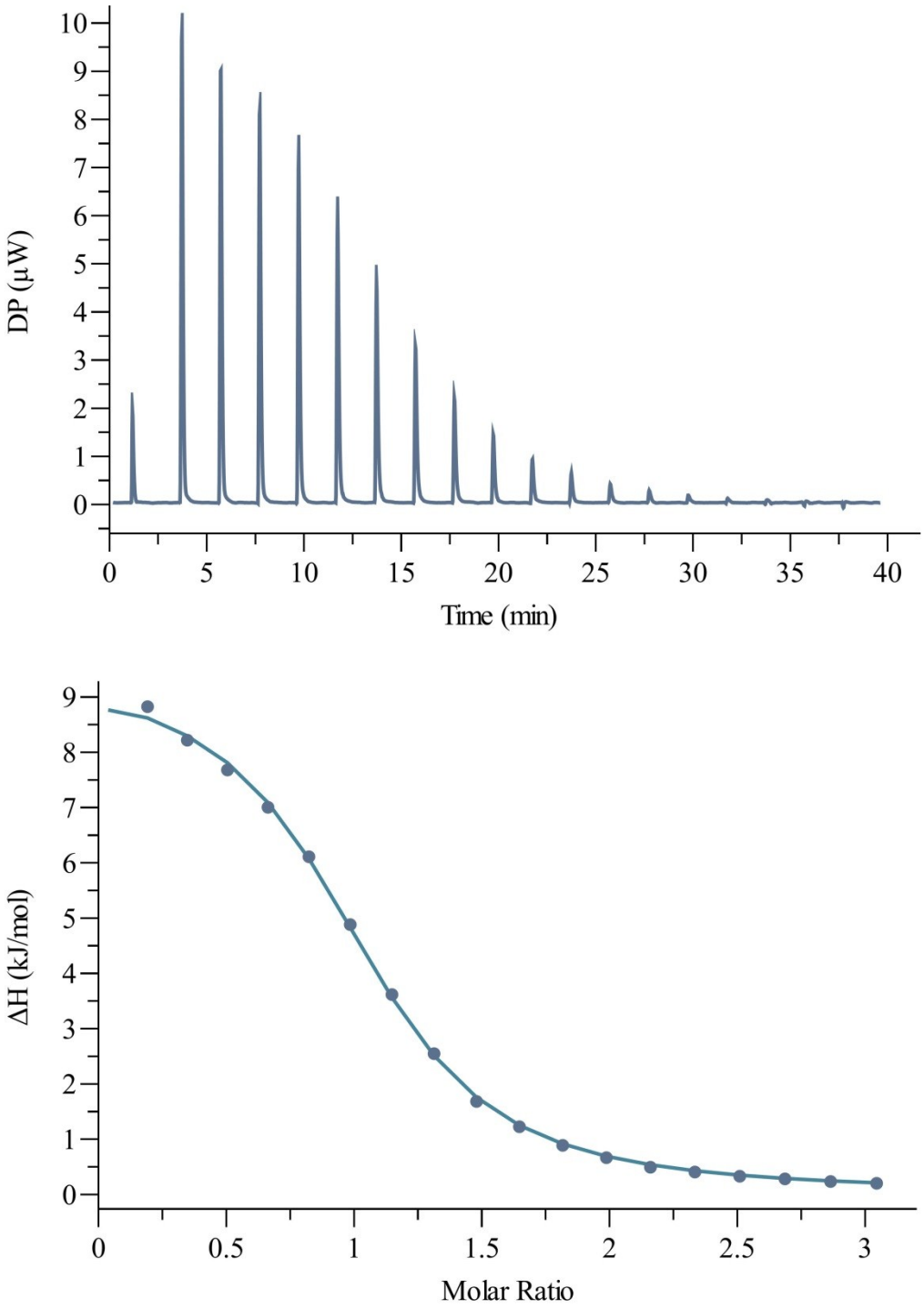

Figure S17. Thermogram for 0.26mM P[6]P·$(Cl)_6$ in 0.05M TRIS buffer (pH=7.22) titrated with **G8** (4mM).

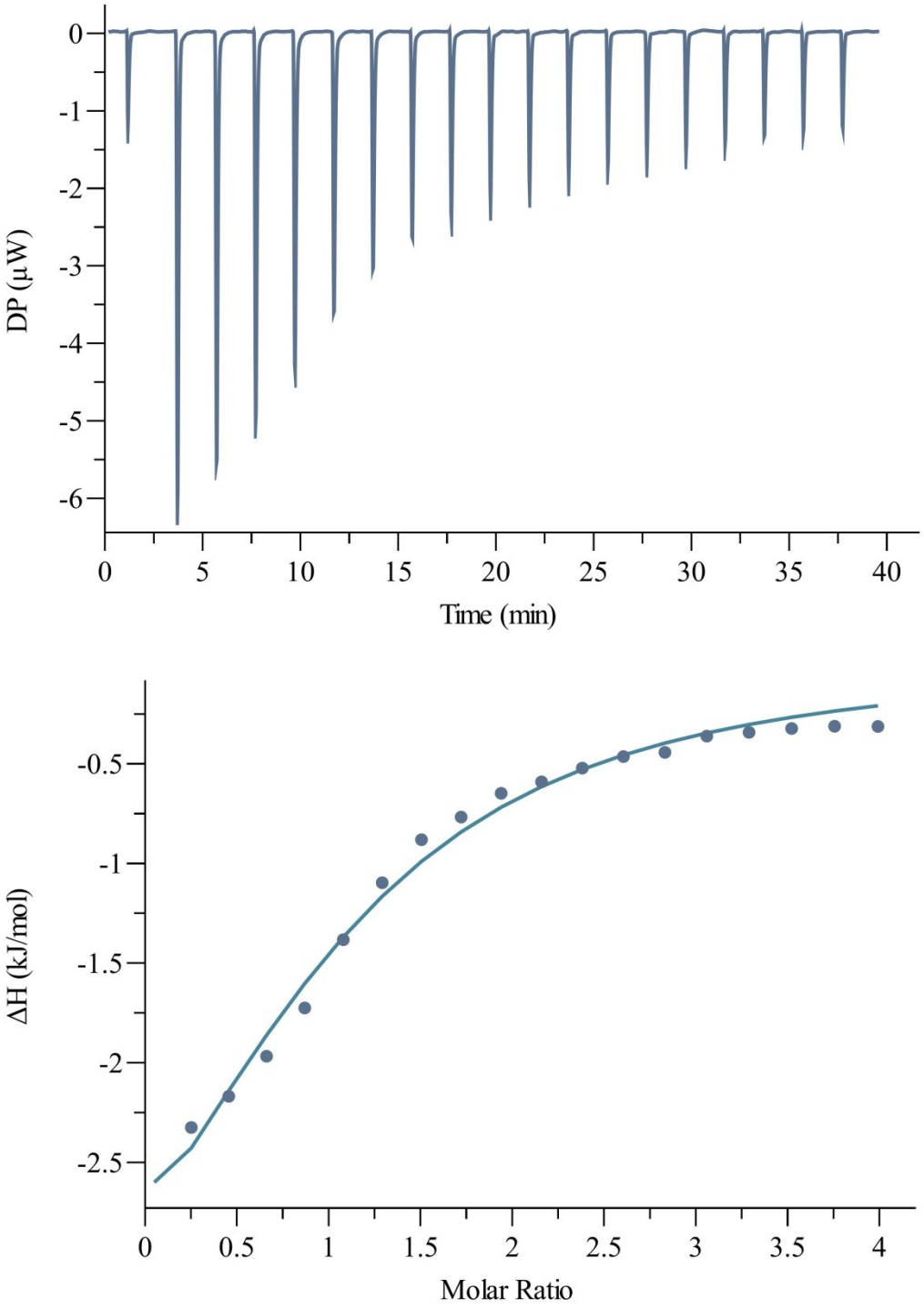

Figure S18. Thermogram for 0.4mM P[6]P·$(Cl)_6$ in 0.05M phosphate buffer (pH= 6.97) titrated with **G8** (8 mM).

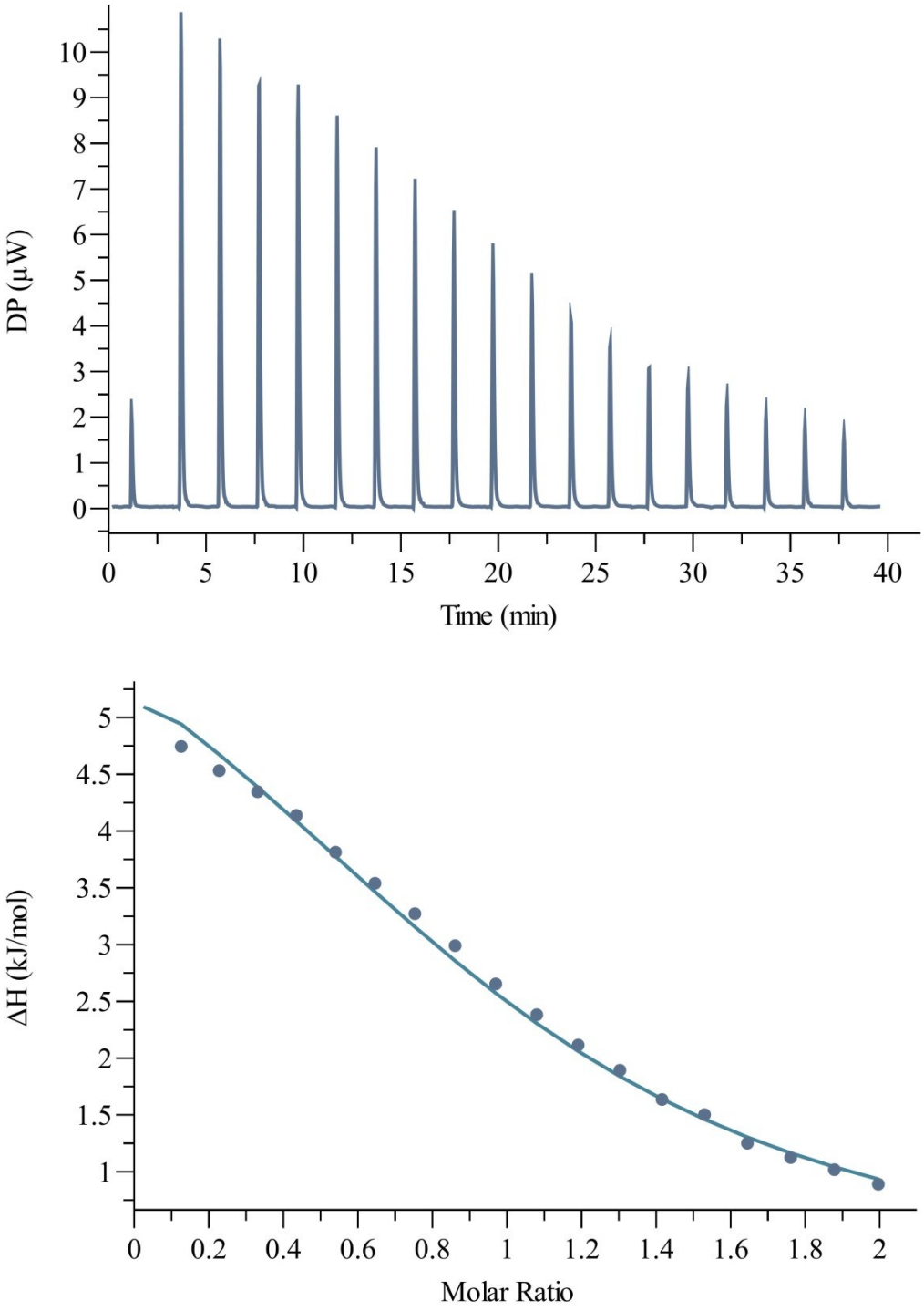

Figure S19. Thermogram for 0.8mM P[6]P·$(Cl)_6$ in 0.05M TRIS buffer (pH= 8.08) titrated with **G7** (8 mM).

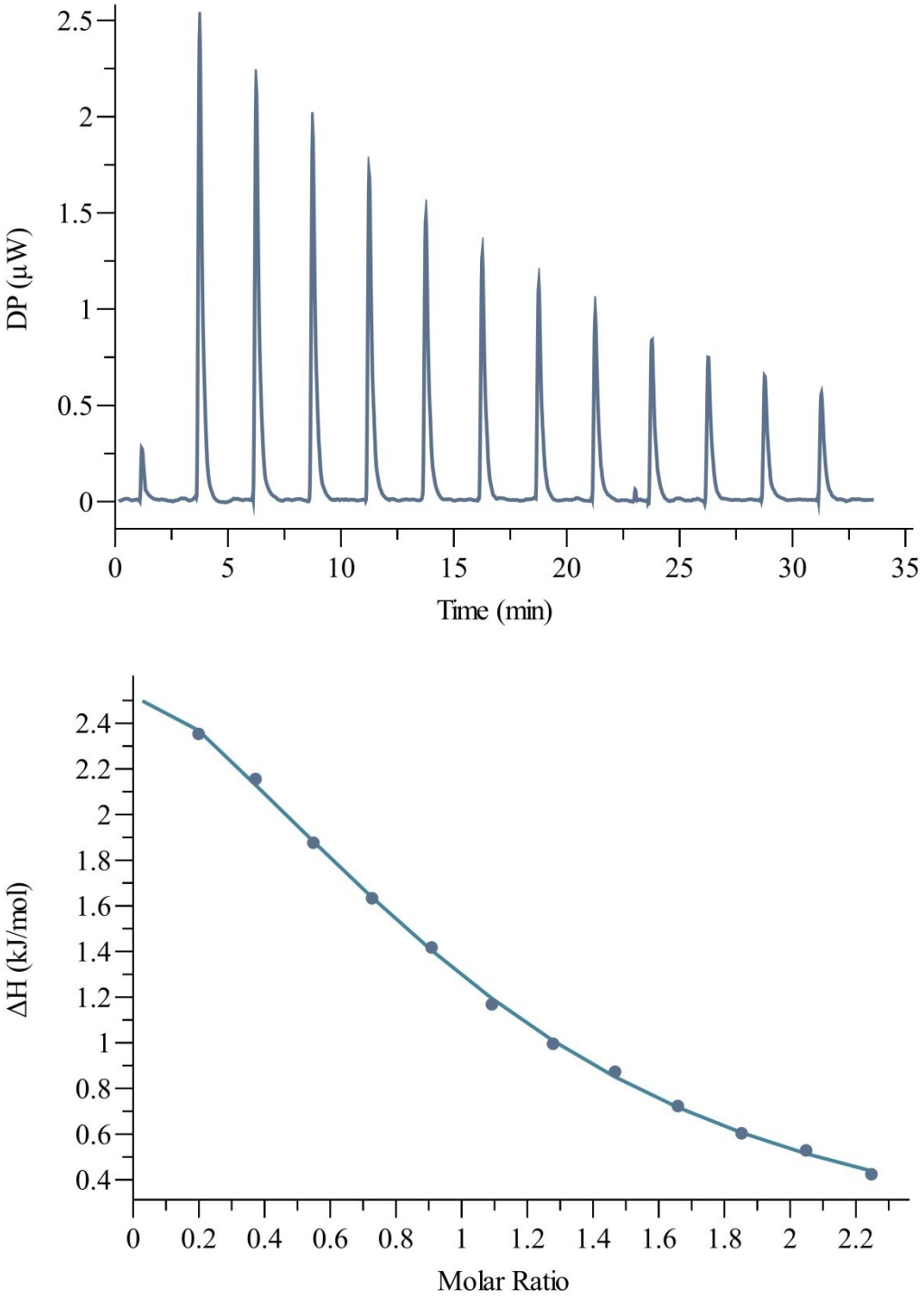

Figure S20. Thermogram for 0.36mM P[6]P·$(Cl)_6$ in 0.05M TRIS buffer (pH= 7.22) titrated with **G7** (4 mM).

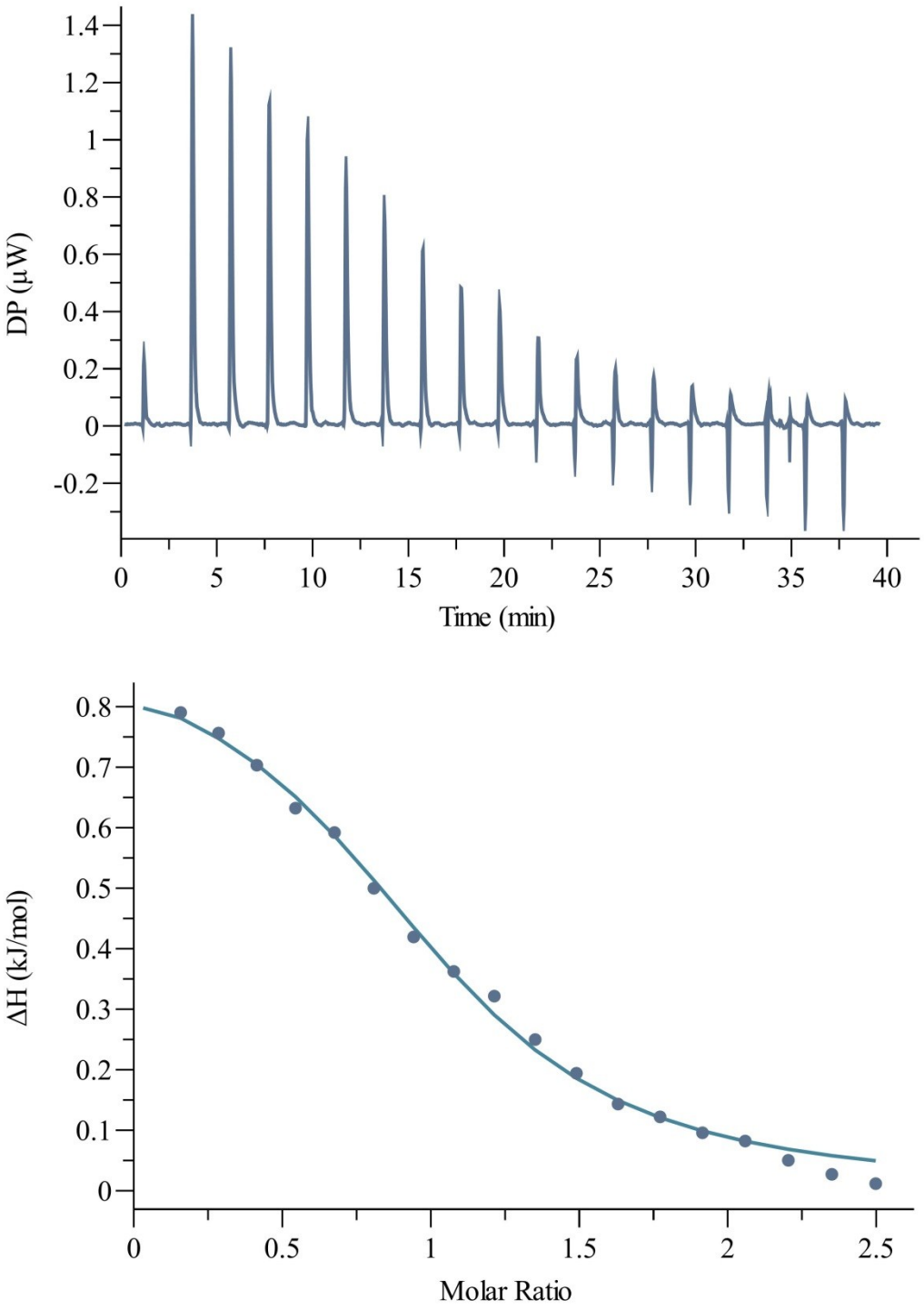

Figure S21. Thermogram for 0.64mM P[6]P·$(Cl)_6$ in 0.1M acetate buffer (pH= 5.85) titrated with **G7** (8 mM).

