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Bonding and Uneven Charge Distribution in Infinite Pyrene π-Stacks

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I. Materials and Methods

All manipulations were carried out using break-and-seal and glove-box techniques under an atmosphere of argon.[1] Fluorobenzene (99%, Sigma Aldrich) was dried over molecular sieves and degassed three times prior to use. Hexanes (99%, Sigma Aldrich) was dried over Na/benzophenone and distilled prior to use. Pyrene (98 %, Sigma Aldrich) was sublimed at 100 °C twice. $GaCl_3$ (99.9 %, Sigma Aldrich) was sublimed at 50 °C prior to use.

Synthesis of $(Py)_2^+(Ga_2Cl_7)^-$

Fluorobenzene (1.5 mL) was added to a custom-built glass system containing pyrene (5.0 mg, 0.025 mmol) and $GaCl_3$ (8.7 mg, 0.050 mmol). The mixture was allowed to stir under argon at 25 °C for three hours in a closed system. The initial pale yellow (neutral ligand) color of the suspension changed to a golden-brown after stirring for 5 minutes and remained the same color until the reaction was stopped. The mixture was filtered through a sintered glass funnel to afford a golden-brown filtrate. The ampule was sealed and placed at –5 °C. Brown needle-shaped crystals were present in solution after 2 weeks (5.4 mg, 55%).

Note: These crystals are very air- and moisture sensitive, which prevented obtaining elemental analysis and spectroscopic data.

II. Crystal Structure Solution and Refinement

Data collection of $(Py)_2^+(Ga_2Cl_7)^-$ was performed on a Bruker D8 VENTURE X-ray diffractometer equipped with a PHOTON 100 CMOS shutterless mode detector and an INCOATEC IμS micro-focus Cu-target X-ray tube (λ = 1.54178 Å) at T = 100(2) K. Data reduction and integration were performed with the Bruker software package SAINT (version 8.38A).[2] Data were corrected for absorption effects using the empirical methods as implemented in SADABS (version 2016/2).[3] The structure was solved by SHELXT[4] and refined by full-matrix least-squares procedures using the Bruker SHELXTL (version 2018/3)[5] software package through the OLEX2 graphical interface.[6] All non-hydrogen atoms were refined anisotropically. The H-atoms were also included at calculated positions and refined as riders, with U_{iso}(H) = 1.2 U_{eq}(C). In $(Py)_2^+(Ga_2Cl_7)^-$, the $(Ga_2Cl_7)^-$ anions were found to be disordered and were modeled with two orientations with their relative occupancies refined. The geometries of the disordered parts were restrained to be similar. The anisotropic displacement parameters in the direction of the bonds were restrained to be equal with a standard uncertainty of 0.004 Å^2. They were also restrained to have the same U_{ij} components, with a standard uncertainty of 0.04 Å^2. Further crystal and data collection details are listed in Table S1.

During analysis of the structure it was found that the U_{eq} values of seven chlorine atoms are not comparable to each other. Specifically, the maximum U_{eq} values are almost twice of the minimum U_{eq} values. Notably, one chlorine atom bridging two gallium centers of the $(Ga_2Cl_7)^-$ unit was especially concerning, as its U_{eq} was found to be much larger than those of terminal Cl-atoms and of two Ga-atoms it connects. Because of this, the anionic unit was modeled as a 2-orientation disorder. After disorder modeling, the R-factors were improved (R1 = 5.01% and wR2 = 15.63% *vs*. R1 = 5.16% and wR2 = 16.20% before disorder modeling).

Moreover, one of the important topics that was discussed in this paper is hydrogen bonding between pyrene's hydrogens and chlorine atoms of the $(Ga_2Cl_7)^-$ unit. The disordered model is believed to present a more accurate model of $(Ga_2Cl_7)^-$ unit in respect to positions of chlorine atoms, thus providing better description of H-Cl hydrogen bonding. Therefore, the disordered model has been chosen over the single component model in this work.

Table S1. Crystallographic data of $(Py)_2^+(Ga_2Cl_7)^-$.

Compound	$(Py)_2^+(Ga_2Cl_7)^-$
Empirical formula	$C_{32}H_{20}Cl_7Ga_2$
M_r	792.07
Temperature (K)	100(2)
Wavelength (Å)	1.54178
Crystal system	Triclinic
Space group	*P*-1
a (Å)	6.7753(3)
b (Å)	13.9706(5)
c (Å)	17.4570(6)
α (°)	79.336(1)
β (°)	82.547(1)
γ (°)	76.051(1)
V (Å^3)	1569.68(10)
Z	2
F(000)	786
μ (mm^{-1})	7.766
ρ_{calcd} (g·cm^{-3})	1.676
Crystal size (mm)	0.40×0.17×0.02
Transmission factors (min/max)	0.662/0.754
Reflections collected	13031
Independent reflections	6223 [R_{int} = 0.0565]
θ range (°) for data collection	3.30-74.64
Data/restraints/parameters	6223/323/435
*R*1,[a] *wR*2[b] ($I > 2\sigma(I)$)	0.0502, 0.1521
*R*1,[a] *wR*2[b] (all data)	0.0544, 0.1555
Quality-of-fit[c]	1.070
Largest diff. peak and hole (ē·Å^{-3})	1.054 and -0.604

[a]$R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]$wR2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]$.
[c]Quality-of-fit = $[\Sigma[w(F_o^2-F_c^2)^2]/(N_{obs}-N_{params})]^{½}$, based on all data.

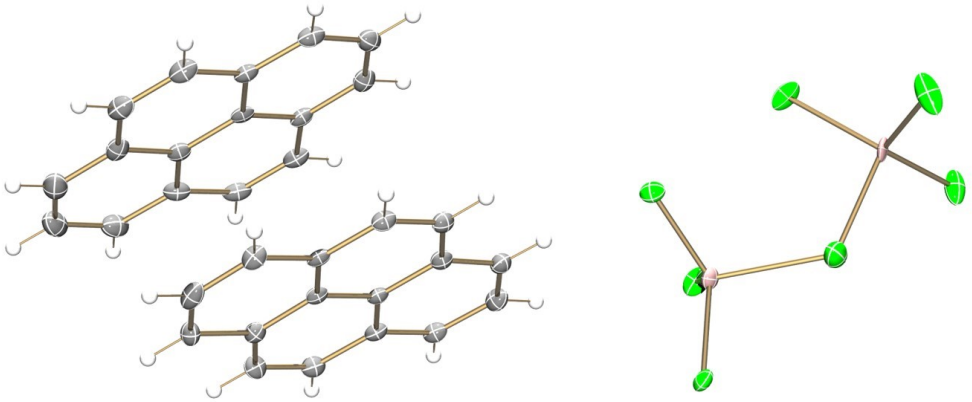


Figure S1. ORTEP drawing of the asymmetric unit of $(Py)_2^+(Ga_2Cl_7)^-$ at the 40% level. The color scheme used: C grey, Cl green, Ga pink, H white.

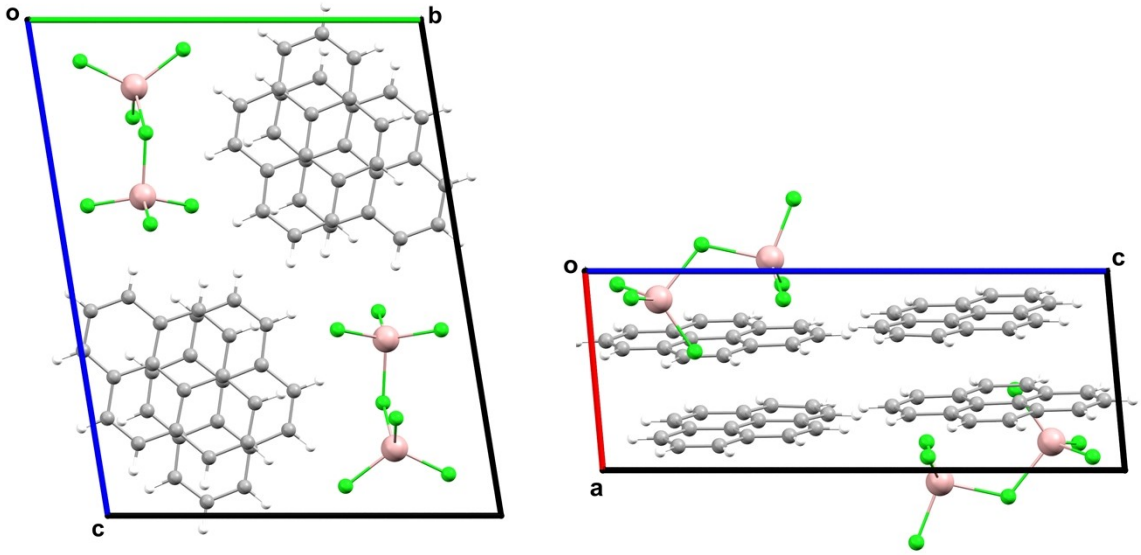
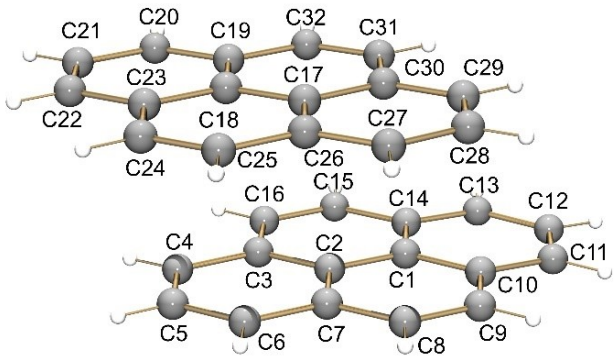


Figure S2. Solid-state packing of $(Py)_2^+(Ga_2Cl_7)^-$ in the unit cell, ball-and-stick models.

Table S2. Selected C–C bond distances (Å) in $(Py)_2^+(Ga_2Cl_7)^-$ along with a labeling scheme.