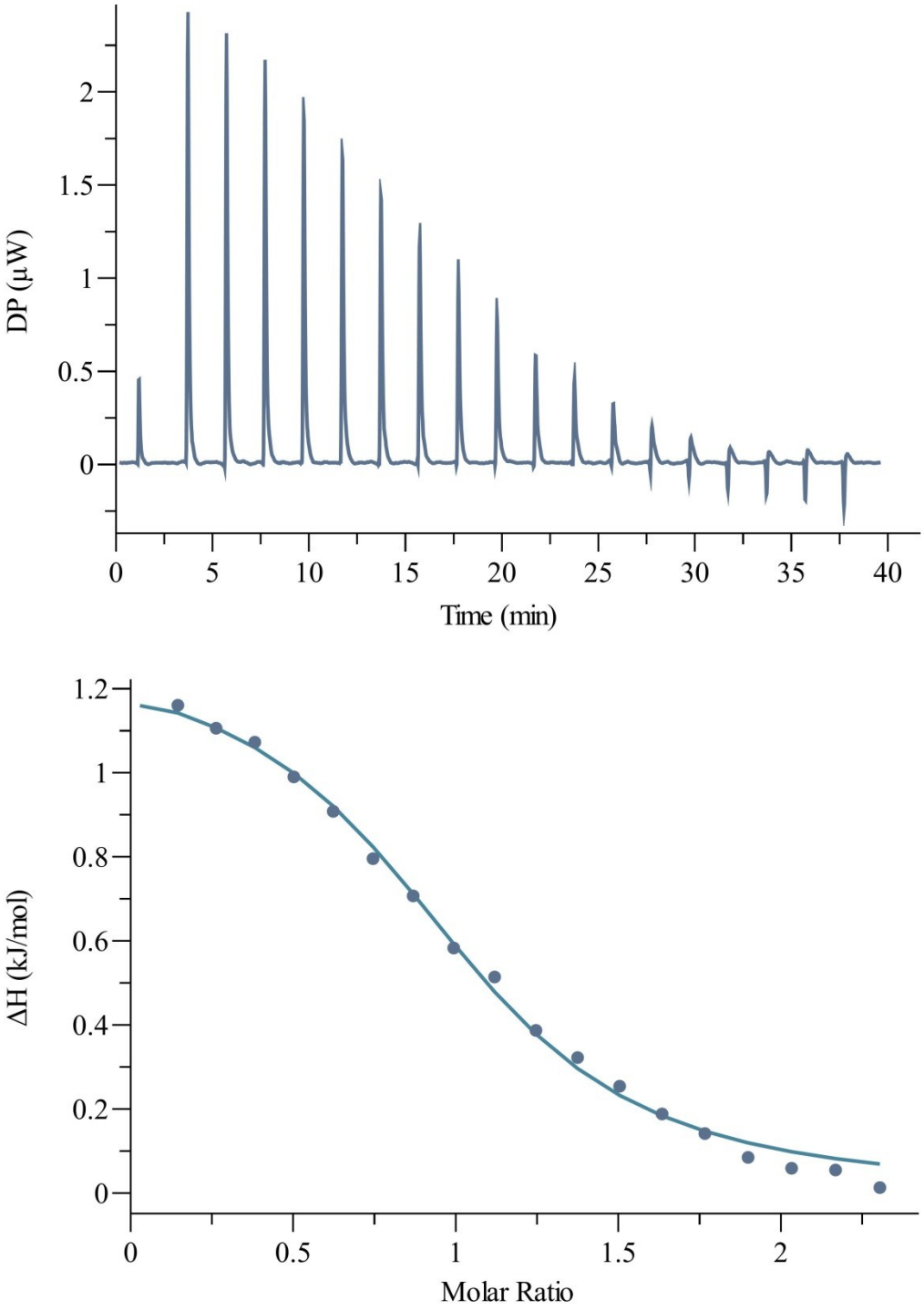

Figure S22. Thermogram for 0.69mM P[6]P·$(Cl)_6$ in 0.1M acetate buffer (pH= 4.86) titrated with **G7** (8 mM).

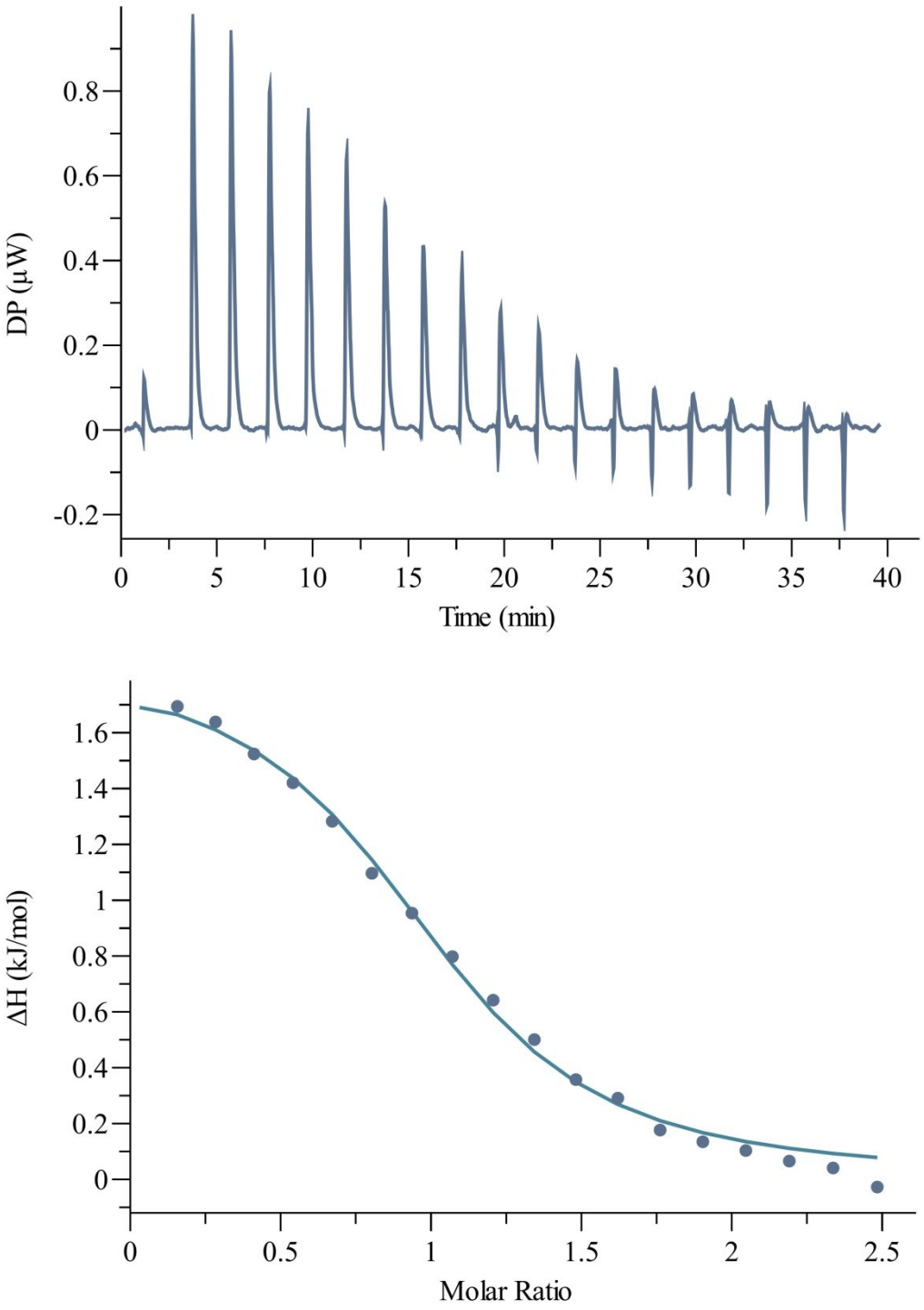

Figure S23. Thermogram for 0.31mM P[6]P·$(Cl)_6$ in 0.1M acetate buffer (pH= 4.11) titrated with **G7** (4 mM).

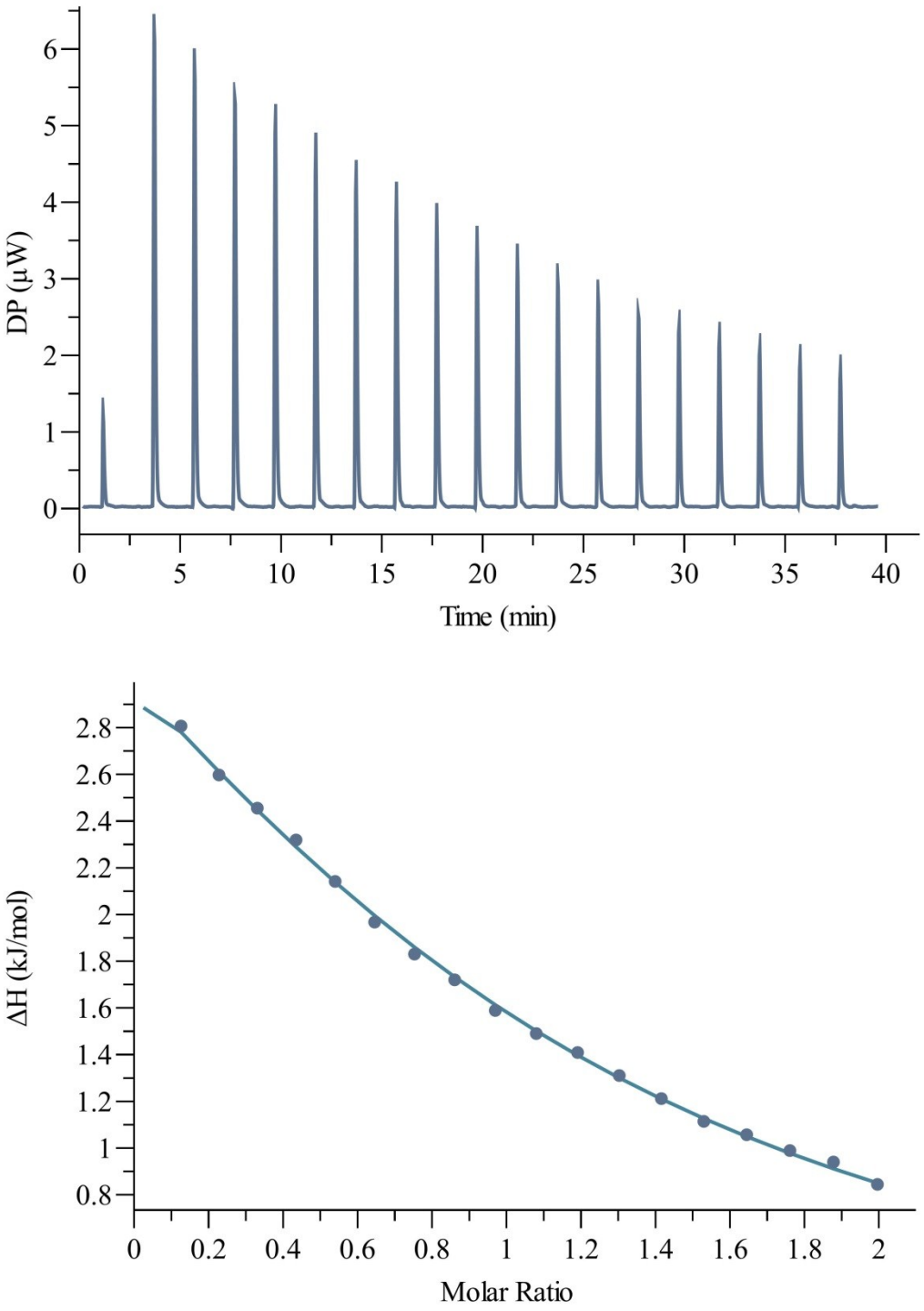

Figure S24. Thermogram for 0.8mM P[6]P·$(Cl)_6$ in 0.05M TRIS buffer (pH= 7.22) titrated with **G6** (8 mM).

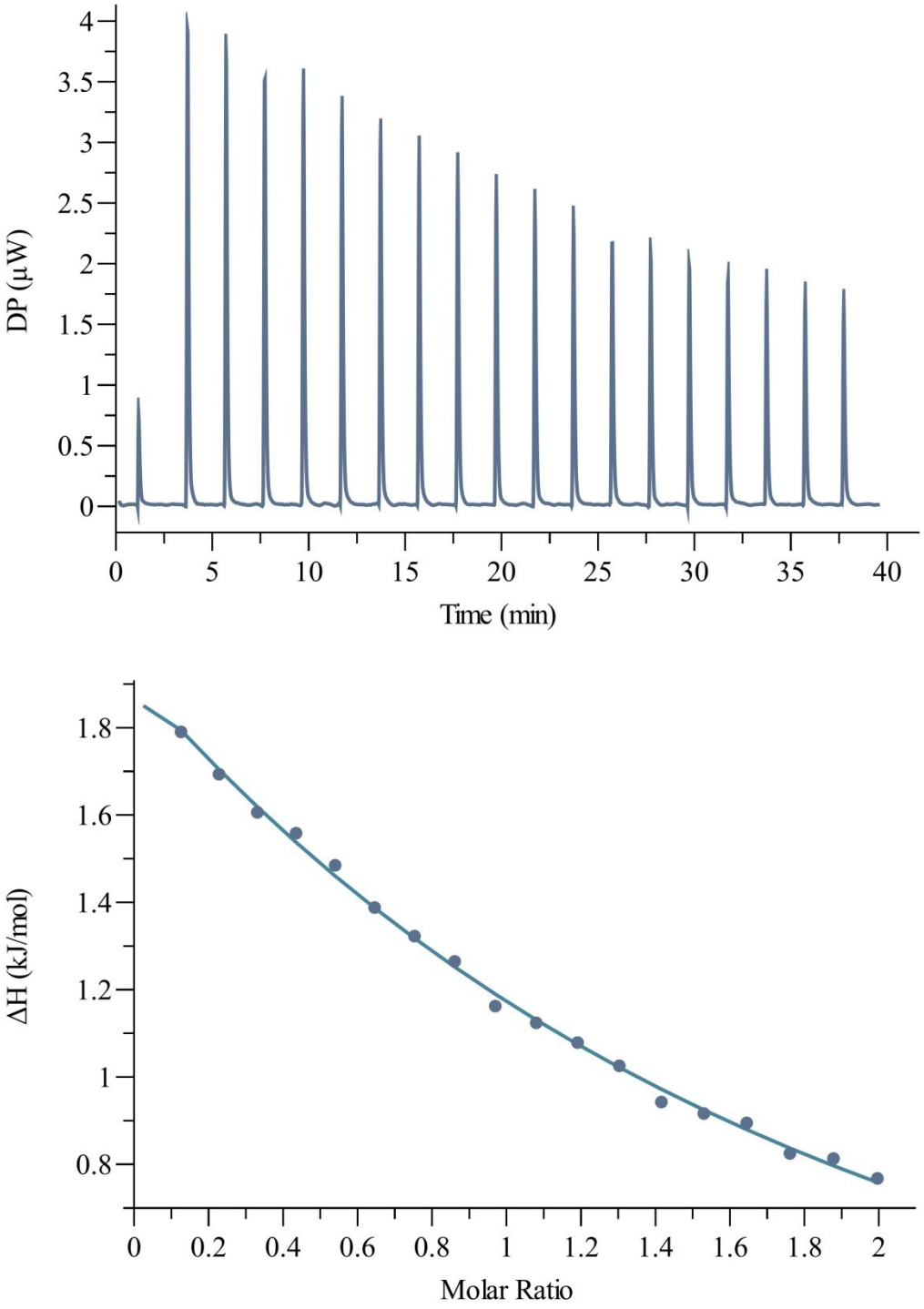

Figure S25. Thermogram for 0.8mM P[6]P·$(Cl)_6$ in 0.05M TRIS buffer (pH= 7.22) titrated with **G5** (8 mM).

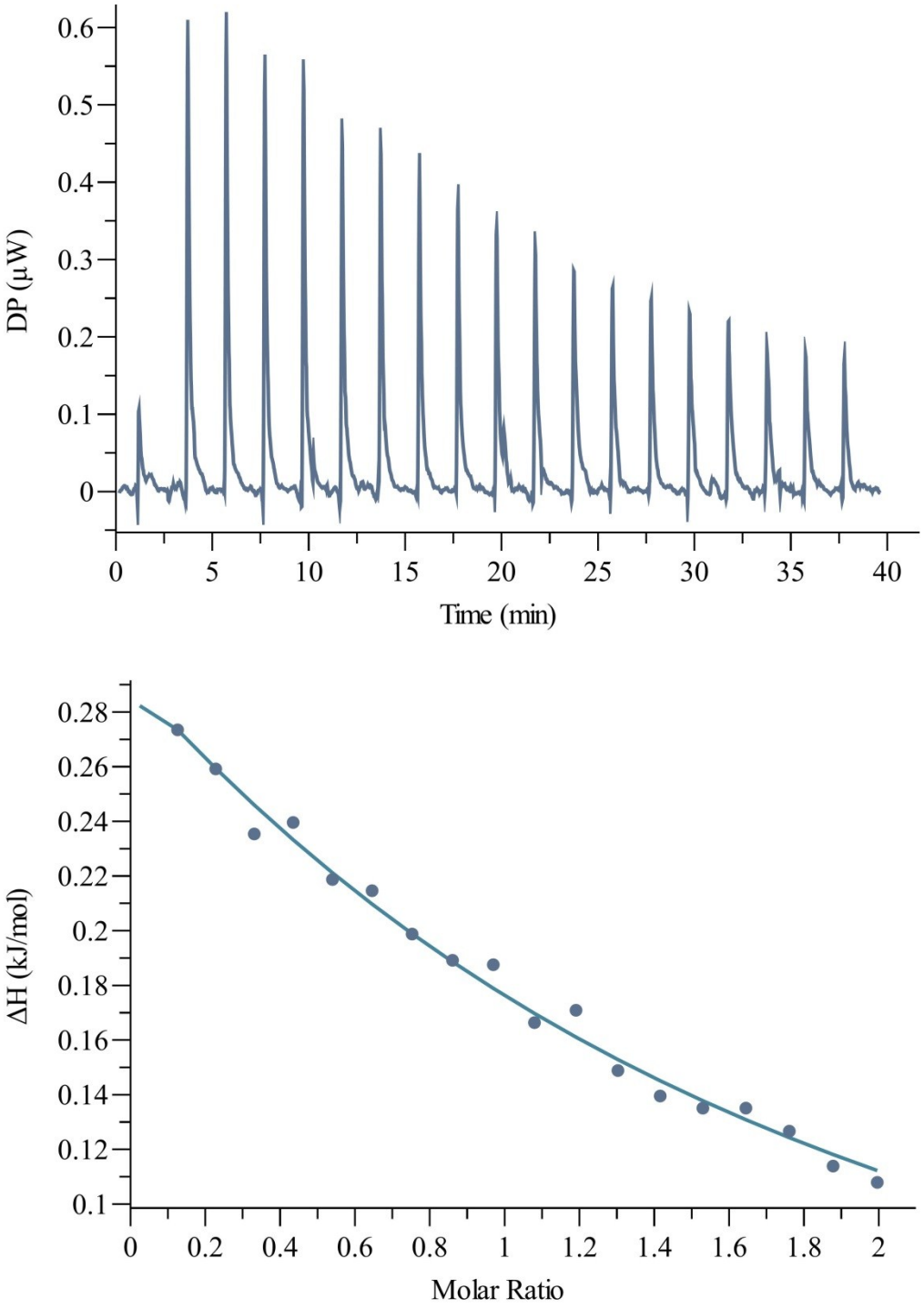

Figure S26. Thermogram for 1.6mM P[6]P·$(Cl)_6$ in 0.05M TRIS buffer (pH= 7.22) titrated with **G4** (16 mM).