Bond	Distance	Bond	Distance
C1–C2	1.419(6)	C17–C18	1.420(6)
C1–C10	1.426(6)	C17–C26	1.428(6)
C1–C14	1.416(6)	C17–C30	1.423(6)
C2–C3	1.413(6)	C18–C19	1.421(6)
C2–C7	1.423(6)	C18–C23	1.428(6)
C3–C4	1.474(6)	C19–C20	1.404(7)
C3–C16	1.404(6)	C19–C32	1.434(7)
C4–C5	1.429(7)	C20–C21	1.391(8)
C5–C6	1.381(7)	C21–C22	1.395(8)
C6–C7	1.451(6)	C22–C23	1.404(7)
C7–C8	1.413(6)	C23–C24	1.441(7)
C8–C9	1.363(7)	C24–C25	1.361(8)
C9–C10	1.426(6)	C25–C26	1.432(6)
C10–C11	1.410(6)	C26–C27	1.397(7)
C11–C12	1.388(7)	C27–C28	1.391(7)
C12–C13	1.396(7)	C28–C29	1.383(7)
C13–C14	1.402(6)	C29–C30	1.406(7)
C14–C15	1.429(7)	C30–C31	1.437(6)
C15–C16	1.368(7)	C31–C32	1.353(7)

Table S3. Distance from the weighted least-squares plane (Å) in $(Py)_2^+(Ga_2Cl_7)^-$.

Position	α	Position	β
C1	0.003	C1	–0.002
C2	–0.009	C2	–0.004
C3	0.009	C7	0.007
C14	0.003	C8	–0.005
C15	–0.003	C9	–0.001
C16	–0.004	C10	0.004
	0.999x – 0.027y –0.047z + 7.961 = 0 (RMSD/A: 0.006)		0.998x – 0.030y – 0.054z + 7.895 = 0 (RMSD/A: 0.004)
Position	γ	Position	ε
C1	0.010	C2	–0.004
C10	–0.009	C3	0.000
C11	0.002	C4	0.001
C12	0.006	C5	0.001
C13	–0.006	C6	–0.004
C14	–0.002	C7	0.006
	0.996x – 0.046y – 0.074z + 7.568 = 0 (RMSD/A: 0.007)		0.999x – 0.022y –0.036z + 8.067 = 0 (RMSD/A: 0.003)
Position	α	Position	β
C17	0.001	C17	–0.001
C18	0.002	C18	0.004
C19	–0.002	C23	–0.005
C30	–0.002	C24	0.002
C31	0.001	C25	0.002
C32	0.001	C26	–0.003
	1.000x – 0.014y – 0.027z + 4.806 = 0 (RMSD/A: 0.002)		0.999x – 0.014y – 0.030z + 4.797 = 0 (RMSD/A: 0.003)
Position	α	Position	β
C17	0.002	C18	0.001
C26	–0.003	C19	–0.001
C27	0.003	C20	0.001
C28	0.000	C21	–0.002
C29	–0.002	C22	0.002
C30	0.001	C23	–0.001
	0.999x – 0.011y – 0.030z + 4.822 = 0 (RMSD/A: 0.002)		0.999x – 0.016y – 0.036z + 4.762 = 0 (RMSD/A: 0.001)

III. Computational Details

1. Mulliken charges in $(Py)_2(Ga_2Cl_7)$ by energy band computations

Table S4. Mulliken charges on each atom in the unit cell in the $(Py)_2(Ga_2Cl_7)$ crystal obtained by using various methods and basis sets. Columns A and B denote pyrene A and pyrene B, respectively, as illustrated in Figure 4. [a]

Method[b]	**UHF**		**UPBE[c]**		**UM05-2X**	
Basis Set	STO-3G		3-21G		3-21G	
Pyrene	A	B	A	B	A	B
	0.034	0.047	0.080	0.066	0.041	0.078
	0.002	0.054	0.025	0.050	-0.004	0.111
	-0.005	0.054	-0.002	0.014	-0.043	-0.012
	-0.018	0.064	0.031	0.052	-0.002	0.095
	-0.021	0.126	0.042	0.094	0.034	0.145
	-0.001	0.055	0.000	-0.017	-0.034	-0.049
	-0.007	0.120	0.064	0.104	0.045	0.150
	0.024	0.050	0.058	0.057	0.061	0.064
	-0.011	0.065	-0.003	0.005	0.017	0.052
	0.005	0.033	-0.001	-0.007	-0.043	-0.038
	-0.019	0.069	-0.009	0.023	0.026	0.064
	0.009	0.078	0.028	0.055	0.040	0.096
	0.008	0.066	0.005	-0.002	-0.037	-0.036
	0.029	0.100	0.047	0.116	0.046	0.192
	-0.010	-0.005	-0.003	-0.003	-0.034	-0.003
	-0.013	-0.005	-0.006	0.008	-0.035	0.001
Q_A or Q_B	0.006	0.971	0.356	0.615	0.078	0.910

$\Delta Q=Q_B-Q_A$	0.965		0.259		0.832	
$Q_{tot}= Q_A+Q_B$	0.977		0.971		0.988	

Method	**UM05-2X**		**UM05-2X**		**UM05-2X**		**UM05-2X**	
Basis Set	6-31G		6-31G(d)		6-311G		6-311G(d)	
Pyrene	A	B	A	B	A	B	A	B
	0.061	0.051	0.054	0.046	0.084	0.036	0.050	0.017
	-0.062	0.110	-0.091	0.075	-0.033	0.198	0.008	0.085
	0.048	0.048	0.087	0.080	0.031	0.005	-0.023	0.020
	-0.005	0.054	-0.042	0.027	0.074	0.100	0.020	0.036
	0.011	0.124	-0.022	0.092	0.075	0.232	0.051	0.143
	0.045	0.014	0.080	0.055	-0.002	-0.078	-0.012	-0.095
	0.017	0.125	-0.023	0.103	0.079	0.189	0.019	0.206
	0.058	0.066	0.077	0.053	0.062	0.058	0.044	0.013
	-0.018	0.019	-0.062	-0.007	0.030	0.086	-0.024	0.151
	0.042	0.055	0.082	0.104	0.002	0.058	0.002	-0.019
	-0.014	0.035	-0.041	-0.006	0.053	0.072	0.014	0.094
	0.042	0.075	-0.003	0.051	0.135	0.178	0.038	0.166
	0.042	-0.009	0.082	0.037	0.004	-0.143	-0.032	-0.057
	-0.020	0.184	-0.044	0.149	0.019	0.251	0.062	0.175
	-0.074	-0.011	-0.029	0.042	-0.241	-0.099	-0.081	-0.073
	-0.096	-0.047	-0.040	-0.014	-0.295	-0.233	-0.071	0.028
Q_A^d, Q_B^d	0.077	0.893	0.065	0.887	0.077	0.910	0.065	0.890

$\Delta Q=Q_B-Q_A$	0.816		0.822		0.833		0.825	
$Q_{tot}=Q_A+Q_B$	0.970		0.952		0.987		0.955	

[a]Crystal (PBC) computations with only half of the unit cell included.
[b]Number of k-points were 1324 for all cases except for PBE, where it was 28.
[c]UPBEPBE keyword in the Gaussian 16 package.
[d]Total charge on pyrene A or pyrene B.

Table S5. Mulliken charges on each atom in the unit cell in the $(Py)_2(Ga_2Cl_7)$ crystal. Columns A and B denote pyrene A and pyrene B, respectively. The charge row is the sum of the charges on each atom in the pyrene molecule. [a,b]

Spin	**Singlet**				**Triplet**			
Method[c]	UHF				UHF			
Basis Set	STO-3G				STO-3G			
Pyrene	A	B	C	D	A	B	C	D
	0.002	0.042	0.002	0.042	-0.006	0.052	-0.006	0.052
	0.007	0.121	0.007	0.100	-0.016	0.082	-0.016	0.070
	0.010	0.100	0.010	0.121	0.000	0.070	0.000	0.082
	-0.008	0.033	-0.008	0.033	-0.012	0.063	-0.012	0.063
	0.005	0.034	0.005	0.034	0.001	-0.007	0.001	0.064
	0.014	0.002	0.014	0.002	0.009	0.064	0.009	-0.007
	0.008	0.045	0.022	0.054	-0.010	0.064	0.018	0.070
	0.022	0.054	0.016	0.045	0.018	0.070	-0.010	0.064
	0.016	0.074	0.008	0.070	0.013	0.095	0.013	0.091
	0.003	0.070	0.003	0.074	-0.007	0.091	-0.007	0.095
	0.011	0.020	0.011	0.020	0.012	0.048	0.012	0.048
	0.007	0.019	0.007	0.019	-0.011	0.046	0.000	0.046

	-0.010	0.013	-0.010	0.013	0.000	0.005	-0.011	0.005
	0.016	0.090	0.016	0.090	0.011	0.085	0.011	0.085
	0.006	0.102	0.006	0.102	-0.008	0.094	-0.008	0.094
	0.005	0.038	0.005	0.038	0.004	0.048	0.004	0.048
Q_A[d], Q_B[d]	0.111	0.857	0.111	0.857	-0.002	0.971	-0.002	0.971
$\Delta Q=Q_B-Q_A$	0.746	-	0.746	-	0.973	-	0.973	-
$Q_{tot}= Q_A+ Q_B$	0.968	-	0.968	-	0.969	-	0.969	-

[a]Crystal (PBC) computations with the full unit cell of the crystal structure of $(Py)_2(Ga_2Cl_7)$.
[b]$E_{triplet} - E_{singlet}$ = -100.6 kcal/mol
[c]Number of k-points were 1324.
[d]Total charge on pyrene A or pyrene B.

Tables S4 and S5 demonstrate the stability of charge distribution among the two types of pyrene molecules in the $(Py)_2(Ga_2Cl_7)$ crystal. The computations were done without geometry optimization. This stability is especially remarkable given that in Table S4 only one half of the unit cell is filled, adding further support for the idea that the main intermolecular interactions are restricted in this case to pyrene-pyrene interactions within the stacks plus the overall electrostatic interactions induced by the charge transfer between the anions and cations.