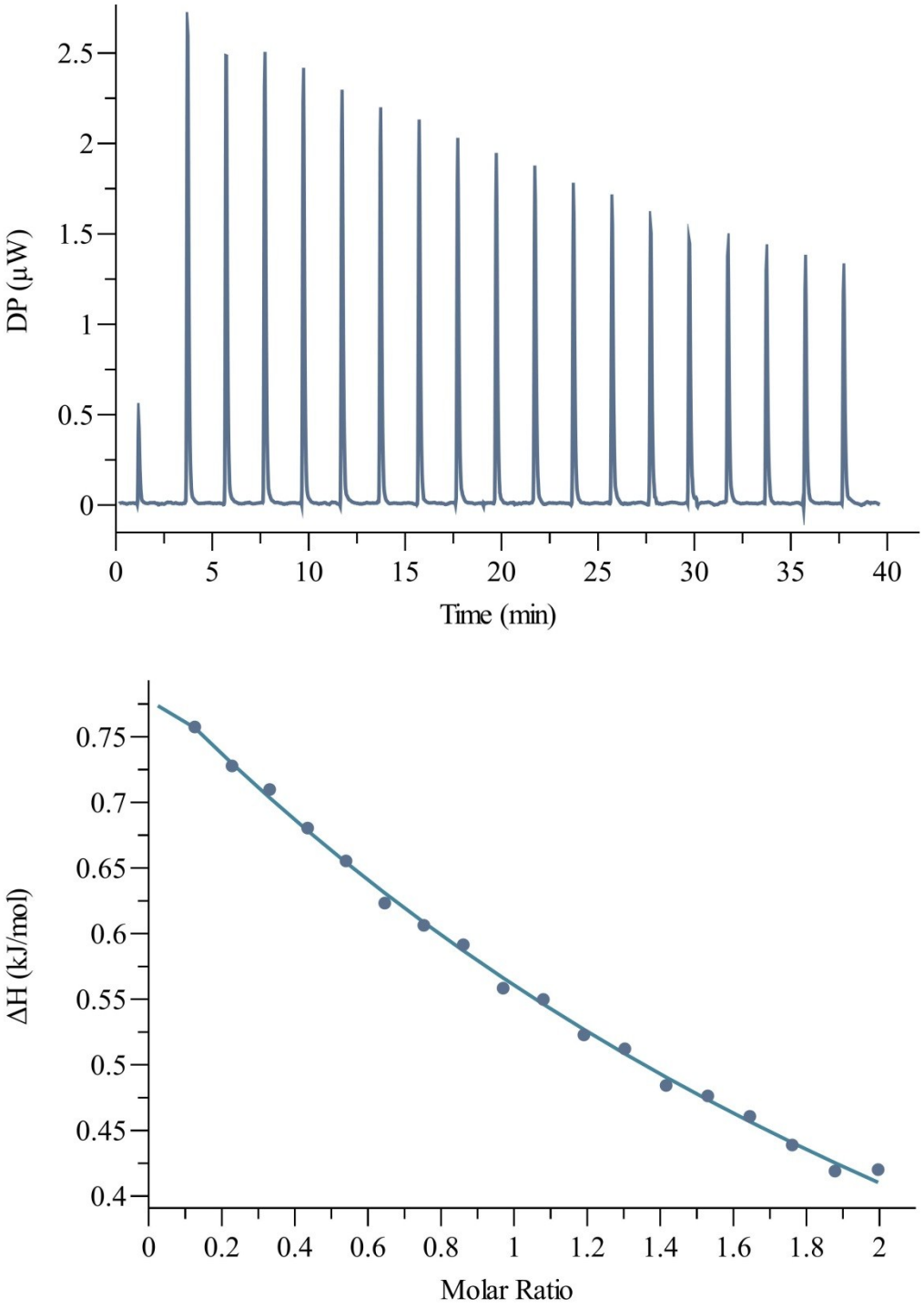

Figure S27. Thermogram for 1.6mM P[6]P·$(Cl)_6$ in 0.05M TRIS buffer (pH= 7.22) titrated with **G3** (16 mM).

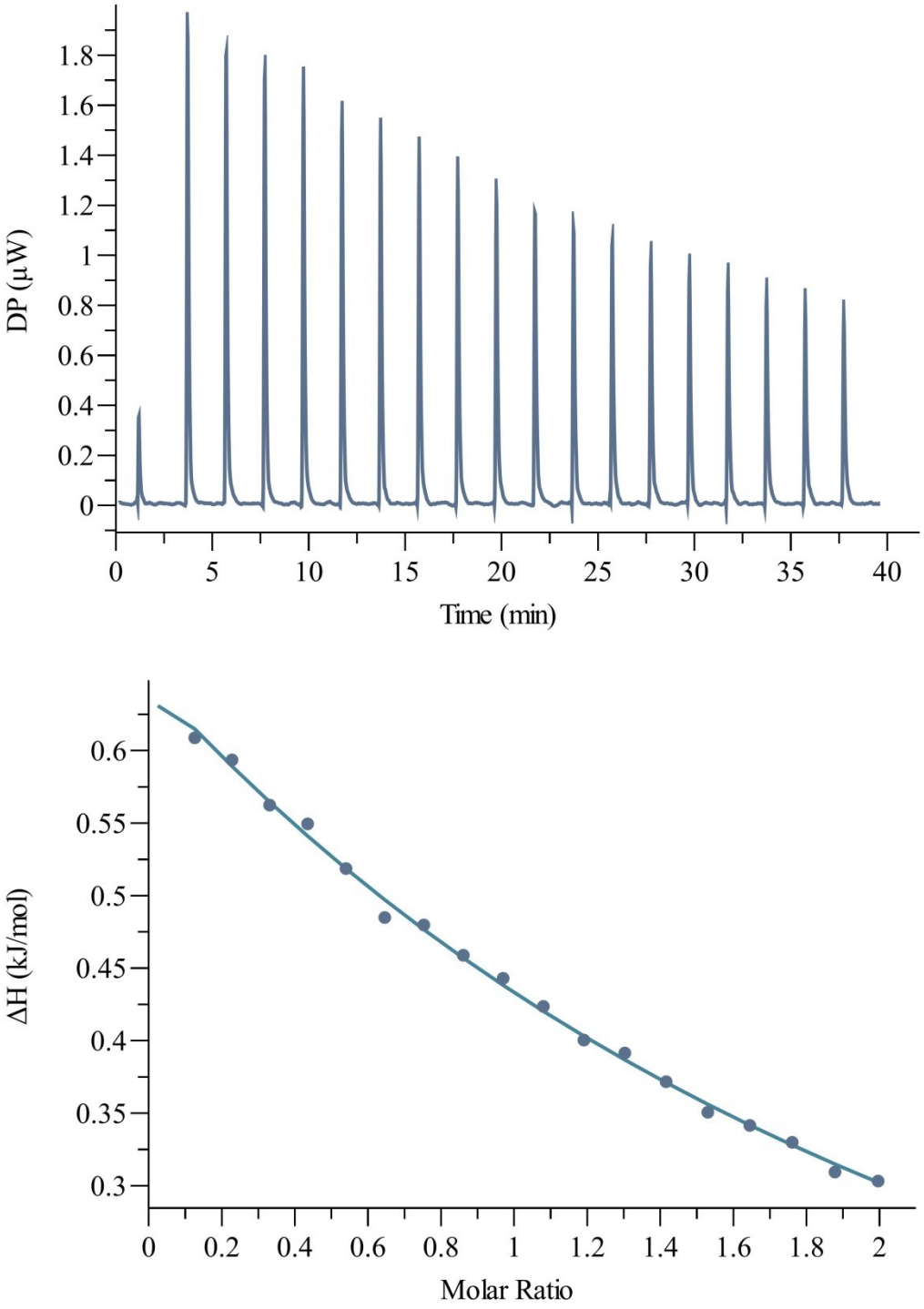

Figure S28. Thermogram for 1.6mM P[6]P·$(Cl)_6$ in 0.05M TRIS buffer (pH= 7.22) titrated with **G2** (16 mM).

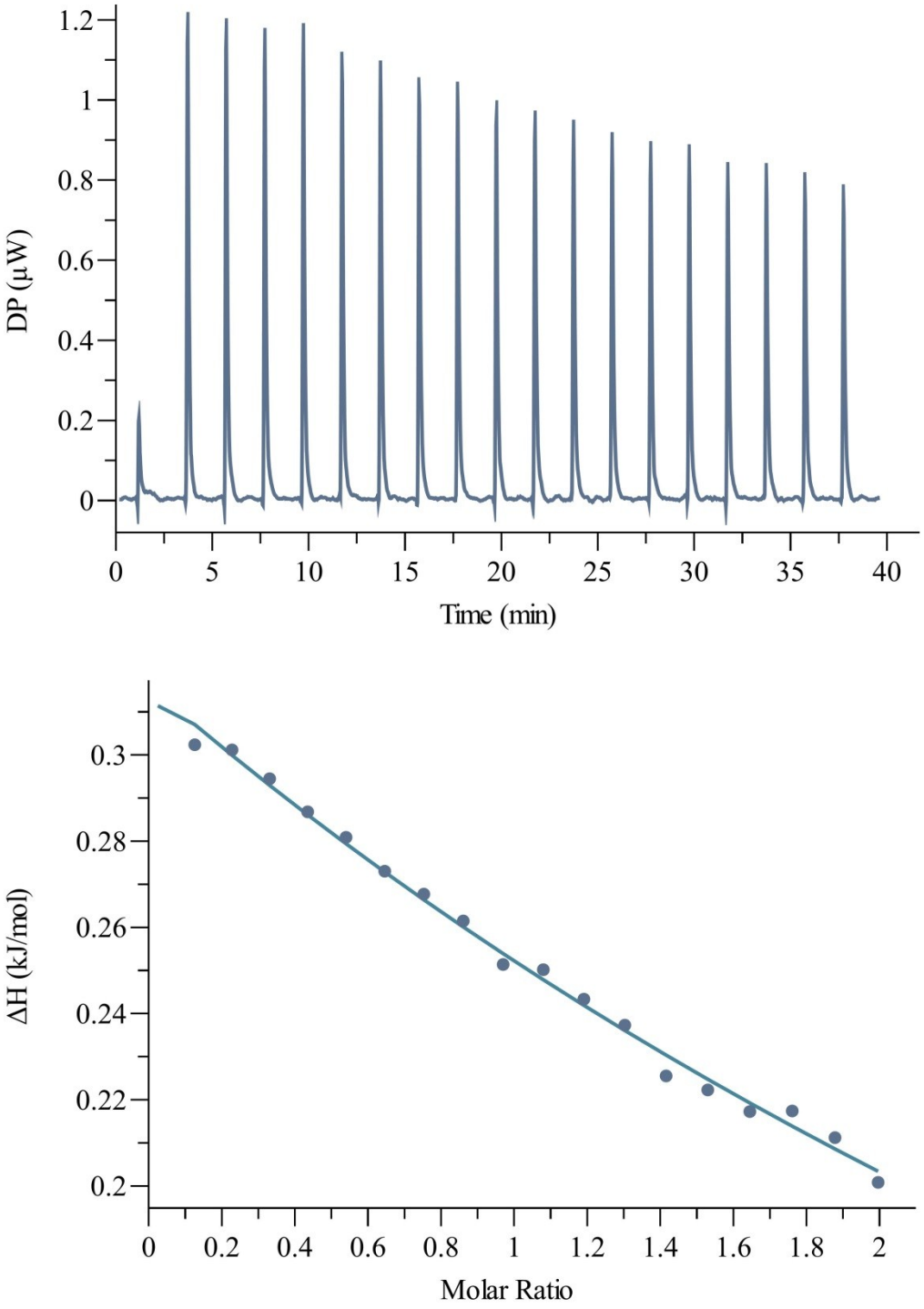

Figure S29. Thermogram for the titration of P[6]P by **G1** (Tris buffer, pH=7.22, 298 K).

5. Computations

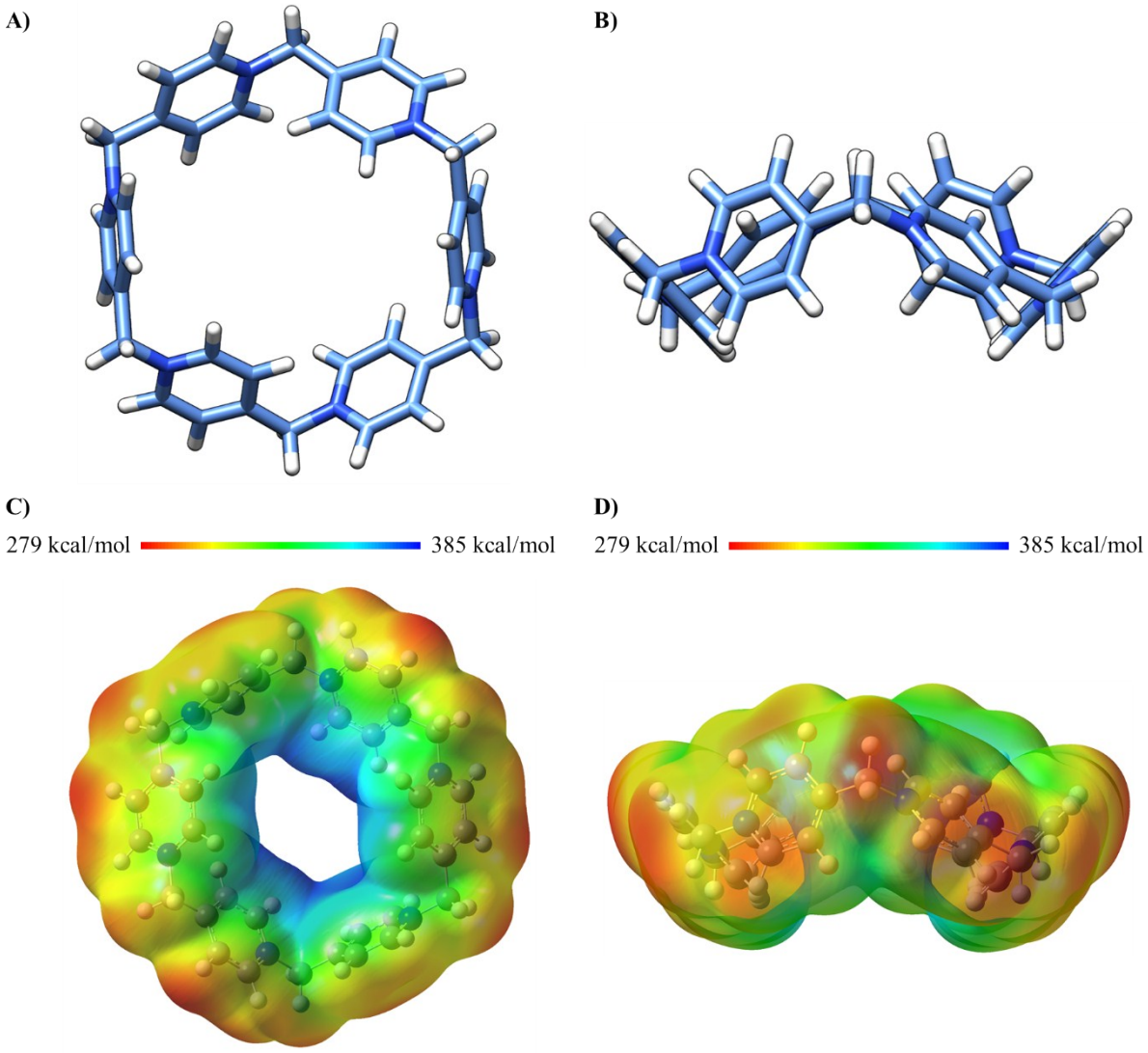

Figure S30. Optimized structure of P[6]P^{6+} seen from the top (A) and from the side (B). Electrostatic potential map of P[6]P^{6+}, top (C) and side (D) view.