2. Correlation of bond length alternation vs. charge in pyrene molecules and their dimers

Figure S3 represents the correlation of bond length alternation (BLA) vs. charge in pyrene molecules and their dimers at their optimized geometries with UM05-2X/6-311G(d). This correlation confirms the dominant role of the HOMO and LUMO orbital patters in determining the relaxation due to both positive and negative charge on the pyrene and its dimers. The negative charge arm of the correlation plays no role in the analysis of the structures of the pyrene salts which in all presented cases are positively charged.

The red line connects points obtained for the monomer with charges of Q= -2, -1, 0, 1, and 2 based on the fully optimized geometries of each charge state. The blue line connects points with charges per pyrene of Q= -1, -1/2, 0, 1/2, and 1 based on the fully optimized geometries of each charge state of the dimer. (All quoted charges are in units of |e|.) The two types of computations yield virtually identical BLA values indicating that this correlation displays a genuine trend because it is not much affected by the intermolecular interactions in the dimer be it of vdW type or pancake bonding. The V shape of the relationship is the consequence of the fact that the HOMO is bonding for r_2 and r_5 and antibonding for r_4, while the LUMO is antibonding for r_2 and r_5 and bonding for r_4.

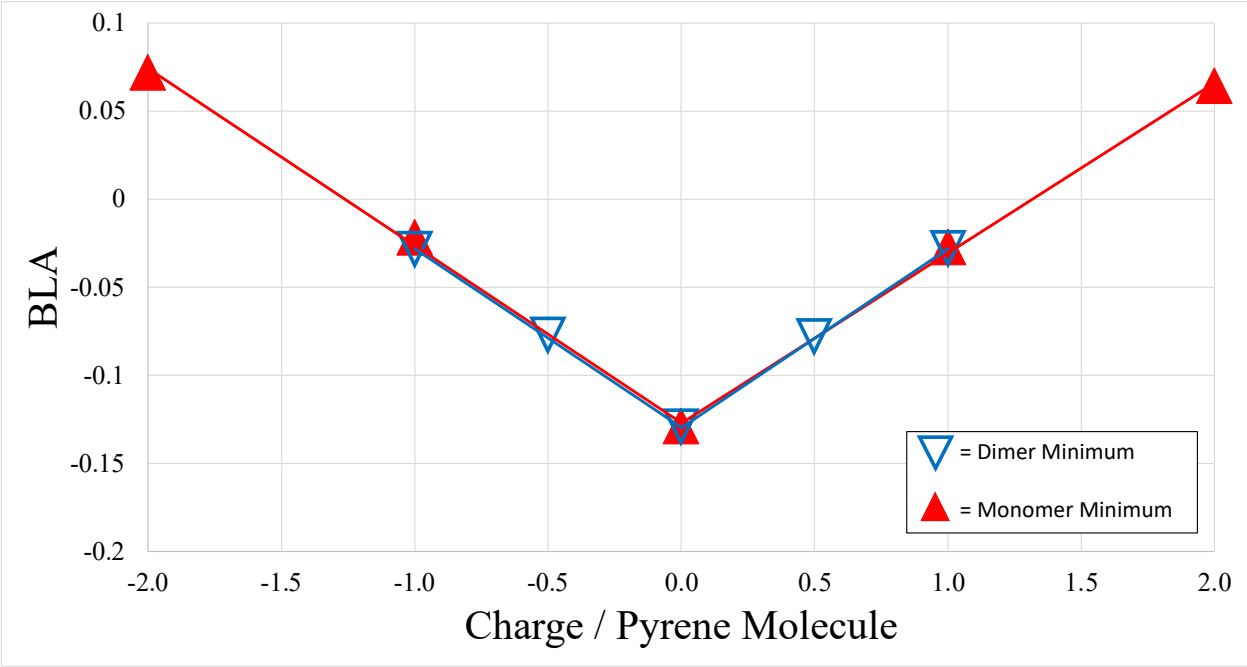


Figure S3. Pyrene bond length alternation (BLA) values, as defined by eq. (2) as a function of charge per pyrene. BLA values were obtained from pyrene monomer (red) and dimer (blue) optimization calculations.

Figure S4 provides two examples of the BLA computation. The two BLA values obtained for the two neutral pyrene crystals differ by ~10%, a representative value for the accuracy of BLA based charge estimates used in this work.

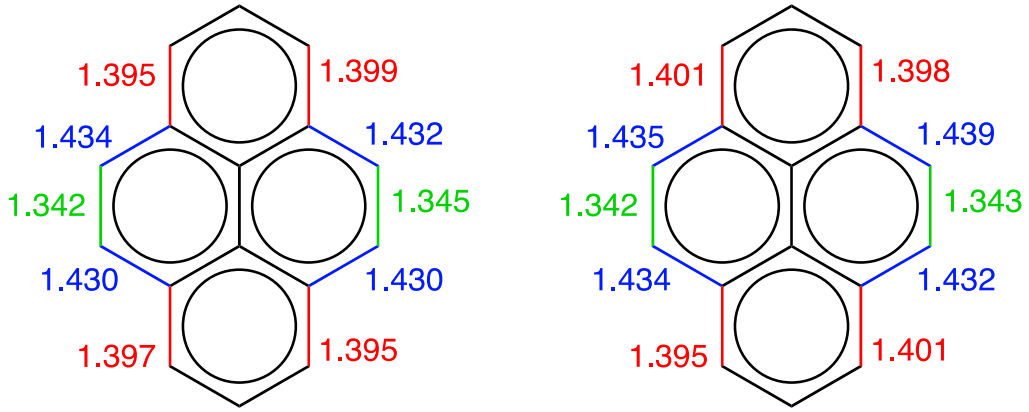


Figure S4. Left: distances in GUQPOZ (left, BLA= −0.118), and PYRENE10 (right, BLA = −0.129 Å). BLA was computed by eq. (2).

Further consistency of the obtained by placing the computationally obtained charge vs. BLA values for the six minima of the $(Py)_2^+$ dimers on the correlation represented in Figure S3, Figure 8 and equ (3a). These data also fit the trendline extremely well as illustrated in Figure S5.

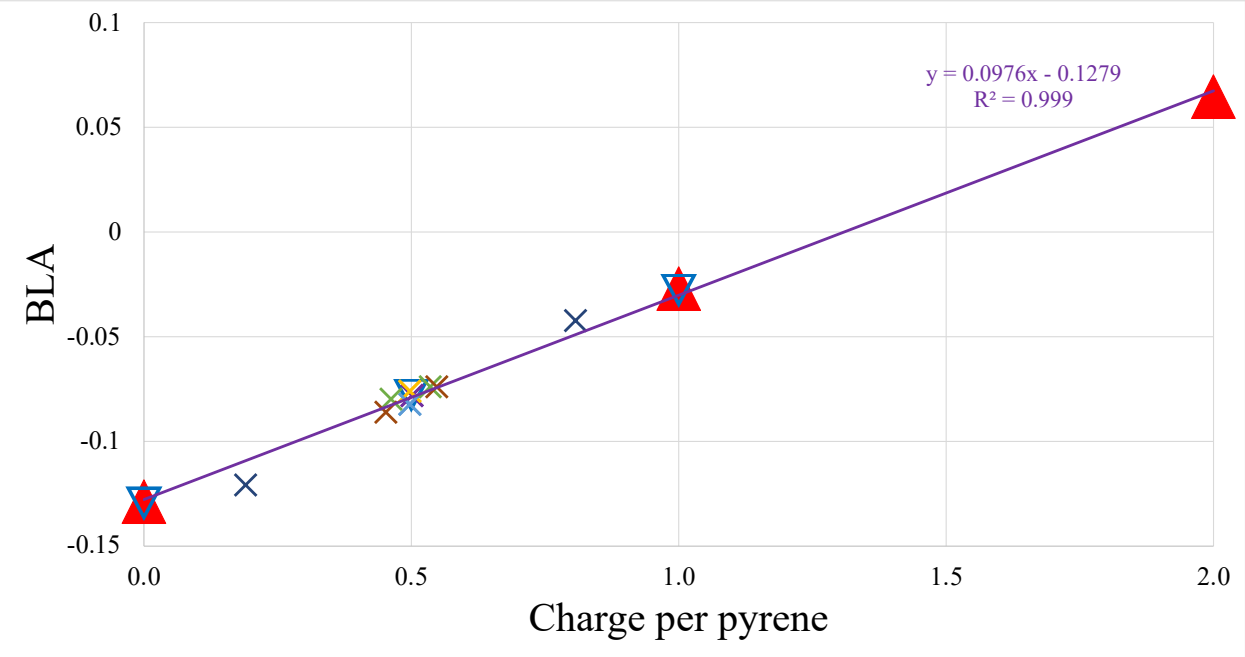


Figure S5. Bond length alternation value plotted against charge per pyrene molecule. Red triangles and blue inverted triangles refer to optimized neutral and charged pyrene monomers and dimers respectively. X's correspond pairwise by color to minima 1-6 of $(Py)_2^+$, with charges on each pyrene obtained from Mulliken population analysis. Minima 1-6 refer to dimer $(Py)_2^+$ minima as listed in Table 1 in the main text. All calculations carried out with UM05-2X/6-311G(d)

3. Analysis of the bond length alternation vs. charge transfer on pyrene-TCNQ complexes

Further validation is presented in conjunction with the data in Table S6. Here we have collected data on the much-studied co-crystals of TCNQ and its derivatives with pyrene in Table S6. Three structures were captured from the CSD with small R-factors. Four types of molecular charge estimates are provided: three for TCNQ, and one from our charge-BLA correlation for pyrene represented by equ. (3) in the main text.

Some of the published values appear to be significantly overestimated. This is especially the case for the disordered two structures PYRTCQ and MIDDIP-UNUPOL which we consider insufficiently accurate. The same is the case for the structure of BITBUD. These are not included in the table.

Ideally, based on unit cell neutrality, the charges on pyrene and TCNQ should add up to zero. This is not the case for any of the computed charges. Some of the estimated charges from the literature on TCNQ are positive, certainly an incorrect result.

The following conclusions emerge: It appears that the charges on both pyrene and TCNQ in the co-crystals where reliable bond length data are available should be less than ± 0.15 e, probably very close to zero. The above range provides an estimate for the error inherent in assessing the value of molecular charge based on equ (3) on pyrenes in their co-crystals with various electron acceptors.

Table S6. Charge transfer estimates for pyrene-TCNQ complexes.

CSD Refcode	PYRTCQ02[7]	PYRTCQ03[8]	PYRTCQ05[9]
R factor from CSD	3.37%	3.44%	3.76%
Z' from CSD	0.5	0.5	0.5
Pyrene:TCNQ ratio	1:1	1:1	1:1
TCNQ charge estimated by publication	-0.13 (HOSE)	-0.02 (C/(B+D)) | -0.045 (FTIR)	-
Charge on TCNQ[b]	-0.110	-0.130	-0.087
Charge on TCNQ[c]	0.016(sic!)	-0.007	-0.007
Charge on pyrene from equ (3)*	0[a]	0.146	0[a]

*This work.

[a]BLA=-0.130 Å for PYRTCQ02 and -0.133 Å for PYRTCQ05, Q=0 is assigned as per comment above equ. (3) in the main text.

[b]Charge estimated by equ (1) from Sanada *et al.*[10]: $q = -41.667\left[\frac{C}{B+D}\right] + 19.818$. B, C, and D refer to C-C bond distances in the TCNQ molecule.

[c]Charge estimated by equ (2) from Yang *et al.*[2] where $\alpha_x, \alpha_0, \alpha_{-1}$ represent the value for (C/B+D) on TCNQ in complex, at neutral charge, and at a -1 charge respectively:

$q = (\alpha_x - \alpha_0)/(\alpha_{-1} - \alpha_0)$

Note that the charge on TCNQ should be negative. All three structures indicate neutral or nearly neutral TCNQ and pyrene molecules in the crystal within the error of 0.15 |e| obtained by all of the methods listed.

4. Analysis of the bond length alternation vs. charge transfer correlation in the pyrene iodide salt $(Py)_{10}(I_3^-)_4(I_2)_{10}$, (CSD refcode BEKQUE[11])

Pyrene charge transfer salts are rare. One with a published XRD crystal structure is that of $(Py)_{10}(I_3^-)_4(I_2)_{10}$ (CSD refcode: BEKQUE).

The 10 unique pyrenes in BEKQUE are distributed between two distinct columns, hereafter termed column A and column B. Column A has the packing pattern, AAAB, alternating between 9 and 5 short C…C contacts. Column B has the same packing pattern, AAAB, alternating between 7 and 3 short C…C contacts. In each column there are 4 distinct pyrene molecules, with the remaining 2 pyrene molecules, 5a and 5b oriented parallel to the columns. Figure 10 contains information on the translations and rotations between the various adjacent molecules (dimers) in the crystal structure

A key difference between the columns is the distribution of short contacts. Column A contains many short H…I_2 and H…I_3^- contacts and short contacts with one of the pyrene molecules parallel to the column. Column B, however, has no such contacts, and is comparatively isolated.

A periodic boundary conditions calculation carried out at the UPBEPBE/STO-3G level of theory indicates a less polarized distribution of charges across all pyrene molecules in both columns (compared with BLA based charges, with near zero charge on the parallel pyrene molecules as indicated by the charges listed in Table S7. Given the size of the unit cell, calculations at higher levels of theory were not possible.

Table S7. Bond length alternation parameters and charges on unique pyrenes in BEKQUE. Periodic boundary conditions calculation was carried out at the UPBEPBE/STO-3G level of theory. BLA values applied to equation 3a adjusted such that the total charge is +4 across the 8 pyrenes in the columns.

Column A Pyrenes	**PBC Charge**	**BLA**	**BLA Charge**	**Column B Pyrenes**	**PBC Charge**	**BLA**	**BLA Charge**
1a	0.421	-0.100	0.434	**1b**	0.338	-0.124	0.186
2a	0.440	-0.093	0.508	**2b**	0.421	-0.078	0.661
3a†	0.453	-0.111	0.323	**3b**†	0.518	-0.066	0.781
4a	0.440	-0.093	0.508	**4b**	0.421	-0.084	0.598
5a	0.002	-0.143	0*	**5b**	0.018	-0.166	0*
Sum	1.756		1.774		1.717		2.226

* BLA value is outside the range for equ (3); charge is assumed to be zero.
† Pyrene 3a is rotated by approximately 60º compared to the adjacent pyrenes.

Orientation of the dimers excised from BEKQUE align closely with Minimum 1 and 2 in the potential energy surface of $(Py)_2^+$ dimers shown in Figure 10, both of which display sufficient orbital overlap for charge delocalization as shown in Figure S8. Contrasting BEKQUE with the $(Py)_2(Ga_2Cl_7)$ crystal, a potential cause for preferential packing in an orientation that prevents delocalization may be the result of differences between the shape of the counterions. I_2 and I_3^- can be more easily interspaced between the columns given their one-dimensional structure, while spatial requirements of the $Ga_2Cl_7^-$ ion are more stringent.

The uneven BLA values in the $(Py)_{10}(I_3^-)_4(I_2)_{10}$ crystal implies an uneven distribution of the charges on the 10 different pyrenes in the unit cell as illustrated in Figure S6. While it is noteworthy that the two different columns appear to have a different total charge (Q[A], and Q[B] in Figure S7), most important is the consistency of the total charge of +4 |e| on all pyrenes perfectly compensating the formal +4 |e| charge on the iodide chains. This consistency lends further support to the BLA vs. charge relationship of equ (3).

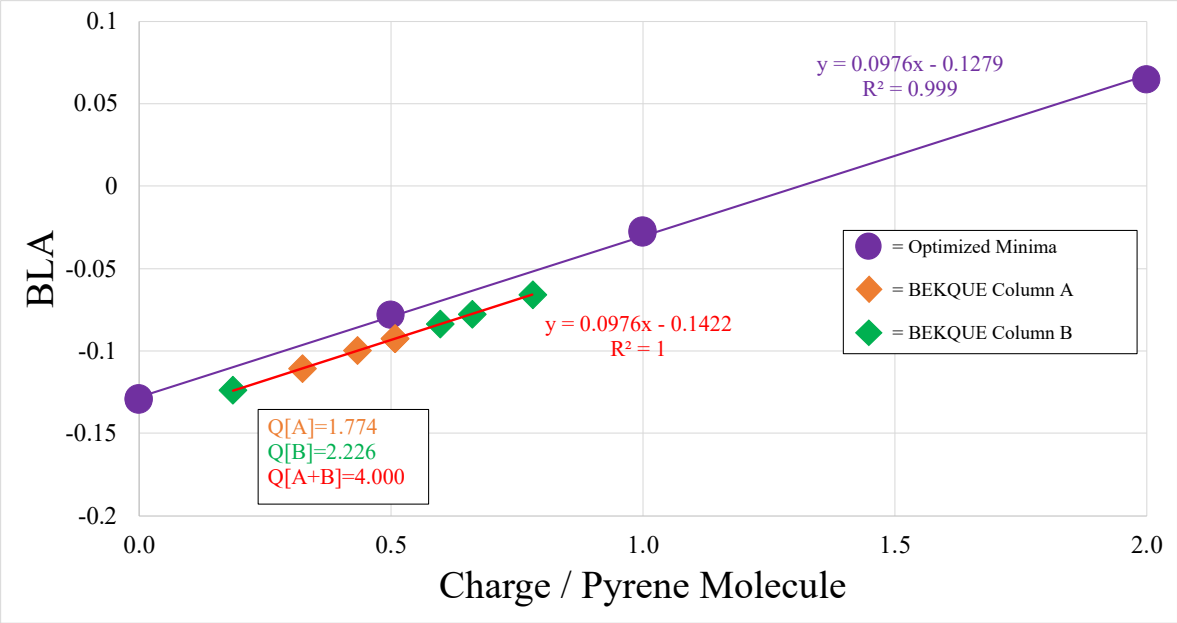


Figure S6. BLA vs. charge for pyrenes. "Minima" refer to the computed values for variously charged monomers and dimers, also shown in Figure 8, together with the trendline of equ (3a). Orange and green diamonds refer to individual pyrenes where the BLA is computed from the crystal structure, and the charge is obtained from the BLA=0.0976 Q-0.1422 relationship, also shown in the graph in orange.

5. Charge localization in the dimer vs. external point charges

The uneven distribution of the position of chlorides in the crystal structure may suggest that the negative charges that they represent are at the origin or enhance the charge localization of the positive charges on every other pyrene.

The anions were represented in these fixed geometry charge distribution computations by a selection of four Cl atom sites closest to the pyrenes in three $(Py)_2^+$ configuration: $(Py)_2$[3], $(Py)_2$[4], where significant charge transfer occurs, and the third at the geometry of Minimum 1 where no charge transfer occurs. Charge transfer values between the two pyrenes in the dimer were computed as a function of the point charge values, q, in the locations of the nearest chloride atoms and are summarized in Figure S7. The charges even at the large values above q=-0.5 |e| indicate no significant change in the ΔQ. This computational modeling indicates that this effect provides at most a small modification of the charge localization and cannot be considered as the main source of charge localization in $(Py)_2(Ga_2Cl_7)$.