C	-0.34932852	4.80634768	-0.34233983	C	-3.49570519	-4.06247697	1.35135646
C	0.75887606	5.57846696	-0.71479263	C	-5.68193609	0.99829892	-0.39553590
C	1.99609463	5.32746243	-0.15195215	C	-1.69223537	5.13412186	-0.96364479
N	2.15347365	4.33273024	0.75484916	H	0.67509251	6.37909881	-1.44147065
C	1.09557040	3.58050983	1.14014725	H	2.87519526	5.90547554	-0.40626533
C	-0.16190448	3.79730184	0.60901956	H	1.28185278	2.81445836	1.88160209
C	4.23888682	1.67730947	1.78034880	H	-0.97258191	3.16941786	0.95814212
C	4.76447162	0.47635296	1.33719930	H	3.96755275	1.76620983	2.82627955
N	5.12762414	0.31637790	0.04255381	H	4.90797410	-0.37133404	1.99490389

C	5.00485811	1.33629323	-0.84151559	H	5.34664346	1.15672628	-1.85266278
C	4.47798961	2.55269540	-0.44513685	H	4.40236249	3.34141787	-1.18525238
C	4.07318020	2.73838748	0.88251785	H	3.46021856	-1.07571987	-2.09731545
C	3.56277977	-1.94219582	-1.45422441	H	1.81019628	-2.90531429	-2.28172007
C	2.62918600	-2.95253852	-1.57479340	H	3.72766692	-5.13338629	0.66713848
N	2.71100628	-4.06690824	-0.80328576	H	5.47131196	-3.39144207	0.96244543
C	3.71775002	-4.21875273	0.08821535	H	-2.87519053	-5.90548993	-0.40624850
C	4.67927154	-3.23222074	0.23950058	H	-0.67508606	-6.37911553	-1.44145036
C	4.61134352	-2.06764307	-0.53130735	H	0.97257429	-3.16939417	0.95811811
N	-2.15347462	-4.33272815	0.75484674	H	-1.28186188	-2.81443465	1.88157605
C	-1.99609200	-5.32747026	-0.15194297	H	-4.90795671	0.37133994	1.99490046
C	-0.75887284	-5.57847538	-0.71478181	H	-3.96753597	-1.76620424	2.82627699
C	0.34932842	-4.80634640	-0.34233924	H	-4.40238069	-3.34142521	-1.18524614
C	0.16190008	-3.79728820	0.60900615	H	-5.34666029	-1.15673230	-1.85265721
C	-1.09557528	-3.58049613	1.14013264	H	-1.81019267	2.90530899	-2.28171734
C	-4.76446192	-0.47635009	1.33719810	H	-3.46021538	1.07571491	-2.09731088
C	-4.23887750	-1.67730671	1.78034794	H	-5.47131323	3.39144420	0.96244159
C	-4.07318157	-2.73838822	0.88251919	H	-3.72766848	5.13338851	0.66713210
C	-4.47800038	-2.55269964	-0.44513308	H	3.38373591	4.08112714	2.43605100
C	-5.00486795	-1.33629723	-0.84151209	H	4.14916268	4.88747773	1.06512599
N	-5.12762375	-0.31637849	0.04255479	H	6.43780018	-1.29343341	0.33229323
C	-2.62918360	2.95253493	-1.57479220	H	6.18114810	-0.83911579	-1.35292358
C	-3.56277740	1.94219244	-1.45422209	H	2.09290453	-6.04476743	-0.51101814
C	-4.61134254	2.06764195	-0.53130698	H	1.57952082	-5.32831419	-2.03252467
C	-4.67927179	3.23222142	0.23949812	H	-3.38373481	-4.08112846	2.43605078
C	-3.71775042	4.21875334	0.08821151	H	-4.14916250	-4.88747875	1.06512601
N	-2.71100534	4.06690673	-0.80328774	H	-6.43779869	1.29343345	0.33229500
C	3.49570467	4.06247645	1.35135652	H	-6.18114847	0.83911565	-1.35292205
C	5.68193673	-0.99829943	-0.39553702	H	-2.09290519	6.04476721	-0.51102535
C	1.69223602	-5.13412319	-0.96364097	H	-1.57951882	5.32830943	-2.03252890

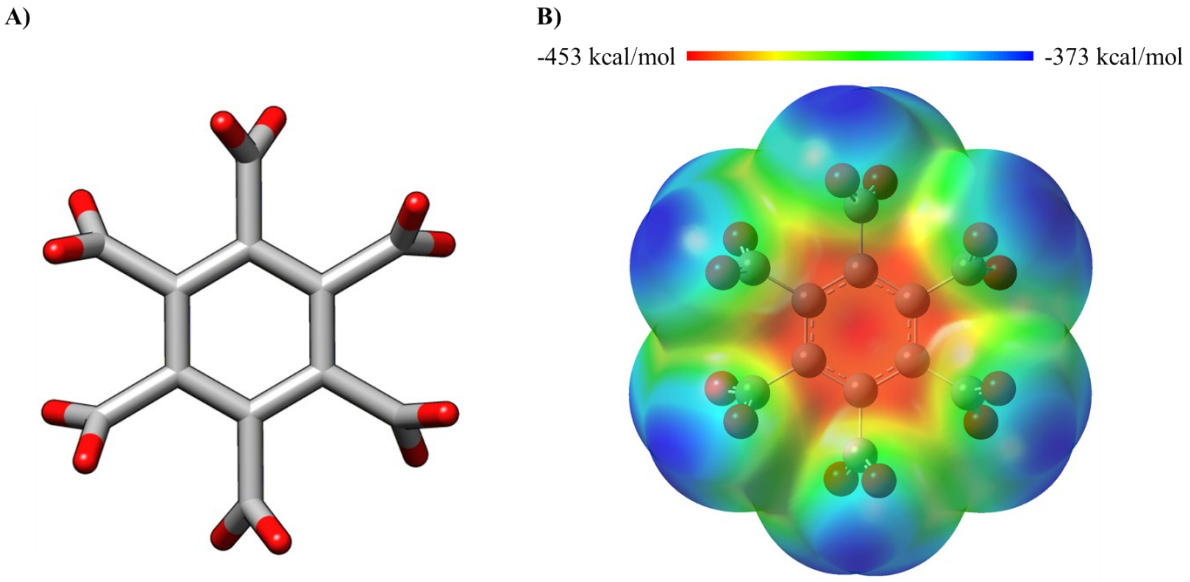

Figure S31. Optimized structure (A) and electrostatic potential map (B) of **G8**.

C	-0.00001123	1.41095776	0.00000348	O	-2.80533514	2.14195304	-1.06562835
C	1.22205872	0.70537294	0.00274372	O	-3.28506962	1.38889767	1.00470643
C	1.22206673	-0.70534833	-0.00272415	O	-2.80533275	-2.14200073	1.06562955
C	0.00001123	-1.41095776	0.00000348	O	-3.28506962	-1.38888300	-1.00467991
C	-1.22205872	-0.70537294	0.00274372	O	0.44856149	-3.52153779	1.03369914
C	-1.22206673	0.70534833	-0.00272415	O	-0.44844203	-3.52153362	-1.03374615
C	-2.54513971	1.47371226	-0.02060887	O	3.28506962	-1.38889767	1.00470643
C	-2.54513370	-1.47373588	0.02062680	O	2.80533514	-2.14195304	-1.06562835
C	0.00004499	-2.94205309	-0.00001526	O	3.28506962	1.38888300	-1.00467991
C	2.54513971	-1.47371226	-0.02060887	O	2.80533275	2.14200073	1.06562955
C	2.54513370	1.47373588	0.02062680	O	0.44844203	3.52153362	-1.03374615
C	-0.00004499	2.94205309	-0.00001526	O	-0.44856149	3.52153779	1.03369914

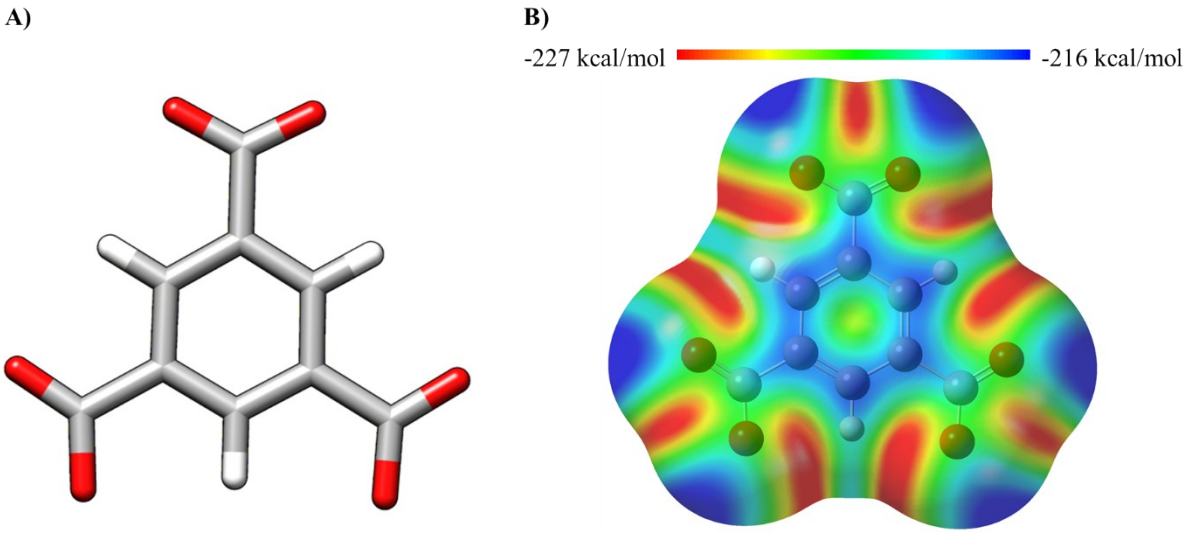

Figure S32. Optimized structure (A) and electrostatic potential map (B) of **G7**.

C	0.69862714	1.20610379	0.00000000	O	3.52605441	1.12740373	0.00000000
C	-0.70352367	1.22308720	0.00000000	O	3.52605400	-1.12740366	0.00000000
C	-1.38934885	-0.00000006	0.00000000	O	-0.79272970	-3.61697123	0.00000000
C	-0.70352367	-1.22308712	0.00000000	O	-2.73941899	-2.47916637	0.00000000
C	0.69862710	-1.20610391	0.00000000	O	-2.73941875	2.47916635	0.00000000
C	1.41452339	-0.00000011	0.00000000	O	-0.79272988	3.61697147	0.00000000
C	2.94627849	-0.00000004	0.00000000	H	1.24087147	2.14416122	0.00000000
C	-1.47346462	-2.54745084	0.00000000	H	-2.47261573	0.00000012	0.00000000
C	-1.47346456	2.54745074	0.00000000	H	1.24087099	-2.14416157	0.00000000

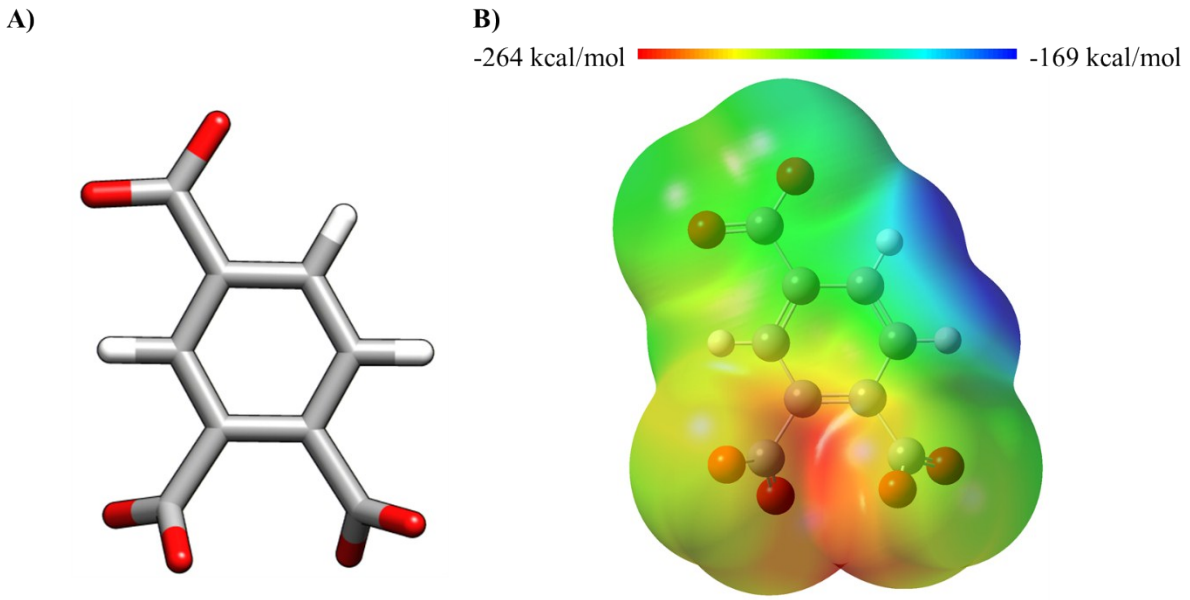

Figure S33. Optimized structure (A) and electrostatic potential map (B) of **G6**.

C	-0.03202072	-1.81576933	0.08170229	O	-2.90368431	-1.91457328	-0.76891275
C	1.34007114	-1.55980991	0.06939227	O	-3.10785431	-0.64536631	1.08846869
C	1.81584381	-0.24190528	0.00464058	O	-1.32496394	2.65971795	0.75278985
C	0.87469107	0.79650579	-0.03258642	O	-2.24387968	1.76920080	-1.10798520
C	-0.50726797	0.55638090	-0.01670130	O	3.66806566	1.26648859	-0.12475274
C	-0.97358872	-0.77418473	0.03977571	O	4.10138874	-0.93964760	0.05407566
C	-2.45540303	-1.12888315	0.11789456	H	-0.38671911	-2.84332103	0.12789211
C	-1.44721852	1.75394185	-0.12439490	H	2.05338498	-2.37750851	0.10846541
C	3.31587733	0.05280408	-0.02423762	H	1.23485053	1.81978710	-0.07873672

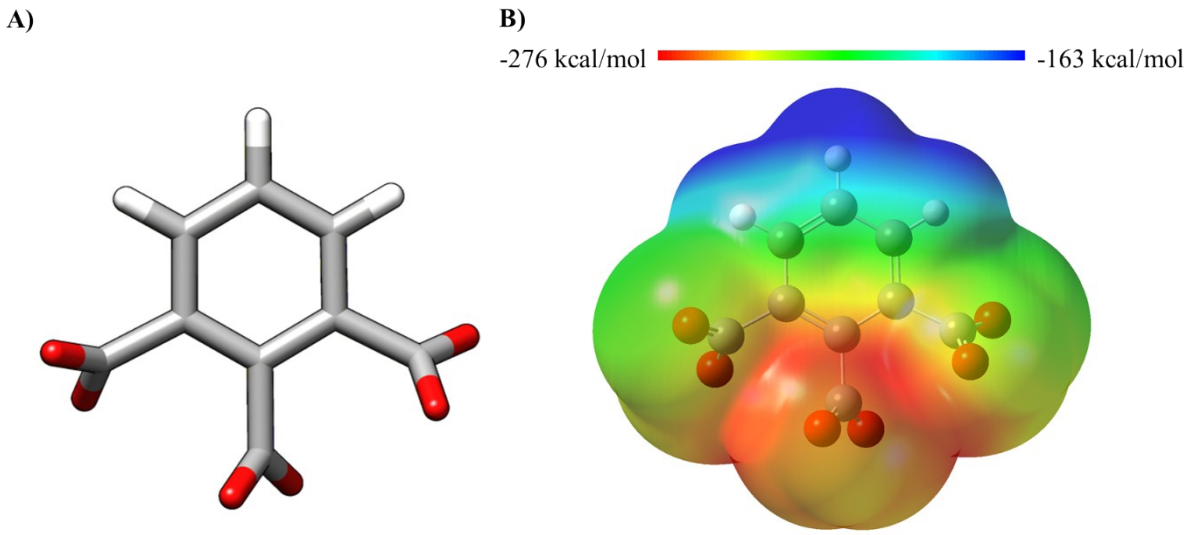

Figure S34. Optimized structure (A) and electrostatic potential map (B) of **G5**.

C	-1.20576242	-2.01569568	0.00629311	O	-3.39582289	-0.15521319	-0.83847850
C	-0.00007192	-2.71961515	-0.00004948	O	-2.80126568	0.79149212	1.12359111
C	1.20566330	-2.01574806	-0.00637768	O	0.52186606	2.20301239	1.00070123
C	1.21938913	-0.61236027	-0.02031883	O	-0.52176607	2.20305234	-1.00084133
C	-0.00000711	0.10114442	-0.00007579	O	2.80142526	0.79140054	-1.12346236
C	-1.21941771	-0.61229397	0.02024089	O	3.39571528	-0.15526821	0.83868746
C	-2.57906070	0.07953425	0.10119051	H	-2.15058254	-2.55441984	0.00949358
C	0.00002756	1.63038461	-0.00006603	H	-0.00009476	-3.80756937	-0.00004070
C	2.57907481	0.07943483	-0.10108824	H	2.15045204	-2.55452847	-0.00952465

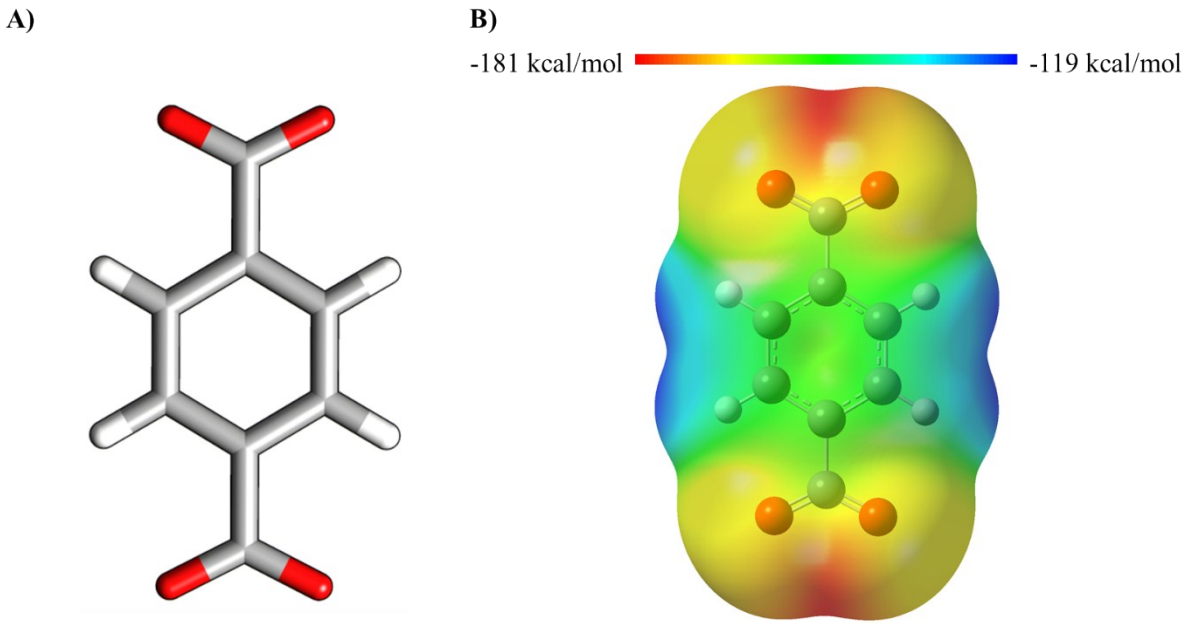

Figure S35. Optimized structure (A) and electrostatic potential map (B) of **G4**.

C	-0.69833405	-1.20372151	0.00024007	O	-3.52880710	-1.12812831	-0.00037952
C	0.69834026	-1.20371951	0.00024186	O	-3.52879897	1.12813315	0.00038383
C	1.42089778	0.00000179	-0.00000380	O	3.52880147	1.12813162	0.00022330
C	0.69833802	1.20371938	-0.00024892	O	3.52879819	-1.12813050	-0.00021524
C	-0.69833733	1.20371345	-0.00024811	H	-1.24582379	-2.14145401	0.00043376
C	-1.42089497	-0.00000213	0.00000304	H	1.24582770	-2.14145502	0.00044213
C	-2.95210448	0.00000062	0.00000196	H	1.24581905	2.14145846	-0.00045046
C	2.95210483	0.00000055	-0.00000060	H	-1.24583200	2.14144716	-0.00043736

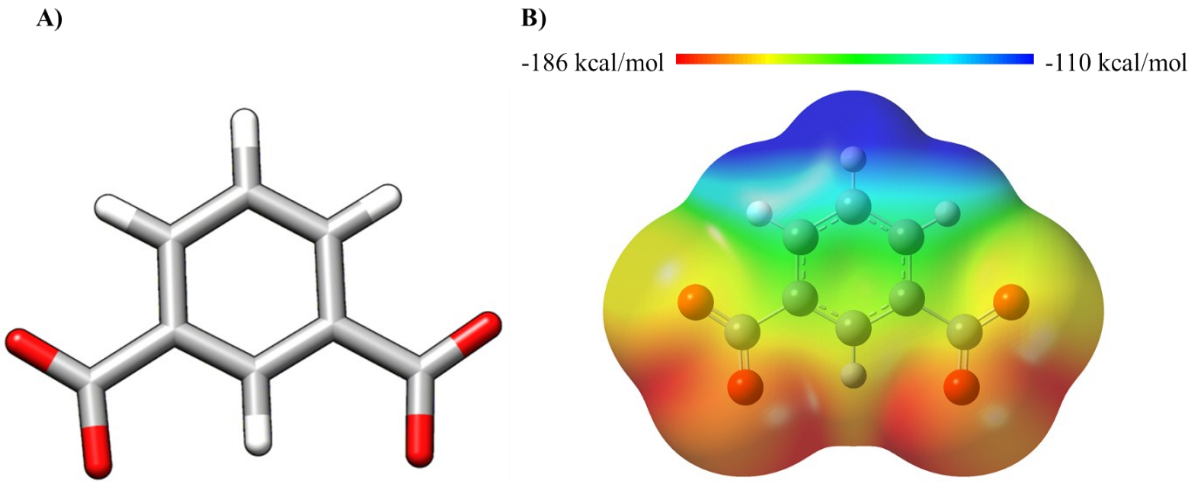

Figure S36. Optimized structure (A) and electrostatic potential map (B) of **G3**.

C	1.21221546	1.55355269	0.00002348	O	3.61703316	0.06158452	0.00025319
C	0.00000008	2.25041999	0.00004260	O	2.47969296	-1.88641002	-0.00041513
C	-1.21221533	1.55355228	0.00003199	O	-2.47969399	-1.88641032	0.00051139
C	-1.22560543	0.15001884	0.00001361	O	-3.61703233	0.06158543	-0.00043098
C	0.00000010	-0.53177125	0.00000258	H	2.15696191	2.08843510	0.00004326
C	1.22560547	0.15001897	-0.00000043	H	0.00000003	3.33845997	0.00006345
C	2.54938528	-0.62147626	-0.00005496	H	-2.15696201	2.08843444	0.00001785
C	-2.54938542	-0.62147608	0.00003050	H	0.00000047	-1.61516138	-0.00000851

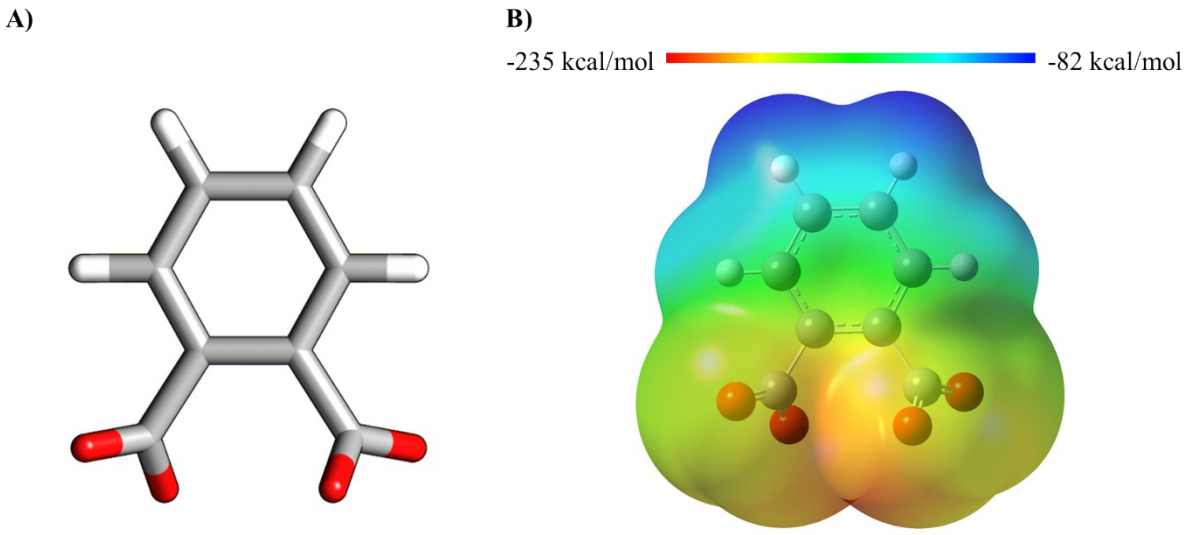

Figure S37. Optimized structure (A) and electrostatic potential map (B) of **G2**.

C	-2.66041184	-0.69796062	-0.03913419	O	1.83640794	-1.25508790	-1.11443000
C	-2.66025332	0.69845231	0.03903090	O	1.23294957	-2.44046396	0.71147938
C	-1.44373397	1.38584315	0.07329041	O	1.83656011	1.25498810	1.11463329
C	-0.21608756	0.70459106	0.03859699	O	1.23361620	2.43990791	-0.71177437
C	-0.21623187	-0.70446200	-0.03848841	H	-3.59821591	-1.24767973	-0.07359559
C	-1.44399383	-1.38554784	-0.07322623	H	-3.59792803	1.24842313	0.07334609
C	1.06680815	-1.52467114	-0.14733720	H	-1.43964780	2.47182021	0.13216744
C	1.06714448	1.52445082	0.14738962	H	-1.43992020	-2.47149130	-0.13191580

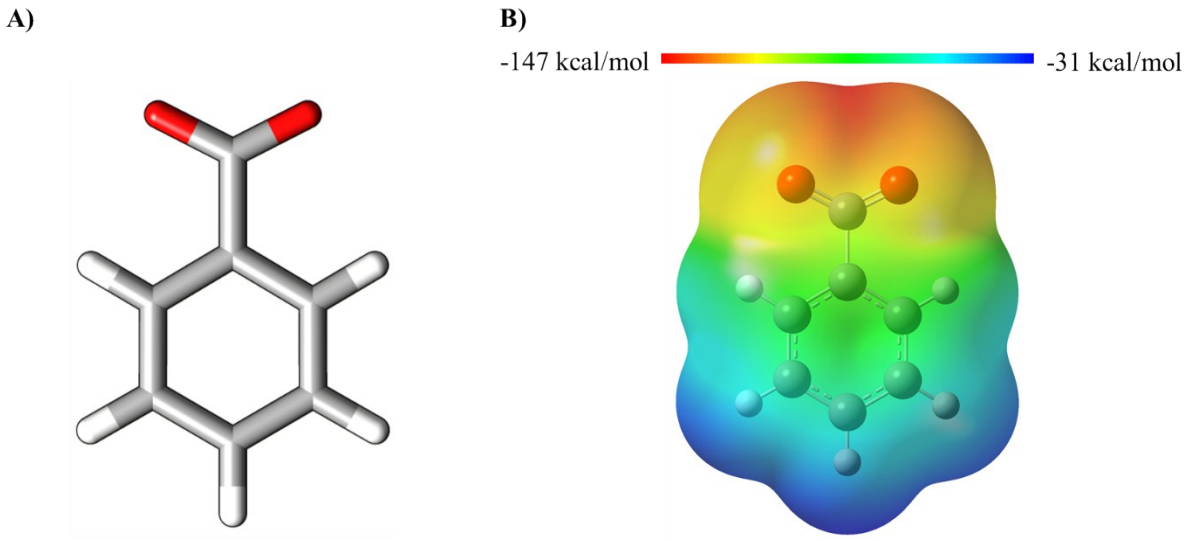

Figure S38. Optimized structure (A) and electrostatic potential map (B) of **G1**.

C	-1.83719630	1.20948817	-0.00022295	O	2.38632884	-1.12834102	0.00001097
C	-0.43889312	1.20646311	-0.00021483	O	2.38632880	1.12834100	-0.00002225
C	0.27880470	-0.00000009	0.00000197	H	-2.37711551	2.15362197	-0.00040342
C	-0.43889310	-1.20646310	0.00021920	H	0.11264949	2.14144657	-0.00038003
C	-1.83719645	-1.20948809	0.00022615	H	0.11264917	-2.14144676	0.00038639
C	-2.54162920	0.00000000	0.00000103	H	-2.37711551	-2.15362198	0.00040656
C	1.81111691	0.00000004	0.00000285	H	-3.62900952	0.00000012	0.00000017

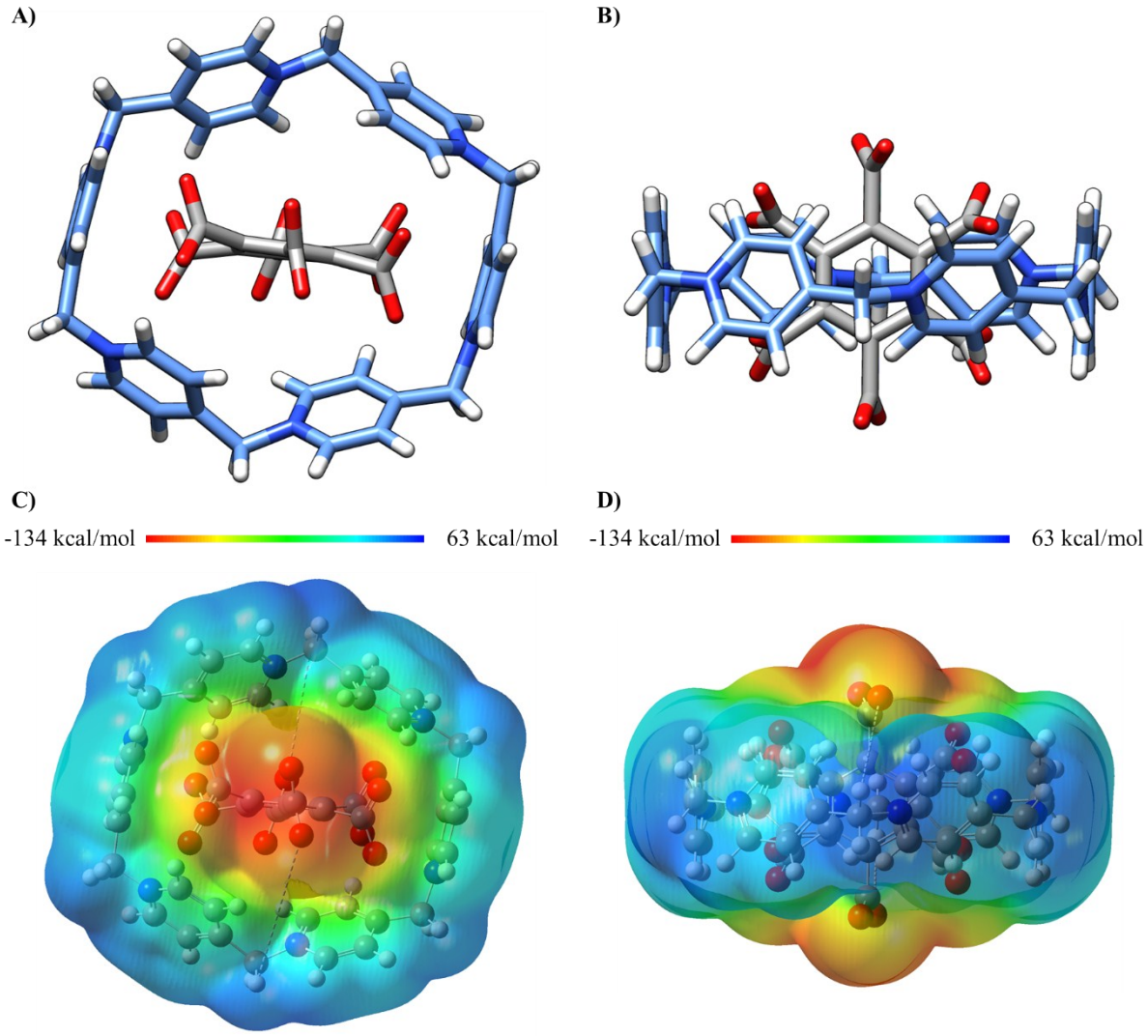

Figure S39. Optimized structure of P[6]P^{6+}·**G8** complex seen from the top (A) and from the side (B). Electrostatic potential map of this complex, top (C) and side (D) view.

C	-3.06872801	3.86164593	-0.08862218	C	-0.00809416	-0.06175688	2.96672318
C	-2.59006483	4.77583775	0.86026633	C	-2.42448767	0.45947909	1.59195294
C	-1.25480643	5.14974165	0.86842694	C	-2.48114535	-0.09453647	-1.52714217
N	-0.37668048	4.64853069	-0.03732733	O	-0.35901810	-1.04159362	-3.49909342
C	-0.81375047	3.74888521	-0.95918517	O	0.35712354	1.09875230	-3.47547866
C	-2.13808541	3.35075230	-1.00625463	O	2.78961271	-0.79037588	-2.35889143
C	3.16477903	4.35236105	-1.07393428	O	3.09965935	1.19101304	-1.35809993
C	4.32940114	3.60920522	-0.96148056	O	2.89122939	0.40877728	2.35750924
N	4.57872685	2.86589447	0.14034162	O	2.83242497	-1.66922326	1.51484883
C	3.67700826	2.83566229	1.14826560	O	-0.18290859	1.03630265	3.57017327
C	2.49246927	3.55623075	1.07795158	O	0.16629223	-1.18934404	3.51431557

C	2.20659657	4.33169891	-0.05005876	O	-2.81241808	1.66372393	1.52596092
C	5.54675713	-0.08441975	-1.14822576	O	-2.91102661	-0.41738075	2.35780877
C	5.24261797	-1.43179019	-1.23370607	O	-3.10427355	-1.17910452	-1.37915159
N	5.05856088	-2.17783156	-0.11139520	O	-2.79481424	0.81511101	-2.35375833
C	5.26874537	-1.62465520	1.10869389	H	-3.24409815	5.21475327	1.60610246
C	5.58841513	-0.27739318	1.23551120	H	-0.86476066	5.86528950	1.58090920
C	5.64545313	0.53902629	0.10421342	H	-0.07971632	3.36603917	-1.65960534
N	0.38053233	-4.63945052	-0.05840173	H	-2.40948572	2.58448795	-1.73354586
C	0.81834283	-3.74002463	-0.98010340	H	3.01676040	4.94009426	-1.97333877
C	2.14269677	-3.34189888	-1.02684915	H	5.07716360	3.59362361	-1.74333307
C	3.07294188	-3.85272905	-0.10860711	H	3.89765424	2.19685677	1.99085890
C	2.59365316	-4.76730859	0.83974142	H	1.80963418	3.49403819	1.91791972
C	1.25840707	-5.14084860	0.84760479	H	5.64774622	0.47520797	-2.06811511
C	-3.67879695	-2.83779851	1.13521997	H	5.11439812	-1.93524221	-2.18047212
C	-2.49292401	-3.55593717	1.06260888	H	5.19815044	-2.28262285	1.96041236
C	-2.20353380	-4.32354316	-0.06990876	H	5.72433287	0.12021900	2.23327934
C	-3.15921587	-4.33810535	-1.09624341	H	0.08438826	-3.35809221	-1.68095323
C	-4.32434589	-3.59582782	-0.98222405	H	2.41405835	-2.57537233	-1.75362456
N	-4.57717837	-2.86034248	0.12407464	H	3.24738574	-5.20631393	1.58577739
C	-5.24236460	1.44706656	-1.22603944	H	0.86803322	-5.85623808	1.56007476
C	-5.54832445	0.09930988	-1.14880705	H	-3.90266567	-2.20624427	1.98224286
C	-5.64332335	-0.53267026	0.09935490	H	-1.81249040	-3.49876786	1.90489301
C	-5.58140559	0.27620134	1.23617720	H	-3.00864645	-4.92005806	-1.99897628
C	-5.26035426	1.62368491	1.11756212	H	-5.06967820	-3.57470319	-1.76624322
N	-5.05291499	2.18485765	-0.09937374	H	-5.11702553	1.95690284	-2.16973893
C	0.99378868	5.25219116	-0.14596819	H	-5.65301830	-0.45371389	-2.07230080
C	5.84062434	2.04894390	0.23526205	H	-5.71546799	-0.12800617	2.23142309
C	4.58486953	-3.59024859	-0.20371434	H	-5.18412415	2.27533458	1.97362153
C	-0.99004148	-5.24316818	-0.16770269	H	1.05903907	5.99871287	0.64804001
C	-5.83914730	-2.04347147	0.22087631	H	1.01565162	5.78488964	-1.09870036
C	-4.58036009	3.59828224	-0.18384667	H	6.29211006	2.28956965	1.19905694

C	-1.22291089	0.06053298	-0.68062451	H	6.50222682	2.41706483	-0.54946393
C	-1.21663718	0.11798161	0.73128211	H	5.09465895	-4.14500424	0.58466159
C	-0.00580755	-0.02757817	1.43036467	H	4.94282796	-3.97866033	-1.16063895
C	1.20786892	-0.14529161	0.72976784	H	-1.05471785	-5.99087935	0.62520573
C	1.21604143	-0.05804410	-0.67980776	H	-1.01197062	-5.77444559	-1.12121462
C	-0.00323495	0.00626952	-1.37907314	H	-6.29281466	-2.28949759	1.18230702
C	-0.00171929	0.02239287	-2.91381278	H	-6.49899180	-2.40681609	-0.56751203
C	2.47560503	0.10943679	-1.52154250	H	-5.09018327	4.14830147	0.60783564
C	2.42161605	-0.47330310	1.58682243	H	-4.93928489	3.99159224	-1.13840938