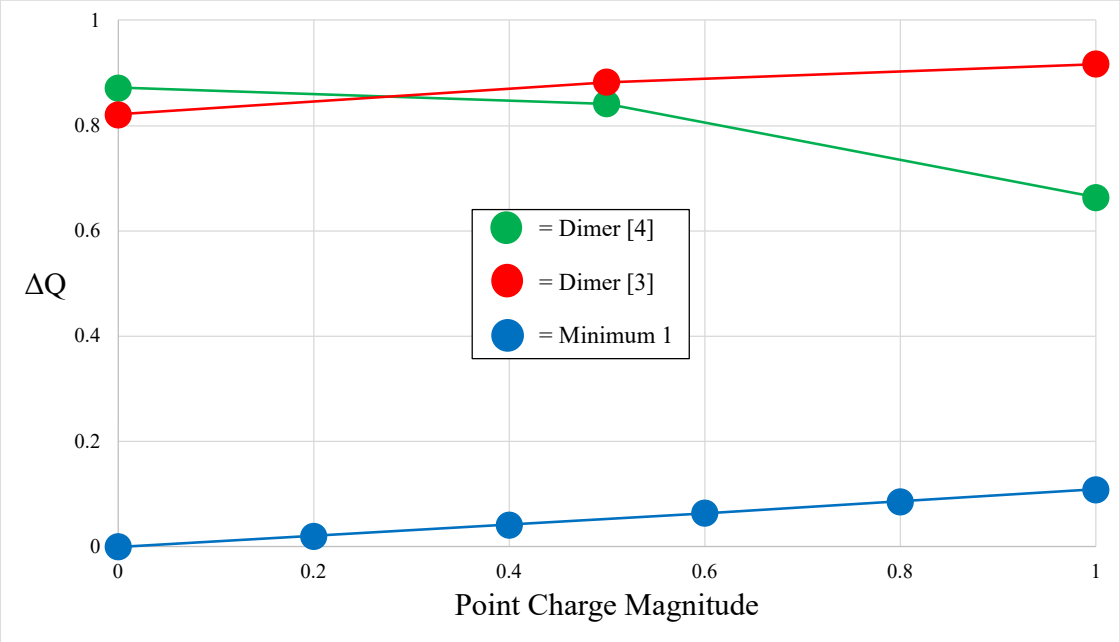


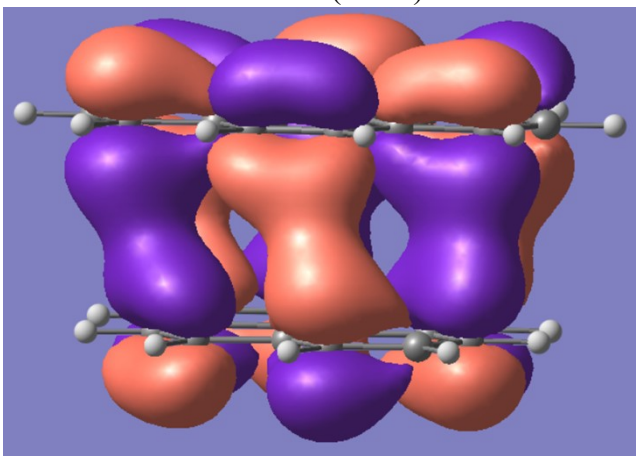
Figure S7. Charge transfer, ΔQ, plotted against point charge magnitude, q. Point charges simulating the influence of the four Cl…H contacts shorter than van der Waals radii were added to dimers $(Py)_2$[4] and $(Py)_2$[3] and Minimum 1. Mulliken population analysis was then carried out with UM05-2X/6-311G(d) with various point charge values.

6. Orbitals of dimers corresponding to the six local minima of the $(Py)_2^+$ dimer

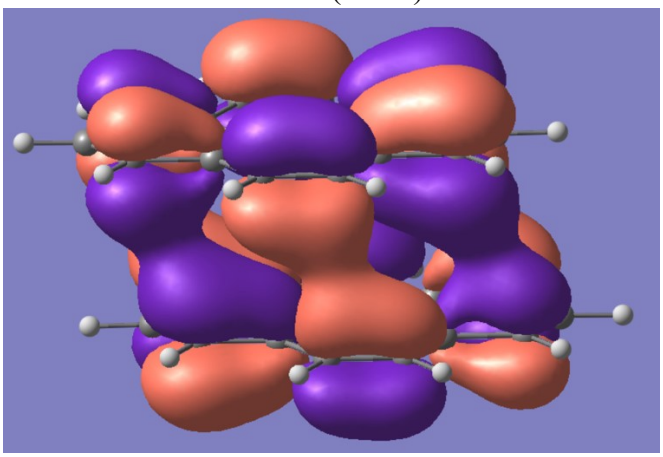
When α and β orbital pictures nearly indistinguishable only one is shown. Their orbital energies are slightly different. The total number of electrons is 211.

Only relevant orbitals are sown. The isovalue is 0.02. HOMO of the neutral dimer is orbital #106. Figure S8 represents the relevant orbitals for the six computed minima of the $(Py)_2^+$ dimer. Figure S9 shows the relevant orbitals for the two types of dimers excised from the $(Py)_2(Ga_2Cl_7)$ crystal structure without further optimization. The level of theory is UM052X/6-311G(d).

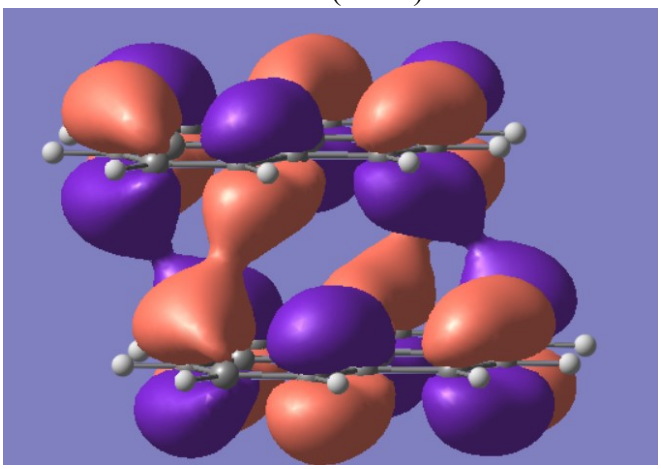
Minimum 1 α-HOMO-1 (# 105)



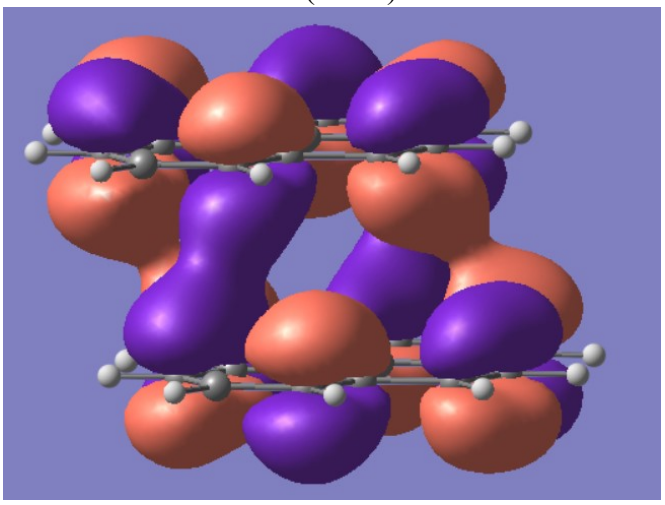
Minimum 2 α-HOMO-1 (# 105)



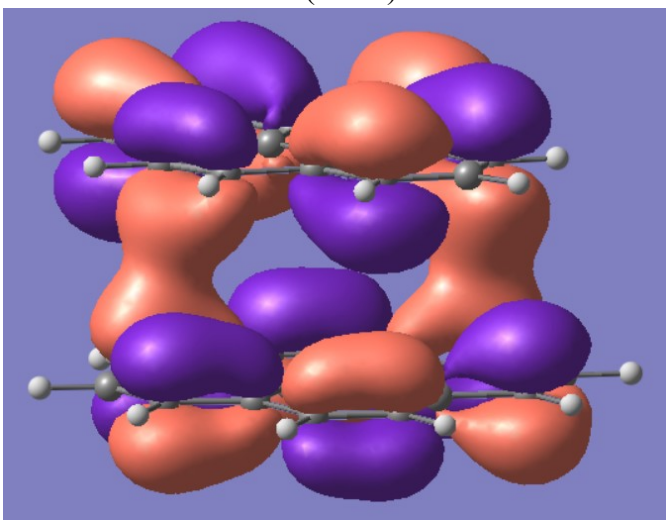
Minimum 3 α-HOMO-1 (# 105)



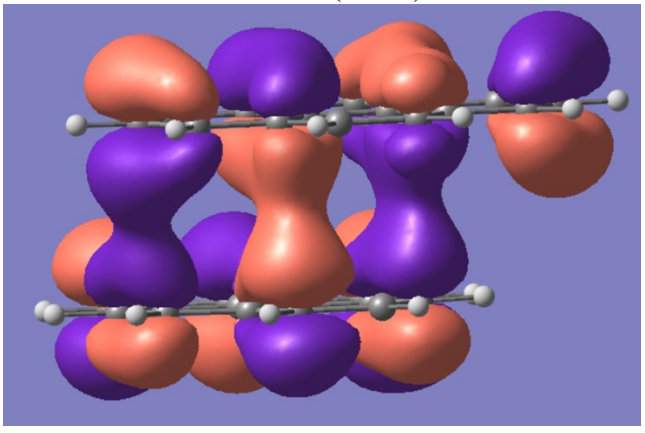
Minimum 3 β-HOMO (# 105)