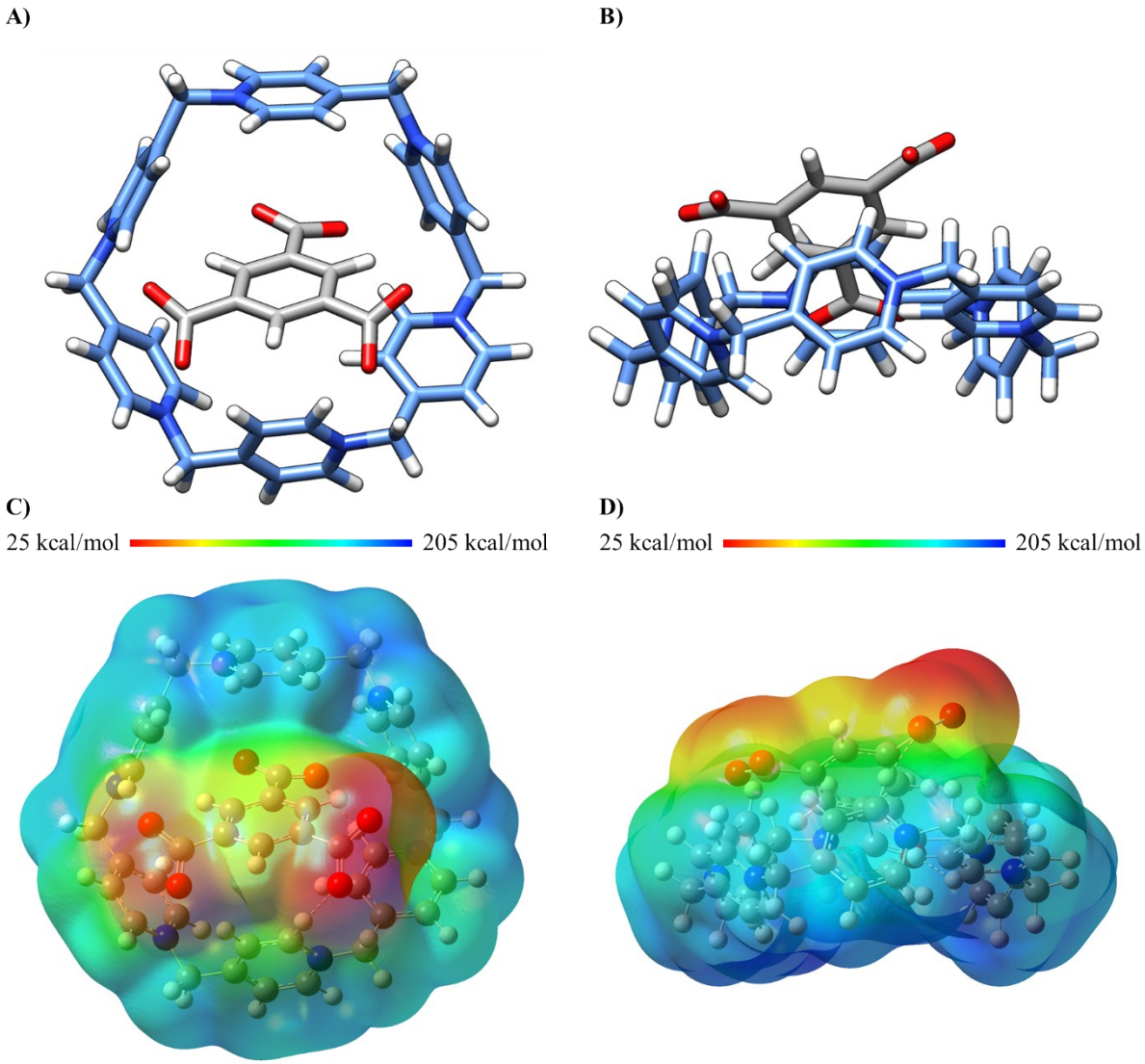

Figure S40. Optimized structure of P[6]P^{6+}·**G7** complex seen from the top (A) and from the side (B). Electrostatic potential map of this complex, top (C) and side (D) view.

C	-0.76696551	-4.64139398	-0.58241265	C	-0.68388598	-2.91122376	3.13256564
C	0.07359051	-5.76023665	-0.67567517	C	1.34849048	0.48604666	-0.05616671
C	1.39043617	-5.60241001	-1.06121866	C	-3.07599480	1.47832942	2.19656505
N	1.88762566	-4.37259294	-1.34794883	O	-1.78096093	-3.55626719	3.07724484
C	1.10027811	-3.27421878	-1.26462174	O	0.40038093	-3.32670154	3.62346027
C	-0.22786178	-3.38998066	-0.89243225	O	1.37017883	1.69325379	-0.43569962
C	4.48089444	-2.04128973	-2.09021429	O	2.12726049	-0.43036702	-0.45768386
C	5.13643412	-0.95252753	-1.54517567	O	-2.87971672	2.73062558	2.19711745
N	5.35521470	-0.87383450	-0.21354783	O	-4.20278633	0.90382531	2.28238967
C	4.94859649	-1.86778234	0.61220483	H	-0.28449376	-6.75841893	-0.44914173

C	4.28760102	-2.97521345	0.11409611	H	2.07030163	-6.43956456	-1.15515061
C	4.02714546	-3.06780052	-1.25813286	H	1.55581929	-2.30254354	-1.43734699
C	5.32152723	2.59974955	-0.53096673	H	-0.80927031	-2.47850587	-0.83186657
C	4.51657755	3.72426396	-0.45656531	H	4.32053555	-2.06681833	-3.16209993
N	3.54909084	3.82039149	0.48457044	H	5.49170613	-0.13052876	-2.15294370
C	3.34373940	2.81142845	1.36277496	H	5.17536620	-1.75589090	1.66434927
C	4.13573489	1.67782030	1.34063074	H	3.98039920	-3.74843927	0.80982140
C	5.14265283	1.55094529	0.37899164	H	6.09520373	2.57302067	-1.29051173
N	-1.29982818	4.77075522	-0.86223126	H	4.64149560	4.56724428	-1.12376572
C	-0.30228336	5.10797058	-1.71576273	H	2.56144970	2.95077230	2.09550134
C	1.00772158	5.18342938	-1.27704438	H	3.94954208	0.91226089	2.08440719
C	1.31050675	4.91985365	0.06409111	H	-0.58419591	5.32256695	-2.73861940
C	0.25817597	4.58040918	0.91985252	H	1.77077858	5.46959361	-1.99179252
C	-1.03814296	4.50101772	0.44007204	H	0.41935726	4.37773770	1.97259505
C	-3.65724023	1.19715644	-2.22472344	H	-1.86771570	4.18574374	1.07069186
C	-2.97784995	2.39885857	-2.20983736	H	-3.39737922	0.39275789	-2.90110332
C	-3.37861740	3.41477332	-1.32779215	H	-2.15517626	2.53073453	-2.90337092
C	-4.45385032	3.16251445	-0.47498442	H	-4.80356958	3.90343291	0.23294933
C	-5.10412464	1.93795197	-0.52077544	H	-5.94137524	1.70406040	0.12166508
N	-4.70867664	0.98353450	-1.39125410	H	-2.92846500	-2.94172507	1.50862250
C	-3.35988169	-2.76435555	0.51992798	H	-4.30212258	-0.90326019	0.97496370
C	-4.12774665	-1.65363952	0.20273433	H	-4.72483719	-2.44518089	-3.05803584
C	-4.62258333	-1.50455803	-1.09801503	H	-3.31556000	-4.37868304	-2.38156468
C	-4.34933165	-2.50329271	-2.04249486	H	3.24264361	-4.17446273	-2.93639140
C	-3.57097315	-3.58901373	-1.68580524	H	3.80444819	-5.18059141	-1.59312193
N	-3.08033281	-3.69561956	-0.42683359	H	6.92819535	0.51285766	-0.27130165
C	3.29145324	-4.25177468	-1.84835629	H	6.38457584	0.07192799	1.34653837
C	6.04563184	0.32908744	0.34226876	H	3.25958535	5.84387846	0.04418528
C	2.72858006	5.06585760	0.59193741	H	2.71748622	5.34715406	1.64633456
C	-2.71805092	4.78136489	-1.33162088	H	-2.71856861	5.19557567	-2.34104141
C	-5.46450679	-0.30213039	-1.48007084	H	-3.26229174	5.47200381	-0.68623218

C	-2.18673308	-4.83049888	-0.08573948	H	-5.83895822	-0.38965400	-2.50109426
C	-1.80582367	-0.67754769	2.66820218	H	-6.32258167	-0.21518046	-0.81219378
C	-1.85777658	0.57495001	2.04226474	H	-2.62343449	-5.74429413	-0.49377490
C	-0.80179096	0.95003071	1.20379141	H	-2.17076152	-4.91303933	1.00620004
C	0.28553093	0.09911540	0.97046828	H	-2.64121480	-1.00116333	3.28195917
C	0.34431950	-1.12085651	1.65793214	H	-0.83250919	1.90046553	0.68835532
C	-0.69946383	-1.52323728	2.50303201	H	1.19425017	-1.77689077	1.50261604

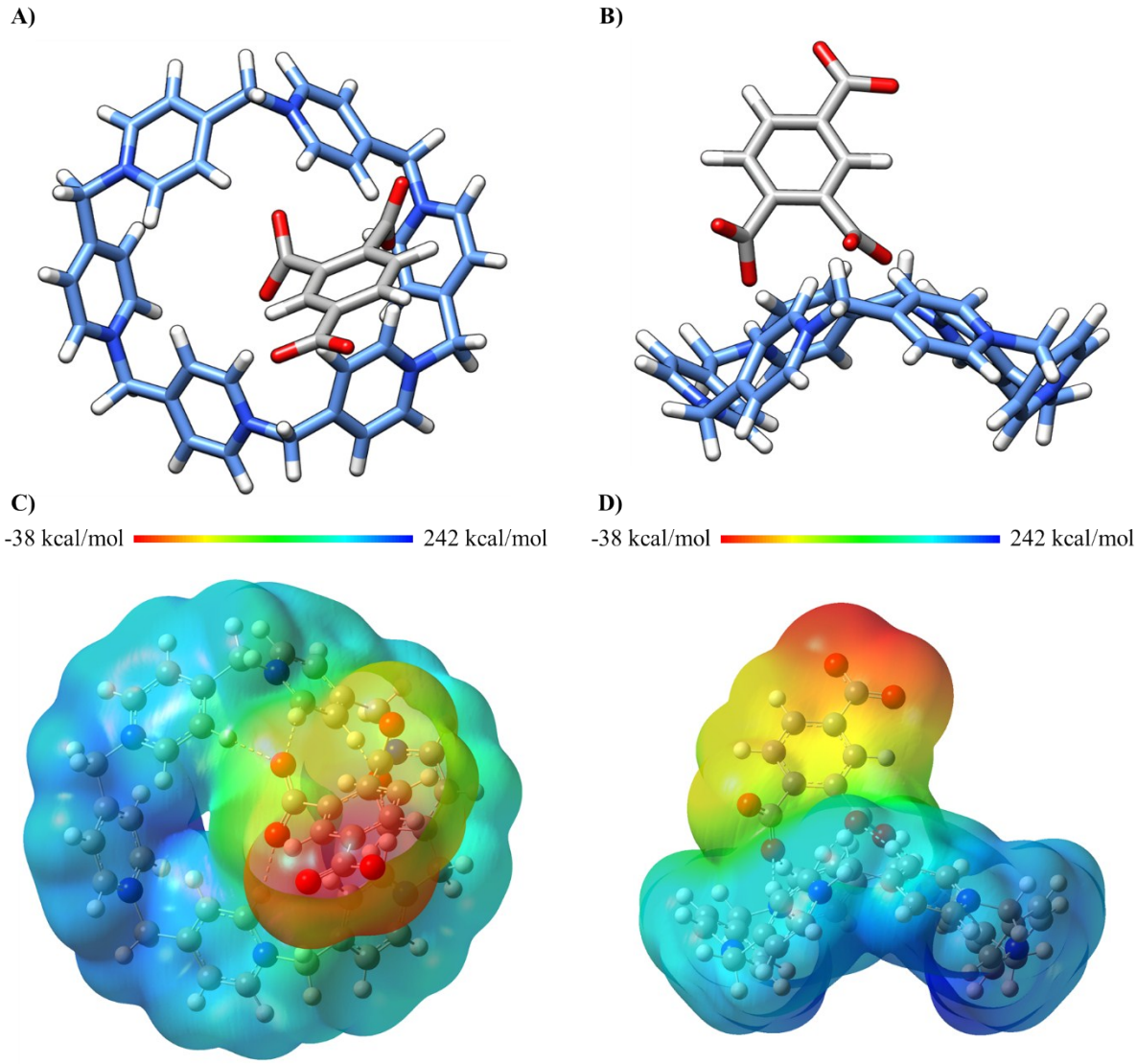

Figure S41. Optimized structure of P[6]P^{6+}·**G6** seen from the top (A) and from the side (B). Electrostatic potential map of this complex, top (C) and side (D) view.

C	0.39871325	4.70349040	-1.35501848	C	0.67517605	-0.22877220	1.88163000
C	-0.68130340	5.57694960	-1.15826582	C	3.02642374	1.68201497	1.41216993
C	-1.48274305	5.43533330	-0.04282003	O	0.10941065	0.87132143	2.15831064
N	-1.24141908	4.45274320	0.86266812	O	0.16800972	-1.16900912	1.19888176
C	-0.20064136	3.60276772	0.69864124	O	2.75125146	1.48572027	0.18506867
C	0.63499885	3.71043405	-0.40095217	O	3.26624771	2.79863673	1.94534686
C	-4.53584684	3.64932815	1.59844500	H	-0.90758038	6.36927072	-1.86342207
C	-5.51543227	2.68657853	1.41615757	H	-2.32240307	6.08917439	0.15430611
N	-5.20812022	1.37119205	1.49259605	H	-0.04894634	2.82414717	1.44329448
C	-3.93980518	0.97429851	1.76742283	H	1.46445124	3.00313715	-0.44840984

C	-2.92412133	1.89510907	1.94076841	H	-4.82309665	4.69295093	1.53596620
C	-3.21481354	3.26415957	1.84965749	H	-6.54690779	2.93934929	1.20651263
C	-5.41118583	-0.48784961	-0.91348274	H	-3.76379774	-0.09093225	1.84205999
C	-4.95973738	-1.51990132	-1.71325202	H	-1.91833192	1.51670669	2.13174021
N	-4.96292545	-2.79869262	-1.25921131	H	-5.37562893	0.52128343	-1.30849538
C	-5.46517324	-3.09974624	-0.03831615	H	-4.57159274	-1.35736646	-2.71078165
C	-5.92387535	-2.09712052	0.80002334	H	-5.45745667	-4.14287433	0.25225051
C	-5.86717004	-0.76308581	0.38364820	H	-6.29090300	-2.37068955	1.78289305
N	-0.10364956	-4.28288916	-1.47114021	H	-0.24096601	-2.82660621	0.03919734
C	-0.78744541	-3.40314542	-0.70375176	H	-2.64273386	-2.51949054	-0.23029067
C	-2.15091227	-3.23750311	-0.87374591	H	-2.57424518	-5.49576984	-3.37891295
C	-2.83693597	-3.98058222	-1.83763296	H	-0.13599690	-5.70581109	-2.99236516
C	-2.10214936	-4.88692166	-2.61569585	H	3.15642442	-0.11335610	-0.96305081
C	-0.74156695	-5.01892318	-2.41546226	H	1.90765744	-2.00955392	-0.03318541
C	3.03801597	-1.03590970	-1.53847308	H	2.63560131	-4.17040346	-3.72280133
C	2.33394002	-2.11312995	-1.02812696	H	3.87968602	-2.18246278	-4.53633377
C	2.15621809	-3.26463214	-1.80316697	H	0.48351992	2.73245279	-3.75555246
C	2.72675636	-3.30138159	-3.08120862	H	1.71189721	0.60922162	-4.09631043
C	3.42601579	-2.20388790	-3.55360929	H	5.17478218	2.49627790	-2.31140261
N	3.56377949	-1.09440265	-2.78788836	H	3.80809860	4.55401858	-2.04195306
C	1.51822755	2.62141344	-3.45671596	H	-2.56259789	5.28614246	2.25737650
C	2.22176629	1.44772049	-3.63534737	H	-1.49279704	4.03573865	2.89812646
C	3.55137840	1.36213324	-3.19864259	H	-7.16534655	0.86182112	0.93916742
C	4.14634338	2.50168537	-2.65358470	H	-6.52221368	-0.04740295	2.31502086
C	3.40222172	3.65840301	-2.49506563	H	-4.52809801	-3.63538746	-3.12943282
N	2.10371537	3.69674019	-2.87151528	H	-4.82805567	-4.80519822	-1.84903294
C	-2.12872153	4.30755597	2.05421760	H	1.53141172	-4.56397642	-0.19203820
C	-6.28355152	0.34738894	1.32602877	H	1.66358217	-5.37134302	-1.75804965
C	-4.33060737	-3.86004367	-2.07882631	H	4.59302565	-0.13479766	-4.34302833
C	1.36842165	-4.44612211	-1.26424727	H	5.26499117	0.13440546	-2.72974975
C	4.33733987	0.07183874	-3.30159959	H	0.66639634	5.10326674	-3.46048950

C	1.27515483	4.89090214	-2.57886448	H	1.94818104	5.73938421	-2.43366372
C	3.48686820	-1.89538362	3.85893521	H	5.49114542	-1.17624755	4.16576311
C	4.53461953	-0.97841690	3.69154280	H	5.17424602	0.87272828	2.79657064
C	4.35175018	0.17198725	2.92250002	H	1.44932132	-2.32674286	3.35416169
C	3.12601207	0.44522230	2.29468138	C	3.66873038	-3.16214880	4.69826456
C	2.06303228	-0.46718397	2.46002205	O	2.67739463	-3.94709034	4.78041147
C	2.26488600	-1.62147423	3.23025218	O	4.79768404	-3.33315340	5.24710318

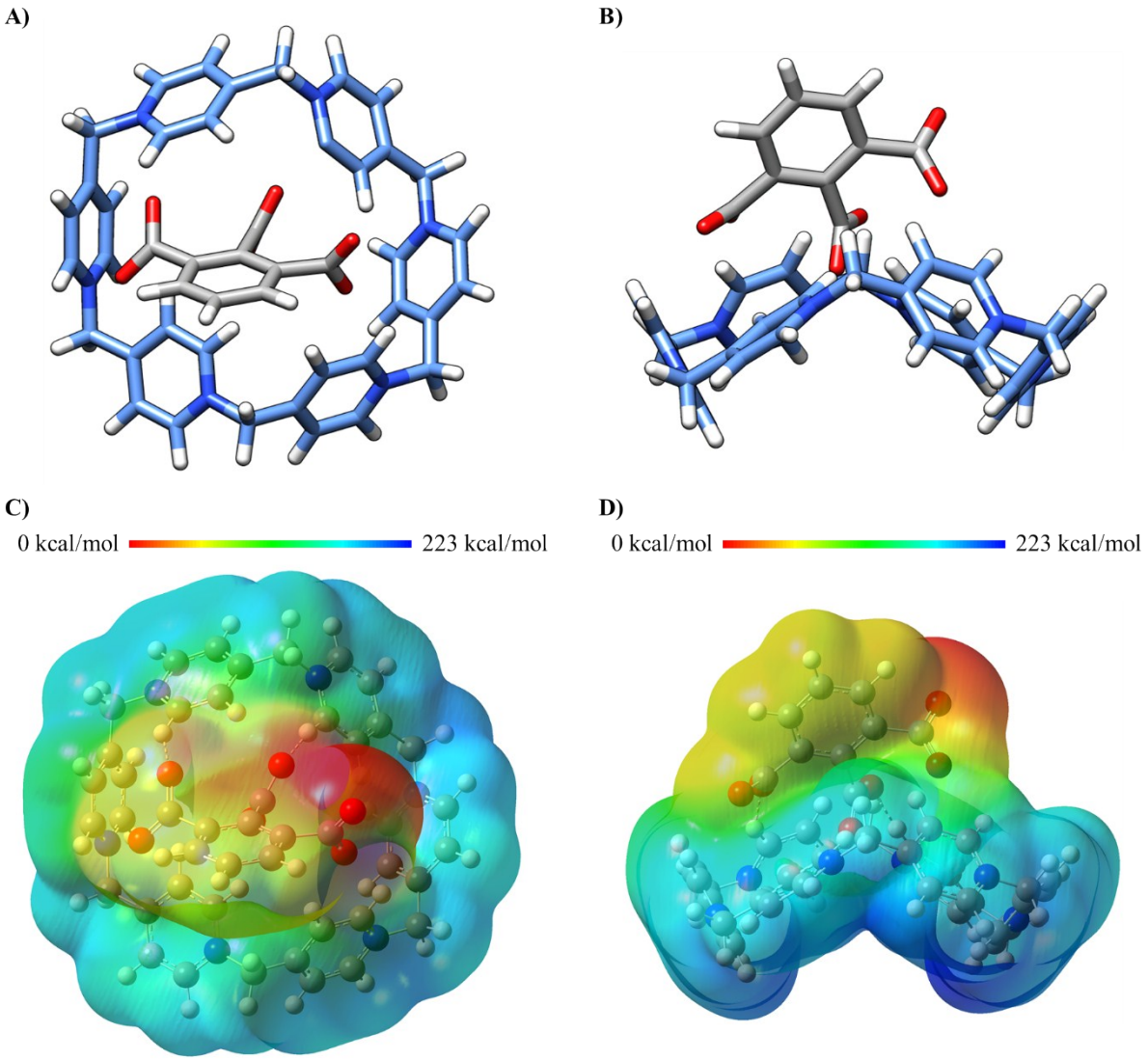

Figure S42. Optimized structure of P[6]P^{6+}·**G5** complex seen from the top (A) and from the side (B). Electrostatic potential map of this complex, top (C) and side (D) view.