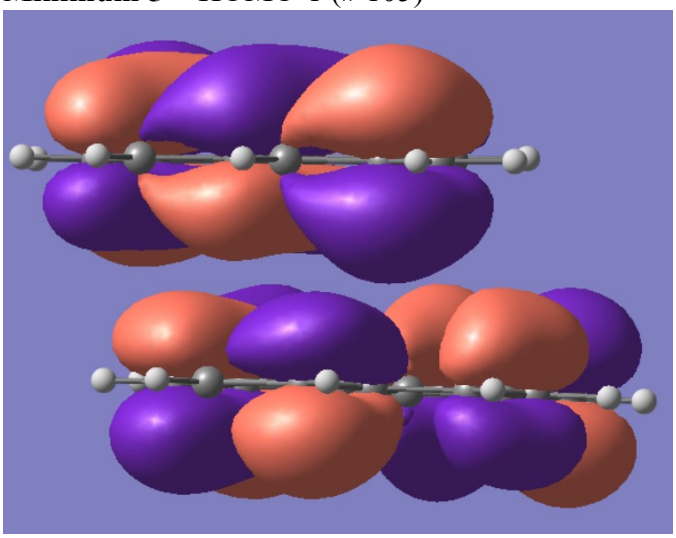
Minimum 4 β-HOMO (# 105)



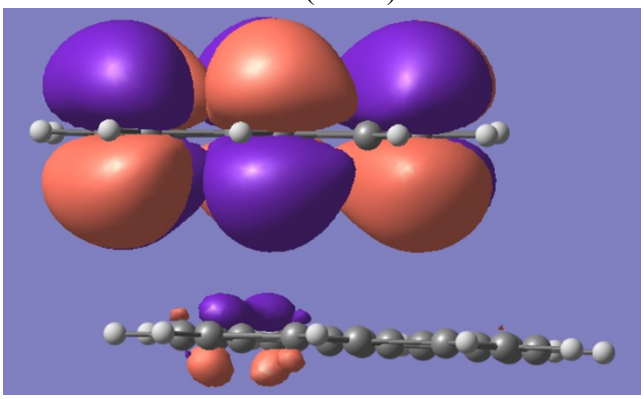
Minimum 5 α-HOMO-2 (# 104)



Minimum 5 α-HOMO-1 (# 105)



Minimum 5 α-HOMO (# 106)



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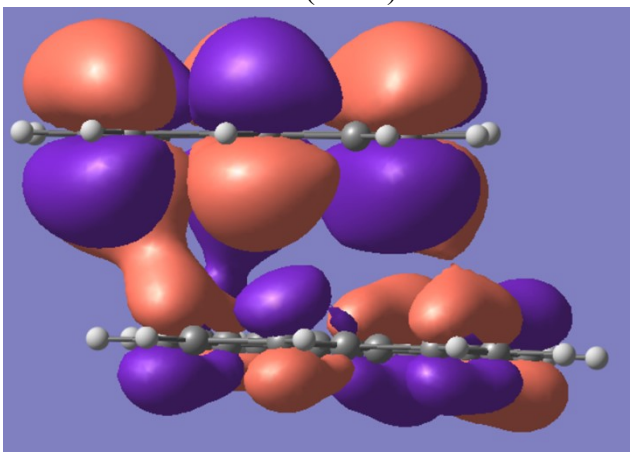
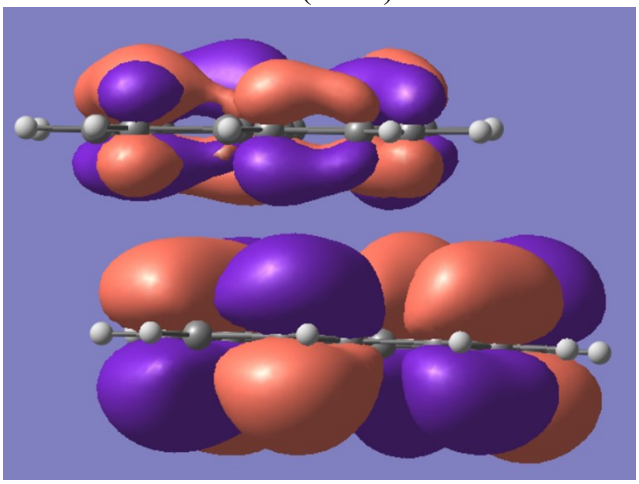
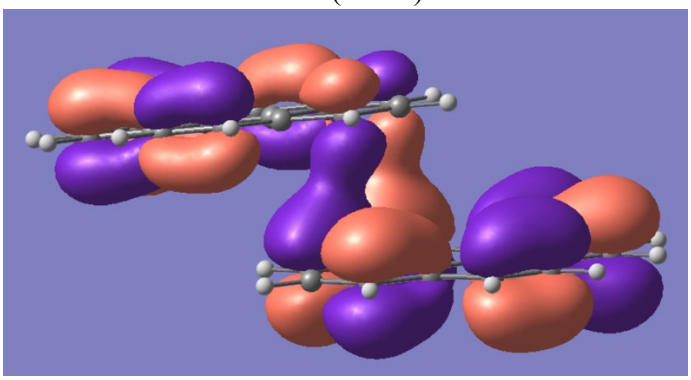


Minimum 5 β-LUMO (# 106)



Minimum 6 α-HOMO-1 (# 105)



Minimum 6 β-HOMO (# 105)

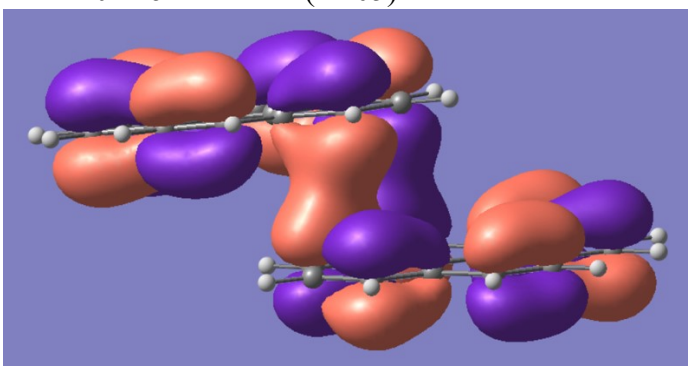
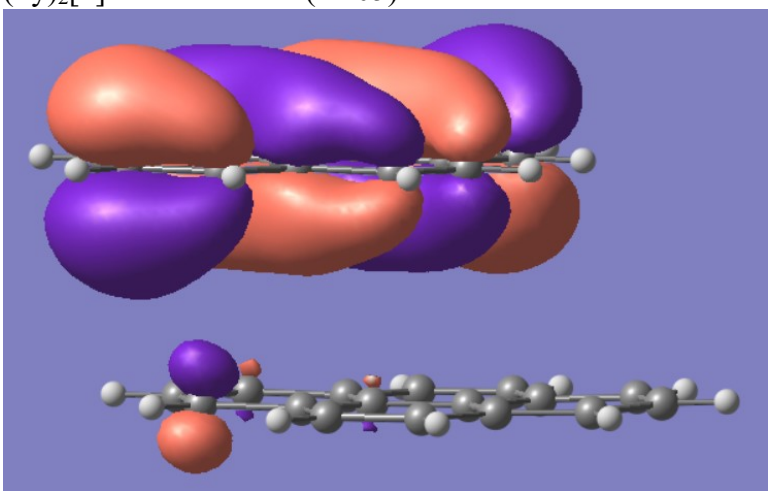


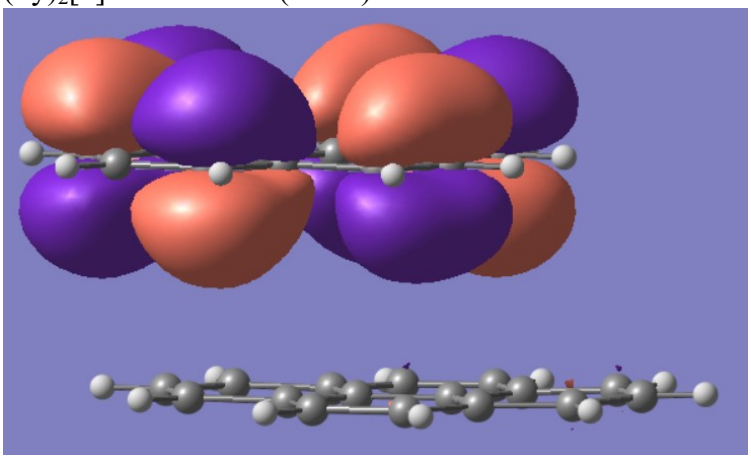
Figure S8. Selected dimer orbitals for the $(Py)_2^+$ dimer at the geometries of the six minima listed in Table 1 and Figure 10 in the main text.

Dimers excised from the $(Py)_2(Ga_2Cl_7)$ crystal structure:

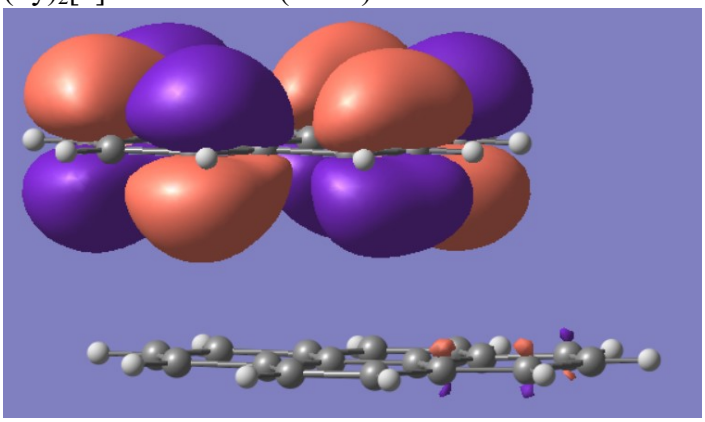
$(Py)_2$[4] – α-HOMO-1 (# 105)



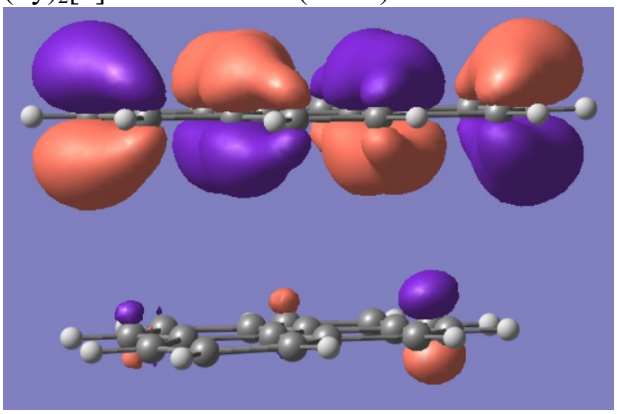
$(Py)_2$[4] – α-HOMO (# 106)