C	3.18101434	4.05970774	-0.71365197	C	-3.10245397	-1.12106820	1.93282052
C	2.66057000	5.36156240	-0.74709758	C	-0.30330354	-0.00106662	1.80964330
C	1.49732158	5.65316801	-0.06285023	C	1.74342450	-1.08716745	3.71625897
N	0.84746149	4.69332271	0.64196644	O	-3.34282550	0.12230788	1.99509697
C	1.32541124	3.42781560	0.69646181	O	-3.73974373	-1.96838986	1.24434821
C	2.48898153	3.09448710	0.02209507	O	0.01333248	1.13349437	2.28241025
C	-2.32759598	5.14943464	-0.28044092	O	-0.33145200	-0.31274075	0.58502307
C	-3.45016072	4.58460089	-0.86096364	O	2.41887305	-1.28183866	2.66162300
N	-3.89876146	3.37105455	-0.45676645	O	2.16490147	-0.56684254	4.78813543

C	-3.26754797	2.68733956	0.52793394	H	3.15074347	6.15692766	-1.29762352
C	-2.13618935	3.21209374	1.12928623	H	1.06501061	6.64565184	-0.05629969
C	-1.64252179	4.45625343	0.72596838	H	0.77303836	2.68076587	1.27873285
C	-4.13933240	1.23409400	-2.83809662	H	2.82720144	2.06854700	0.10080065
C	-3.85928719	-0.03836019	-3.29527140	H	-2.00892654	6.12635042	-0.62654075
N	-4.26669217	-1.12881653	-2.59422416	H	-4.00881432	5.07833241	-1.64581991
C	-4.97205094	-0.99659191	-1.44723790	H	-3.65032157	1.71215769	0.83063778
C	-5.28395532	0.26207735	-0.95896119	H	-1.63924061	2.61031728	1.88527933
C	-4.85132225	1.40110707	-1.64050151	H	-3.79566182	2.08082213	-3.42167194
N	-0.42084322	-4.16092029	-1.20648925	H	-3.30860426	-0.22368347	-4.20871516
C	-0.80456886	-2.90871700	-0.86995451	H	-5.24358833	-1.90317692	-0.92337793
C	-1.91301127	-2.32739406	-1.45803885	H	-5.84069996	0.32863430	-0.03233706
C	-2.65334526	-3.03489956	-2.40581681	H	-0.24511033	-2.35415162	-0.12108906
C	-2.22866994	-4.32858788	-2.74469731	H	-2.16928596	-1.33193900	-1.12163257
C	-1.11511853	-4.86990479	-2.13306639	H	-2.75985645	-4.92896243	-3.47535061
C	3.68693905	-2.44620976	0.04023731	H	-0.76006025	-5.86778833	-2.35598668
C	2.50748439	-3.13711400	0.25113418	H	4.06778545	-1.75183297	0.77929029
C	2.03173125	-4.01575251	-0.72775821	H	1.99778301	-2.93928772	1.18970466
C	2.78505488	-4.17952381	-1.89795040	H	2.47833224	-4.85547731	-2.68848182
C	3.96204179	-3.47057589	-2.06330494	H	4.57956892	-3.56752970	-2.94710004
N	4.39307717	-2.61553900	-1.10328876	H	3.64019282	1.97684441	-3.12368231
C	4.29458454	1.52239410	-2.39083464	H	4.08460019	-0.46139098	-3.11361749
C	4.55588553	0.16672206	-2.36618388	H	6.67601386	0.17152236	0.29680032
C	5.40033410	-0.36087895	-1.37960373	H	6.12245324	2.59205783	0.15883844
C	5.99855411	0.52080798	-0.47406826	H	-0.46025045	6.11960298	1.44555371
C	5.70614357	1.87349642	-0.53581561	H	-0.29077456	4.64008649	2.39780606
N	4.84994537	2.34984796	-1.46991069	H	-5.45391827	3.46476327	-1.86265545
C	-0.40325841	5.03313133	1.38669590	H	-5.89819046	2.74580088	-0.30862164
C	-5.12546671	2.78237046	-1.07846981	H	-3.76399750	-2.43370593	-4.15187746
C	-3.89997922	-2.48391307	-3.06909657	H	-4.75000061	-3.14410013	-2.87930593
C	0.74273387	-4.78357677	-0.50588028	H	0.49774901	-4.82578401	0.55661187

C	5.66095961	-1.85198489	-1.29097115	H	0.83572348	-5.80466293	-0.87522663
C	4.47002834	3.78262921	-1.46438941	H	6.13153831	-2.21440250	-2.20657348
C	-2.28189220	-2.67793981	3.71818611	H	6.31914461	-2.08975037	-0.45443171
C	-1.32767757	-3.14847532	4.62226498	H	4.38145021	4.10850097	-2.50353117
C	-0.04648336	-2.59420419	4.62020582	H	5.29253329	4.34543246	-1.01656116
C	0.29811866	-1.58366182	3.70919544	H	-3.28275392	-3.10251751	3.70983705
C	-0.67223580	-1.09531691	2.80694605	H	-1.58117200	-3.93986236	5.32412803
C	-1.97434015	-1.64444644	2.82053666	H	0.70308037	-2.95144893	5.32260331

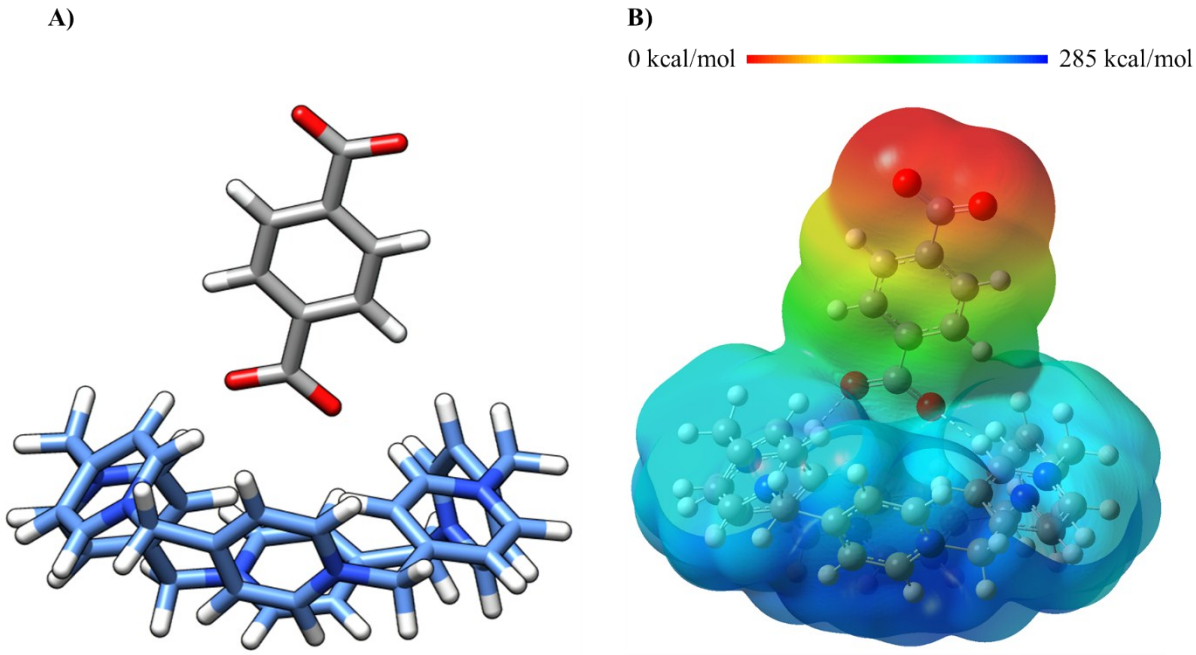

Figure S43. Optimized structure (A) and electrostatic potential map (B) of P[6]P^{6+}·**G4** complex.

C	-4.20681609	3.08195215	-0.96290740	C	2.76609246	-1.87234100	-2.37577734
C	-4.01878694	4.47113026	-0.92899367	C	0.92252783	-0.17854383	-1.90031450
C	-2.76117626	4.99878235	-1.14437494	O	0.52421779	1.01174742	-2.09622886
N	-1.69963331	4.18725543	-1.38112024	O	0.31733102	-1.04753939	-1.20491546
C	-1.85122860	2.84245591	-1.43050095	H	-4.84205104	5.15127891	-0.73989213
C	-3.09733147	2.27392553	-1.22360300	H	-2.57473026	6.06496395	-1.13672774
C	0.57520263	5.40921989	0.68398761	H	-0.97160259	2.22633968	-1.64000943
C	1.42979003	5.17020088	1.74770317	H	-3.16390016	1.19413099	-1.27699431
N	2.28443568	4.12041684	1.72094871	H	-0.08463435	6.26739483	0.74246142
C	2.33205927	3.29445767	0.64697452	H	1.45251620	5.79873985	2.62844880
C	1.48916132	3.48366558	-0.43195704	H	3.04969007	2.48463609	0.68128853
C	0.58367884	4.55219227	-0.42256481	H	1.52538424	2.77111900	-1.25304744
C	1.77573298	2.07080918	3.95856325	H	0.92947235	2.74571683	4.01811818
C	1.60871545	0.77150741	4.39613266	H	0.67057216	0.40634727	4.79532389
N	2.63169031	-0.11801396	4.32426049	H	4.62451730	-0.49575189	3.85981859
C	3.85086781	0.26155611	3.87568756	H	5.05018552	1.81939142	3.06169176
C	4.06574607	1.55610642	3.43154458	H	0.61320062	-2.26019604	0.37016430
C	3.01224805	2.47543191	3.43470274	H	1.64033451	-0.80626016	2.04638514

N	0.59091574	-3.94319702	1.63871180	H	1.70991499	-4.16229035	4.78695437
C	0.85885388	-2.64475984	1.36275907	H	0.67072301	-5.52354519	2.99567305
C	1.44520228	-1.83536910	2.32141853	H	-3.49361025	-3.11584452	-2.11148515
C	1.76140635	-2.35016251	3.58156434	H	-1.12213052	-3.73629332	-1.72261409
C	1.48046042	-3.70121671	3.83252113	H	-2.25827859	-4.97415284	2.26666515
C	0.89916216	-4.47569246	2.84847300	H	-4.57669288	-4.29877423	1.73065312
C	-3.16318209	-3.52251389	-1.16404098	H	-5.10393407	1.10235304	1.36014367
C	-1.84695262	-3.87745480	-0.92939532	H	-5.02483067	-1.36371643	1.56306156
C	-1.47842769	-4.39536192	0.31712785	H	-6.22860979	-1.59963962	-2.59124221
C	-2.47316618	-4.55915739	1.28878803	H	-6.25573103	0.88557861	-2.63376311
C	-3.77609712	-4.18685907	1.01095393	H	-0.47738312	5.83934664	-1.79641566
N	-4.10088560	-3.66507316	-0.19660329	H	0.06367674	4.31321889	-2.50530422
C	-5.33407148	0.45655189	0.52200513	H	2.99452008	4.62604778	3.62919253
C	-5.29392603	-0.92107753	0.61060821	H	4.22675794	4.01726706	2.51627131
C	-5.58826733	-1.70022489	-0.51742217	H	1.74667543	-1.54403909	5.57752693
C	-5.96692016	-1.04839672	-1.69496666	H	3.34836893	-1.96948115	4.98617366
C	-5.99258023	0.33617469	-1.73857780	H	0.56574151	-4.70534158	-0.31595539
N	-5.65885650	1.06391406	-0.64732648	H	0.01190103	-5.82701988	0.92915233
C	-0.34392371	4.77459436	-1.60514634	H	-6.13476614	-3.61618622	0.31918058
C	3.20521362	3.87033506	2.87077582	H	-5.81045240	-3.65858893	-1.41632277
C	2.39055475	-1.53298544	4.69449710	H	-6.01606475	2.94354735	0.19977140
C	-0.03896734	-4.79248788	0.58690480	H	-6.26685671	2.85803402	-1.53957174
C	-5.49791502	-3.21506866	-0.47081289	H	4.37266950	-3.24098270	-2.82612691
C	-5.60471675	2.54300335	-0.72974438	H	4.69059876	0.64584576	-4.59600178
C	3.96997506	-2.24408777	-2.97669895	C	6.00293951	-1.75368557	-4.44245305
C	4.68158490	-1.34341012	-3.78420337	O	6.42688277	-2.92198027	-4.19929761
C	4.14951295	-0.05781222	-3.97048860	O	6.57012444	-0.89325269	-5.17799146
C	2.94755091	0.31613126	-3.36596102	H	2.22461551	-2.58123000	-1.75773052
C	2.23618422	-0.58559604	-2.55819779	H	2.54628656	1.31360762	-3.51708610

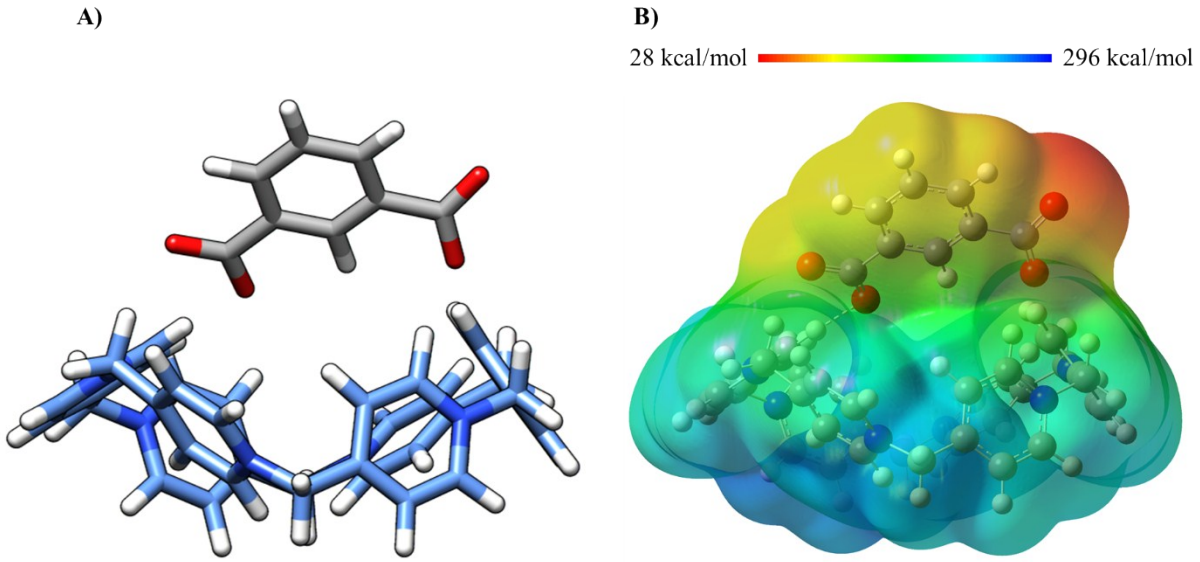

Figure S44. Optimized structure (A) and electrostatic potential map (B) of P[6]P^{6+}·**G3** complex.