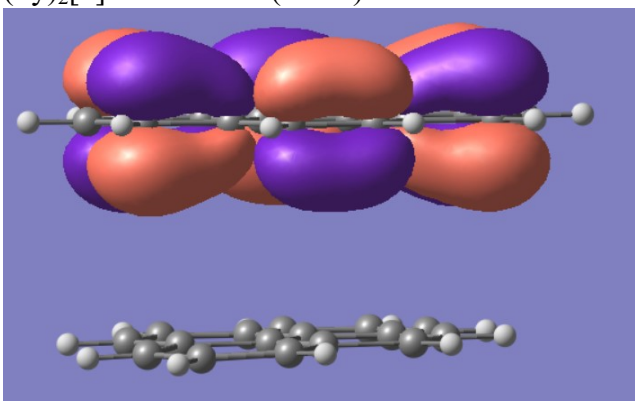
$(Py)_2$[4] – β-HOMO (# 105)



$(Py)_2[3]$ – α-HOMO-1 (# 105)



$(Py)_2[3]$ – α-HOMO (# 106)



$(Py)_2[3]$ – β-HOMO (# 105)

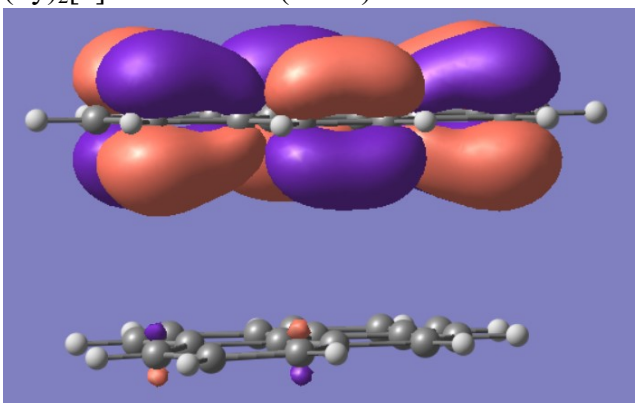


Figure S9. Selected dimer orbitals for the $(Py)_2[3]$ and $(Py)_2[4]$ dimer at the geometries excised from the crystal structure and referred to in Table 1 and Figure 10 in the main text.

7. Cartesian coordinates of six minima of the $(Py)_2^+$ dimer cations

Minimum 1
E_{tot} (UM05-2X/6-311G(d)) = -1231.443922 Ha

C	1.82224600	-0.43036900	1.62642500
C	0.68603700	1.74341500	1.63544200
C	-3.05678400	-0.23998800	1.60885400
H	-3.97005600	0.34048200	1.61437800
C	-1.82223200	0.43152300	1.62611200
C	0.62778800	-0.32841900	-1.63098800
C	-0.68602300	-1.74225600	1.63650500
C	-0.62778800	-0.32726200	1.63117300
C	0.62780200	0.32841800	1.63098500
C	1.94381500	2.37385700	1.62142100
H	1.98945700	3.45507700	1.63492700
C	-0.62780200	0.32726200	-1.63117200
C	-1.82224600	-0.43152200	-1.62610700
C	0.52926100	-2.48387500	1.65462100
C	-1.73834400	1.85372700	1.64215700
H	-2.65463200	2.42877700	1.65560500
C	-0.68603600	1.74225600	-1.63650000
C	0.52924700	2.48387500	-1.65462000
H	0.47887500	3.56486000	-1.67505100
C	1.73834400	1.85256400	-1.64335900
H	2.65463200	2.42760400	-1.65719200
C	3.05679900	0.24112900	1.60877300
H	3.97007100	-0.33933800	1.61467300
C	1.73835700	-1.85256400	1.64335300
H	2.65464500	-2.42760500	1.65718400
C	-1.94380100	-2.37270600	1.62285300
C	-3.11258400	-1.62750500	1.61062100
C	-0.52924700	2.48504600	1.65306700
H	-0.47887600	3.56604300	1.67283300
C	-3.05679800	0.23998900	-1.60883700
H	-3.97007000	-0.34048200	-1.61435300
C	-3.11259800	1.62750600	-1.61059900
H	-4.07068100	2.12779700	-1.61354800
C	1.82223200	0.43036900	-1.62643200
C	0.68602200	-1.74341500	-1.63544800
C	-1.94381400	2.37270700	-1.62283700
H	-1.98945500	3.45391800	-1.63701100

C	-1.73835900	-1.85372600	-1.64215400
H	-2.65464700	-2.42877500	-1.65559900
C	3.11260000	1.62864700	1.60967100
H	4.07068300	2.12894000	1.61233200
C	-0.52926200	-2.48504500	-1.65307000
H	-0.47889200	-3.56604300	-1.67283700
C	3.05678500	-0.24113000	-1.60878900
H	3.97005700	0.33933700	-1.61469600
C	1.94380000	-2.37385700	-1.62143300
H	1.98944100	-3.45507700	-1.63494000
C	3.11258400	-1.62864800	-1.60968900
H	0.47888900	-3.56486000	1.67505600
H	-1.98944100	-3.45391800	1.63703100
H	-4.07066700	-2.12779600	1.61358000
H	4.07066700	-2.12894100	-1.61235600

Minimum 2

E_{tot} (UM05-2X/6-311G(d)) = -1231.440091 Ha

C	-2.26838800	0.00002300	2.49631400
C	-1.61800400	1.20252200	2.26420400
C	-0.28790400	1.22604600	1.81280200
C	0.38126300	0.00001300	1.58170200
C	-0.28790700	-1.22601400	1.81282300
C	-1.61800600	-1.20248100	2.26422400
C	0.40994000	2.44681500	1.58125100
C	1.72122400	0.00000800	1.12347200
C	2.39062800	1.22648000	0.89698800
C	1.70440900	2.44739400	1.14911100
C	3.72579200	1.20184700	0.44524900
H	4.24268700	2.13909400	0.28531500
C	4.38242700	-0.00000200	0.22680100
C	3.72578800	-1.20184600	0.44526400
C	2.39062400	-1.22646900	0.89700500
C	1.70440200	-2.44737800	1.14914700
C	0.40993400	-2.44678900	1.58128900
H	-0.10024200	-3.38153400	1.77341200
H	2.22710100	-3.38198700	0.99238100
H	-0.10023400	3.38156600	1.77335700
H	-3.28764700	0.00002700	2.85474900
H	-2.12670200	2.13950900	2.45080000
H	-2.12670200	-2.13946600	2.45083900

H	2.22711100	3.38200000	0.99233400
H	5.41005700	-0.00000600	-0.10736000
H	4.24268000	-2.13909600	0.28534200
C	-4.38242300	-0.00000300	-0.22679400
C	-3.72578900	1.20184300	-0.44526400
C	-2.39062600	1.22646700	-0.89700300
C	-1.72122200	-0.00000900	-1.12346700
C	-2.39062600	-1.22648100	-0.89698700
C	-3.72578700	-1.20185100	-0.44524100
C	-1.70440500	2.44737800	-1.14914700
C	-0.38126100	-0.00001200	-1.58170000
C	0.28790600	1.22601600	-1.81282200
C	-0.40993800	2.44679100	-1.58128900
C	1.61800300	1.20248500	-2.26422500
H	2.12669900	2.13946900	-2.45084100
C	2.26838600	-0.00001900	-2.49631700
C	1.61800300	-1.20251900	-2.26420700
C	0.28790500	-1.22604400	-1.81280500
C	-0.40994000	-2.44681500	-1.58125700
C	-1.70440700	-2.44739600	-1.14911600
H	-2.22710900	-3.38200100	-0.99234300
H	0.10023500	-3.38156400	-1.77336900
H	-2.22710600	3.38198600	-0.99238400
H	-5.41005300	-0.00000100	0.10737000
H	-4.24268600	2.13909200	-0.28535300
H	-4.24268000	-2.13909800	-0.28530600
H	0.10023700	3.38153700	-1.77341300
H	3.28764400	-0.00002100	-2.85475600
H	2.12670000	-2.13950600	-2.45080900

Minimum 3

E_{tot} (UM05-2X/6-311G(d)) = -1231.433880 Ha

C	-4.16141400	-1.66605700	0.27169300
C	-4.34351100	-0.41447300	-0.30350400
C	-3.37974500	0.59372400	-0.15275500
C	-2.21418800	0.32416400	0.60435100
C	-2.02966300	-0.95017200	1.19430400
C	-3.01926100	-1.93538800	1.00827300
C	-3.54159900	1.88671000	-0.73681800
C	-1.22431200	1.32431000	0.75952700
C	-1.40166800	2.59354700	0.15708500