C	6.04304744	-0.45270924	0.08845310	C	-3.40991883	1.91649894	2.34594305
C	5.90689712	0.47392083	-0.95204917	C	-2.13721420	2.63142943	1.90661046
C	5.62030938	1.79662381	-0.66391520	C	-4.86768561	-1.64573254	2.32968870
N	5.47601915	2.20706998	0.61862715	O	-1.18683720	1.91535998	1.46580402
C	5.63972828	1.33969124	1.64634705	O	-2.11153897	3.89599698	2.00279425
C	5.92211689	0.00675671	1.40588387	O	-4.03080883	-2.20253442	1.54380984
C	3.35732666	5.05282699	-0.23325088	O	-5.80594598	-2.23428532	2.92903307
C	2.03473174	5.33572907	-0.52985510	H	6.01748612	0.18484644	-1.99102667
N	1.04274481	4.53590572	-0.07329114	H	5.49644613	2.54649672	-1.43516115
C	1.31012233	3.45028502	0.69745569	H	5.54022846	1.74100929	2.64666455
C	2.61977431	3.13189377	1.01100771	H	6.04524062	-0.65129264	2.25849835
C	3.67023767	3.93070766	0.54311658	H	4.12887910	5.70895901	-0.61991647
C	-0.24057634	3.00706595	-2.19485833	H	1.74049734	6.18412673	-1.13502749
C	-0.89703334	2.15529573	-3.06224759	H	0.44159341	2.86947009	1.03731936
N	-2.24310875	2.21102219	-3.20509886	H	2.79350051	2.25513093	1.62526483
C	-2.96867113	3.14316075	-2.53704996	H	0.83545993	2.91360697	-2.11249766
C	-2.35574051	4.01172575	-1.65665170	H	-0.37561102	1.40553237	-3.64446102
C	-0.97088427	3.93526717	-1.44257021	H	-4.03707093	3.14991970	-2.71298262
N	-3.18807384	-2.58586566	-2.00769286	H	-2.96957046	4.72627269	-1.11986727
C	-3.41920061	-1.44502389	-1.31392568	H	-3.66752682	-1.55715399	-0.25469923

C	-3.33923177	-0.21787602	-1.94763141	H	-3.52939736	0.66802034	-1.35280251
C	-3.01901510	-0.14609308	-3.30705112	H	-2.56397153	-1.35309963	-5.05759469
C	-2.80698490	-1.34392613	-4.00088702	H	-2.74255391	-3.50041833	-3.82706640
C	-2.89853627	-2.55108319	-3.33092454	H	0.12574811	-3.58545852	1.97568820
C	-0.25118149	-4.01521094	1.05582250	H	-2.10241998	-2.94778449	1.04051254
C	-1.47298667	-3.66222201	0.51439082	H	-1.37873452	-5.76223874	-2.16831164
C	-1.90263872	-4.26571603	-0.67708778	H	0.79194711	-6.30976114	-1.09763613
C	-1.08584230	-5.23733259	-1.26627665	H	4.06871984	-2.01884286	-1.48566255
C	0.12750499	-5.56199050	-0.68320605	H	2.08286653	-3.40217743	-1.02826248
N	0.53296997	-4.94482038	0.45229219	H	4.23711049	-5.13410572	2.30685581
C	4.05155359	-2.71576120	-0.65769904	H	6.15503987	-3.68299793	1.70832740
C	2.94779695	-3.50215140	-0.38375447	H	5.79822528	4.25711491	0.31225749
C	2.97905497	-4.39047234	0.69676946	H	5.30170282	3.81754841	1.94738918
C	4.15110847	-4.46015935	1.46157975	H	-0.44319058	5.88230811	-0.69012594
C	5.23058719	-3.65717837	1.14639730	H	-0.95303415	4.69510653	0.54408053
N	5.16766450	-2.79152583	0.10535990	H	-2.36481577	1.07842522	-4.96744751
C	5.11797510	3.62885047	0.88757208	H	-3.91821183	1.55603881	-4.28184865
C	-0.37437373	4.83505121	-0.38642837	H	-3.99180433	-3.78366376	-0.49476420
C	-2.92126145	1.18273462	-4.03536732	H	-3.58276871	-4.64661282	-1.99508170
C	-3.24568845	-3.89287437	-1.28425859	H	2.06753876	-6.33184757	0.76075679
C	1.83195225	-5.30909421	1.06678624	H	1.69446764	-5.32160581	2.14946920
C	6.33305589	-1.91243717	-0.21456431	H	6.57181156	-2.05354449	-1.26913997
C	-4.45961090	2.63043222	2.94336880	H	7.17941679	-2.26798051	0.37450649
C	-5.62194549	1.96893261	3.35013065	H	-4.35353702	3.70138938	3.08576227
C	-5.74829862	0.58992435	3.16086097	H	-6.43017822	2.52863565	3.81529427
C	-4.71714891	-0.14242207	2.55163876	H	-6.64691991	0.06940646	3.47733871
C	-3.55535849	0.53460558	2.15495363	H	-2.74619086	-0.01923761	1.69289381

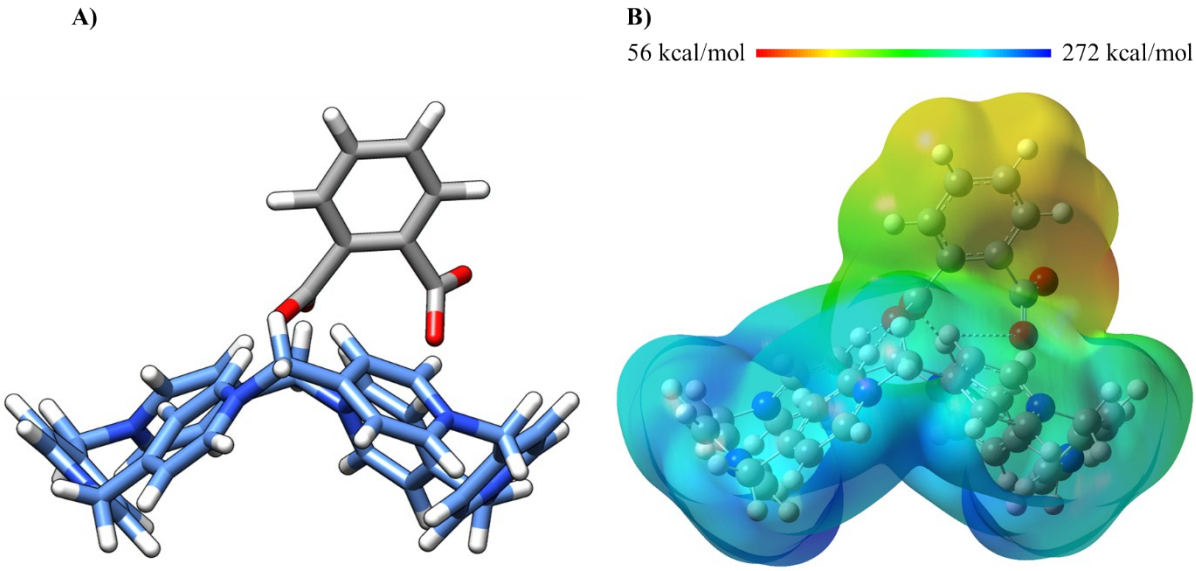

Figure S45. Optimized structure (A) and electrostatic potential map (B) of P[6]P^{6+}·**G2** complex.

C	1.83512284	3.80157130	-1.98405185	C	1.54792466	-1.18453450	4.32543587
C	1.00141652	4.91393796	-2.17296065	C	0.52255760	-0.01470386	2.35796154
C	0.07101385	5.24574987	-1.20815139	C	3.31352293	1.15027514	1.82358743
N	-0.05187635	4.50015752	-0.08021368	O	0.18969048	1.20088113	2.23243378
C	0.74537688	3.42616461	0.12791171	O	-0.08925613	-1.00608413	1.85909426
C	1.69756313	3.05860401	-0.80862003	O	3.10035564	0.66309907	0.66826415
C	-3.48808881	4.65619672	0.19126827	O	3.79968275	2.28756911	2.06800578
C	-4.65286210	3.91852126	0.05446189	H	1.06789984	5.53000592	-3.06317170
N	-4.71810560	2.64567642	0.50873873	H	-0.58672853	6.09957135	-1.30763299
C	-3.64915573	2.07607278	1.12075909	H	0.60701874	2.85219020	1.04179609
C	-2.45975132	2.76452940	1.26621085	H	2.31535192	2.19652447	-0.55433974
C	-2.36232519	4.07997769	0.78947453	H	-3.48216083	5.67477722	-0.18017790
C	-5.08461788	0.26631841	-1.35627492	H	-5.54201782	4.31953730	-0.41482995
C	-4.81958479	-1.02455268	-1.77037185	H	-3.77313498	1.06450117	1.48558954
N	-5.22281894	-2.08546418	-1.02646876	H	-1.62325221	2.24938360	1.74016431
C	-5.94760387	-1.90579529	0.10294035	H	-4.73039175	1.08645641	-1.97046194
C	-6.23562314	-0.62943327	0.55731011	H	-4.27155291	-1.24496902	-2.67777387
C	-5.76897125	0.48212525	-0.15164397	H	-6.25013466	-2.79715956	0.63788243
N	-0.88384514	-4.55208563	-0.03745782	H	-6.79263892	-0.52243054	1.48109527
C	-1.41254971	-3.37714834	0.37590606	H	-0.82330926	-2.74999070	1.04076633

C	-2.66852289	-2.98439028	-0.05290373	H	-3.03829379	-2.03472997	0.31250498
C	-3.40542868	-3.80060621	-0.91520072	H	-3.35391404	-5.69206941	-1.99075517
C	-2.83288962	-5.01374720	-1.32403714	H	-1.09670321	-6.29354206	-1.16104678
C	-1.57570131	-5.36656116	-0.87310859	H	3.23409280	-1.19327809	-0.10609376
C	2.94548396	-2.19098827	-0.44537398	H	1.47257431	-2.43219317	1.06028915
C	1.95380549	-2.90366932	0.20619024	H	2.00352276	-5.66923674	-1.77808761
C	1.57601126	-4.16715477	-0.26137418	H	3.76015099	-4.30112787	-2.87205960
C	2.23995738	-4.68957179	-1.37778748	H	1.70521042	1.33025795	-3.90616045
C	3.22476521	-3.94295095	-2.00201585	H	2.37728540	-1.03381552	-3.57611795
N	3.55483942	-2.71284788	-1.53934472	H	5.93485355	0.40822616	-1.57708762
C	2.62406606	1.06577005	-3.39804555	H	5.12388183	2.72254256	-1.98918089
C	3.01779250	-0.24254221	-3.20339203	H	-1.25180932	5.93770233	0.85953192
C	4.20826273	-0.51452115	-2.51388857	H	-0.62581293	4.67640360	1.92432301
C	4.99845490	0.56021733	-2.10138030	H	-6.65035861	2.44260685	-0.28079052
C	4.56460598	1.85688600	-2.32053335	H	-6.45818593	1.84892534	1.37465650
N	3.38367991	2.09123972	-2.93597053	H	-4.82972448	-3.51221972	-2.50947214
C	-1.07147099	4.86686999	0.94694582	H	-5.52570852	-4.15796222	-1.02644464
C	-5.99506456	1.87968891	0.38665402	H	0.50514876	-4.77496195	1.51455174
C	-4.79306746	-3.44885938	-1.41943934	H	0.58361260	-6.01864136	0.26261073
C	0.47755026	-4.94884479	0.43777590	H	4.89388677	-2.45886692	-3.13336947
C	4.63652552	-1.93472852	-2.21067433	H	5.50960799	-1.94754906	-1.55597240
C	2.86393550	3.47471244	-3.04989862	H	2.43484178	3.58999327	-4.04718277
C	2.59180837	-1.46944421	5.20908972	H	3.71250722	4.15966766	-2.97658340
C	3.84908631	-0.89474450	4.99855763	H	2.42408976	-2.13352024	6.05352663
C	4.04215613	-0.03793274	3.91201722	H	4.67324304	-1.11126535	5.67394425
C	3.00014122	0.25589549	3.01798883	H	5.01829058	0.41099986	3.74507493
C	1.73156249	-0.32295512	3.23166809	H	0.56872458	-1.62942179	4.48519891

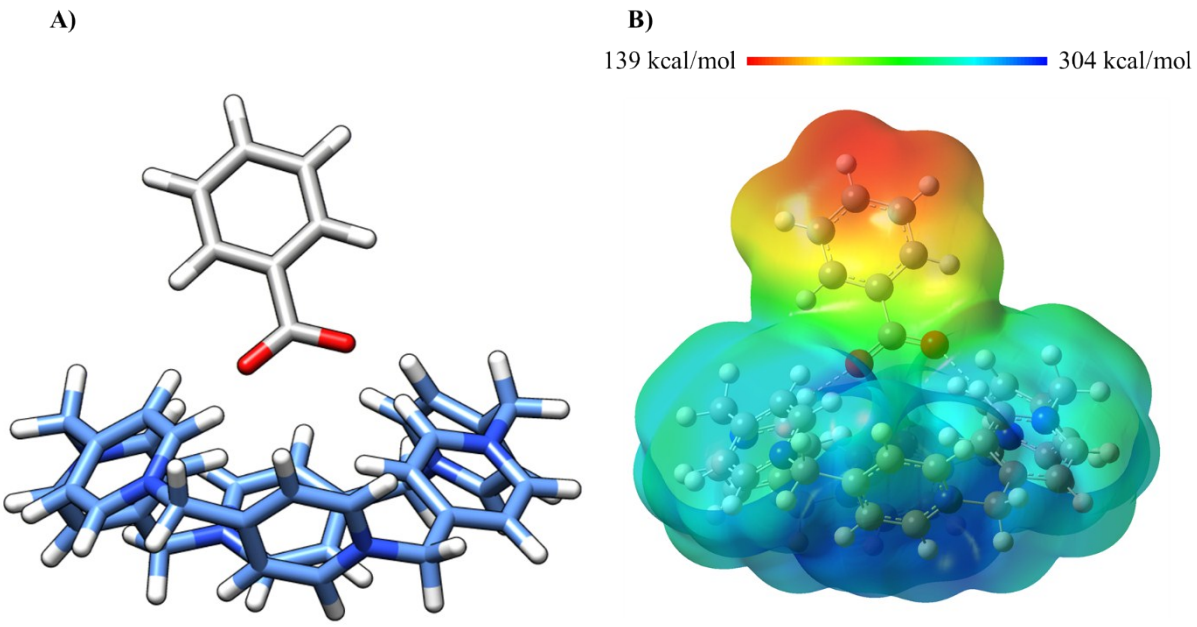

Figure S46. Optimized structure (A) and electrostatic potential map (B) of P[6]P^{6+}·**G1** complex.

C	-1.59885664	-3.79203386	-2.20360625	C	-0.94600065	-0.87158130	3.80362729
C	-0.75358663	-4.87949694	-2.46753716	C	-1.67992196	-0.09324394	4.71246423
C	0.33051985	-5.12186698	-1.64755597	C	-0.36469170	-0.24854646	2.53932131
N	0.59232770	-4.31761035	-0.58611910	O	0.29316694	-1.00521861	1.76329474
C	-0.20773875	-3.26229988	-0.30511879	O	-0.57947242	0.98726601	2.35000667
C	-1.30576299	-2.98400478	-1.10202209	H	-0.92975688	-5.54603983	-3.30486489
C	3.91013301	-3.83186990	-0.82445253	H	1.00384680	-5.95275398	-1.81431738
C	4.91896976	-2.89600600	-0.98589597	H	0.03387436	-2.64042484	0.55726195
N	4.93523706	-1.76745512	-0.23862116	H	-1.91174971	-2.12907894	-0.82863103
C	3.97983411	-1.54360656	0.69707287	H	3.93736630	-4.72515850	-1.43787474
C	2.94696069	-2.44200931	0.88577752	H	5.71857326	-3.02065719	-1.70479110
C	2.89176931	-3.60627395	0.10854917	H	4.06302282	-0.63312695	1.27615316
C	4.62173508	0.80958636	-1.86045552	H	2.18392420	-2.19744795	1.61957526
C	4.03926658	2.04393726	-2.07263374	H	4.40863483	0.01399228	-2.56511220
N	4.26264856	3.06909227	-1.21191836	H	3.38016926	2.24261304	-2.90860104

C	5.10579795	2.92396901	-0.16261539	H	5.25433258	3.79035530	0.47012576
C	5.71110011	1.70362207	0.08947735	H	6.36157029	1.61658931	0.95247251
C	5.44397609	0.61133892	-0.74228888	H	0.02607414	2.56769437	1.25624279
N	-0.32327976	4.49905294	0.49372405	H	2.23615203	2.38208562	0.21993249
C	0.42895947	3.38450282	0.65212646	H	1.69566361	6.35189354	-1.43168336
C	1.67654010	3.29479378	0.05667449	H	-0.51374628	6.41126601	-0.31636410
C	2.16923661	4.35266419	-0.71191703	H	-4.12303428	0.63178932	0.50430014
C	1.36759472	5.49472244	-0.85365240	H	-2.41572625	1.96784015	1.70394519
C	0.13079220	5.54498095	-0.24205734	H	-3.28601657	5.22414112	-1.02518443
C	-3.89121208	1.64554496	0.20399789	H	-4.91048787	3.73431054	-2.15670265
C	-2.95689534	2.41388762	0.87224427	H	-2.34311803	-1.18039278	-4.03963572
C	-2.69831567	3.71983065	0.43603344	H	-3.47714250	0.94286316	-3.43598536
C	-3.42105428	4.21390602	-0.65593266	H	-6.10023462	-1.35704084	-0.87100069
C	-4.33820846	3.40023473	-1.30084611	H	-4.86264469	-3.39554872	-1.57817496
N	-4.55216075	2.13320726	-0.87455850	H	2.10008993	-5.61658784	0.07439135
C	-3.17322867	-1.15607444	-3.34470450	H	1.40126917	-4.58722261	1.32765462
C	-3.81705108	0.01424423	-2.99161586	H	6.65767904	-1.10475701	-1.23763587
C	-4.86704780	-0.02280719	-2.06329554	H	6.61293059	-0.73247165	0.48999801
C	-5.27654351	-1.26569730	-1.57016858	H	3.41058572	4.51321421	-2.46478142
C	-4.60249868	-2.41358774	-1.95322231	H	4.14845036	5.14859097	-0.99962863
N	-3.55465752	-2.34209654	-2.80692144	H	-1.53550870	4.23863916	2.18163263
C	1.76302808	-4.60503487	0.29881853	H	-1.96446933	5.61938417	1.16583872
C	6.01899496	-0.75591263	-0.42462775	H	-5.93599737	1.82009882	-2.42202038
C	3.52542563	4.34174190	-1.39202325	H	-6.34707035	1.03784278	-0.88961285
C	-1.66375752	4.57193585	1.15119327	H	-2.44459140	-3.48663960	-4.16056550
C	-5.53197398	1.25302211	-1.58225200	H	-3.46753577	-4.41587160	-3.07218745

C	-2.78259435	-3.56622090	-3.12501124	H	-2.42501405	-2.46490756	7.04597877
C	-2.21033013	-0.66180984	5.87400404	H	-1.12673516	-3.86328336	5.44547678
C	-2.01365025	-2.02129123	6.14266368	H	-1.82835279	0.96057724	4.49895925
C	-1.28391082	-2.80657221	5.24295483	H	-2.77596907	-0.04597940	6.56907937
C	-0.75474807	-2.23367033	4.08310263	H	-0.18599642	-2.83778662	3.38326112

6. References

[1] Z. Liu, Q. Lin, Q. Huang, H. Liu, C. Bao, W. Zhang, X. Zhong, L. Zhu, *Chem. Commun.* **2011**, *47*, 1482-1484.

[2] Agilent Technologies, *CrysAlisPro*, Version 1.171.35.21b.

[3] L. J. Farrugia, *J. Appl. Cryst.* **2012**, 45, 849-854.

[4] G. M. Sheldrick, *Acta Cryst*. *Sect. A* **2008**, 64, 112-122.

[5] E. F. Pettersen, T. D. Goddard, C. C. Huang, G. S. Couch, D. M. Greenblatt, E. C. Meng, T. E. Ferrin, *J Comput Chem*. **2004**, 25(13), 1605-12.

[6] Frisch MJ et al. (2009) Gaussian 09, Revision B.01. Gaussian, Inc., Wallingford CT.

[7] Dennington R, Keith T, Millam J (2009) GaussView, Version 5, Semichem Inc., Shawnee Mission, KS.