C	-2.59013900	2.84900400	-0.58614000
C	-0.39707800	3.57153100	0.31396100
H	-0.54143800	4.54731500	-0.13120600
C	0.74833100	3.29787200	1.03276300
C	0.93330100	2.04156100	1.61173800
C	-0.04910900	1.04697000	1.49928000
C	0.10652300	-0.23965800	2.09567300
C	-0.85152400	-1.20081400	1.95404500
H	-0.72567900	-2.16988700	2.41796700
H	1.00584100	-0.44493600	2.66202900
H	-4.44173400	2.09308300	-1.30073000
H	-4.91717700	-2.42884800	0.15030700
H	-5.24004000	-0.20568200	-0.87237900
H	-2.88037400	-2.90855200	1.46053200
H	-2.72734500	3.82629200	-1.02962700
H	1.50946400	4.05634800	1.14919300
H	1.83920300	1.82870700	2.16436000
C	-0.74833200	-3.29786900	-1.03276800
C	-0.93329800	-2.04156000	-1.61174800
C	0.04911200	-1.04697000	-1.49928700
C	1.22431100	-1.32430900	-0.75952800
C	1.40166200	-2.59354600	-0.15708100
C	0.39707300	-3.57152800	-0.31395900
C	-0.10651600	0.23965800	-2.09568400
C	2.21418800	-0.32416400	-0.60434900
C	2.02966800	0.95017100	-1.19430700
C	0.85153100	1.20081200	-1.95405400
C	3.01926700	1.93538500	-1.00827500
H	2.88038500	2.90854700	-1.46054000
C	4.16141600	1.66605400	-0.27169000
C	4.34350800	0.41447100	0.30351200
C	3.37974100	-0.59372400	0.15276300
C	3.54159100	-1.88671000	0.73683100
C	2.59013100	-2.84900200	0.58615100
H	2.72733400	-3.82628900	1.02964000
H	4.44172300	-2.09308300	1.30074600
H	-1.00583000	0.44493600	-2.66204600
H	-1.50946400	-4.05634500	-1.14920100
H	-1.83919600	-1.82870700	-2.16437700
H	0.54143000	-4.54731100	0.13121000

H	0.72569000	2.16988500	-2.41798000
H	4.91718100	2.42884300	-0.15030400
H	5.24003500	0.20568000	0.87239200

Minimum 4

E_{tot} (UM05-2X/6-311G(d)) = -1231.433822 Ha

C	0.30489200	-0.05460000	1.73008800
C	1.06014000	-2.18648200	0.78598600
C	4.50633900	-0.26419600	-0.74711600
H	5.23622700	-0.83393900	-1.30704600
C	3.37355200	-0.91668400	-0.23941800
C	-1.65286400	1.16837500	-0.69433300
C	2.62148400	1.21704000	0.70485100
C	2.42537800	-0.17141000	0.49849800
C	1.26844300	-0.80757900	1.01240800
C	-0.10721000	-2.79183500	1.29025600
H	-0.25982600	-3.85094100	1.12978400
C	-2.02326100	-0.19503000	-0.80297500
C	-1.16433700	-1.11037700	-1.45746000
C	1.63905400	1.94964200	1.42502500
C	3.13846700	-2.30915800	-0.45871600
H	3.86862100	-2.87663000	-1.02062100
C	-3.24742600	-0.64187300	-0.24809200
C	-4.09795900	0.30003200	0.40087600
H	-5.04043300	-0.04320700	0.80668400
C	-3.74026500	1.60984900	0.50854000
H	-4.39675100	2.31539400	1.00059700
C	-0.84937600	-0.70314900	2.21886900
H	-1.58561300	-0.12486600	2.76180900
C	0.51752200	1.33390900	1.91883300
H	-0.22514900	1.90927500	2.45570000
C	3.76971700	1.83188400	0.17701200
C	4.70037000	1.09569700	-0.53887300
C	2.02605900	-2.91935400	0.03424100
H	1.86424900	-3.97648600	-0.13166300
C	-1.53537900	-2.46253000	-1.51891400
H	-0.87866500	-3.16487700	-2.01617200
C	-2.74663100	-2.89823900	-0.98300700
H	-3.02483700	-3.93960500	-1.06302900
C	-2.50510400	2.08237000	-0.02790900
C	-0.42357500	1.61170400	-1.23806100

C	-3.59354500	-2.00313300	-0.35932500
H	-4.53733200	-2.34039800	0.04880400
C	0.05523000	-0.63396900	-2.02481600
H	0.69999200	-1.33570300	-2.53749700
C	-1.04210500	-2.05687800	2.00857000
H	-1.92741200	-2.54237800	2.39275300
C	0.41471700	0.67583500	-1.91379800
H	1.34739200	1.02429700	-2.33878900
C	-2.11359400	3.42737100	0.08145400
H	-2.77179400	4.12890300	0.57704900
C	-0.06174800	2.96100600	-1.08629600
H	0.87932500	3.30074700	-1.49961500
C	-0.90465200	3.85774100	-0.44004200
H	1.79025900	3.00862900	1.58734700
H	3.92467700	2.89025800	0.34154400
H	5.58205300	1.57928700	-0.93409700
H	-0.61898600	4.89636600	-0.35168200

Minimum 5

E_{tot} (UM05-2X/6-311G(d)) = -1231.433257 Ha

C	-0.37281300	-1.27214700	1.45376400
C	-0.77287900	1.14236800	1.55503800
C	-4.49308000	0.57920100	-0.40023600
H	-5.11950700	1.43417700	-0.61710400
C	-3.25635300	0.78186100	0.24888500
C	2.15270700	-0.37103400	-0.75897900
C	-2.86276200	-1.63643400	0.17312300
C	-2.43856600	-0.33872500	0.53723300
C	-1.19680300	-0.15735900	1.18415500
C	0.47475700	1.30057900	2.20382700
H	0.79111200	2.29328400	2.49371200
C	1.46899900	0.86051500	-0.94697200
C	0.22409500	0.88509900	-1.62521900
C	-2.01935200	-2.74242600	0.45493800
C	-2.80855100	2.07103000	0.61798500
H	-3.43169400	2.92773900	0.39803000
C	2.03332200	2.06481000	-0.45554500
C	3.30833700	2.01712500	0.20476600
H	3.74353000	2.94518900	0.55244400
C	3.96354500	0.84624700	0.37332800

H	4.93059800	0.82403700	0.85914400
C	0.87636000	-1.06275700	2.08766700
H	1.51876600	-1.91470000	2.26748500
C	-0.80852100	-2.56407200	1.07134300
H	-0.16799400	-3.41243300	1.27194800
C	-4.10783100	-1.79197300	-0.47050000
C	-4.90972800	-0.69493800	-0.75277500
C	-1.59772900	2.24625300	1.25247700
H	-1.26867400	3.23922200	1.52607200
C	-0.42785900	2.10666000	-1.80243300
H	-1.36918400	2.13157700	-2.33647300
C	0.13340400	3.28894000	-1.32120800
H	-0.37559600	4.22890300	-1.48614200
C	3.40578200	-0.39375300	-0.09471400
C	1.58280500	-1.57773600	-1.23776800
C	1.34391200	3.27051700	-0.65117500
H	1.78354600	4.19344100	-0.29529600
C	-0.32537000	-0.35071500	-2.10916900
H	-1.27046800	-0.32229500	-2.63700600
C	1.28111000	0.20521200	2.47232500
H	2.23474400	0.34290300	2.95915500
C	0.32357000	-1.52557900	-1.92323000
H	-0.09359900	-2.44861700	-2.30461200
C	4.05586200	-1.61370500	0.08861400
H	5.01696300	-1.63332700	0.58575500
C	2.26411800	-2.78196300	-1.02584400
H	1.83612900	-3.70404100	-1.39809500
C	3.48518500	-2.79708600	-0.36998500
H	-2.34612100	-3.73529600	0.17567900
H	-4.43620900	-2.78557400	-0.74512200
H	-5.86096700	-0.83495600	-1.24491700
H	4.00656900	-3.73332900	-0.22694000

Minimum 6

E_{tot} (UM05-2X/6-311G(d)) = -1231.427691 Ha

C	-0.61836500	2.96773900	-1.05573100
C	-1.90519500	3.16666800	-0.58774400
C	-2.77075600	2.07839700	-0.35765100
C	-2.31099600	0.76970900	-0.62826400
C	-0.99641800	0.56724200	-1.12254000

C	-0.15906500	1.68057800	-1.31473800
C	-4.09421000	2.25979500	0.14173400
C	-3.16281400	-0.33960700	-0.40564500
C	-4.47074500	-0.13699500	0.09082500
C	-4.91191100	1.19309100	0.35893200
C	-5.29919000	-1.25417700	0.30116000
H	-6.30162500	-1.10115300	0.67833700
C	-4.85013900	-2.53590900	0.02695500
C	-3.56523300	-2.73814500	-0.46069200
C	-2.70450800	-1.65278800	-0.68216300
C	-1.38217500	-1.82784000	-1.17636400
C	-0.55530800	-0.75448600	-1.39004300
H	0.44494100	-0.90677600	-1.77365900
H	-1.03324300	-2.82965400	-1.39222000
H	-4.44208100	3.26418900	0.34298700
H	0.03186600	3.81393500	-1.22626900
H	-2.26258600	4.16949100	-0.39368000
H	0.84703700	1.52509800	-1.68208100
H	-5.91505600	1.34232400	0.73542700
H	-5.50312600	-3.38110800	0.18974400
H	-3.22037800	-3.74011200	-0.68000400
C	-0.45321700	-0.21085200	2.00124500
C	0.11602900	-1.40651500	1.58793400
C	1.39569200	-1.43323100	0.99275600
C	2.09505000	-0.21488400	0.81493600
C	1.51725500	1.00345600	1.24760800
C	0.22874700	0.98214700	1.82333700
C	2.00081900	-2.64860500	0.56029400
C	3.37701900	-0.21501000	0.20783800
C	3.95296100	-1.43262200	-0.22774600
C	3.22779500	-2.64724900	-0.03029600
C	5.22011000	-1.41040400	-0.82723800
H	5.66381700	-2.33975800	-1.15905700
C	5.90604200	-0.21585700	-0.99021000
C	5.34733000	0.97876100	-0.55779600
C	4.08258600	1.00155000	0.04513200
C	3.48568900	2.21282900	0.51374800
C	2.25407900	2.21414400	1.09252600
H	1.81494400	3.13793300	1.44555000
H	4.03787500	3.13713300	0.40513800

H	1.46947200	-3.57881700	0.71386800
H	-1.43474300	-0.20885000	2.45372500
H	-0.41318300	-2.33887700	1.73447400
H	-0.21840300	1.91609400	2.13786200
H	3.67823100	-3.57695500	-0.35229800
H	6.88342300	-0.21597000	-1.45083500
H	5.89106500	1.90626100	-0.67960600

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